Fabrication and characterization of nanomaterials grown by electron beam induced deposition process

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FABRICATION AND CHARACTERIZATION OF
NANOMATERIALS GROWN BY ELECTRON BEAM INDUCED
DEPOSITION PROCESS

By

Juntao Li

A Dissertation
Submitted to the University at Albany, State University of New York
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the Requirements of the Degree of
Doctor of Philosophy

College of Nanoscale Science and Engineering

2010
FABRICATION AND CHARACTERIZATION OF
NANOMATERIALS GROWN BY ELECTRON BEAM INDUCED
DEPOSITION PROCESS

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Juntao Li

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Abstract

Platinum- and tungsten-containing materials were grown on bulk substrates from a variety of precursors including (CH$_3$)$_3$CH$_2$C$_5$H$_4$Pt, W(CO)$_6$, WF$_6$, and Pt(PF$_3$)$_4$ in either a high vacuum dual beam focused ion beam/scanning electron microscope (FIB/SEM) or an environmental scanning electron microscope (ESEM). The effects of deposition conditions on the growth kinetics, microstructure and composition of the grown materials, structural and chemical homogeneity of impurities inside the deposits as well as the resistivity were investigated.

First, Pt-containing deposits were grown in high vacuum SEM using (CH$_3$)$_3$CH$_2$C$_5$H$_4$Pt. The deposits consisted of platinum nanocrystals embedded in an amorphous matrix and intermixed with the amorphous oxide on a Si substrate. The extent of intermixing scaled with the electron beam fluence delivered to the material during EBID, and during post-growth electron beam irradiation in high vacuum (in the absence of the precursor). Second, ESEM was used to perform deposition using WF$_6$. The deposits consisted of WO$_3$ nanocrystals embedded in an amorphous matrix. Oxide formation was attributed to residual oxidizers present in the ESEM chamber during EBID. Under conditions of fixed low electron flux, the WO$_3$ grain size and the degree of deposit crystallinity increased with time. These changes correlated with the degree of electron energy deposition into the material during growth. Third, W-containing nanowires were grown using W(CO)$_6$ in high vacuum SEM. With increasing electron beam energy, the resistivity increased from $2.0 \times 10^7$ $\mu\Omega$ cm to $1.2 \times 10^9$ $\mu\Omega$ cm, while the carbon sp$^2$/sp$^3$ bond ratio decreased from 1 to 0.6. The increase in resistivity was attributed to the decreasing fraction of graphitic (sp$^2$) bonded carbon inside the deposits. Finally, Pt-
containing nanowires were grown from \((\text{CH}_3)_3\text{CH}_3\text{C}_5\text{H}_4\text{Pt}\) in high vacuum SEM and \(\text{Pt(PF}_3)_4\) in ESEM. The resistivity (~\(10^4\) μΩ cm) from nanowire grown from \(\text{Pt(PF}_3)_4\) was about four orders of magnitude smaller than that (~\(10^8\) μΩ cm) from those grown from \((\text{CH}_3)_3\text{CH}_3\text{C}_5\text{H}_4\text{Pt}\). Cross-sectional TEM analysis revealed that the nanowires formed by decomposition of \(\text{Pt(PF}_3)_4\) have a higher degree of crystallinity and a larger size grain size and higher grain packing density compared to those by \((\text{CH}_3)_3\text{CH}_3\text{C}_2\text{H}_4\text{Pt}\).
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<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AES</td>
<td>Auger Electron Microscopy</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
</tr>
<tr>
<td>BCC</td>
<td>Body-Centered Cubic</td>
</tr>
<tr>
<td>BF</td>
<td>Bright Field</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscattered Electron</td>
</tr>
<tr>
<td>CBED</td>
<td>Convergent Beam Electron Diffraction</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge Coupled Device</td>
</tr>
<tr>
<td>CL</td>
<td>Cathodeluminescence</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DEA</td>
<td>Dissociative Electron Attachment</td>
</tr>
<tr>
<td>DF</td>
<td>Dark Field</td>
</tr>
<tr>
<td>EBID</td>
<td>Electron Beam Induced Deposition</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron Backscattered Diffraction</td>
</tr>
<tr>
<td>EDS/EDX</td>
<td>Electron Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>ELE</td>
<td>Energy Loss Electron</td>
</tr>
<tr>
<td>ELNES</td>
<td>Energy Loss Near Edge Structures</td>
</tr>
<tr>
<td>ESEM</td>
<td>Environmental Scanning Electron Microscopy</td>
</tr>
<tr>
<td>FEA</td>
<td>Field Emitter Array</td>
</tr>
<tr>
<td>FED</td>
<td>Field Emission Display</td>
</tr>
<tr>
<td>FEG</td>
<td>Field Emission Gun</td>
</tr>
<tr>
<td>FFT</td>
<td>Fast Fourier Transform</td>
</tr>
<tr>
<td>FIBID</td>
<td>Focused Ion Beam Induced Deposition</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>FSE</td>
<td>Forward Scattered Electron</td>
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<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>GIF</td>
<td>Gatan Image Filter</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>IFFT</td>
<td>Inverse Fast Fourier Transform</td>
</tr>
<tr>
<td>LACO</td>
<td>Linear Combination of Atomic Orbital</td>
</tr>
<tr>
<td>MC</td>
<td>Monte Carlo</td>
</tr>
<tr>
<td>MO</td>
<td>Molecular Orbital</td>
</tr>
<tr>
<td>NBD</td>
<td>Nano-Beam Diffraction</td>
</tr>
<tr>
<td>NEXAFS</td>
<td>Near Edge X-ray Absorption Fine Structures</td>
</tr>
<tr>
<td>PE</td>
<td>Primary Electron</td>
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<tr>
<td>PEELS</td>
<td>Parallel-collection Electron Energy Loss Spectroscopy</td>
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<tr>
<td>RT</td>
<td>Room Temperature</td>
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<tr>
<td>RTA</td>
<td>Rapid Thermal Annealing</td>
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<tr>
<td>SAD</td>
<td>Selected Area Diffraction</td>
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<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single-Wall Carbon Nanotube</td>
</tr>
<tr>
<td>RGA</td>
<td>Residual Gas Analyzer</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultrahigh Vacuum</td>
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<tr>
<td>VRH</td>
<td>Variable Range Hopping</td>
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<tr>
<td>ZL</td>
<td>Zero Loss</td>
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<td>Symbol</td>
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<td>$\Phi$</td>
<td>Work function</td>
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<td>$\phi$</td>
<td>Tilt angle</td>
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<td>$\sigma_k$</td>
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<td>$\tau$</td>
<td>Surface residence time</td>
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<td>Ionization potential</td>
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<td>$E_f$</td>
<td>Fermi level</td>
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<tr>
<td>$f$</td>
<td>Electron flux</td>
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<tr>
<td>$I_k$</td>
<td>Signal integral for edge K</td>
</tr>
<tr>
<td>$I_0$</td>
<td>Zero-loss integral</td>
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</table>
\( I_p \)  
Electron beam current

\( J \)  
Precursor molecule flux

\( L \)  
Camera length

\( m_0 \)  
Electron rest mass

\( n \)  
Surface adsorbate number density

\( N \)  
Areal density

\( P \)  
Pressure

\( R \)  
Deposition rate

\( s \)  
Sticking coefficient

\( V \)  
Volume

\( Z \)  
Atomic number

\( \Delta \)  
Signal integration width

\( \Delta_E \)  
Energy loss
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1. Introduction

The ability to manipulate and process materials at the nanoscale with excellent reproducibility is important to the advancement of the nanotechnology field.\textsuperscript{1-6} This type of materials processing is becoming increasingly important to the integrated circuit manufacturing industry, where minimum feature sizes are approaching current fabrication limits. Consequently, there has been a surge in demand for the improvement of existing processing techniques as well as for the development of novel fabrication methods.

Conventional material deposition techniques currently used for the fabrication of micron or sub-micron structures in microelectronics devices do not allow the site-specific deposition of materials on the substrate. Instead, materials are deposited on the whole planar substrate and the pattern is defined by a combination of photolithographic patterning and etching processes. In the photolithography process, a light sensitive polymer material, photoresist is first spin coated on the substrate. A photomask with the desired patterns is positioned above the photoresist, and UltraViolet (UV) light is focused onto the photoresist through the photomask. The light that passes through the photomask (transparent area) causes the photoresist to polymerize and become insoluble. The area that is covered and protected by the opaque area of the photomask does not polymerize and can therefore be dissolved away in the developing process. Once the resist pattern is formed on the substrate, the material which is not covered by the patterned resist is removed by a subsequent following etching process. Finally, the remaining resist is
removed from the surface of the substrate, resulting in a patterned thin film layer that is a negative image of the photomask. However, the formation of a given pattern involves several complex steps, such as photomasks, resists, photolithography, wet etching, and/or selective etching which result in costly processes and generally require planar substrates. Alternative techniques are needed for nanofabrication, rapid device prototyping, 3D complex structure fabrication.

One subset of nanofabrication technology is referred to as “direct-write” processes.⁴,⁷-¹⁷ In these processes, photoresists are not necessarily used to transfer patterns, since features are typically defined directly on the substrate. In this manner, the intermediate step of resist patterning is not required and structures at nanometer scale can be produced within a single process step. In addition, direct-write processes are also advantageous for rapid device prototyping⁶,¹⁰,¹⁸-²¹ due to the capability of fabricating devices without the cost and time constraints of mask set fabrication. Among the different site-selective deposition techniques, the electron beam induced deposition (EBID) process has received considerable attention in recent years as a viable nanoscale processing technique.

Electron beam induced deposition is a local chemical vapor deposition technique. It is similar to normal chemical vapor deposition (CVD) or atomic layer deposition (ALD) process, except for the energy needed to dissociate the precursor molecules comes from electrons, not heat. Generally, there are different ways to introduce the precursor gases. Either the gas can be introduced into the local area for deposition by a gas injection system attached to a normal high vacuum scanning electron microscope (SEM)²²-²⁴, or the whole chamber is filled up with gas by using a modified transmission electron...
microscope (TEM)\textsuperscript{7,9,25-28} or an environmental SEM (ESEM)\textsuperscript{13,29-33} It is initiated by electrons that dissociate precursor molecules adsorbed to a substrate surface, giving rise to deposition in the vicinity of an electron beam. The volatile reaction by-products are pumped away by the vacuum system. The technique is capable, in principle, of depositing any material provided a suitable CVD precursor is available.

Controlled electron beam induced deposition must be performed in a vacuum environment to reduce electron-gas molecule scattering and deposit contamination. Most of the previous EBID studies were performed in conventional SEM using low-energy electrons in the range of 1-30 keV.\textsuperscript{12,24,31,34-38} Recently, 200 keV high-energy electrons have been used to achieve a better spatial resolution in TEM\textsuperscript{7,28,39}, or scanning transmission electron microscopes (STEM)\textsuperscript{12}, due to the reduction of probe size and smaller electron-solid interaction volume for a thin film substrate. In addition to these high vacuum instruments, ESEM has also been used to perform EBID experiments.

To date, most work on the nanostructure of EBID-fabricated materials has focused on metal-containing materials.\textsuperscript{2,16,18,21,24,29,30,36,38,40-44} Typically, the deposits are nanocomposites consisting of metal crystallites (with diameters in the range of 1 to 10 nm) embedded in an amorphous carbon-rich matrix\textsuperscript{7,13,25,26,35,36,42,43,45-52} composed of reaction byproducts and impurities present at the substrate surface during EBID. The chief impurities are carbon and oxygen, resulting from incomplete decomposition of the organometallic precursor and incorporation of the reaction fragments on the deposited metal-containing films. In contrast, metal films deposited by chemical vapor deposition techniques but using the same precursor typically have very high purity levels.\textsuperscript{53-60} High impurity content degrades the conductivity of the deposited metals.\textsuperscript{10,20,24,35,36,38,52,61-65}
Consequently, the effects of deposition conditions on the structural and chemical homogeneity of impurities need to be investigated. In addition to organometallic precursors, deposits made by several metal-containing inorganic precursors were also investigated in this work.

The height of EBID structures is generally at the micron or sub-micron scale, which is lower than or comparable to the penetration range of the energetic electrons typically used for EBID.\textsuperscript{66,67} As a consequence, while electron irradiation initiates EBID through the dissociation of adsorbates, it also serves to deposit energy into underlying EBID-grown material and may give rise to material modification during growth. However, there are as yet no definitive reports on the electron beam induced material modification on the deposit nanostructure and composition.

Finally, the typical feature sizes are on nanometer scale, making the conventional structural and chemical characterization of EBID deposits challenging. Material characterization by TEM has played an important role in the development of nanotechnology. The application of TEM techniques to nanomaterials studies have been remarkably increased as the techniques were improved in TEM, especially in last 20 years.\textsuperscript{68-70} The highly coherent field emission electron sources and electron energy loss spectroscopy (EELS)\textsuperscript{71} combined with energy dispersion spectroscopy (EDS) analysis make TEM a powerful analytical technique. Imaging, electron diffraction and spectroscopy could be obtained from a single instrument. The analytical capability of TEM makes it a perfect technique to study the nanostructure and composition of EBID-grown materials.
The following chapters include a literature overview of the electron beam induced deposition technique. In this chapter, the principles and history of EBID are discussed. Some application examples of EBID, such as mask repair, site-specific nanocontact and interconnect, field emitters are also presented. Different aspects of EBID in high vacuum SEM system and environmental SEM are described and compared. The fundamental EBID mechanisms as well as the available theoretical models for EBID process, including continuum models\textsuperscript{23,32,50} and three-dimensional Monte Carlo models\textsuperscript{11,72} are discussed in the theory and simulation chapter (Chapter 3).

Chapter 4 describes, in detail, the experimental setup and experiments conducted to prepare the EBID samples grown in both high vacuum SEM and environmental SEM systems. The general principles of the characterization techniques and the corresponding quantification analysis process are covered in this chapter. In this study, an \textit{in-situ} lift-out site-specific TEM sample preparation method was used to prepare the cross-sectional TEM samples from the EBID deposit in a FIB/SEM dual beam system (Chapter 5). A comprehensive TEM analysis of the nanostructure and composition of the deposit was performed using a high-resolution analytical TEM. In order to explain the evolution nanostructure of the deposits, Monte Carlo simulations of electron energy deposition\textsuperscript{31,73} during the growth were performed.

The ultimate goal of this research is to study the electron beam induced materials modification effects during the EBID process. It is hoped that the effects discussed in this work can potentially be used to control the nanostructure and functionality of EBID fabricated materials. Starting from Chapter 6, the following several chapters include the main findings of the experiments conducted in this work. In chapter 6, the nanostructure
of Pt-containing nanocomposites grown by room temperature EBID using (CH₃)₃CH₅C₅H₄Pt precursor in a high vacuum SEM system is studied. The intermixing of the nanocomposite with an amorphous oxide overlayer on a Si substrate, microstructures and compositions of the deposits are investigated. Possible mechanisms behind the observed changes in nanostructure, and implications for the functionality of materials grown by EBID are also discussed.

As mentioned before, environmental SEM can also be used for EBID study. For an environmental EBID instrument setup, no gas injection needle is used and the whole chamber is filled with precursor gas. Compared to the electron beam induced chemistry in high vacuum conditions, ESEM beam chemistry has several advantages.

- The ESEM chamber is filled with precursor gas and can be operated at relative high chamber pressure.⁷⁴,⁷⁵ This is different from the high vacuum SEM system. Using the gas injection system normally attached a high vacuum SEM system, the precursor is delivered into the local area on the substrate, where the local precursor pressure is relatively high and the precursor pressure inside the chamber has a large gradient. In ESEM system, the precursor pressure at the deposition location is uniform and can be measured accurately. Since the gas pressure is a very important factor in EBID process, knowing the accurate precursor pressure can result in better understanding of the physical phenomena taking place during deposition.

- It has the ability to remove contamination, which is generally a problem for high vacuum electron beam induced chemistry. Oxygen and water vapor can be used to volatize the carbonaceous materials on the sample surface and
inside the deposits. ESEM system can also perform gas mixture beam chemistry. \(^\text{6,13,29,30}\)

- It can overcome problems caused by charging when an insulating or poorly conductive substrate is used. EBID is often impaired by charging of substrate or deposits that can dissipate the excess charge created by the electron beam. Charging will cause defocusing and deflection of the beam, which lead to distortion and degrade the spatial resolution of the EBID structures. \(^\text{5,76-78}\)

In this study, ESEM was also used to perform electron beam induced deposition. In chapter 7, evolution of the nanostructure of deposits grown by EBID using a WF\(_6\) precursor in an ESEM system is investigated. Monte Carlo simulations of electron energy deposited into the materials are used to explain the electron beam induced material modification occurring during EBID, such as the degree of crystallinity, grain size, grain packing density, etc.

Since many of the most promising EBID applications entail the production of site-specific contacts and interconnects in devices, a significant fraction of the EBID literature is focused on the resistivity and composition of metallic deposits. However, reports of resistivity and composition contain inconsistencies and unexplained dependencies on experimental parameters such as the electron beam current and current density used for growth. This indicates that the conductivity of these materials depends not only on composition, but also the deposit nanostructure which may be a function of growth parameters. For example, deposits with high metal content have lower resistivity than those with relative lower metal concentration deposited under different experimental conditions. This indicates that the fundamental electron transport mechanism for this kind
of disorder system (metal nanoparticles randomly distribute among amorphous matrix) does not depend on the composition solely, the metal grains size and packing density, the electron tunneling mode, electron-electron interaction\textsuperscript{79,80}, and the inter-grain conductance\textsuperscript{80,81} will also influence the measured conductivity.

In addition, previous experimental results indicate that the degradation of resistivity was caused mainly by the inclusion of carbon atoms. Although significant progress has been made on reduction of impurity incorporation using \textit{in-situ}\textsuperscript{6,30} or \textit{ex-situ}\textsuperscript{24,46,65} methods, less attention has been paid to the characterization and quantification of the nature of the amorphous carbonaceous species inside the deposits. In chapter 8, I presented a detailed electrical and microstructural characterizations of EBID tungsten deposits from W(CO)\textsubscript{6}, and elucidate the relationship between deposition conditions and the degree of structural and chemical homogeneity as well as the resistivity of electron beam induced tungsten deposits. In this work, four-point probe instead of two-point probe measurement was used to measure the resistivity of the EBID line deposits. One reason is that the deposited feature sizes are in nano/micrometer scale, which makes the normal resistivity measurement method fail. Additionally, using four-point probe method can eliminate the relative high contact resistance between these line deposits and the metal figures. Specifically, the relationship between resistivity and impurity carbon sp\textsuperscript{2}/sp\textsuperscript{3} bond ratio inside the tungsten-containing deposits grown from W(CO)\textsubscript{6} were investigated. In addition, the resistivity of Pt line deposits fabricated using Pt(PF\textsubscript{3})\textsubscript{4} in environmental SEM and (CH\textsubscript{3})\textsubscript{3}CH\textsubscript{2}C\textsubscript{5}H\textsubscript{4}Pt in standard SEM were also measured and compared. Cross-sectional TEM analysis was performed on these line deposits to evaluate the degree in crystallinity, grain size, and grain packing density.
The thesis concludes with chapter 9 that includes a summary and future directions of the work presented, followed by the appendices.
References


Chapter 2

2. Literature overview

2.1. Principle of EBID

Focused electron beam induced deposition is similar to ion beam induced deposition, except that an electron beam is used to initiate the decomposition process of the organometallic precursor molecules in EBID. EBID is the process by which a solid material can be deposited onto a solid substrate by means of an electron-mediated decomposition of a precursor molecule (a molecule containing the species to be deposited). An ideal EBID process can be visualized as shown in Figure 2-1. The primary energetic electron beam is focused on a substrate surface that is covered with adsorbed precursor molecules. The rate at which molecules arrive at the position of the electron beam is limited by two factors: the adsorption and diffusion rate of the molecules. When primary electrons strike the surface they are scattered either elastically (backscattered) or inelastically inside the substrate. These scattering processes create secondary electrons that are emitted backward into the vacuum chamber. These lower-energy (< 50 eV) electrons have nearly optimal cross sections for fragmenting precursor molecules through electron-molecule collisions, which disassociate adsorbed molecules resulting in a solid deposit on the substrate and volatile by-products, which subsequently desorb from the surface and are pumped out by the vacuum system.
Figure 2-1. An illustration of an ideal EBID process.

(a) Substrate is exposed to the precursor; (b) Molecules are absorbed on the surface; (c) Electrons initiate dissociation reaction; (d) Solid material remains on the surface. (From Ref.1)

The electron beam induced deposition has unique properties that make it an attractive alternative method to the focused ion beam (FIB) induced deposition technique, which is widely used in both academia and industry. The electron beam diameter can be smaller than the focused ion beam diameter, and the current densities can be higher for electron beam compared with the ion beam. Electron beam induced depositions are easier to control than ion beam induced depositions that are complicated by the inherent sputtering action of the ion. Electron beam induced depositions do not result in substrate
damage (such as heating, sputtering, ion implantation) compared to the ion beam induced depositions. Consequently, while FIB processing is a very effective technique in many microscale applications, an alternative damage-free site-selective processing technique (EBID) is needed for emerging nanoscale processing applications.

2.2. History of EBID

The earliest report of EBID was a common effect in electron microscopy known as carbon contamination or carbon staining. Deposition of insulating films under electron irradiation, due to the presence of organic contaminants in vacuum systems, was detected for the first time in 1934. An electron microscope was used for the first time to study similar deposition in 1954. The solid thin polymer films were produced by electron bombardment in the presence of oil vapor. Nanometer scale (8 nm) carbon contamination structures were fabricated in a scanning transmission electron microscope in 1970. The first metal containing deposits were obtained by using a metal halide (WF₆) vapor as precursor in the vacuum chamber of a scanning electron microscope. The first three-dimensional metal-containing metal nanostructures were deposited using the focused electron beam of a conventional SEM in 1988.

With advances and development in high-resolution electron microscopes, including SEM and TEM, high-resolution nanofabrications via EBID have become a hot research topic. Experiment results show that the EBID spatial resolution, defined as the lateral size of a singular deposited dot or line, always exceeds the diameter of the electron beam. EBID spatial resolution is limited by the electron flux profile at the substrate surface, which is determined by the electron beam diameter and by the spatial distribution...
of secondary and backscattered electrons (SE and BSE)\textsuperscript{8-12} emitted from the substrate, both of which extend beyond the incident position of the primary electron beam. EBID on bulk substrates is typically performed by scanning electron microscope using electron beam energies in the range of 1–30 keV. The size of EBID-grown features, such as dots, pillars and wires is typically in 10-100 nm range.\textsuperscript{11,13-16} Higher resolution has been achieved by minimizing the electron dose, yielding dots and wires with diameters in the range of 4–30 nm.\textsuperscript{17-21} Recently, further enhanced spatial resolution has been achieved using high energy (100-300 keV) electron beams, thin substrates (10-30 nm) and low electron doses. EBID-grown nanodots and nanowires with sub-5 nm diameters have been reported,\textsuperscript{9,22-29} with smallest nanodots with average size of 0.7 nm at full width at half maximum\textsuperscript{27}. Such high-resolution results from minimal beam-solid interaction volume and efficient electron transmission through the substrates and deposits.

In addition to the aspect of spatial resolution enhancement, a large fraction of the EBID publications have also been focusing on fabrication of nanostructures using various precursor gases. In the past twenty years, a variety of metal materials have been deposited using a focused or a broad electron source including copper,\textsuperscript{30-33} chromium,\textsuperscript{34} gold,\textsuperscript{13,35-37} iron,\textsuperscript{38,39} platinum,\textsuperscript{7,40-47} tungsten,\textsuperscript{7,8,10,21,28,48-54} nickel,\textsuperscript{55} rhodium,\textsuperscript{56} cobalt,\textsuperscript{57} molybdenum.\textsuperscript{46}

### 2.3. Applications of EBID

#### 2.3.1. Mask repair

One of the commercial applications of EBID technique is the damage-free electron beam mask repair tool\textsuperscript{58,59} used widely in semiconductor industry. The main
advantages of e-beam mask repair include superior resolution and accuracy for repair and no mask structure modification during imaging. Unlike traditional FIB mask repair tools, electron beam induced chemical processes will not introduce unwanted side effects, such as ion implantation or sputtering. In addition to its damage-free repair capabilities, the e-beam tool is also a fully functional SEM that can be used for any metrology applications of a standard critical-dimension SEM (CD-SEM) and defect review SEM. This benefit means that the repair and defect characterization can be done in the same tool, which can increase the throughput. Furthermore, commercial modern electron microscopes with advanced electron optics system are well developed, operating over a wide range of beam energies and currents. The state-of-the-art e-beam mask repair tool has been shown to be suitable for the current generation of semiconductor technology. Research results show that the performance of the tool is also extendible to 45 nm node and beyond. Figure 2-2 shows a clear defect before and after repair for a binary Cr-on-glass (COG) mask.58,59

![Figure 2-2. E-beam mask repair for a clear defect.](image)

SEM micrographs showing defect site before (a) and after repair (b). The width of the equal lines and spaces is 620 nm (4X). (From Ref. 58,59)
2.3.2. Site-specific nano-contacts and nano-interconnects

Synthesis of one-dimensional nanostructures, including nanowires and nanotubes is attracting increasing attention in nanoscience and technology.\textsuperscript{61} The physical properties, such as electrical and optical properties of these nanostructures are important for their potential applications in nanoelectronics, photonics, etc. Since the traditional electrical test structures are made by conventional photolithography techniques, many complex and time-consuming process steps are required. In addition, locating and aligning a single nanowire or nanotube precisely across electrodes is a challenging problem. Since EBID is actually a local chemical vapor deposition technique using a fine focused electron beam to dissociate the metal-containing precursor molecules on the substrate surface, it has much higher flexibility to perform site-specific depositions and provide a unique solution for electrical contact on these nanowires and nanotubes. As mentioned before, electron beam deposited electrical contacts have been realized by using various metal-containing precursors. Gold- and Platinum-containing precursors are most often used for fabricating electrical contacts due to the low resistivity of the as-deposited metallic pads or wires. Focused electron beam induced deposition of gold lines on a SiO\textsubscript{2} substrate has been used to connect a single wall carbon nanotube (SWNT) to the Cr/Au electrode pad for measuring its electrical properties, as shown in Figure 2-3. Electron beam deposited electrical contacts have also been realized from trimethylcyclopentadienyl-platinum [(CH\textsubscript{3})\textsubscript{3}CHC\textsubscript{5}H\textsubscript{4}Pt], an organometallic precursor generally used for Pt deposition.
Figure 2-3. Electron beam fabricated electrical contacts and connections.

(a) Electron beam deposited gold lines to connect a single wall carbon nanotube (CNT) to prefabricated gold electrodes. (From Ref. 13); (b) Electron beam assisted deposition of Pt contacts to a Y-junction nanotube. (From Ref. 44)

Since the first metal containing deposits were obtained by using a metal halide (WF₆) vapor as precursor in the SEM vacuum chamber back in 1980s, many of the most promising EBID applications entail the production of site-specific contacts or interconnects in devices, as evidenced by the relatively large body of literature focusing on conductivity of metallic EBID-fabricated deposits. However, reports of resistivity and composition contain inconsistencies and unexplained dependencies on experimental parameters such as the electron beam current density used for growth. This indicates that the fundamental electron transport mechanism for this kind of disorder system (metal nanoparticles randomly distribute among amorphous matrix) does not depend on the composition solely. The metal grains size and packing density, the electron tunneling mode, electron-electron interaction⁶²,⁶³, the inter-grain conductance⁶³,⁶⁴, etc. will also influence the measured conductivity. Hence, in this work, a systematic investigation of microstructures of EBID metal deposits as well as the chemical bonding of amorphous carbonaceous matrix inside the deposits as function of deposition conditions was performed. The research goal is to elucidate the relationship between deposition
conditions and the degree of structural and chemical homogeneity as well as the resistivity of electron beam induced metal deposits.

2.3.3. Field emitter

One type of nanostructure fabricated by EBID that has a number of applications is the nanopillar. These structures are grown by a stationary focused electron beam in spot mode producing a high-aspect ratio pillar after a certain period of time. So far, several types of nanopillars have been made using EBID, including platinum,\textsuperscript{65,66} cobalt,\textsuperscript{57} carbon,\textsuperscript{35} and tungsten.\textsuperscript{11,53,67} Nanopillars with a diameter of 50-100 nm were successfully fabricated with EBID in the last two decades. Due to their geometrical properties, high aspect ratios, small tip radii of curvature, and conductivity, EBID nanopillars exhibit excellent field emission characteristics and would be promising candidates for use in cold field emission electron sources, supersensitive sensors and nanoelectronics.

A field emitter array (FEA) is one of the most important key devices, as a cold electron source, for vacuum microelectronic applications. Most FEAs have been fabricated using semiconductor processing that is used for integrated circuit fabrication, such as the Spindt-type field emitter.\textsuperscript{68} Field emission displays (FED) are drawing attention as one of the cadicate for flat panel displays. Recently, fast prototyping of vacuum microelectronic device structures using focused ion beams (FIB) and electron beams has been demonstrated.\textsuperscript{41,43,65,69,70} As mentioned before, the gallium contamination and damage of the sample surface caused by ion implantation during the ion beam induced deposition of emitters restrict the application of focused ion beam. Alternatively, electron beam induced deposition (EBID) is free of these problems, and its spatial
resolution is higher than that of FIB. Figure 2-4(a) shows a single Pt nanopillar of a high-aspect-ratio (up to 1 µm height and down to 50 nm diameter) grown in the conventional dry-etched gate opening by EBID. Figure 2-4(b) shows a field emitter array fabricated by FIB etching of the gate openings and subsequent electron beam induced deposition of Pt nanotips. Figure 2-4(c) shows the current-voltage ($I$-$V$) characteristics of one of these FEAs before and after Pt deposition in a high vacuum chamber. The corresponding linear dependence of the Fowler–Nordheim plot (Figure 2-4(d)) indicates that electron emission takes place via field emission.

### 2.3.4. Nanotips for scanning probe microscopes

Due to their high-aspect-ratio, electron beam deposited nanotips can be used as scanning probes for scanning probe microscopes, such as atomic force microscope (AFM). Depending on the gas molecules within the SEM vacuum chamber, high-aspect-ratio nanopillars that are carbonaceous, diamond-like, or metallic can be fabricated. Figure 2-5 shows how the electron beam induced grown nanotips are fabricated on the pre-made AFM tip arrays on a four-inch Si wafer. Control of the electron beam and stage can be done automatically by software system during the entire production process. One application example from the semiconductor production field is shown in Figure 2-6. It can be clearly seen that AFM image obtained by using EBID supertip can get more detail information of both bottom and sidewall of the dense photoresist lines, such as the line edge roughness, sidewall angle, etc.
Figure 2-4. Pt field emitter fabricated by electron beam induced deposition.

(a) SEM micrograph of a Pt emitter fabricated by electron beam induced deposition. The beam exposure time is 30 seconds; (b) Field emitter array produced by FIB etching of the gate openings and subsequent EB-induced deposition of Pt tips; (c) I-V characteristics of a prototype FEA before and after Pt deposition; (d) Corresponding Fowler-Nordheim plot of the I-V curve. (From Ref. 65)

Figure 2-5. Fabrication process of the ultrafine scanning probes on AFM Si tip.

Fabrication process of the ultrafine scanning probes on unprocessed AFM Si tips made by conventional wet-etching techniques. SEM image shows that the needle-shaped structure has a diameter of about 50 nm. (Image courtesy of Armin Kriele, NanoTools GmbH)
2.4. Instrumentation for EBID

In EBID, a highly focused electron beam is used to decompose the precursor molecules. So in principle any type of vacuum instrument with an electron source and a gas injection system for delivering precursor gas into the vacuum chamber can be used to perform deposition. Modified scanning electron microscopes are most often used. The system is generally equipped with some type of gas injection system that allows precursor to flow into the vacuum chamber from a source located either inside or outside of the chamber. Figure 2-7 shows a general schematic diagram of an EBID system built on a normal SEM.

Figure 2-6. AFM images obtained by using EBID supertip and normal AFM tip.

(a) A photoresist trench with a depth of 500 nm and width of 140 nm is characterized by AFM with a nanotip. (b) The trench structure is correctly displayed in the AFM image due to the sharp tip which can be inserted into the bottom of the trench. (c) AFM image of the same trench using conventional AFM probe shows an imprecise result.
A general schematic diagram of an EBID/IBID system built on a normal SEM. Internal/external gas injection system are shown. (From Ref. 1)

In addition to these high vacuum instruments, environmental scanning electron microscope (ESEM) have also been used to perform EBID experiments. A main difference between high vacuum EBID and environmental EBID instrument is the precursor gas delivering method. For a high vacuum SEM instrument, precursor gas is generally introduced into the vacuum chamber by a special gas injection needle (as shown in Figure 2-7). The local precursor gas pressure close to the deposition area is relatively high compared with the whole chamber pressure. For an environmental EBID instrument setup, no gas injection needle is used and the whole chamber is filled with precursor gas. Compared to the electron beam induced chemistry in high vacuum conditions, ESEM beam chemistry has several advantages. First, the ESEM chamber is filled with precursor gas and can be operated at relative high chamber pressure. Second,
unlike the gas injection system normally used in a high vacuum SEM system, the precursor pressure at the deposition location can be measured accurately. Since the gas pressure is a very important factor in EBID process, knowing the accurate precursor pressure can result in better control over the physical phenomena taking place during deposition. Third, it has ability to remove contamination, which is generally a problem for high vacuum electron beam induced chemistry. Oxygen and water vapor can be used to volatize the carbonaceous materials on the sample surface and inside the deposits. Furthermore, using ESEM system can also perform mixed-gas beam chemistry. Finally, it can overcome problems caused by charging when an insulating or poorly conductive substrate is used. EBID is often impaired by charging of the substrate or deposits that cannot dissipate the excess charge created by the electron beam. Charging will cause defocusing and deflection of the beam, which lead to distortion and degradation of the spatial resolution of the EBID structures.\textsuperscript{11,71} In addition, the ESEM image resolution has been achieved \textasciitilde1 nm\textsuperscript{72} under optimized conditions for the microscope, which indicates the EBID feature size in the similar range is achievable.\textsuperscript{11}

Recently, transmission electron microscopes (TEM) and scanning transmission electron microscopes have both been used to fabricate nanostructures. The probe size of electron beams can be reduced to sub-nanometer in TEM/STEM with field emission guns, and this would lead to a reduction in size of the fabricated structures as compared with those produced by typical SEMs. Another advantage is the small amount of backscattered electrons emitting from the thin specimen substrate generally used in TEM or STEM. This enables the dissociation reaction to occur in an extremely limited area around the probe and therefore contribute to achieve nanometer-sized structures.
In addition, TEM plays a crucial role in nanomaterials research and characterization, where high resolution is needed to observe atomic nanostructures and their properties. EBID materials normally contain metal nanocrystals embedded in an amorphous matrix, which are particularly suited for TEM characterization because the crystal size of nanomaterials is typically comparable to or below the required thickness for electron transparent samples in TEM. This make it possible to prepare, image and analyze EBID samples by the exact same TEM without breaking the vacuum conditions and sample transferring. No additional TEM sample preparation is needed, which is a time-consuming process and will cause damage to the specimen during the sample preparation process (such as focused ion beam damage, which will be discussed later in this dissertation). Given the available commercial in situ TEM holder, environmental changes (i.e., heating, electrical bias) can be applied to the sample and the sample response can be observed and recorded in real time.

2.5. Structures of deposited materials

The earliest observation of EBID was mainly the carbon contamination during electron microscopy. The modern microscopes have much better vacuum conditions which make metal-rich materials deposition possible. However, the residual background vapors and precursor fragments may still contribute to the deposit, which make characterization of EBID materials critical. Generally, the deposits consist of metal nanocrystallites embedded in an amorphous carbon matrix. Several publications have addressed the issue of contamination, composition, and structure of EBID materials for a variety of deposition precursors. Among these materials, Au-, W- and Pt-
containing material are most often studied due to their potential applications in nanocontacts or interconnects.

2.5.1. Gold deposition

Madsen et al.\textsuperscript{37} presented an \textit{in situ} method for the highly conductive attachment of carbon nanotubes by the use of an EBID gold-carbon composite material deposited using a gold containing precursor, dimethylacetylacetonate gold(III). TEM analysis of the soldering material revealed a gold-carbon composite structure with a porous crust of 3-5 nm nanoparticles around a dense core, as shown in Figure 2-8.

More detailed work on the properties of environmental EBID gold deposited with a variety of beam and chamber conditions using same precursor were reported by Mølhave et al.\textsuperscript{76} Their results indicated that the use of a carrier or background gas could influence the structure and morphology of the resultant gold nanorod deposit. Different

Figure 2-8. TEM image of EBID Au tip.

TEM image of EBID Au tip, showing a dense core encapsulated in a porous crust. In the inset, the porous crust structure with 3-5-nm nanoparticles can be seen. (From Ref. 37)
background gases, including nitrogen and water vapor, were used in their experiments and the TEM analysis showed that the deposited tips may contain three distinct types of concentric layers, which can be referred as core, crust, and contamination layers\textsuperscript{76}. Figure 2-9 shows the three-dimensional structures made by EBID under different deposition conditions. Tips deposited in 1 Torr N\textsubscript{2} consisted of gold nanocrystals (diameter 3-5 nm) embedded in an amorphous carbon matrix, which are similar to nanostructures fabricated in a traditional SEM. Tips deposited using 0.9 Torr H\textsubscript{2}O vapor as chamber gas contained a central core of dense gold surrounded by a crust. In addition, a contamination layer, which consisted of amorphous carbon with lower gold content than the crust was observed on the side facing the following second deposition. High-resolution TEM analysis and EDX analysis indicated the inner core contained polycrystalline gold whose grain size is much larger than those of small gold nanocrystals embedded in the amorphous carbon matrix in the outer crust shell. The authors attributed these effects to

Figure 2-9. TEM image of the apex of a Au tip deposited in nitrogen and water vapor.

(a) TEM image of the apex of a tip deposited in nitrogen. (b) TEM image of the tip apex with a gold core deposited in water vapor. (c) TEM image showing an asymmetric contamination layer on an EEBD tip deposited in water vapor. The thicker layer on the left-hand side (indicated by the arrow) was caused by a later deposition of a tip a few micrometers to the left.(From Ref. 76)
the diffusion of the gold cluster during deposition and electron beam irradiation with presence of water vapor.

2.5.2. Tungsten deposition

It is well known that tungsten hexacarbonyl and tungsten hexafluoride precursors are capable of producing tungsten deposits from focused EBID processing. Consequently, tungsten is the one of the most commonly reported EBID materials in the literature. Liu et al.\textsuperscript{77} studied structure and composition of tungsten wire deposited on a molybdenum substrate using W(CO)\textsubscript{6} precursor and 20 keV electron beam in a SEM. The as-deposited structure of the tungsten wire was composed of homogeneous nanocrystallites with sizes of 2-4 nm, which were embedded in an amorphous matrix. Post-annealing process at 900 °C indicated that crystallization of the deposited structure took place. Heterogeneous polycrystalline grains of tungsten, tungsten carbide and tungsten oxide were observed in the tungsten wire. However, microdiffraction analysis from as-deposited tungsten nanoparticles in the pores of the anodic porous alumina by Xie, et al.\textsuperscript{78} indicated that except for the pure W crystal, the diffraction rings corresponding to the strongest peak and the largest inter-planar spacing peak for other possible candidate phases were not observed in the pattern. The nanocrystallites were identified to be the equilibrium phase of bcc structure metal W at room temperature. Tungsten structures deposited in a high-resolution TEM (HRTEM) using W(CO)\textsubscript{6} precursor and 200 keV beam energy were shown to be nanocrystalline tungsten embedded in an amorphous tungsten matrix. These nanocrystals ranged from 1.5 to 2.0 nm in size and were composed of W, WC,WO\textsubscript{2}, and WO\textsubscript{3} at room temperature.\textsuperscript{79}
Tungsten hexafluoride (WF$_6$) precursor gas is a potential candidate precursor for producing high purity deposits presumably because it does not contain carbon and oxygen. Klein et al.$^{52}$ investigated the effects that the electron beam scanning conditions have on the deposit characteristics. The nanowires were grown in both vertical manner via a stationary electron beam and lateral manner via a scanning electron beam on the edges of holes in a lacey-carbon-film-coated on the TEM Cu grid. They found that slow, one-dimensional lateral scanning produced textured $\beta$-tungsten nanowire cores surrounded by an oxide secondary layer, while stationary vertical growth leaded to single-crystal [100]-oriented W$_3$O nanowires.

2.5.3. Platinum deposition

Post-deposition treatments are usually applied to improve the properties of the deposit and to remove unwanted fragments. Thermal annealing either performed in vacuum or in the presence of the reactive gases is generally used to remove the impurity in the deposits (such as amorphous carbon, hydrocarbon contaminants). Several papers discussed the effects of thermal annealing process (up to 500 °C) on the purity, nanostructures as well as resistivity of EBID deposits, including Au- and Pt-containing materials. Botman et al.$^{80}$ described a method applied to Pt and Au containing structures deposited using EBID, consisting of a post annealing treatment in a reactive atmosphere of oxygen, whereby the amount of carbon in the structure is greatly reduced. It has been found that post-treatment can increase the purity of Pt from 15 at.% to 70 at.% and Au from 8 at.% to 60 at.% . The corresponding resistivity of these structures has also been improved by up to four orders of magnitude, to achieve $(1.4 \pm 0.2) \times 10^4 \mu\Omega$ cm for Pt.
deposits and \((2.2 \pm 0.5) \times 10^4 \, \mu\Omega \text{ cm}\) for Au deposits, respectively. The heat treatment changed the microstructures of the deposits, which can be seen clearly in Figure 2-10. Larger-size grains were obtained after annealing process for both Au and Pt samples.

![STEM images for the gold and platinum deposits.](image)

Figure 2-10. STEM images for the gold and platinum deposits.

STEM images for the gold deposit without (a) and with (b) treatment at 500 °C in O\(_2\), and for the platinum deposit without (c) and with (d) treatment at 500 °C in O\(_2\). (From Ref. 80)

A carbon-free precursor has also been used for Pt deposition. Wang, *et al.*\(^{47}\) investigated electron-beam-induced deposition of Pt thin films on a Cr-coated Si(100) substrate by using an inorganic precursor, Pt(PF\(_3\))\(_4\). Pt content reached 60 at. % for a 3 kV e-beam flux of \(2.1 \times 10^{-3} \, \text{A}\cdot\text{cm}^{-2}\), a precursor pressure of \(2 \times 10^{-5} \, \text{Torr}\) with a substrate temperature of 80 °C. They also found that the phosphorous content could be reduced by introducing oxygen into the reaction chamber. This effect was attributed to the oxidation of phosphorus to form a gas-phase by-product.

Takeguchi *et al.*\(^{81}\) fabricated self-standing nanowires on the edge of a molybdenum film using Pt(PF\(_3\))\(_4\) precursor, followed heating at about 400 K in vacuum.
Before treatment, the as-deposited nanowires were composed of an amorphous phase, of which the dominant composition was platinum but containing a small amount of phosphorus impurity which was confirmed by electron energy loss spectroscopy (EELS) analysis. After heating treatment, the as-deposited nanowires became single-crystal platinum with a large grain size and the phosphorus content disappeared. Figure 2-11 clearly shows the difference in nanostructure before and after annealing treatment. The EELS analysis indicated that the phosphorus concentration dropped to an undetectable level after the heating process.

Figure 2-11. TEM and EELS analysis of EBID Pt nanowire.

TEM images of the as-deposited Pt nanowire before (a) and after (b) heat treatment in vacuum at 400K for 10 minutes. (c) EELS spectra showing change of phosphorus content before and after the heating. (From Ref. 81)

2.6. Electron transport properties

The fundamental electron transport properties of EBID fabricated nanowires have been investigated by several groups. Rotkina et al.\textsuperscript{16} studied the electrical characteristics of the nanowires that were formed by focused electron beam induced dissociation of a Pt-
containing \((\text{CH}_3)_3\text{CH}_2\text{C}_5\text{H}_4\text{Pt}\) precursor. They concluded that current-voltage characteristics were strongly nonlinear at 4.2 K. A voltage gap of order 0.1-0.2 V was observed at the lowest temperatures which was attributed to the single-electron tunneling via Pt nanocrystals formed in the wires during their fabrication. Further evidence for this nonlinearity that persisted to room temperature has also been provided by subtracting the surface (silicon nitride) leakage current at room temperature from the measured transport current in the Pt/C nanowire. In the further experiment that incorporated nanowire into three-terminal transistor structures, a gate-induced modulation of this voltage has been found. However, Coulomb oscillations were not observed due to the increasing surface leakage current with increasing gate bias.

This metal delocalized deposition effects have been systematically investigated by Gopal et al.\textsuperscript{45} In their work, they patterned pairs of closely separated Pt nanowires and measured the leakage current between them. They proposed that the delocalization of metal was due to the broadening by emitted secondary electron induced deposition outside the exposed area as well as the thermally assisted diffusion of the deposited metal atoms with electron beam heating the substrate.

Due to the fact that material structures and compositions may be modified by the heat generated during the resistivity measurement, rapid thermal heating (RTA) was used to improve the contacts between nanowire and metal electrode and to stabilize the composition of the nanowire.\textsuperscript{16} Resistivity measurement results from these annealed Pt nanowire shows drastic drop down to a few mΩ cm (about four orders) while they have not reached the true metallic regime. The authors attributed this to the granular structures of the metal wires even after annealing. Figure 2-12 shows the high-resolution
transmission electron microscopy (HRTEM) images taken before and after the annealing. Heat treated material shows larger grain size and higher packing density.

![HRTEM micrographs of the Pt/C nanowire.](image)

**Figure 2-12.** HRTEM micrographs of the Pt/C nanowire.

HRTEM micrographs of the Pt/C nanowire, deposited onto a Si$_3$N$_4$ membrane: the image of as deposited material (a) and the image taken after the thermal annealing at 600 °C (b). (From Ref. 16)

Different models and mechanisms have been proposed for electron transport properties of Pt nanowires fabricated by EBID technique. Tsukatani et al.\textsuperscript{43} investigated the current-voltage characteristics of Pt nanowires fabricated by EBID using a source of gas of C$_8$H$_{14}$Pt at a temperature range of 4.2 -300 K. Temperature-dependence of the resistance as well as the Coulomb oscillations have been observed at temperature up to 200K. They attributed the exponential temperature dependence of the resistance of the Pt nanowire to variable range hopping (VRH) conduction mechanism, where the possible candidate for the localized electrons is a Pt nanocrystal or an isolated electron site in the amorphous carbon matrix.
Electron transport properties of another type of metal nanowires grown by focused ion beam induced deposition (IBID) technique have also been reported in the literature. Even though both electron beam and focused ion beam deposited Pt nanowire have similar nanostructures, which are polycrystalline and contain nanometer-size Pt nanocrystals embedded in an amorphous carboneous matrix, they exhibit very different electrical characteristics. Further investigation by Lin et al. into the temperature-dependent (0.1K-300K) resistivity of the Pt nanointerconnects formed on SiO₂ substrate by focused ion beam induced deposition technique proposed different electron transport mechanism. Unlike the electron beam deposited nanowires with room temperature resistivity generally of 20-100 Ω cm, these Pt nanowires had a room temperature resistivity less than 500 μΩ cm and showed the metallic dependence of the resistivity vs the temperature. These nanowires shows behavior typical of dirty metals, including a resistivity variation at higher temperature (30-300K) which can be well described by the interference of electron-phonon scattering and elastic electron scattering from the boundaries and defects.13 The most important difference between Pt nanowire grown by EBID and IBID is the presence of Ga in IBID nanowires, which is due to the unintentional incorporation of Ga⁺ ions into the deposited nanowires during the dissociation process of the precursor.82-84 It is possible that the Ga can actually increase the conductivity of the nanowires fabricated by IBID, possibly by doping the C matrix in which the Pt nanocrystals are embedded.
2.7. Purity and resistivity measurement

From the above discussion, it has shown that electron beam induced deposition using organometallic precursors typically result in low purity metal deposits. The chief impurities are carbon and oxygen, resulting from incomplete decomposition of the organometallic precursor and incorporation of the reaction fragments on the deposited metal films. As a result, as-deposited nanowires normally have relatively high resistivity compared to the corresponding metal, which is not preferable for EBID applications in nanocontacts and interconnects. The materials composition and resistivity of the deposits (e.g. W, Pt, Au) as a function of the most important EBID parameters, including beam energy, beam current, substrate and deposition temperature are reported in Table 2-1. The variation in the deposit composition and properties with varying experimental conditions indicates the complex reactions during the deposition process. Even though some of the experimental data cannot be meaningfully compared with each other due to the differences in instrumental setups and deposition conditions, some general trends in material compositions and properties still can be observed.

From Table 2-1, it can be seen that an increase in primary electron beam current generally results in a high metal content in the deposits. There are two main effects on the final deposits with an increasing beam current, which may explain this observation. First, an increase in beam current can increase the desorption rate of the molecules (including both partially dissociated precursor molecules and the corresponding fragments or ligands). For instance, Li et al.\textsuperscript{89} investigated the temperature dependence of the electron beam induced deposition of tungsten under two conditions of beam energy and beam current using WF\textsubscript{6} as the precursor gas. It was suggested that secondary electron
stimulated desorption of fluorine species dominated at high beam current. This will lead to higher concentrations of nonvolatile metal material in the final deposit. Another effect is the electron beam induced heating on the deposit during deposition process. Utke et al. studied the thermal effects during the deposition of cobalt-containing tips using Co$_2$(CO)$_8$ as precursor gas. It was found that the cobalt content of the deposit increased with increasing beam current in the range of 20 pA to 3 μA with a beam energy of 25 keV. Higher beam currents will introduce a structural change to polycrystalline and corrugated surface morphology, which was attributed by the authors to increase in beam-induced heating and the subsequent thermal decomposition of precursor. Similar experimental results have also been reported for EBID deposits using other metal-containing precursor molecules.

The effect of primary electron beam energy on the resistivity of W deposition from W(CO)$_6$ between 0.06 and 20 keV has been studied by Hoyle et al. The measured resistivity of the deposits formed using low primary energies (below 2 keV) was found to drop up to 4 orders of magnitude. The lowest measured resistivity was $6 \times 10^{-4} \, \Omega \text{ cm}$ for a primary energy of 0.25 keV, which was still about 2 orders of magnitude larger than that of bulk tungsten ($5 \times 10^{-6} \, \Omega \text{ cm}$). The authors attributed this dependence of resistivity on beam energy to two factors. First, low energy electrons (<1 keV) have a higher dissociation cross-section for the precursor molecules compared with those with high energy (20 keV). The secondary electron yield increases with increasing incident primary electron energy. The increasing number of emitted low energy electrons can effectively increase the desorption of nonmetallic species resulting in a higher metallic content in the final deposit.
Table 2-1. Properties of W, Pt, Au containing deposits.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Precursor</th>
<th>Deposit Properties</th>
<th>E (keV)</th>
<th>Ip</th>
<th>T (°C)</th>
<th>Substrate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>W(CO)₆</td>
<td>55 at. %W, 30 at.%C, 15 at. %O (EDX), Rₑ=10⁴</td>
<td>0.25</td>
<td>10nA</td>
<td>-3</td>
<td>Si₃N₄</td>
<td>7</td>
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<tr>
<td>W</td>
<td>W(CO)₆</td>
<td>Rₑ=10⁴</td>
<td>5</td>
<td>1nA</td>
<td>20</td>
<td>Au/GaAs</td>
<td>48</td>
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<tr>
<td>W</td>
<td>WF₆</td>
<td>70 at. %W (AES)</td>
<td>3</td>
<td>5.5μA</td>
<td>-180</td>
<td>Ni</td>
<td>85</td>
</tr>
<tr>
<td>W</td>
<td>WF₆</td>
<td>66 at. %W (AES)</td>
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<td>1.5μA</td>
<td>160</td>
<td>SiO₂</td>
<td>6</td>
</tr>
<tr>
<td>W</td>
<td>WCl₆</td>
<td>58 at. %W, 6 at. %Cl, 8 at. %C, 18 at. %O (EDX)</td>
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<td>40pA</td>
<td>RT</td>
<td>Au/Cr on SiO₂</td>
<td>6</td>
</tr>
<tr>
<td>Pt</td>
<td>CpPt(Me₃)</td>
<td>13 at. % Pt (AES)</td>
<td>20</td>
<td>1.1nA</td>
<td>RT</td>
<td>SiO₂</td>
<td>46</td>
</tr>
<tr>
<td>Pt</td>
<td>CpPt(Me₃)</td>
<td>21.5 at.%Pt, 73 at. %C, 5.5 at. %O(AES) Rₑ=3</td>
<td>15</td>
<td>-</td>
<td>RT</td>
<td>SiO₂</td>
<td>41</td>
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<tr>
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<td>CpPt(Me₃)</td>
<td>13 at. % Pt (EDS)</td>
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<td>RT</td>
<td>SiO₂</td>
<td>46</td>
</tr>
<tr>
<td>Pt</td>
<td>CpPt(Me₃)</td>
<td>21.5 at.%Pt, 73 at. %C, 5.5 at. %O(AES) Rₑ=3</td>
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<td>70</td>
<td>RT</td>
<td>SiO₂</td>
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<td>Cr on Si</td>
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<tr>
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<td>15 at.%Pt</td>
<td>20</td>
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<td>RT</td>
<td>Si</td>
<td>80</td>
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<tr>
<td>Pt</td>
<td>MeCpPtMe₃</td>
<td>70 at.%Pt after annealing in O₂</td>
<td>5-30</td>
<td>~2nA</td>
<td>RT</td>
<td>SiO₂</td>
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<tr>
<td>Pt</td>
<td>MeCpPtMe₃</td>
<td>Rₑ=10⁻³–10⁴</td>
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<td>~2nA</td>
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<td>43</td>
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<tr>
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<td>-</td>
<td>RT</td>
<td>SiO₂</td>
<td>43</td>
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<tr>
<td>Au</td>
<td>(Me₂)Au(tfac)</td>
<td>3 at. % Au</td>
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<td>100pA</td>
<td>RT</td>
<td>SiO₂</td>
<td>41</td>
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<tr>
<td>Au</td>
<td>(Me₂)Au(tfac)</td>
<td>10 at. % Au</td>
<td>300</td>
<td>1nA</td>
<td>RT</td>
<td>SiO₂</td>
<td>41</td>
</tr>
<tr>
<td>Au</td>
<td>PF₃AuCl</td>
<td>Pure Au</td>
<td>25</td>
<td>300pA</td>
<td>RT</td>
<td>SiO₂</td>
<td>35</td>
</tr>
<tr>
<td>Au</td>
<td>(Me)Au(hfac)</td>
<td>50 at. % Au with Ar/O₂</td>
<td>10-30</td>
<td>-</td>
<td>RT</td>
<td>ITO</td>
<td>36</td>
</tr>
<tr>
<td>Au</td>
<td>Me₂Au(tfac)</td>
<td>35 wt.% Au e-(EDX) Rₑ=10⁹</td>
<td>25</td>
<td>100pA</td>
<td>RT</td>
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<td>25</td>
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<td>RT</td>
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<td>88</td>
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<td>dimethyl-gold-acetylacetone (DGAA)</td>
<td>Rₑ=2×10⁻⁴</td>
<td>5-20</td>
<td>200pA</td>
<td>RT</td>
<td>SiO₂</td>
<td>76</td>
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</table>

Properties of W, Pt, Au containing deposits obtained from the organometallic precursors by electron-beam-induced deposition. AES: Auger Electron Spectroscopy; EDX: Electron Dispersive X-ray spectroscopy; Rₑ indicates the resistivity ratio to the pure metal (ρₑdeposit / ρₑpure metal). Resistivity for pure metal: ρₑW = 5.6×10⁻⁶ Ω cm, ρₑPt = 1.05×10⁻⁵ Ω cm, ρₑAu = 2.44×10⁻⁶ Ω cm.
2.8. Summary

Until recently, most work on the nanostructure of EBID-fabricated materials has focused on metal-containing materials. Typically, the deposits are nanocomposites consisting of metal crystallites with diameters in the range of 1-10 nm, embedded in an amorphous matrix composed of reaction byproducts and impurities present at the substrate surface during EBID. It has been found that the thermal treatments on the EBID deposits can effectively increase the metal concentration in the deposit and the resistivity of these metal-containing deposits. The widely scattered resistivity data reported in the literature as a function of deposition parameters are intended to show a significant correlation with the nanostructures and chemical compositions of the metal-containing deposits. A systematic investigation of the structural and chemical character of the metal-containing deposits is necessary in order to understand how composition and nanostructure affect the electrical performance. In this work, the modifications of the nanostructures of the EBID deposits during the deposition process as well as post electron irradiation process have been investigated.


2.9. References


Chapter 3

3. Theory and simulation of EBID

In this chapter, different aspects of electron beam-solid interactions are discussed, including elastic and inelastic scattering, secondary electron generation and emission. These phenomena can have effects on the EBID growth process and on the properties of the deposited materials. Furthermore, possible electron-molecule interaction processes during EBID are discussed. Finally, a brief overview is given on the previous simulation works on the electron beam induced deposition process, including phenomenological EBID growth rate model, two-dimensional (2D) EBID growth model using raster electron beam, 2D and 3D Monte Carlo simulations based on electron-solid interactions.

3.1. Electron beam-solid interactions

3.1.1. Electron scattering

A finely focused electron beam with an energy range of 1-30 keV is generally used in EBID. When these energetic electrons hit the solid surface, a series of complicated interactions between electrons and the electrostatic fields of the substrate atoms will occur. These interactions, also called scatterings, can be divided into two categories: elastic and inelastic scattering depending on energy loss during the scattering process.

Elastic scattering involves Coulomb interaction with the atomic nucleus. The extensive electric field close to each nucleus can deflect the incident electron into a large
angle. Most of the electrons travel further away from the center of an atom, where the electrostatic field decreases quickly. As a result, these electrons are scattered through smaller angles. Elastic scattering usually involves negligible energy exchange when the scattering angle is small. The scattering process causes the electron beam to spread out laterally from the initial electron incident location. Some of the incident electrons which undergo elastic scattering maybe emitted out from the substrate after numerous scattering events as backscattered electrons. This process called backscattering provides an important class of information for SEM imaging.

Simultaneously with elastic scattering, inelastic scattering also occurs as a result of Coulomb interaction between incident electron and the outer atomic electrons surrounding each nucleus. Unlike elastic scattering, inelastic scattering involves a kinetic energy loss of an incident electron resulting from interactions between incident electron and the inner- and outer-shell electrons. During the interaction process of an incident electron with an inner-shell electron whose ground stage energy lies typically hundreds or thousands of eV below the Fermi level of the solid, the inner-shell electron may be excited into a higher energy state if it absorbs enough energy comparable to or exceeding the its binding energy, leaving an vacancy in the inner shell of the atom. As a result, the primary electron loses same amount of energy and the atom is left in an excited state. During the electron relaxation process, the outer shell electron or the inner shell electron of lower binding energy will jump and fill the hole and the excess energy is released as emission of characteristic X-Ray photon or radiationless Auger electron emission. For those excited outer-shell atomic electrons, if they have enough energy to reach the
surface and overcome the surface barrier, they may be emitted as secondary electrons (see Figure 3-1).

Figure 3-2 shows the intensity distribution\(^1\) of the various types of electrons emitted from a target under electron bombardment. Secondary electrons (SE) are specimen electrons with an average energy distribution of (0 to 50 eV), peaking in the range of 3-5 eV. SEs are usually used as signals for SEM imaging because they come from a shallow depth, providing high-resolution topographical images. Backscattered electrons (BSE) consist of high-energy electrons from the electron beam, which are reflected or back-scattered out of the specimen interaction volume by elastic scattering interactions with specimen atoms. In addition to those secondary electrons (SE\(_I\)), generated by the primary electrons emitting out from the primary beam incident position on the sample surface, secondary electrons (SE\(_II\)) can also be generated by the backscattered electron when they escape out of the surface. These low energy (< 50 eV) secondary electrons play a very important role in the dissociation process of the precursor molecules in EBID, which will be discussed in the following sections.
V.L. is vacuum level, V.B. valence band, C.B. conduction band, C.L. cathode luminescence, $\chi$ the electron affinity, $\Phi$ the work function, $E_f$ the Fermi level, $E_b$ the binding energy. The primary and secondary processes show the generation and emission of secondary electron, Auger electron, plasmon, X-ray photons during the electron solid interaction.
3.1.2. The electron-solid interaction volume

When the primary electrons propagate into the substrate, they will gradually lose energy via inelastic scattering until they are eventually thermally stable. The maximum depth below the substrate surface that the electrons can reach is called the penetration depth or the electron range\(^2\). The volume, shown as pear-shaped in cross-section inside the substrate, contains most of the scattered electrons and is called the interaction volume. The interaction volume is defined by energy loss through inelastic scatterings interactions and backscattering through elastic scatterings. The penetration depth and the shape of interaction volume of the electron beam are a function of the incident angle, beam energy,

Figure 3-2. Complete energy distribution of electrons emitted from a target.

Complete energy distribution of electrons emitted from a target, including secondary electrons (SE), backscattered electrons (BSE). AE, ELE and P donate Auger electron, energy loss electron, and primary electron. \(E_0\) is the primary electron beam energy.(From Ref. 1)
and the average atomic number (Z) of the substrate. Monte Carlo electron trajectory simulation\textsuperscript{2-5} is often used to predict the electron penetration depth and interaction volume. A lower-electron-energy beam generates a smaller interaction volume, as shown in Figure 3-3.

![Figure 3-3. Monte Carlo electron-trajectory simulations.](image)

Monte Carlo electron-trajectory simulations of the interaction volume in iron as a function of beam energy: (a) 10 keV, (b) 20 keV, and (c) 30 keV. (From Ref. 6)

**3.2. Low energy electron-molecule interaction**

EBID is initiated by dissociation of gaseous precursor adsorbates by energetic electrons crossing a substrate surface, forming reactive products that give rise to deposition. The knowledge of the fundamental electron impact reaction mechanism is
crucial to obtain full control of the EBID deposits’ physical and chemical properties, such as the purity and resistivity. Various interaction processes are involved in the complex electron-molecule collisions, such as excitation, ionization, attachment, and dissociation. Among these elementary processes, those that may lead to the dissociation of the precursor molecules are more important in EBID since one of its ultimate purposes is to obtain high purity metal deposits from inorganic or organometallic precursors. The dissociation process itself also contains different sub-processes including dissociative excitation, dissociative ionization, and dissociative attachment. Even though other mechanisms are also present during the electron-molecule interaction, here we only focus on the electron-impact dissociation mechanism.

Unlike electron-atom collisions, electron-molecule collisions are much more complicated. A simple diatomic molecule is used as an example to describe the electron-molecule interaction process.\textsuperscript{33,34} When a projectile electron is temporarily captured by a molecule, resonant scattering between the electron and molecule will occur. A resonant state can be considered as negative ion formed by the electron that temporarily occupies an orbital of this molecule. The transient molecular anions have more decay channels than their atomic counterparts due to the additional degrees of the freedom introduced by nuclear motion.
Figure 3-4. Electron induced reaction pathways for a diatomic molecule AB.

Source: Adapted from Ref. 33 and reproduced by Arumainayagam (Ref. 34).

Figure 3-4 illustrates the possible reaction pathways of a diatomic molecule AB. Electron impact excitation, electron attachment and electron impact ionization are the three main reaction pathways during the electron-molecule interaction. The departing electron may leave the molecule in an excited state \( AB^* \). \( AB^* \) may return to ground state, dissipating its excess energy via photon emission and/or energy transfer to neighbouring molecules. If the resulting excited neutral state is dissociative, \( AB^* \) may dissociate into two neutral radicals or an ion-pair (known as dipolar dissociation). Electron attachment to form a transient ion will also occur during electron-molecule interaction. Autodetachment, associative attachment and dissociative electron attachment (DEA) are the three possible decay pathways for this transient ion. Finally, the incoming electron can directly ionize
the molecule AB to yield AB^+*, which may further fragment, as shown in Figure 3-4. Detailed discussions can be found in references^{33,34}.

Each of these above mechanisms can be described by an energy dependent cross section $\sigma(E)$. $\sigma(E)$ (cm^2) is generally expressed as the probability that an electron induces the scission of a bond in a precursor molecule. The larger the cross section, the larger the probability that a bond in the molecule can be broken. This parameter, specific for each type of precursor molecule, in practice is only well known for a few simple gases. Among these gases, electron interaction with Tetrafluoromethane (CF_4), a halogenated etch gas molecule mostly used in semiconductor processing, has been extensively investigated. For example, electron impact cross sections for dissociative ionization,^7 neutral dissociation,^8-10 and dissociative electron attachment ^11,12 of CF_4 have been reported. The electron impact dissociation cross sections of CF_4 has a threshold at 10-50 eV and a maximum value at 70–100 eV with slowly decreasing values on both lower and higher energies.\(^12,13\)

Experiments to measure dissociation cross section for the precursor molecules normally used in EBID are difficult to perform. For most of the gas precursors used in EBID, there are not enough complete experimental data. This is due to the difficulties in detecting the neutral products resulting from the dissociation, as well as the multitude of possible dissociation pathways, which increase with the complexity of the molecules. Recent experiments on determination of electron induced dissociation of several carbonyls and Cu-containing precursor molecules have shown that low-energy electrons are closely relevant for the deposition process. Hoyle \textit{et al.}^14 studied focused electron beam induced deposition from W(CO)_6 at beam primary energies between 0.06 keV and
Decomposition cross sections of $\text{W}(\text{CO})_6$ for primary energies below about 1 keV were found to be about a factor of 4 larger than those at 20 keV. Figure 3-5 shows the electron impact decomposition cross section for $\text{W}(\text{CO})_6$ and secondary electron (SE) yield of pure W. Clearly, the cross section and the secondary yield have a relatively large overlap among the primary electron beam energy range. This indicates the low energy secondary electrons play a very important role in the decomposition process. In addition, the lower resistivity of the deposits formed using low primary energies indicated higher metallic content, which was attributed to the higher decomposition efficiency at low energies.

Figure 3-5. Electron impact decomposition cross section and SE yield of pure tungsten.

Electron impact Decomposition cross section for $\text{W}(\text{CO})_6$ and secondary electron (SE) yield of pure tungsten. (From Ref. 15 and 14)

Mezhenny et al.\textsuperscript{16} investigated the effects of low energy electron impact on the molecule $\text{Cu}(\text{I})(\text{hfac})(\text{vtms})$ decomposition on clean Si(111) in an ultrahigh vacuum
(UHV) chamber with a base pressure of ~5×10^{-11} Torr. The electron energy threshold for decomposition was found to be 4±0.5 eV. It suggested that a DEA process was the main decomposition channel of the molecule in this threshold region. In addition to using experiments to measure the molecular dissociation cross sections, the energy dependence of the cross sections have also been modeled or calculated in theoretical ways. Mitsuishi et al. \cite{17} calculated the energy-dependent dissociation cross section for W(CO)₆ using the method described in reference. \cite{13} In their Monte Carlo simulations, the cross section peak position was chosen to be at 100 eV with a threshold value at 35.5 eV. These studies clearly indicate that dissociation mechanisms, including dissociative ionization, neutral dissociation, and dissociative electron attachment have cross sections that have their maximum far below the primary beam energy (1-30 keV) generally used in EBID. \cite{13} Generally, the energy-dependent dissociation cross section has a relative large overlay with the energy spectrum of the low-energy electrons, which suggest that the secondary electrons generated during deposition process might dominate the dissociation process. \cite{18} More detailed studies of the electron-impact dissociation cross sections of the precursor molecules used in EBID are still needed to clarify the complex mechanisms behind the electron beam induced chemistry.

### 3.3. EBID simulations and models

In order to elucidate the complex electron-solid-adsorbed precursor molecules interactions associated with EBID, experimental studies have been carried out to determine the specific type of electrons responsible for the dissociation process of the precursor molecules. Among these experiments, understanding and improving the
resolution limits have been attracted much attention in the EBID community. Kohlmann-von Platen et al.\textsuperscript{19} investigated dissociation of precursor gas W(CO)$_6$ with the aim of determining the resolution limiting parameters during EBID process. They found that the surface growth was correlated to the number of secondary electrons (SE) emitted by the primary electron beam from the W needle surface and demonstrated that the beam diameter mainly limits the deposit resolution. Hiroshima et al.\textsuperscript{20} deposited W wires from the EBID of WF$_6$ precursor by a beam raster process and also attributed nanopillar diameter growth to SE stimulated deposition. Koops et al.\textsuperscript{21} concluded that BSE’s induced deposition at the flanks of growing features and limited the aspect ratio achievable by an electron-stimulated process. Recently, Rack et al.\textsuperscript{22} deposited high-aspect ratio W pillar from the EBID of WF$_6$ over the electron beam energy range (500 eV-20 keV) on SiO$_2$ substrate. It suggested that primary, secondary, and backscattered electron all contributed to the total volume of the deposited nanopillar due to the large overlap of between the integrations of these three types of electrons and a dissociation cross section for WF$_6$.

Furthermore, thin specimen substrates (e.g., TEM Cu grid with thin carbon film, Silicon nitride membrane substrate) and high kinetic energy (100-300 keV) were also applied to improve the ultimate EBID resolution. Thinner substrates (30-100 nm) have less scattering events and high energy electron beam used in scanning transmission electron microscope usually has the smallest primary beam size. Recently, further enhanced spatial resolution has been achieved using high energy (100-300 keV) electron beams, thin substrates (10-30 nm) and low electron doses. EBID-grown nanodots and nanowires with sub-5 nm diameters have been reported.
One of the most practical interests for EBID is how material is deposited by electron beam under given experimental conditions. However, the EBID process actually involves a very complex reaction system. The deposition rate or the shape evolution of the deposits are determined by various experimental parameters, such as

- The impinging precursor molecule flux
- The sticking coefficient
- The volume of the deposited molecules
- The adsorption time of molecule
- The dissociation cross section by electron impact
- The surface diffusion coefficient of the molecule

![Figure 3-6](image)

**Figure 3-6.** Precursor molecule depletion and replenishment in an ideal EBID process.

The nonvolatile dissociation products form the deposit and the volatile fragments are pumped away. (From Ref.15)

Hence, modeling and simulating the various inherent material parameters and variables in the EBID process is useful to predict the general trends of the deposition profile.
Currently, there are two categories of modeling work including continuum model and Monte Carlo electron-solid interaction model, which have been reported in the EBID literature. Some examples of these models will be discussed in the following sections.

### 3.3.1. Continuum model

Growth rate, in terms of deposited volume (nm$^3$) or deposit height (nm) per unit time is one of the most often measured EBID parameters. The measurements of the growth rate as a function of the experimental conditions can be used to evaluate the growth efficiency. Other practical reasons for measuring the growth rate are, for instance, to determine the rate of contamination growth in an electron optical system, to find suitable growth conditions for the fabrication of applications, or to study fundamental aspects of the deposition process.$^{18}$

Given a system with rotational symmetry, the steady-state deposition rate ($R$) as a function of distance ($r$) from the center of the primary beam can be expressed as:

$$R(r) = Vn(r)\int_0^{E_0} \sigma(E)f(r, E)dE$$  \hspace{1cm} (3.1)

where $V$ is the decomposed precursor molecule volume, $n(r)$ is the surface adsorbate number density, and $E_0$ is the primary beam energy. The energy dependent dissociation cross-section $\sigma(E)$ determines the probability that an electron induces the scission of a bond in a precursor molecule, leading to the deposition of nonvolatile fragments or volatile by-products. The $f(r, E)$ is the flux distribution of electrons crossing the substrate, including the incident primary electron beam as well as the emitted secondary and
backscattered electrons. The entire energy spectrum is responsible for the dissociation of surface adsorbed molecules.

Most of the continuum models are based on the time-dependent macroscopic model for focused ion beam induced deposition.\textsuperscript{23-27} Similar considerations apply for EBID where the surface density of molecules the EBID process can be described by a differential adsorption equation consisting four terms: adsorption, diffusion, desorption and decomposition. Adsorption is governed by the local precursor flux $J$, the sticking coefficient of the molecule $s$, and the surface coverage $n/n_0$ (where the density of a full monolayer is $n_0$). Surface diffusion to the irradiated area from the surrounding surfaces depends on the concentration gradient as well as the surface diffusion coefficient $D$. Spontaneous desorption of physisorbed molecules after a residence time $\tau$ is a function of substrate temperature. Precursor dissociation is governed by the product $\sigma(E)f(r,E)n$. Thus the change in particle density $\partial n/\partial t$ is given by:

$$\frac{\partial n}{\partial t} = sJ\left(1 - \frac{n}{n_0}\right) + D\left(\frac{\partial^2 n}{\partial r^2} + \frac{1}{r} \frac{\partial n}{\partial r}\right) - \frac{n}{\tau} - \frac{\sigma fn}{\text{decomposition}}$$

(3.2)

There are some limitations for this model. For example, there exists very little fundamental data (such as adsorption energy, adsorbate diffusion coefficients, sticking coefficients, and dissociation cross sections) for the precursors of interest to EBID. This lack of information caused several research groups to use different expressions to approximate the real dissociation cross sections\textsuperscript{31,35,36} and make various assumptions in their simulations. Such models do, however, offer valuable insights into the phenomena
that occur and can be manipulated to predict deposit dimensions and growth rate, which in turn control the deposition process. For example, Rykaczewski et al.\textsuperscript{28} predicted the three-dimensional morphology and the growth rate of carbon nanopillars using a comprehensive dynamic model coupling surface diffusion, electron transport and scattering, electron density distributions. Toth et al.\textsuperscript{29} compared competitive electron beam induced deposition and etching processes by incorporating the additional terms for adsorption and diffusion of etch precursors into the above equation. They demonstrated athermal electron flux controlled transition between material deposition and etching. The dependence of ultimate etching/deposition profile on various parameters including the electron-impact dissociation cross sections for deposition and etching precursor molecules and electron flux distribution were investigated. More recently, this group has extended their model by incorporating a radially-symmetric electron flux profile, and surface diffusion of adsorbates to demonstrate how simultaneous EBID and electron beam induced etching (EBIE) has the potential to greatly improve the resolution of nanostructures fabricated on both bulk and thin substrates by using the effects of adsorbate depletion to induce an abrupt transition between deposition and etching.\textsuperscript{30} Figure 3-7 (a) shows the steady state growth rate (molecules/Å\textsuperscript{2}/s) plotted as a function of radius (r) from the beam axis, calculated using a deposition precursor partial pressure of 10^{-2} Pa at a number of currents. Evolution of the pillar growth rate profiles can be clearly seen while the beam current is increased. The transition was attributed to the depletion of deposition precursor adsorbates under the beam causes the etching rate to exceed that of deposition, giving rise to a purely ring-like deposition profiles as shown in Figure 3-7(b).
Figure 3-7. Growth rate and surface plot as a function of radius (r) from the beam axis.

(a) Growth rate plotted as a function of radius (r) from the beam axis, calculated using currents of 0.4, 0.5, 0.52, 0.55, 0.6, 0.7, 0.8 and 1 nA. (b) Surface plots of the 0.4, 0.5 and 0.6 nA deposition rate profiles (linear scale) (P = 10^-2 Pa). (From Ref. 30)

3.3.2. Monte Carlo model

As the spatial resolution of EBID is related to the distribution of electrons contributing the dissociation of the precursor molecules, Monte Carlo (MC) simulation is helpful for understanding the EBID process. The advantage of using MC simulations to model the EBID process is that the trajectories of all the primary electrons and the backscattered electrons as well as the generated secondary electrons can be traced together with their corresponding energies as they pass through any surface and material (see Figure 3-8). By tracking the electron position, each time an electron traverses the surface (either the substrate or the freshly deposited material), the probability of dissociation event leading to deposition is determined. Several models based on Monte Carlo simulations have been reported in the literature.
Silvis-Cividjian et al.\textsuperscript{31} developed a 2D EBID model based on electron interactions with the thin solid target (10 nm carbon film) in order to elucidate the limits of resolution. This model showed that the diameter of the carbon contamination tip saturated with increasing electron exposure time (as shown in Figure 3-9), which confirmed the major influence of the secondary electrons on the EBID resolution.

Figure 3-8. Electron types involved in EBID process.

Deposition events induced by various possible sources of electrons. (From P.D. Rack’s presentation at 1\textsuperscript{st} International Workshop on Focused Electron Beam Induced Processing (FEBIP), Delft, Netherlands, June 2008)
Figure 3-9. 2D EBID growth model.

(a) A sequence of cross-sectional simulated profiles for a singular contamination dot grown by a zero-diameter electron beam; (b) Time evolution of the dot geometry: the dot height (●), the dot diameter measured at the base (▲), and the dot diameter measured at half maximum height (■). (From Ref. 31)

One of the purposes in EBID simulation is to determine the probability for electron-impact precursor molecule dissociation, the variable $\sigma(E)$ mentioned before. We already know that the molecules are more likely dissociated by those low energy electron generated by electron-solid interactions. So in Silvis-Cividjian’s MC model, contribution to deposition from primary electrons (PEs), backscattered electrons (BSEs) and forward-scattered electrons (FSEs) are not considered due to the energies of these electrons are much higher than that of the secondary electrons (SEs).\textsuperscript{31} However, this model clearly demonstrated the importance effects of SE dissociation on lateral broadening of nanopillars, while the deposit morphology could be underestimated due to neglecting the scattering effects occurred in the thin substrate and the as-grown material.

Even though SEs induced deposition have been widely accepted in the EBID community, recent research results have also shown that other electron species other than SE can initiate molecule dissociation. In some circumstance, these electrons can actually
dominate the growth characters such as the growth rate and morphology. Fowlkes et al.\textsuperscript{22} developed a 3D MC simulator in which SEs as well as PEs, BSEs and FSEs were all tracked during EBID process. They demonstrated that the relative contribution to vertical tungsten nanopillar growth for PE electrons was even higher than that of SE over the primary beam energy range of 500 eV-20 keV. Liu et al.\textsuperscript{32} confirmed the role of primary electrons during deposition in their 3D dynamic MC simulation, showing the preferential growth of deposit along the incident direction of the electron beam (20-200 keV) on both side of a 10 nm-thick tungsten substrate. SEs and BSEs emitting from the top surface of substrate were attributed to the deposition of the upside part, while the transmitted PEs and SEs emitting from the bottom surface were attributed to the deposition of the downside part and the contribution of PEs is more significant that that of SEs.\textsuperscript{32} Recently, Smith et al.\textsuperscript{22} systematically studied the growth characteristics of the EBID tungsten nanopillar from WF\textsubscript{6} on W substrate using a 3D MC simulator. It successfully recorded the deposition events caused by various electrons including SE, PE, BSE, FSE. Figure 3-10 displayed the 3D grown structure with spheres representing deposited atoms resulting from each type of electron-initiated dissociation events. Simulations involved pillars grown under reaction-rate-limited regime (precursor flux >> electron flux) and mass-transport-limited regime (electron flux >> precursor flux) using 1 keV and 5keV primary electron beams. The effects of the beam energy on the growth rate and morphology of the W nanopillar were investigated. It suggested that the shape and morphology of the pillar structure were independent of the primary electron beam energy over the energy range 1-5 keV for the reaction-rate-limited condition. One significant result from this work was that vertical pillar growth rates were faster at lower beam
energies while still maintaining high lateral resolution, which is preferable for EBID as a mask repair tool where contamination and throughput issues are most often concerned.

Figure 3-10. W pillar growth, simulated under reaction-rate-limited conditions.

Two million electrons have been simulated. The deposited atoms are classified into five categories, depending on the type of electron species initiating dissociation events (red = PE, green = FSE, blue = BSE, yellow = SEI, and cyan = SEII). (From Ref. 22)

3.4. Summary

In summary, even though the current available models have capability to predict the growth rate, and morphology of the EBID deposits, no model is currently capable of predicting internal microstructure (e.g., metal grain size, packing density), or bonding
structure, all of which strongly influence the material properties and functionalities of the deposit. One important challenge for EBID modeling work is that very little fundamental data (such as dissociation cross sections, adsorbate surface diffusion coefficients, sticking coefficients for most metal-containing precursor molecules used in EBID experiments) are available. Many authors have used modified models (i.e., use modified ionization cross section instead of the dissociation cross section\textsuperscript{22}, or use dissociation cross section data from other molecules to substitute the original complex inorganic or organometallic precursor molecules\textsuperscript{31}). As a result, the accuracy of the EBID models might be limited.
3.5. References


Chapter 4

4. Experimental setup

In this chapter, the generic experimental setups are described, including the EBID instruments, precursor gases, deposition parameters, substrates. The details for each experiment will be described in the Chapter 6 to 8, respectively.

Two scanning electron microscope systems were used for the electron beam induced deposition experiments. A high vacuum SEM instrument, FEI Nova Nanolab 600 SEM/FIB dual beam system was used to perform deposition experiments using organometallic precursors, including methyl cyclopentadienyl (trimethyl) platinum (IV) \([(\text{CH}_3)_3\text{CH}_3\text{C}_5\text{H}_4\text{Pt}]\), and tungsten hexacarbonyl \([\text{W(CO)}_6]\). A modified FEI Sirion NC 600 environmental SEM system was used to perform W and Pt deposition using carbon-free precursors, including tungsten hexafluoride\([\text{WF}_6]\) and tetrakis (trifluorophosphine)-platinum (0) \([\text{Pt(PF}_3]_4)\). The main features of these apparatus are described in Section 4.1. The precursor details are described in Section 4.2. The EBID deposition experimental parameters, such as electron beam parameters, substrates, etc. are described in Section 4.3. Monte Carlo simulations of electron energy deposition profiles are described in Section 4.4. The analytical characterization techniques are summarized Section 4.5.
4.1. Deposition system overview

4.1.1. FEI Nova Nanolab 600 dual beam system (high vacuum deposition)

The complete overview of the dual beam system is shown in Figure 4-1. The High-resolution Field Emission-SEM column with a Schottky thermal field emitter is oriented normal to the sample surface, while the ion column is oriented at approximately 52 degrees from the vertical SEM column, as shown in Figure 4-2. Both beams coincide at a crossover point 5 mm below the objective lens of the SEM. The geometrical arrangement of the two columns enables perpendicular tilt of the sample to the ion beam in the coincidence point for FIB deposition or milling.

Both electron and ion beam can be used to perform beam assisted depositions. High-resolution SEM column is used for SEM viewing of the sample afterwards. The
resolution is 1.5 ~ 2.0 nm at the beam coincidence point (working distance = 5 mm) for beam energy of 5 to 15 keV. FIB is also used to prepare cross-sections for SEM viewing and TEM sample preparation.

A computer controlled gas injection system is used to handle three different gases for metal (Platinum, Tungsten) deposition and insulator enhanced etching (XeF₂). To complete the analytical capabilities of the system the specimen chamber is equipped with several analytical attachments like energy dispersive x-ray detectors for EDS analysis as well as an electron backscattered diffraction detector for EBSD analysis.

![Figure 4-2. CCD image of the experimental setup inside the vacuum chamber.](image)

4.1.2. FEI Sirion NC 600 environmental SEM system (low vacuum deposition)

EBID experiments have also been carried out using a customized FEI Sirion NC 600 ESEM system. A schematic illustration of the system is shown in Figure 4-3. Similar to normal SEM, low vacuum SEM is also a high-resolution technique with the ability to
obtain secondary electron images of specimens, specially the uncoated, nonconductive specimens.

In the general ESEM operation process, a small amount of imaging gas (e.g., water, nitrogen) is introduced into the specimen chamber, resulting in a chamber pressure of a range of 0.1 to 20 Torr.\(^1,2\) The gas molecules are ionized by the energetic primary electrons, as well as by those emitted from the specimen (e.g., backscattered electrons). Gas molecules ionized by the electrons inside the chamber can effectively neutralize the charge from the sample. Secondary electron (SE) images can be obtained using a gaseous secondary electron detector. On this instrument, a new Helix detector is used to collect secondary electrons. Since the chamber pressure is relatively high compared the normal SEM system, pressure limiting apertures (PLA), located in the final lens of the electron column are essential for ESEM to maintain a good vacuum in the electron column chamber while the gas are present in the specimen chamber. This is realized by pumping the regions below, between, and above the PLA separately to provide a graduated vacuum from as high as 50 Torr in the sample chamber to \(10^{-6}\) Torr (or better) in the column and emission chamber, as shown in Figure 4-3.

Residual gas analysis (RGA) of precursors in the ESEM chamber was performed using a differentially pumped RGA (Pfeiffer ThermoStar GSD 300T, modified to eliminate the heated quartz capillary supplied with this unit). Neutral gas molecules are leaked into the RGA unit, where they are ionized using an electron source and analyzed using a Prisma Quadrupole mass spectrometer (QMS 200). The details of RGA analysis are described in Appendix II.
4.2. Choice of precursors

The choice of precursor is mostly determined by the fact whether it is readily available. In most cases, inorganic or organometallic molecules, which are commonly used in ALD/CVD metal deposition processes, can be used as precursors for EBID. Many different precursors have been tried for EBID. Among them, W(CO)\textsubscript{6} and (CH\textsubscript{3})\textsubscript{3}CH\textsubscript{3}C\textsubscript{5}H\textsubscript{4}Pt are the most popular organometallic precursors and WF\textsubscript{6} and Pt(PF\textsubscript{3})\textsubscript{4} are the most frequently used inorganic carbon-free precursors for metal containing deposits during EBID process. The inorganic precursor has the potential for producing high purity deposits presumably because it does not contain carbon and oxygen. In this work, the above four precursors are selected for EBID experiments. Both organometallic
and inorganic carbon-free precursors are available for the same metal containing deposits. Organometallic precursors were used to produce carbon-containing deposits, which will be studied by EELS analysis to extract the impurity carbon chemical bonding information.

### 4.2.1. Precursors for high vacuum EBID

In this research, two precursors were used to perform the EBID deposition experiments in high vacuum environment, including tungsten hexacarbonyl \([\text{W(CO)}_6]\) and methylcyclopentadienyl (trimethyl) platinum (IV) \([(\text{CH}_3)_3\text{C}_5\text{H}_4\text{Pt}\)]. A brief summary of these two precursors is listed in Table 4-1. The crucible temperature was set as 45°C and 50°C for Pt precursor and W precursor, respectively. The precursor vapor was delivered using a capillary-style gas injection system. The distance between the bottom of the precursor injection needle and the sample surface was about 100 µm at 5 mm working distance. A detailed analysis of gas flow and the local pressure distribution nearby the sample surface can be found elsewhere.³

### 4.2.2. Precursors for ESEM EBID

Two precursors were used to perform the EBID deposition experiments in environmental SEM (low vacuum environment), including tungsten hexafluoride \([\text{WF}_6]\) and tetrakis(trifluorophosphine)platinum(0) \([\text{Pt(PF}_3)_4]\). A brief summary of these two precursors is listed in Table 4-2. These precursor gases have the potential for producing high purity deposits presumably because they do not contain carbon and oxygen. The precursor gas flow control valve was adjusted to achieve a stable specimen chamber pressure of 100 mTorr to 150 mTorr, depending on specific precursors (i.e., \(P_{\text{WF}_6}:100\) mTorr and \(P_{\text{Pt(PF}_3)_4}:120-150\) mTorr).
Table 4-1. W(CO)$_6$ and MeCpPt[Me]$_3$ precursor properties.

<table>
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<th>Trimethyl(methylcyclopentadienyl)platinum(IV)</th>
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</thead>
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<td></td>
</tr>
<tr>
<td>Name</td>
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<tr>
<td>Other name</td>
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Table 4-2. WF₆ and Pt(PF₃)₄ precursor properties.

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4.3. EBID deposition parameters

The electron energy \( (E_0) \) used for deposition is varied from 5 to 30keV. The electron probe current \( (I_p) \), measured by focusing the electron beam in a Faraday cup on the sample holder, is varied from hundreds of pA to several nA. EBID can be performed by operating the electron beam in spot mode (stationary beam) or scanning mode (line scanning). In line scanning mode, the beam energy and current are 20 keV and 2.0 nA, respectively. The working distance is 5 mm. The focused electron beam is set line scan mode with a line scan time ranging from 0.0256 ms (fast scan) to 512 ms (slow scan) at a field of view of 20 \( \mu \)m. The total deposition time is 5 minutes for each line deposit.

In spot mode, the electron beam is located at a point on the substrate. The beam can be moved in x-y directions from the microscope control console in customer service mode. To study the effects of electron flux and fluence on the microstructure and composition of materials fabricated by EBID, the electron beam diameter was varied by changing the excitation current of the objective lens, yielding accurate control over the electron flux at the substrate surface. All other microscope parameters were unchanged. Prior to EBID, the working distance was set to 5 mm and the electron beam was focused onto the sample surface. Test structures were then deposited as a function of the change in objective lens excitation current, and the deposit diameters were measured. The dependence of beam diameter on lens excitation (in terms of working distance) can be obtained, as shown in Figure 4-4.
Figure 4-4. EBID test structures.

(a)-(b) SEM images (taken using a sample tilt of 52°) of the EBID Pt test structures, the scale marker is 5µm; (c) calibration curve of deposit size as a function of the position of the focal plane below the pole piece.

The diameter of the electron beam used in this work has a range of several hundreds of nanometers to several microns. For the deposits versus electron flux experiments, the deposition time for each deposit is 2 minutes. In order to prepare large disk-like structures (see Figure 4-5) for Auger and cross-sectional TEM analysis, the objective lens current was fixed at a value that yielded a highly defocused electron beam for deposition. All EBID was performed using a stationary electron beam, eliminating ambiguities arising from EBID growth kinetics caused by changes in pixel overlap and dwell revisit times.
Figure 4-5. SEM image of the large Pt deposit.

SEM image of the Pt deposit (taken using a sample tilt of 52°). Deposition conditions: $E_0 = 20$ keV, $I_p = 2.0$ nA, spot mode, $t_d = 45$ minutes, $(\text{CH}_3)_2\text{CH}_3\text{C}_2\text{H}_4\text{Pt}$, $WD = 9$ mm.

For ESEM EBID experiments, the beam energy was fixed at 20keV and beam current was varied from tens of pA to tens of nA. Similar to the high vacuum EBID experiments, spot mode (stationary beam) or scanning mode (line scanning) were also applied to make disk-like and line deposits. In line scanning mode, two set of samples were made. The first set of line deposits were fabricated using an electron beam with fixed energy of 20 keV and current of 3 nA. The line scan time was from 0.21 ms to 233 ms. Line scan length (i.e., field of view) is 20 μm and the total deposition time was 5 min for each line deposit. Line deposits were also made using various beam current (40 pA-4 nA) to study the resistivity as function of beam current.

For deposits made in spot mode, the electron beam diameter was controlled in the same manner as mentioned in previous section. All the depositions were performed at
beam energy of 20 keV and various beam current of tens of pA to tens of nA. Deposition time was generally 1-32 minutes for different experimental purposes. Large deposits were also prepared for Auger and TEM analysis.

4.4. Substrate for EBID

Most of the depositions are done on Si substrate. In some cases the substrate choice depends on the characterization technique. (i.e., silicon nitride membrane for TEM and EELS analysis). The following substrate have been used: commercial p-type Si (100), Silicon nitride membrane substrate (30 nm), four-point probe substrate (5 nm Cr and 100 nm Au on a Si substrate with a 1000-nm-thick thermally grown SiO2 layer, patterned by general lithography and wet-etching techniques).

Prior to deposition, the bulk substrates are cleaned by rinsing first in acetone, then deionized water ultrasonic bath and dried with a N2 spray. After the bulk substrates are transferred into the vacuum chamber, an Evactron 25 De-Contaminator [XEI Scientific, Inc] (0.4 Torr of air, 13 Watts, 1 hour) so as to volatilize residual hydrocarbons on the substrate surface and inside the vacuum chamber.

In ESEM EBID experiments, bulk and thin substrate were used. Bulk substrates include p-type Si (100), n-type GaAs (100) and four-point probe substrate. The substrates were first annealed at 110°C in air for about 2 hours, then plasma cleaning was performed. Four-point probe substrate was also used to measure the resistivity of line deposit from Pt(PF3)4.
4.5. Monte Carlo simulations of electron interactions

This section gives a brief overview on the physical processes that occur when an electron beam interacts with a solid target and how Monte Carlo methods can be used to simulate these processes. A detailed mathematical description of the mathematics is outside the scope of this work, and comprehensive treatment of this simulation method can be found in references4,5.

When a high-energy electron beam hits the solid surface, a series of complicated interactions between electrons and the electrostatic fields of the substrate atoms will occur. These interactions, also called scatterings, can be divided into two categories: elastic and inelastic scattering depending energy loss during the scattering process. During elastic scattering, the incident electron is deflected to a new trajectory with no energy loss. After several elastic scattering events, the electrons will spread out and some of them may escape the sample surface as backscattered electrons. The incident electrons will also gradually lose their energy with distance travelled via inelastic scattering. Kinetic energy is transferred to the substrate, producing signals that can be used for imaging and elemental analysis in electron microscopy, such as secondary electrons, auger electrons, and characteristic X-rays. A number of mathematical models have been developed to describe the probability of an electron undergoing elastic and inelastic scattering event. Mott’s elastic scattering cross-section6 is most often employed for elastic scattering modeling. For inelastic scattering, the Bethe's stopping power7 equation is used to describe the rate of energy loss with distance travelled.

In a Monte Carlo simulation, the electron trajectory is recorded in a stepwise manner from its entry point until it loses all of its energy and stops in the solid or until the
electron is backscattered. At each point, the probability of the electron undergoing scattering, the scattering angle, distance between scattering events and the rate of energy loss is calculated from appropriate physical models. The location of the electron within the sample and its kinetic energy is constantly updated with time. In order to obtain a statistical distribution of the electron scattering events, a large number of simulated electrons and random numbers need to be used to describe the stochastic process. As a result, the accuracy of any simulation depends on the models and assumptions and is only as accurate as the formulae and tabular data that are used to describe the various processes. Improvements to the approximations adopted to describe the elastic and inelastic scatterings in the past several decades have demonstrated that Monte Carlo method has become a powerful tool for simulating the distributions of secondary, backscattered and transmitted electrons, energy dissipation and generation of characteristic X-rays.

In this work, Monte Carlo simulations were performed using the package CASINO,\(^8\) which was originally developed by the research team of Raynald Gauvin at Université de Sherbrooke, Canada. Mott’s elastic cross-sections\(^6\), and a modified expression for the Bethe stopping power\(^7\) are implemented in this version of CASINO. Simulations of electron energy deposition into the sample at different stages of deposit growth in EBID were performed and depth-resolved energy deposition profiles were obtained using the methodology described by Toth and Phillips\(^9\).

Specifically, each simulation was performed using \(10^5\), 20 keV primary electrons. Densities of 7.16, 5.32 and 2.33 g/cm\(^3\) were used for WO\(_3\), GaAs and Si, respectively. As for Pt deposit prepared in high vacuum SEM instrument, the substrate was approximated
by bulk Si (i.e., the SiOₓ overlayer was ignored), and the EBID-grown nanocomposite by bulk PtₓC₁₋ₓ with a Pt atomic fraction of 0, 0.2, 0.4 and 0.6, respectively. The densities for amorphous C and pure Pt were assumed to equal 2.2 g/cm³ and 21.5 g/cm³, respectively.

4.6. Analytical characterization techniques

Analytical characterization of EBID structures includes morphological, structural and chemical analysis. In this chapter, several different characterization techniques for EBID deposits have been discussed. Morphological analysis has been performed with scanning electron microscopy (SEM), environmental scanning electron microscopy (ESEM), focused ion beam (FIB), and transmission electron microscopy (TEM). Structural characterization has been carried out by selected-area electron diffraction (SAED), Convergent beam electron diffraction (CBED) using TEM. Chemical composition has been studied by Auger electron spectroscopy (AES), energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS). The electrical properties of EBID metal line deposits have been measured by four-point probe method. The detailed analytical characterization techniques are discussed in the following sections.

4.6.1. Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) analysis was carried out mainly FEI Nova 600 NanoLab SEM/FIB dual beam system to measure the topography and dimension of EBID deposits. It has a high-resolution field emission SEM column with a monopole magnetic immersion final lens and Schottky thermal field emitter. An energetic electron beam (1-30 keV) is focused into an approximately nanometer size spot on the specimen. When the electrons hit the specimen surface, various signals, including secondary
electrons (SE), backscattered electrons (BSE), Auger electrons, X-ray photons can be generated during electron-specimen interactions. Secondary electrons (SE) are collected by an Everhart-Thornley (E-T) detector or a through lens detector (TLD) and can be used to form a variety of images by modulating the brightness of a cathode ray tube (CRT) synchronized with the scan on the specimen. The SEM column on this dual beam system has a resolution of 1-5 nm depending on the sample, current column conditions and skill of the operator. For a primary electron beam energy of 20 keV and 5 mm working distance (mostly used in this work), the resolution is 1.5 – 2.0 nm.

### 4.6.2. Focused Ion Beam (FIB)

Focused ion beam (FIB) on the dual beam system mentioned before was used to prepare the cross-sections for SEM viewing. FIB system is similar to SEM in that it involves scanning a highly focused ion beam (rather than electrons) over a sample. The ions are field extracted from a liquid metal ion source\(^{10,11}\) (LMIS) which consists of a tungsten needle with a radius of curvature of 1 μm wetted by a liquid metal. High intensity electric field (~10\(^8\) cm/V) is applied on the wetted tip to form a Taylor’s cone with a radius of curvature of about 10 nm from which the ions are field extracted and ionized. The current density of extracted ions can be on the order of ~10\(^8\) A/cm\(^2\)). Gallium (Ga)\(^{12,13}\) is the most commonly used liquid metal for commercial FIB instruments. Once the Ga\(^+\) ions are extracted form the source, they are accelerated through a potential down to the ion column. The typical accelerating voltages range from 5 to 30 keV. Then the ion probe is formed by the condenser lens and focused on the specimen by the objective lens of the ion column. Similar to electron-solid interactions, the bombardment of energetic ions to the specimen surface will generate secondary
electrons (and ions), which can be collected to form an image of the surface of the sample. The ion beam allows the milling of small trenches and holes in the sample at well localized sites, so that cross-sectional images of the structure can be obtained either by SEM or FIB imaging. Another important application for FIB is site-specific cross-sectional TEM sample preparation. In this work, all of the TEM samples are made by using the dual beam systems.

4.6.3. Transmission Electron Microscopy (TEM)

One of the typical characters of nanophase materials is the small particles. As has already been shown that the EBID materials are generally nanocomposites where the metal crystals are in nanometer scale. Although some structural information can be obtained by X-ray diffraction techniques, direct imaging of the nanoparticles and the internal structures is only possible using transmission electron microscopy (TEM).

To date, the analytical transmission electron microscopy has been well established as one powerful analytical technique in materials science because specimens can be well-characterized at the nanoscale using a combination of imaging, analytical, and electron diffraction techniques. TEM is unique because it can provide a real space image of with atomic resolution as well as chemical information at a spatial resolution of 1 nm or better. Electron diffraction in TEM can provide information on the lattice parameters and orientation of the nanocrystals. Convergent beam electron diffraction (CBED) can determine the structure, symmetry details and atom positions in a crystal as small as several nanometers in size. The microscope used for this work was a JEOL 2010F high-resolution TEM with a Zirconated tungsten thermal field emission tip operating at an acceleration voltage of 200 kV. It has a spatial resolution of 1.9Å and a lattice resolution...
of 1.02 Å. Since TEM was the primary characterization tool used in this work, some details about major techniques used in TEM will be discussed in the following subsections.

4.6.3.1. The illumination system

The conventional TEM illumination system takes the electrons emitting from the gun and transfers them to the specimen giving either a broad parallel beam or a focused beam. This is usually done by adjusting the first two condenser lens (C1, C2) located below the gun system. The electron beam is refocused by adjusting C2 before the objective lens resulting in a more coherent beam, as shown in Figure 4-6(a). The parallel illumination is essential to obtain sharpest diffraction patterns and the best image contrast. Small illumination area can be achieved by simply changing the C2 lens to focus the beam on the specimen, as shown in Figure 4-6(b). A focused beam is usually used when local chemical analysis is required, i.e., the elemental identification of specific grain or precipitate in the specimen. A convergent beam is also often used to generate the micro- or nano-diffraction pattern to identify the grain structure at nanometer scale.
4.6.3.2. The imaging system

There are two basic operation modes for TEM, imaging mode and diffraction mode which can be switched easily between each other. In imaging mode, the objective lens forms a diffraction pattern in the back focal plane with electrons scattered by the sample and recomines them to generate an image in the image plane (intermediate image 1). In diffraction mode, the intermediate lens selects the diffraction pattern formed in the back focal plane of the objective lens and forms an image in its image plane (second intermediate image). This image (diffraction pattern) is magnified and projected on the viewing screen. The Figure 4-7 shows the paths of the electron beam after passage through the specimen in diffraction (Figure 4-7A) and imaging mode (Figure 4-7B). Switching from real space (image) to reciprocal space (diffraction pattern) is easily achieved by changing the strength of the intermediate lens. For instance, in diffraction...
mode, the intermediate lens is weakened so that the diffraction pattern in the back focal plane of the objective lens can be projected on the screen.

![Figure 4-7. TEM imaging system.](image)

The two basic operation modes of the TEM imaging system (A) projecting the diffraction pattern on the viewing screen and (B) projecting the image on the screen. (From Ref.14) The intermediate lens is weakened so that the diffraction pattern in the back focal plane of the objective lens can be projected on the screen.

It can be seen in Figure 4-7(A) that an aperture is inserted at the image plane of the objective lens to define the region of which the diffraction is obtained. This diffraction pattern is called selected-area diffraction (SAD) pattern. This technique is used to obtain certain information for a single large grain or large precipitate in a specimen. Due to the limit of the size of the aperture and the demagnification back to the plane of the specimen, the minimum selected area is normally several hundred nanometers. As a result, if a material is polycrystalline and grain size is very small, many grains will contribute to the diffraction pattern, and a ring pattern, instead of spots, is formed. The diffraction pattern for polycrystalline specimens can be seen in Figure 4-8,
which contain the SAD pattern taken from the Pt-containing specimen and sputtered Pt thin film studied in this work, as shown in Figure 4-8(a). The two patterns show clear difference because the grain size for these two polycrystalline materials is different. In Figure 4-8(b) the grain size is smaller than in Figure 4-8(c), so the rings consist of continuous rings pattern. For a larger grain size, as shown in Figure 4-8(c), the rings are made up of discrete spots. It should be noted that the width of the continuous rings of diffraction intensity in Figure 4-8(b) becomes broader and can be used as an inverse measurement of the grain size. In addition, the high-resolution TEM image showed in Figure 4-8(a) reveals that the sputtered Pt has a much larger grain size than the Pt nanocomposite deposit.

Figure 4-8. Selected area diffraction patterns.

(a) High-resolution TEM image of containing both sputter Pt thin film and EBID Pt-containing deposit on single crystalline Si substrate. Selected area diffraction pattern of (b) electron beam deposited Pt-containing specimen, (c) sputtered Pt specimen and (d) single crystalline [100] Si substrate.
As mentioned before, there are a large number of nanocrystals in the area selected by the SAD aperture even when the smallest aperture is used. Under this circumstance, the diffraction pattern will contain crystallographic information from all of the selected nanocrystals, which is not what we want. For instance, if we want to identify the structure of one specific nanocrystal, the SAD pattern fails to reveal the crystallographic information from this specific nanocrystal. Another important technique in TEM, convergent beam electron diffraction (CBED) can solve this problem and provide complementary diffraction information from the specimen. Instead of using the parallel beam illumination in SAD, the electron beam is focused to form a small probe on the surface of the specimen with convergence semiangle being determined by the condenser aperture. The beam convergence in CBED gives rise to a pattern of disks of intensities rather than the sharp diffraction spots shown in Figure 4-8(d).

Figure 4-9 shows the high-resolution TEM image of the electron beam deposited W-containing specimen from WF<sub>6</sub> as well as the corresponding CBED pattern taken from one of the nanocrystal marked by red dashed circle, as shown in inset of Figure 4-9. This pattern proves that it is a single crystal and the set of spots can be indexed as bcc WO<sub>3</sub>. In addition to the application of phase identification shown above, CBED has other important applications, such as evaluation of lattice strain in microscopic regions<sup>15-19</sup>, defects in crystals,<sup>20,21</sup> and point and space group symmetry.<sup>22-24</sup> Since these techniques are not used in this work, no more details of these techniques are discussed here. If readers are interested in these subjects, please refer to the above references (and the references therein).
4.6.3.3. **Mechanisms for contrast formation**

The imaging mode in TEM can be divided into two categories: Bright Field (BF) and Dark Field (DF) mode, depending on the signals used to form the amplitude contrast image on the viewing screen or negative film. The direct transmitted beam is used to form BF images while some of the diffracted beams in the SAD pattern are used to form DF images. This can be done by inserting objective aperture to select whether the direct beam spot or the diffracted beam spot in the diffraction pattern formed in the back focal plane of the objective lens (see Figure 4-7) to form an image.
In TEM, scattering and diffraction of electrons are mainly responsible for image formation. Mass-thickness contrast arises from the elastic scattering of the electrons. A certain portion of the incident electrons is scattered into directions different from the primary beam direction. The factors that influence the electron scattering include the atomic number of specimen atoms, density of specimen, thickness of specimen, and the energy of electrons.\textsuperscript{14} The brightness of the image is determined by the intensity of the electron beam leaving the bottom specimen surface and pass through the objective aperture. Dense or thicker areas in the specimen will scatter more electrons off axis than the light or thinner areas, resulting in fewer electrons from the higher mass-thickness region landing on the screen, which appears darker in the BF images. This mass-thickness contrast can be clearly seen in Figure 4-8. The sputtered Pt thin film is much darker than the EBID Pt-containing nanocomposite materials because the density of the Pt film is much higher than that of the later one. In the routine operation of TEM, objective aperture is often used to enhance the image mass-thickness contrast by limiting the angles of electron scattering collection. A smaller objective aperture will give a higher image contrast because of the absence of contribution of electrons scattered into higher angles to the formation of image.

The incident electron beam can be seen as a plane wave with a mono-wavelength (2.5 pm at 200 keV), which is less than the atomic spacings for most of the crystalline materials. Bragg diffraction occurs at the lattice planes when it passes through the atoms in the crystals, as shown in Figure 4-10. Those scattered waves interfere with each other and undergo constructive interference when Bragg equation\textsuperscript{29} is obeyed.
\[ n\lambda = 2d \sin \theta_B \]  \hspace{1cm} (4.1)

where \( n \) is integer, \( \lambda \) wavelength, \( d \) is the distance between two lattice planes, and \( \theta_B \) is the scatter angle between the incident beam and the lattice plane, which is also called Bragg angle. From this equation, the path difference can be a whole number of wavelength only at certain (Bragg’s) angles.

Figure 4-10. Bragg diffraction.

Bragg description of interaction of the electron beam with the lattice planes of a crystalline specimen. The planes are separated a distance \( d \) and scattered at angle \( \theta_B \). The path difference is \( 2d\sin\theta_B \).

The diffraction contrast is generated from Bragg diffraction of the electron beam as it passes through the specimen. Objective aperture inserted into the back focal plan of objective lens allows those electrons that pass through the specimen without being diffracted to contribute the formed image. Regions in the specimen that strongly diffract electrons turn out to be dark, while regions that do not scatter electrons appear to be bright. TEM image shown in Figure 4-8(a) displays the diffraction contrast of the Pt nanocrystals embedded in an amorphous carboneous matrix, where the amorphous and crystalline phases can clearly be seen.
Diffraction contrast is a dominant mechanism for imaging crystalline specimens. However, the resolution of this imaging technique is limited to 1-3 nm. In order to resolve the structures at atomic scale, phase contrast imaging technique is often used for high-resolution TEM analysis. Phase contrast originates from interference between unscattered electrons and diffracted electrons, which have phase differences. Each pair of interfering beams will give rise to a set of lattice fringes in the images. A good example of phase contrast image is also shown in Figure 4-8(a). Lattice fringes of sputtered Pt, Pt nanocrystals in the EBID deposit, single crystalline Si are clearly seen. Phase contrast imaging is the highest resolution TEM imaging technique and has spatial resolution of less than 1 Å. However, the attainable resolution in phase contrast image is often limited by several factors, such as the performance of the instrument, the experience of operator, and specimen thickness.\textsuperscript{14}

4.6.4. Auger Electron Spectroscopy (AES)

Auger Electron Spectroscopy (AES) is a surface-sensitive analytical technique that utilizes a high-energy electron beam as an excitation source. Auger process is a multi-electron process, which involves transition between core and valence electron energy states.

The basic Auger process starts with a removal of an inner shell atomic electron to form a vacancy. Several processes are capable of producing the vacancy, but bombardment with an electron beam (3-20 keV) is most commonly used. Both primary and core electrons leave the system and the initial inner shell vacancy is filled by an electron from a higher energy shell. The relaxation process of this atom can be accomplished either by emission of characteristic X-Ray photon or radiationless Auger
transition, in which the energy gained by the electron dropping into a deeper level is transferred to electron of the same or different shell. The later electron is then emitted with a characteristic Auger energy, leaving the atom in double ionized state (two vacancies in different or the same core levels). The process of an excited ion decaying into a doubly charged ion by ejection of an electron is called the Auger process. The energy of the Auger electron is characteristic of the element, and can thus be used to identify the element. For low atomic number elements, the most probable transitions occur when a K-level electron is ejected by the primary beam, an L-level electron drops into the K shell and fill the vacancy, and another L-level electron is ejected. Higher atomic number elements have LMM and MNN transitions that are more probable than KLL. The Auger process is shown in Figure 4-11.

In this work, AES was used to determine the elemental composition and depth of profiles of the EBID deposit. The analysis has been performed on deposits with dimensions larger than the lateral resolution (circular deposit with a diameter of 10-20 μm), in order to avoid detection of substrate elements. The experiments were performed using a Perkin-Elmer PHI 660 scanning Auger microscope operated at beam energy of 10 keV and current of 1 μA (beam diameter ~ 1μm). Depth profiling was performed using an in-situ, 3 keV Ar+ ion source. Samples were tilted 30° from normal beam incidence toward the Ar+ ion gun to increase the sputtering rate. Sample rotations during sputtering are used to improve the uniformity of sputtering. The Ar+ sputter and Auger acquisition times were 30 and 48 s, respectively.
4.6.5. Energy Dispersive X-ray Spectroscopy (EDS)

Energy Dispersive X-ray Spectroscopy (EDS) is an analytical technique generally used for high Z element chemical compositional analysis. Most of the EBID materials contain metal, metal oxide, metal-carbide nanocrystals embedded in an amorphous matrix. These heavy elements, such as Pt, W, Au, and Cu are easy to detect using EDS due to their high X-ray yield. EDS in TEM or SEM has several advantages over other spectroscopic techniques such as Auger or EELS. EDS data acquisition and interpretation are easier compared to other spectroscopic techniques such as Auger or EELS. The energy of the electron beam for EDS analysis performed in conjunction with SEM instruments is typically in the range 5-30 keV. For EDS system attached TEM, the beam energy is usually 100-300 keV dependent on specific TEM instruments.

When the electrons hit the specimen surface, the incident electrons experience inelastic collisions with atoms in the sample resulting in X-rays emission from the
material. The X-ray generation process is also shown in Figure 4-11. During the electron relaxation process, a higher energy level electron will decay and jump to fill the core vacancy. In order to make this transition, the electron must emit a photon of energy equivalent to the energy difference between its initial and final states. This energy is characteristic of the specific atom involved in the excitation and relaxation process and falls into the X-ray spectrum.

During the electron relaxation process, an L-shell electron may drop to fill the inner K-shell (as indicated in Figure 4-11), lowering the energy of the atom and emitting $K\alpha$ X-ray. If an electron from the outer M-shell (not shown in Figure 4-11 for simplicity) fills the K-shell vacancy, $K\beta$ X-ray will be emitted. Similarly, if an L-shell electron is ejected and an electron from the M-shell fills the vacancy, $L\alpha$ X-ray will be emitted. The most probable transition when a K-shell vacancy is generated is the L to K transition because they are adjacent energy shells. As a result, the $K\alpha$ line in the spectrum is always more intense than $K\beta$ line. The $K\beta$ line is of higher energy than $K\alpha$ line due to the higher energy difference between M and K shells compared to that between L and K shells.

As mentioned before, when a beam of energetic electrons hit the specimen, they will undergo a series of scattering events along each electron’s pathway until they are attenuated completely or exits from the opposite surface of the specimen. The scattering processes will increase the electron-solid interaction while electron beam penetrate the substrate. So the X-ray photons can be generated from a larger region than the actual electron beam irradiation area, which will introduce analysis errors since information gathered may come from other regions of different compositions.
Even though EDS systems are normally found on scanning electron microscopes, there are certain advantages to using EDS in TEM. The main advantage is the improved spatial resolution due to the following reasons. One is that thin specimen (generally <100 nm) and extremely fine electron probe (0.5-2 nm) used in TEM will result in less electron scattering while the electrons transverse the specimen. Another reason is that the electron mean free path for both elastic and inelastic scattering increase with the electron energy.\textsuperscript{25,26} The higher electron energy (typical range from 100 to 400 keV) used in TEM compared with 5-30 keV used in SEM can effectively reduce the scattering effects. Consequently, the total electron-solid interaction volume is much smaller compared to the bulk sample, which results in more localized X-ray excitation region and a higher spatial resolution.

The EDS measurements were carried out using a JEOL 2010F, field emission gun transmission electron microscope operating at 200 kV and equipped with an EDAX X-ray energy-dispersive spectrometer with a super-ultrathin window in order to detect low atomic number elements such as carbon and oxygen. A double-tilt beryllium sample holder was used. The measurements were performed with an electron probe diameter of about 1 nm. During the EDS measurements, the specimen was always tilted towards the detector over an angle between 20 and 30\degree. The dead time was maintained between 20\% and 40\% by adjusting time constants, corresponding to an energy resolution relative to Mn Ka varying from 135 to 140 eV respectively.
4.6.6. Electron Energy Loss Spectroscopy (EELS)

4.6.6.1. General principles

Electron Energy-Loss Spectroscopy (EELS) is the analysis of the energy distribution of electrons that have interacted inelastically with the specimen. Transmission EELS is usually carried out using a TEM, which also offers imaging and diffraction capabilities that can be used to identify the structure of the materials being analyzed. Since the TEM specimen should be thin enough for electron transparency, the elastic and inelastic scattering take place inside the sample and information about internal structure can be obtained by passing the transmitted beam into a spectrometer. Also because the electron beam can be focused into a very small diameter, this can yield highly localized information due to the small electron-specimen interaction volume. In EELS, we study directly the primary processes of electron excitation, each of which results in a fast electron losing a characteristic amount of energy. The beam of transmitted electrons is directed into a high-resolution electron spectrometer, which separates the electrons according to their kinetic energy and produces an electron energy loss spectrum showing the scattering intensity as a function of the decrease in kinetic energy of the fast electron. Figure 4-12 shows the schematic configuration of electron energy spectrometer in TEM.

Because both inelastic scattering and elastic scattering electrons are collected by spectrometer, there are principal regions such as zero-loss peak, low-loss region and high-loss region providing different information about the specimen. A typical electron energy loss spectrum, recorded from a thin specimen over a range of about 1000 eV, is shown in Figure 4-13. The zero-loss peak, which consists primarily of elastic forward scattered electrons, but also contains electrons that have suffered minor energy losses.
The low-loss region up to an energy loss of ~50 eV contains electrons which have interacted with the weakly bound outer-shell electrons of the atoms in the specimen.

Figure 4-12. Electron energy loss spectrometer attached to TEM.

The Parallel-collection electron energy loss spectrometer is interfaced to a TEM after the final viewing screen. An entrance aperture selects the electrons on the optic axis and disperses them via a magnetic prism and projects them onto a cooled Charge-Coupled Device (CCD). (EELS Imaging and Analysis School 2007)

Electrons in the high-loss region have interacted with the more tightly bound inner-shell or “core” electrons. Three different regimes of energy losses can give us different information about the specimen. The zero-loss peak can be used to define the energy resolution, which is essential in calibrating the spectrum and measuring the thickness of the specimen. Valence and conduction electron densities can be calculated by measuring the position of the plasmon peaks. Elemental concentration and chemical bonding information can be obtained by analyzing the energy loss near edge structures (ELNES).
Electron energy loss spectrum of a high temperature superconductor (YBa$_2$Cu$_3$O$_7$) with the electron intensity on a logarithmic scale, showing the zero-loss peak, plasmon peaks and ionization edges arising from each element (Courtesy of D. H. Shin, Cornell University)

Ionization losses occurring in the core-loss region is important for EELS elemental analysis because the process is characteristic of the atom involved and so the signal is a direct source of elemental information, just like the characteristic X-ray. In order to ionize the atom, a specific minimum-energy transferred from the beam electron to the inner-shell electron is required to overcome the binding energy of the electron to the nucleus. Therefore, it is possible to ionize an atom by the transfer of $E > E_c$. However, the chances of ionization occurring become less with increasing energy above $E_c$, because the value of the ionization cross section decreases with increasing energy. As a result, the ionization-loss electrons have an energy distribution that ideally shows a sharp rise to a maximum at $E_c$, followed by a slowly decreasing intensity above $E_c$ back toward the background. In energy loss spectrum, the ionization edges are superimposed on the
background arising from plural inelastic scattering. ELNES represents the joint density of occupied and unoccupied states, which will be discussed further in section 4.4.6.4.

4.6.6.2. EELS Experimental conditions determination

Prior to collecting the spectra, experimental conditions should be chosen carefully. The most important two parameters are the convergent angle of the beam (α) and the collection angle (β) for the spectrometer. Convergence angle α is the range of angles incident upon the specimen, which is determined by condenser system settings and can be measured on calibrated diffraction pattern. Collection angle β is the maximum scattering angle included in EELS data for parallel illumination. The convergent angle of the beam (α) and the collection angle (β) for the spectrometer should be defined accurately, because the quantification analysis will need the scattering cross section parameter, which is calculated using collection angle. Recent developments in high brightness field-emission guns (FEGS) and highly efficient parallel-collection EELS (PEELS) systems have made the detection more effective, and EELS is mostly performed in the TEM. There are two common modes used to acquire EELS: image-coupled (diffraction mode) and diffraction coupled (image mode) in the conventional TEM condition. The details of the calculations are described in Appendix III.

In addition to convergence and collection angle, knowing of other angles involved in scattering process, such as characteristic scattering angles and cut-off angles are also important to set up the EELS acquisition correctly. The characteristic scattering angle at energy loss $\Delta_E$ can be calculated using the following equation\textsuperscript{25}

$$\theta_{E} = \frac{\Delta_{E}}{2E_0}$$  \hfill (4.2)
Where $\Delta_E$ is the energy loss (edge energy), $E_0$ is the kinetic energy of incident electron.

Due to the relativistic particle mechanics, the denominator in above equation should be corrected as

$$\theta_E = \frac{\Delta_E}{\gamma m_0 v^2} = \frac{\Delta_E}{(1 - v^2 / c^2)^{-1/2} m_0 v^2} = \frac{\Delta_E}{m_0 c^2 \beta^2 / \sqrt{1 - \beta^2}}$$

(4.3)

where $\beta = v / c = 0.695$ for 200keV electron, $m_0 c^2 = 511$ keV

For example, for Si K-edge, $\Delta_E = 1839$ eV, then corrected characteristic scattering angle

$$\theta_E = 5.36 \text{ mrad}$$

The cut-off angle is the angle at which the EELS signals drop to zero. If the collection angle is smaller than this angle, the scattered electron cannot be detected by the spectrometer.

The cut-off angle can be calculated as

$$\theta_c = \sqrt{2 \theta_E}$$

(4.4)

For example, for Si K-edge, $\theta_c = \sqrt{2 \theta_E} \approx 103$ mrad.

Generally, the collection angle is set as two or three times of the characteristic scattering angle to efficiently collect the major inelastically scattered (mostly forward scattered) electrons into the spectrometer. The characteristic scattering angles and cut-off angles for some elements involved in this work are listed in Table 4-3.
Most representative EELS shown in this work were collected under the conditions as follows: image-coupled diffraction mode, entrance aperture 2 mm, camera length 60-150 mm, convergence angle 3~5 mrad, corresponding collection angle 5~11 mrad, energy dispersion of 0.3-1 eV/ch and accumulated acquisition time for 5–30 s.

<table>
<thead>
<tr>
<th></th>
<th>Si-L</th>
<th>P-L</th>
<th>C-K</th>
<th>O-L</th>
<th>F-K</th>
<th>W-M</th>
<th>Si-K</th>
<th>Pt-M</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE (eV)</td>
<td>99</td>
<td>132</td>
<td>284</td>
<td>532</td>
<td>685</td>
<td>1809</td>
<td>1839</td>
<td>2122</td>
</tr>
<tr>
<td>θ_e (mrad)</td>
<td>0.29</td>
<td>0.40</td>
<td>0.83</td>
<td>1.55</td>
<td>1.99</td>
<td>5.27</td>
<td>5.36</td>
<td>6.18</td>
</tr>
<tr>
<td>2θ_e (mrad)</td>
<td>0.58</td>
<td>0.77</td>
<td>1.66</td>
<td>3.09</td>
<td>3.99</td>
<td>10.54</td>
<td>10.71</td>
<td>12.36</td>
</tr>
<tr>
<td>3θ_e (mrad)</td>
<td>0.87</td>
<td>1.15</td>
<td>2.48</td>
<td>4.65</td>
<td>5.99</td>
<td>15.81</td>
<td>16.07</td>
<td>18.54</td>
</tr>
<tr>
<td>θ_c (mrad)</td>
<td>24.08</td>
<td>27.75</td>
<td>40.74</td>
<td>55.59</td>
<td>63.17</td>
<td>102.67</td>
<td>103.49</td>
<td>111.18</td>
</tr>
</tbody>
</table>

The spectrometer energy resolution is defined as the full width at half maximum (FWHM) of the zero-loss (ZL) peak. The energy resolution is dependent on several factors, such as energy spread of the electron source, spectrometer energy dispersion, size of the entrance aperture, the magnitude of any aberrations in the spectrum plan, the stability of the high voltage and the magnetic prism and the lens currents, etc. A tungsten source has the worst energy resolution (~ 2.5 eV), and a LaB₆ is slightly better than W at 1.5 eV while a cold field emission gun (FEG) gives the best value (0.3eV). For 2010F TEM instrument used in this work, a Schottky thermal field emitter is used. During the Gatan image filter (GIF) alignment process, the ZL peak should be focused in order to obtain a sharp and symmetrical peak. Figure 4-14 shows that the FWHM of the Gaussian-fitted peak is used to determine the spectrometer energy resolution. The measured energy resolution is about 1.5 eV. In our EELS experiments, spectrometer dispersions of 0.5 and 1 ev/channel were also used to obtain spectrum from a larger energy loss range. It should
be noted the energy resolution might be degraded by using large energy dispersion value or entrance aperture.

![Figure 4-14. Determination of EELS energy resolution.](image)

Measurement of spectrometer energy resolution. The ZL peak was collected using 0.3eV/channel and 2 mm entrance aperture.

### 4.6.6.3. EELS elemental quantification analysis

At higher energy loss, the intensity in the spectrum falls dramatically (see Figure 4-15(a)) but superposed on this decline are ionization edges, representing the excitation of core electrons belonging to inner atomic shells. Because the ionization threshold occurs at the binding energy of each shell (k = K, L, etc.), which is known for all elements, the element responsible for each ionization edge can be identified. Background model is fitted using a pre-ionization edge-fitting region, and extrapolated to model the background intensity below the edge signal. Power-law form is most commonly used to model the background intensity (see Figure 4-15(a)).

Moreover, the amount of each element can be quantified by measuring the intensity $I_k$ (above background) of the edge, integrated over a convenient energy range $\Delta$.
as shown in Figure 4-15. Knowing the angular range $\beta$ of the scattering allowed into the energy-loss spectrometer, the cross section $\sigma_k(\beta, \Delta)$ for inner-shell scattering can be calculated and the areal density ($N$ atoms per unit area of specimen) obtained from the following equation\textsuperscript{25}

\[
\text{Areal density } N = \frac{I_k(\beta, \Delta)}{I_0(\beta)\sigma_k(\beta, \Delta)}
\] (4.5)

Where

$I_k$ is the signal integral for edge $K$ without plural scattering, $I_0$ is the zero-loss integral, $\beta$ is effective collection angle, $\Delta$ is the signal integration width, $\sigma_k(\beta, \Delta)$ is the partial scattering cross-section (see Figure 4-15(b)). By measuring the integral $I_0$ over an equal energy range $\Delta$ in the low-loss region, absolute and standardless quantification is therefore possible.

Although the above equation can be used to measure the absolute areal density $N$ of a given element, absolute quantification is not required in most cases. Instead, the ratio of two elements is obtained from the ratio of the core-loss intensities and cross-sections, based on Eq. (4.5) and without need to measure the low-loss integral. For example, core-loss spectroscopy can be used to measure the local atomic fraction of two elements (A and B) in an alloy or a composite material. Given the same integration window is used for both edges for element A and B, Eq. (4.5) gives

\[
\frac{N_A}{N_B} = \frac{I_A(\beta, \Delta)}{I_0(\beta, \Delta)} \frac{\sigma_B(\beta, \Delta)}{\sigma_A(\beta, \Delta)}
\] (4.6)
The partial scattering cross sections are calculated using Hartree-Slater method and they have already been integrated into the EELS quantification analysis software. Figure 4-16 gives an example of EELS quantification analysis of carbon to oxygen atomic ratio inside the electron-beam-induced deposition of tungsten thin film on a TEM Cu grid.

Figure 4-15. EELS relative quantification analysis.

(a) Power-law background model is fitted using a pre-ionization edge-fitting region, and extrapolated to model the background intensity below the edge signal. $\Gamma$ is the background fitting window, $\Delta$ is the signal integration window, $I_b$ is the background intensity, $I_k$ is the signal intensity; (b) the extracted signal integral; (c) The extracted signal integrals for two specific elements. (From Ref. 25)
Figure 4-16. An example of EELS quantification analysis.

The specimen is electron-beam-induced deposition of W thin film on TEM Cu grid using beam energy of 30keV and beam current of 0.63nA. The carbon to oxygen atomic ratio is about 6.

4.6.6.4. Extracting chemistry from ELNES

ELNES can be explained in term of molecular orbital (MO) theory: the local band structure is approximated as a linear combination of atomic orbitals (LCAO) of the excited atom and immediate neighbors. Because ELNES is analogous to near-edge x-ray absorption fine structures (NEXAFS) which is also widely utilized in physics and chemistry of condensed matter, a schematic diagram of NEXAFS of graphite is used to describe the electronic transitions, as shown in Figure 4-17. For graphite, three of the four valence electrons of each carbon are sp$^2$ hybridized, resulting in three $\sigma$ bonds to the nearest carbon atoms, the remaining unhybridized p electron contributes to a delocalized $\pi$ orbital. The corresponding antibonding orbitals are designated as $\pi^*$ and $\sigma^*$, which are the empty states into which core electrons can be excited, giving rise to distinct peaks in the K-edge spectrum. Fine details near the absorption threshold give information on the chemical state of the element. Specifically, transitions to bound states give information on bonding. Figure 4-18 shows the energy loss near edge structures around the C peak at
285 eV for 3 different forms of carbon: graphite, fullerene and diamond, showing the difference in bonding state and local electronic state.

Figure 4-17. Near edge X-ray absorption fine structures (NEXAFS) of graphite.

The near edge X-ray absorption fine structures (NEXAFS) of graphite arise from electronic transitions of an inner shell electron to energy levels which are normally unoccupied in ground state. The lowest unoccupied molecular orbital (LUMO) is $\pi^*$ orbital. (From Ref. 28)

The sharp peak at absorption edge corresponds to the excitation of carbon K-shell electron (1s electron) to empty anti-bonding $\pi$ orbital. It should be noted that there is no such a peak for diamond, because no $\pi$ electrons are present.
As mentioned in the introduction chapter, focused electron beam induced deposition (EBID) using organometallic precursors typically results in low purity metal deposits. The chief impurities are carbon, resulting from incomplete decomposition of the organometallic precursor and incorporation of the reaction fragments on the deposited metal films. Due to its unique advantage of sensitivity to low-Z materials and nanoscale spatial resolution, electron energy loss spectroscopy becomes a very useful technique to study the structural and chemical homogeneity of the EBID materials.

The properties of carbon materials are known to be related to the different bonding states of carbon atoms in the material. Carbon bonds predominantly in two ways: sp² configuration with carbon bonded to three other atoms in a planar geometry, or in tetrahedral sp³ coordination. The physical properties, such as electrical, optical properties
of carbon materials are strongly influenced by the proportion of \( \text{sp}^2/\text{sp}^3 \) bond ratio of carbon atoms in the material.

Previous experimental results indicated that the degradation of resistivity was caused mainly by the inclusion of \( C \) atoms. Although many advances have been made on reduction of impurity incorporation using \textit{in-situ} or \textit{ex-situ} methods, less attention has been paid to the characterization and quantification of the nature of the amorphous carbonaceous species inside the deposits. Most characterization techniques for EBID deposits, including Auger electron microscopy (AES), energy dispersive spectroscopy (EDS), and secondary ion mass spectroscopy (SIMS) can not obtain the chemical bond information of the carbon impurities, which is very important for the electrical characteristics of the deposits. In this work, the impurity carbon \( \text{sp}^2/\text{sp}^3 \) bond ratios inside the electron beam deposited tungsten-containing deposits were examined in a JEOL 2010F transmission electron microscope (TEM) equipped with a Gatan GIF 200 electron energy loss spectrometer. The details of determination of impurity carbon \( \text{sp}^2/\text{sp}^3 \) bond ratios are described in Chapter 8.

\textbf{4.6.7. Four-point probe method}

The resistances of the EBID line deposits from Pt(PF$_3$)$_4$ and (CH$_3$)$_3$CHC$_2$H$_4$Pt were measured via four-point probe method. In this method, an EBID line deposit is grown across the four low resistivity metal electrodes P1, 2, 3, 4, as shown in Figure 4-19. A driving current \( i_{14} \) is forced to flow through the outer electrodes (P1 and P4) and the voltage drop \( V_{23} \) between the inner electrodes (P2 and P3) is measured. The current flowing through P2 and P3 is forced to be zero. The advantage of using four-point instead of two-point probe is that the contact resistance between deposit and the metal electrode
can be canceled out. The resistance of the structure can be calculated: \( R = \frac{V_{23}}{i_{12}} \). The corresponding resistivity can also be calculated by using following equation:

\[
R = \rho \frac{L}{A} \rightarrow \rho = \frac{RA}{L}
\]  

(4.7)

where \( L \) is the length of the measured structure between P2 and P3 (m), \( A \) is the area of the cross-section (m\(^2\)), and \( \rho \) is the resistivity (\( \mu \)Ω·cm). The cross-section area is measured by SEM on the FIB cross-sections of the line deposit after the resistance measure has been done.

![Figure 4-19. The schematic diagram of four-point resistivity measurement method.](image)

The patterns for the four terminal electrodes (shown in Figure 4-20(a)) were deposited successively of 5 nm Cr and 100 nm Au by electron beam evaporator on a Si substrate with a 1000-nm-thick thermally grown SiO\(_2\) layer, using general lithography and wet-etching techniques. This gives a resistance of a few tens of ohms for the gold electrodes. Before deposition, the Si substrate was put into plasma cleaner for 2 minutes to remove the hydrocarbon contamination on the surface of Au electrodes and SiO\(_2\). For
the electrical studies, the Pt nanowires were used to connect four-terminal gold electrode contact structures, as shown in Figure 4-20(b).

Prior to measurement, four W needles are polished using sand paper to remove the oxide layer and dusts to obtain good electrical contact to the Au pad. The electrical properties of the structure were measured at room temperature, using a Keithley 4200-SCS Semiconductor Characterization System for current-voltage characteristics measurement. The forced current was kept in pA to nA range to avoid any nanostructure change or burn out due to the heat generated during measurement. The cross-section area of the Pt deposits was measured by SEM image of FIB cross-section on the line deposits. After resistance measurement, a 75nm Au-Pd thin film was sputter coated on the wafer and the line deposits cross sections were prepared and imaged by using FEI Nova 600 Nanolab SEM/FIB dual beam system.

![Figure 4-20](image)

Figure 4-20. Scanning electron micrographs of the four terminal electrodes.

(a) Four-point probe pattern fabricated using general lithography and wet-etching techniques (image was taken using environmental SEM to avoid charging). (b) The SEM image of the electron beam deposited Pt line across the four electrode fingers.
4.7. References


Chapter 5

5. TEM sample preparation

5.1. Introduction

In order to obtain high quality TEM images, the sample should be thin enough for electron transparency. Generally, the thickness in the region of interest should be around 100 nm or less. There are several different ways to make TEM samples. As mentioned in previous chapter, the sizes of EBID deposit prepared for this work are generally from several hundred nanometers to a few microns. The traditional mechanical polishing method is unable to handle this in such a small scale. Alternative site-specific TEM sample preparation methods with high precision and accuracy are needed to make the cross-sectional TEM samples on these small features.

Since the initial development of focused ion beam (FIB) technology\(^1\) in the 1970’s, FIB instruments have been widely used in many different areas, including site-specific failure analysis of semiconductor devices, TEM sample preparation and nano-machining. Compared with conventional mechanical TEM sample preparation method, FIB TEM sample preparation method has the following advantages: 1) site-specific target area can be located with a high spatial accuracy of within tens of nanometers by using FIB; 2) FIB sample preparation is fast, which is generally 2-3 hours; 3) FIB preparation techniques is generally independent of the nature of the material and can handle various materials; FIB process can be easily adjusted to meet the requirements for specific materials; 4) the preparation of cross sections with near parallel sides, enabling quantitative compositional analysis to be performed over the entire area of a cross-section specimen.
During the development of FIB technique, different site-specific cross-sectional TEM sample preparation methods have been proposed. In 1989, Kirk et al.\textsuperscript{2} reported the use of FIB as a new technique for preparing a cross-sectional specimen which was known as “trench” method later on. The sample preparation started from mechanically polishing the bulk sample down to an approximately 50 μm lamella which still contains the region of interest and then using the FIB to cut two trenches, one from each side, leaving behind a thin electron-transparent lamella supported by bulk material on two opposite sides. This method was applied to several device materials with small modifications depending on the characteristics of the observed area\textsuperscript{4,5}, and was known as the “trench” method. This method is also frequently called the H-bar technique due to its geometry (shown in Figure 5-1). Similar to this method, Overwijk et al.\textsuperscript{6} proposed a novel scheme in 1993 for the preparation of TEM specimens that was later referred to as the “lift-out” method. In this

![Figure 5-1. H-bar FIB TEM sample preparation technique.](image)

(a) Schematic illustration of the H-bar focused ion beam (FIB) technique. Material on both sides of a region of interest is FIB-milled until it is electron-transparent. (b) SEM image showing the top-down view of an H-bar FIB specimen in progress. The metal sample was mechanically thinned to ~40 mm and glued to a transmission electron microscope (TEM) half-grid. (Figure courtesy of Richard Young, FEI Company, from Ref. 3)
method, the specimen is cut from the substrate and subsequently transported to a standard TEM specimen holder, allowing for the FIB milling time to be minimized. The lift-out technique has the advantages in processing silicon devices and semiconductor, where the fabricated area conditions such as the dimensions and sputtering ratio have similar objectives and a high throughput is required.

Figure 5-2. *Ex-situ* lift-out TEM sample preparation technique.

Preparation of a cross-section specimen by the lift-out technique, (a) deposition of a platinum strip over the region of interest as protection layer, (b) cutting of the staircase trenches on both sides, (c) thinning of a cross-section specimen until it is about 500 nm thick, (d) tilting of a sample by 45° and cutting of its base, (e) further thinning of a cross-section specimen until it is about 70 nm thick, and (f) cutting of the edges of a cross-section specimen to free it from the substrate and pluck it out and transfer it to TEM sample holder. (From Ref. 7)

Both of these methods have been used for preparing TEM samples from a wide range of materials, including semiconductors, metals and ceramics. The main limitation of “trench” method is that the sample geometry limits the angles of tilt possible in a TEM.
For example, if a trench is 50 μm long and a cross section is 4 μm high then the maximum possible angle of tilt is only 3°. Another problem associated with trench method is that during energy dispersive x-ray (EDX) analysis electrons scattered from the cross section can irradiate the sidewalls and generate additional X rays, which will introduce artifacts to the chemical analysis results.

The lift-out technique involves cutting out a cross-section specimen from its substrate (shown in Figure 5-2) and transferring it onto a thin support membrane using a micromanipulator. One main problem encountered when using the lift-out technique is that a cross-section specimen can sometimes be lost. It can drop off the tip of the glass needle while it is being transferred to the TEM grid or if the needle vibrates during the plucking process it can spring away from the needle and the staircase shaped cuts due to the electrostatic charges on the tip or the sample surface. Therefore, the yield is generally 50%-70%. The two techniques outlined above have their own advantages and disadvantages. These advantages and disadvantages of the two techniques are summarized in Table 5-1.

Table 5-1. Trench and lift-out sample preparation technique.

<table>
<thead>
<tr>
<th></th>
<th>Trench technique</th>
<th>Lift-out technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-FIB preparation time</td>
<td>0.5–1 h</td>
<td>None</td>
</tr>
<tr>
<td>Post-FIB preparation time</td>
<td>None</td>
<td>0.5–1 h</td>
</tr>
<tr>
<td>Yield</td>
<td>90%–100% (material dependent)</td>
<td>50%–95% (material dependent)</td>
</tr>
<tr>
<td>EDS analysis problems</td>
<td>Secondary signals from sidewalls</td>
<td>No secondary signals</td>
</tr>
<tr>
<td>Tilting in TEM</td>
<td>Limited by trenches</td>
<td>Limited by TEM</td>
</tr>
<tr>
<td>Surrounding substrate left intact</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Comparison of the trench and the lift-out techniques.(From Ref. 7)
In 1999, Ohnishi et al.\textsuperscript{9} developed a new focused ion beam micro-sampling technique which involved using a metal needle being inserted into the specimen position under vacuum in the FIB specimen chamber to pick up the micro-sized sample and mount it on a standard TEM sample holder. Since the size of a sample prepared by the micro-sampling method is similar to that obtained by the lift-out method, there are some identical advantages. Furthermore, this method has a good repeatability for FIB milling, which is a very important factor for the FIB sample preparation because the microstructure of most materials must be observed to check the sample thickness by the TEM before the final milling.

With the continuous shrinking in size of semiconductor devices, there is a high demand on the metrology and characterization tools in respect of accuracy and resolution. The resolution of typical single-beam focused ion beam (FIB) instruments is not sufficient any more to meet the necessary accuracy and precision. In order to overcome this problem, new generation FIB tools have been combined with a high-resolution SEM column that is used to monitor FIB process on a nanometer scale. These integrated tools are often called as FIB-SEM dual beam system. These dual beam systems enable both the observation and direct control of the FIB operation process in real time. In addition to the enhancement of accuracy and spatial resolution, the electron beam can also provide analytical capabilities such as scanning transmission electron microscopy (STEM), energy dispersive spectroscopy (EDS), and electron backscattered diffraction (EBSD).

5.2. Ion beam damage during TEM sample preparation

We have already known that FIB TEM sample preparation has many advantages over conventional mechanical and argon ion milling. For example, the electron-
transparent area can be located with high precision and accuracy; milling time is shorter, and flat, parallel-sided specimens can be readily prepared. However, the use of a high energetic (typically 30 keV) gallium ion can also introduce damage and implantation of the milling species into the surface as well as the sidewalls of the cross-sectional specimen during the FIB-assisted metal deposition (e.g. Pt and W protection layer) and FIB imaging and milling. The formation and depth of the ion beam-induced damage depends on the ion species, the incident energy, the angle of incidence and the material itself. Langford et al.\textsuperscript{7} summarized the projected range of gallium implantation into silicon and the number of vacancies generated per incident ion at different incident energies and angles of incidence (shown in Table 5-2) calculated using SRIM program\textsuperscript{10}.

Table 5-2. Penetration depth, vacancies per ion, and sputter yield of gallium.

<table>
<thead>
<tr>
<th>Energy (keV)</th>
<th>Incident angle</th>
<th>Lateral depth (nm)</th>
<th>Longitudinal depth (nm)</th>
<th>Vacancies per ion</th>
<th>Sputter Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>90</td>
<td>26</td>
<td>72</td>
<td>575</td>
<td>17</td>
</tr>
<tr>
<td>30</td>
<td>10</td>
<td>9.4</td>
<td>26.5</td>
<td>211</td>
<td>17</td>
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<tr>
<td>10</td>
<td>10</td>
<td>5.3</td>
<td>14.2</td>
<td>167</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>2.1</td>
<td>8.1</td>
<td>104</td>
<td>14</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>1.3</td>
<td>4.0</td>
<td>26</td>
<td>4</td>
</tr>
</tbody>
</table>

Data were taken from Reference 7.

In the following sessions, more details on \textit{in-situ} lift-out TEM sample preparation for EBID deposits made in both environmental scanning electron microscope (ESEM) and high vacuum SEM instrument using SEM-FIB dual beam systems will be discussed. First, the ion beam damages and artifacts, particularly in electron-beam-induced deposits, including W and Pt-containing deposits will be investigated. Then the protection techniques for cross-sectional TEM sample preparation of EBID deposits, including
single sputter coated AuPd thin film and AuPd/Ir thin films to reduce the damage generated by 30keV Ga\(^+\) ion beam during FIB imaging and deposition will be presented. Finally, the effectiveness of these protective coatings will be evaluated.

5.3. *In-situ* lift-out cross-sectional TEM sample preparation

5.3.1. EBID sample preparation

EBID samples made two systems are described. First, EBID was performed using an FEI Sirion NC 600 ESEM, a field emission gun (FEG) magnetic immersion lens ESEM system modified to enable the delivery of WF\(_6\) into the specimen chamber.\(^{11}\) The substrate was (100) p-type Si plasma cleaned prior to EBID to remove residual surface hydrocarbons,\(^{12}\) which resulted in the formation of an approximately 5 nm thick SiO\(_x\) overlayer. Tungsten hexafluoride\(^{13-17}\) (WF\(_6\)) was used as the EBID precursor. The entire ESEM chamber was filled to a pressure of 21 mTorr. All depositions were performed at room temperature, with the electron beam energy and current fixed at 20 keV and 1.16 nA. The electron beam diameter was controlled by the objective lens current\(^{18}\) and the deposition time was varied to make the electron beam fluence constant used for EBID.

Similarly, EBID Pt samples were prepared by using a FEI Nova 600 Nanolab high-resolution field emission SEM/FIB dual beam system. All depositions were performed at room temperature, with the electron beam energy and current fixed at 20 keV and 2 nA. Trimethyl–methylcyclopentadienyl–platinum [(CH\(_3\))\(_3\)CH\(_3\)C\(_5\)H\(_4\)Pt] was used as the EBID precursor. The base pressure of the vacuum chamber prior to introducing precursor gas was less than 2.6\(\times\)10\(^{-6}\) Torr, and the stable precursor pressure during deposition experiments was approximately 5\(\times\)10\(^{-6}\) Torr. The distance between the bottom of the precursor injection needle and the sample surface was about 100 \(\mu\)m at
5mm working distance. In addition to the sample that has series of disk-like Pt deposits with different diameters (from hundreds of nanometers to several microns), a small Pt pillar and a large Pt deposits were grown by a focused and extensively defocused electron beam, respectively. For the single Pt pillar, (100) Si substrate was used as before. For large Pt deposit, a perfect crystal (SrTiO₃) was used as substrate due to the fact of absence of amorphous region on it. Thus, we can evaluate the effectiveness of the protection layer for FIB-TEM sample preparation.

5.3.2. Sputtered coated thin films as protection layer

After SEM imaging of the deposits, samples were taken out of the chamber and were sputter coated with a gold-palladium protective film in Sputter Coater (Denton Desk IV). The sputter coating was carried out at 1.4 kV voltage and 40 mA plasma current in an argon gas atmosphere with the pressure ~50 mTorr. For the sample used to evaluate the effectiveness of protection from single AuPd thin film, the thickness of the coated AuPd film was controlled around 100 nm. For samples used to evaluate the effectiveness of protection from Ir/AuPd thin films, Emitech K575 turbo sputtering coater was used to coat Ir film. It has been found that the grain size of Ir is smaller that that of AuPd due to the low working pressure (7.5×10⁻⁴ to 7.5×10⁻⁵ Torr).

Thus, the effect of variation in film property to protect the initial structure of the specimen can be studied. The Ir film (~40 nm) was first sputter coated on the substrate with EBID deposits, followed by the AuPd film (~50 nm) sputter coated on top of the Ir film.

5.3.3. Cross-sectional TEM sample preparation

A single cross-section of each sample described above was prepared for transmission electron microscopy (TEM) by a typical “in-situ lift-out” method described
elsewhere\textsuperscript{20,21} using a 30 keV Ga\textsuperscript{+} focused ion beam (FIB) on a FEI Nova 600 Nanolab dual beam system. The first step is to align the SEM and FIB columns and perform eucentric height adjustment. Since the sample tilt angle has different values relative to electron or ion column, here sample stage tilt (i.e., angle between the target surface and the plane normal to the electron column axis) is denoted by $\Phi$ throughout the following sections unless otherwise indicated.

A large EBID Pt deposit, as shown in Figure 5-3(a) [SEM image, $\phi=52^\circ$] was used to show the typical steps of \textit{in-situ} lift-out TEM sample preparation method. In general, a thin protection layer, such as Pt, W or oxide, has to be deposited in the region of interested using ion beam-induced deposition to avoid the ion damage, the “curtain” effect and to reduce the rounding of the top of a cross-section specimen during ion milling. Figure 5-3(b) [SEM image, $\phi=52^\circ$] shows the $25\times3\times3\mu$m FIB-Pt platinum strip, deposited on the specimen surface using 460 pA beam current and 30-keV beam energy. In order to reduce the ion beam damage during the Pt deposition, low energy ion beam can be used to perform Pt strip deposition\textsuperscript{7,22-24}. The main drawback of a low energy ion beam is that both the image resolution and etch rate are lowered. The first staircase shaped trenches are milled on both sides of the region of interest, using large beam currents (9.3-21 nA). The dimensions of the staircase-shaped trench cuts are generally determined by the sizes of the features of interest, the geometry requirement that the cross-section specimens have to be lifted out and mounted onto a TEM sample grid and the total time required for the preparation of the cross-section specimen. The nominal width ($w$) of the rectangular defined by the FIB pattern generation software should be equal or larger than twice the nominal depth ($z$) in order to avoid redeposition during the
ion milling. The front and back side trench normally have same dimensions which allow SEM viewing of the specimen from both sides. In our experiments, we routinely prepare cross-section specimens that are 20–25 μm long and 5–10 μm deep and for silicon cross-section specimens. The beam current is then reduced to 2.8 nA, and the area on either side of the region of interest is milled by scanning the ion beam in a line at the edges of the region between the staircase shaped cuts and moving it inwards until the cross-section is about 2μm thick. In this procedure, the rectangular milling boxes are created using a “clean up cut” algorithm, which can remove the redeposited materials on both sidewalls of the cross-section and the bottom of the trenches close to the cross-section. Figure 5-3(c) [SEM image, φ =0°] shows the SEM image of a clean cut cross-section of the region of interest. Then the sample stage is tilted back to 0°. In FIB imaging mode, bottom and one sidewall cuts are created by using a 6nA beam current. In this procedure, the normal rectangular algorithm is used since the milling depths should be same for both two cuts. The 2-3μm thick micro-specimen, as shown in Figure 5-3 (d) [SEM image, φ =0°] is free on one side and the bottom, but still attached to the substrate via a micro-bridge on the other side. A more clear view is shown in Figure 5-3(e) [FIB image, φ =0°]. The W needle is inserted and manually moved to the specimen until it touches the free side of the micro-specimen via the omniprobe control buttons. A 1 μm×1 μm Pt square is deposited to attach the sample to the W needle using low current (93pA) ion beam, as shown in Figure 5-3(e). The thickness of this Pt deposit is usually 0.7-1 μm. The next step is to release the specimen free by cutting out the micro-bridge using a medium current (2.8-6.5nA) ion beam. Figure 5-3(f) [FIB image, φ =0°] shows the cross-section sample has been welded on the W tip securely and starts being lifted out of the trench. Then the
sample is transferred and attached to a TEM grid via large area FIB Pt deposit, as shown in Figure 5-3(g) [FIB image, $\phi = 0^\circ$]. Finally the micro-specimen is cut free from the W tip, as shown in Figure 5-3(h) [FIB image, $\phi = 0^\circ$]. Until now, the 2-3 $\mu$m thick micro-specimen has been lifted-out from the substrate and mounted on the TEM Cu grid.

The sample stage is tilted back to $52^\circ$ in order to make the ion beam perpendicular to the top surface of the cross-section sample for the following thinning procedure. The area on either side of the region of interest is thinned by scanning the ion beam in a line at the edges of the region until the cross section is 200-300 nm thick. Several milling sections may be used and the corresponding ion beam current decreases from a few nA to several hundreds of pA. The ion beam current should be less than 100pA during the final milling process in order to obtain high precision milling performance due to the smaller beam size. The ion beam profile is reported to be Gaussian$^{25,26}$ shape with long tails and the sputter yield is dependent on the incident angle of the ion beam, which result in a cross-section specimen being tapered in profile. The slightly sloping sidewalls are often shown as white regions on either side of the cross-section specimen in the ion beam images. These effects need to be corrected since it is necessary for the specimen to have uniform thickness (parallel sidewalls) for quantitative compositional analysis (i.e., EDX and EELS) over a cross-section specimen. Tilting the specimen by a small angle to the ion beam ($\pm 1-2^\circ$) can reduce the amount of tapering. The specimen is tilted by $2^\circ$ (Stage tilt $\phi = 54^\circ$) and the white region at the lower sidewall is polished by using cleaning cross-section procedure. Then the specimen is tilted by $-2^\circ$ (Stage tilt $\phi = 50^\circ$) and the white region at the upper sidewall is polished in the similar manner. This thinning procedure is repeated in small steps until specimen is thin enough (<100nm) for electron transparence.
Figure 5-4 shows a comparison of TEM cross-section specimens prepared with/without tilting the specimen. It is clearly seen that tilting a small angle to the ion beam during the final milling can effectively reduce the tapering effects and the specimen has nearly parallel sidewalls. The specimen should be constantly monitored by SEM during the final milling process. This is very important in the TEM sample preparation process since some of the specimen cross-section need to be located at the right center of several deposits. Constant SEM viewing can lower the risk of overmilling of the features from either side of the lamella. Figure 5-3(i) [SEM image, φ=50º] shows the final TEM cross-section specimen which is ready for TEM imaging.

One advantage of in-situ lift-out TEM sample is that the specimen can be thinned further either by FIB or low energy Ar⁺ ion miller if the specimen thickness is still too thick to obtain high quality TEM images. In this work, post-FIB polishing of the TEM specimen was performed by using Gatan Ar⁺ ion miller. Two broad argon beams (2 keV, 1 mA) with an incident angle of 15º to the sidewall surface of the cross-section were used to polish the specimen and remove the amorphous damage layer on the sidewalls of the lamella. The Ominprobe Cu grid was placed with the Pt deposition upward, to face the up-to-down Ar⁺ beam, so that the Cu grid does not block the ion beam (Figure 5-5). The ion milling time was 15-20 minutes. TEM analysis was carried out using a JEOL 2010F TEM operating at 200 keV.
Figure 5-3. *In-situ* lift-out TEM sample preparation technique.

Typical steps of *in-situ* lift-out TEM sample preparation method. (a) EBID Pt sample is sputter-coated with a thin Ir/AuPd protection layer; (b) FIB-Pt or W strip is deposited by FIB as a protection layer of the sample; (c) back and front trench is milled by FIB (d) bottom and one sidewall is cut free; (e) the omniprobe (W tip) is attached and welded to the micro-sample; (f) the micro-sample is released by cutting the other sidewall bridge; (g) the micro-sample is attached and welded to the TEM grid; (h) the micro-sample is cut free from the W tip; (i) the micro-sample is thinned down to electron transparent (thickness < 100nm)
Figure 5-4. Removal of tapered cross section by small angle tilted ion beam.

(a) FIB cross-section specimen prepared without tilting the sample into the ion beam during the final thinning. (b) FIB cross-section specimen prepared by tilting the sample by ±1.2° into the ion beam during the final thinning. (From Ref. 7)

Figure 5-5. Schematic of Ar⁺ ion milling process
5.3.4. TEM analysis results

5.3.4.1. FIB damage on EBID deposit and Si substrate

Figure 5-6(a) and (b) show scanning electron micrographs of materials deposited using WF$_6$ precursor and electron beams with decreasing electron flux and constant electron fluence. Figure 5-6(c) shows cross sectional SEM image of the TEM sample that was polished down to a thickness of 100nm. A damaged layer with granular structure can be clearly seen on top of the tungsten deposits and Si substrates between two deposits in the high magnification SEM image shown in Figure 5-6(d).

A more detailed view of the damaged layer can be obtained using high-resolution TEM, as shown in Figure 5-7. Significant ion beam damage can be observed on top of both the tungsten deposits and the Si substrate adjacent to the main deposits. The total thickness of the damage layer in the EBID deposit is 68 nm, which consists of 60 nm of partially amorphous material and 8 nm of a distinctly different appearance (dark layer in Figure 5-7(c), whose identity will be described later using energy dispersive X-ray spectroscopy (EDS). Qualitatively similar damage is found between the deposits, although it is shallower. High magnification bright field TEM images in Figure 5-8(a) show that there are two obvious damage layers on the Si substrate (regions “2” and “3”) just as there were in the EBID deposit. Unlike in the EBID deposit, however, the two damage layers in the substrate are comparable in thickness, 25 nm and 35 nm respectively.
Although it seems counterintuitive that the 30keV Ga\(^+\) ion beam causes less damage in a low-Z material like Si, this result is consistent with other literature reports.\(^{22,24,27}\) In those experiments, a (100) single crystalline Si substrate was used to investigate Ga\(^+\) ion damage and the thickness of the amorphous layer is about 40 nm. In the samples used for this study, it is possible that the original oxide layer (5 nm) and the “halo” deposition (~5-10 nm) around the main deposits retard the incoming Ga ions to some extent, which results in lower Ga ion penetration depth compared to previous data.\(^{22}\) EDS was used to determine whether the damage caused by the Ga\(^+\) ion beam was accompanied by any compositional changes. Six points (marked by “1” to “6”) in Figure 5-8(a) were interrogated using a 2 nm electron probe and 60 second collection time. Figure 5-8(b) shows the EDS spectra collected. In the region between the deposits, the 35nm damage layer (region 2) mainly consists of Si and Ga, while the upper (dark) layer
(region 3) was mixture of Ga, Pt, and Si. The dark particles (20-30 nm) on top of tungsten deposit were W and Pt, presumably intermixed by sputtering of the tungsten surface by the Ga$^+$ ions as the Pt nanoparticles were being deposited.

Figure 5-7. FIB damage formed during sample preparation.

(a) Bright field transmission electron micrographs of FIB-induced damage on the sample shown in Figure 5-6, generated by a 30keV focused Ga$^+$ ion beam, (b) and (c) high magnification TEM images of damage layer on top of W deposit.
Figure 5-8. EDS analysis on the FIB damage region.

(a) High magnification TEM image showing the ion beam damage on the Si substrate between two deposits (as indicated by arrows in Figure 5-7(a)), and (b) Energy dispersive spectra taken from the positions labeled by numbers in (a). Cu x-rays (Cu Kα and Kβ originate from the TEM sample grid).
5.3.4.2. **Au-Pd sputter coatings with thicknesses up to 100nm**

To eliminate the possibility that the observed damage was not due to the FIB processing but rather due to exposure of the Si substrate to the potentially corrosive fluorine liberated from the WF$_6$ precursor during electron irradiation, a control Si sample was inserted in the EBID chamber and exposed to the precursor without exposure to electrons.

A 100 nm thick Au-Pd protection layer (see Figure 5-9) was sputter-coated on half of the sample using a standard argon sputter coating system with a physical sputter shield to leave the other half of the sample uncoated. This half would thus be exposed to the Ga$^+$ ion beam directly during FIB-Pt layer deposition, and be used as a benchmark for the efficacy of the Au-Pd layer's protective ability. The SEM image shows the discontinuous topography and the columnar microstructures (Figure 5-9 inset) of the Au-Pd coating.

![Figure 5-9. Sputter coated AuPd thin film.](image)

Scanning electron micrograph image (taken at sample tilt of 52°) of the 100nm AuPd sputter coated on Si substrate (inset: high magnification image showing the columnar structure)
Figure 5-10 shows a series of cross-sectional TEM images demonstrating the efficacy of the Au-Pd coating. Clearly, the damage is worst in the region without Au/Pd protection, where the damage layer is about 60 nm deep, while under the Au-Pd layer only a very thin native oxide layer can be seen [Figure 5-10(b)].

Figure 5-10. AuPd thin film as protection layer for TEM sample preparation.

(a) Cross sectional TEM images show the effectiveness of the 100nm Au/Pd coatings, (b) High magnification image of the interface between Au-Pd and Si substrate; (c) High magnification image of interface under the gap between two Au-Pd grains.

Figure 5-11 is the high magnification TEM image of the cross section of Si substrate without Au-Pd protection layer. It can be clearly seen that three regions corresponds to different mass-thickness contrast observed in the image (marked by “1” to “3”). The arrowhead shows the original Si substrate surface before any exposure to Ga⁺
ion irradiation. Region “1” (~25nm in thickness) shows a diffusion region which consists of dark particles with size increasing towards the above FIB Pt layer. The transition from dark to bright in contrast indicates that this region is result of sputtered and redopsited Pt and Si mixture. Region “2” (~15nm in thickness) is completely amorphous and has a slightly higher density than the low part of region “1”. This is possibly the result of competition between sputtering and deposition at the early stages of the ion-beam-induced deposition process.\textsuperscript{22,28,29} Region 3 (~ 46 nm in thickness) is the focused ion beam induced damaged layer in crystalline Si substrate. The thickness of this amorphous layer is nearly proportional to the range of Ga ion implantation.\textsuperscript{30,31} The total thickness of the bottom damage layer in crystalline Si after ion-beam induced Pt deposition (61 nm, i.e. the overall thickness of region “2” + region “3”) is in good agreement with previous experimental data.\textsuperscript{32}

![Figure 5-11. TEM image of the cross section of Si substrate without protective layer.](image)

The above results indicated that the damage layer (~ 60 nm) was not caused by the exposure of the Si substrate to the potentially corrosive fluorine liberated from the
WF$_6$ precursor$^{35,36}$ Problems still arise for FIB-TEM sample preparation because the sputter coated Au/Pd layer is not continuous. At the junction of two Au-Pd grains, the high energy Ga$^+$ ions can still penetrate into the substrate and cause damage to the underlying materials (e.g. amorphisation of crystalline Si substrate, as indicated by the arrowhead in Figure 5-10(c)). It is clearly that actual penetration depth of ion implantation of gallium ions in polycrystalline gold is much greater than that predicted from TRIM simulations.$^{22}$ Thus it is concluded that single Au-Pd thin film may not be the best solution for TEM sample preparation. Next, Ir/AuPd double protection layers will be discussed.

5.3.4.3. Ir/AuPd sputter coatings

Since discontinuous Au-Pd thin films can not successfully protect a sample during FIB-deposition, next a double protection layer for the TEM sample preparation was investigated. In this section, several examples were used to demonstrate the effectiveness of this Ir/AuPd double layer in protecting EBID metal deposits. As mentioned before, a 40 nm Ir film was first sputter coated on the substrate with EBID deposits, followed by a 50 nm Au-Pd thin film sputter coated on top of the Ir film. The cross-sectional TEM sample was prepared using the method described in previous section.

A. Evaluation on Pt deposits on Si substrate

Figure 5-12 shows another application example of the Ir/AuPd protective layer on cross-sectional TEM sample preparation. The sample was prepared used the same method, except that the deposition time was not compensated with the electron beam
size and each of the four deposits (shown in Figure 5-12(a)) was grown for 2 minutes. This results in the decreasing electron flux with constant electron dose on each deposit.

Figure 5-12(b) shows the cross-sectional TEM image of deposit indicated by arrow (shown in Figure 5-12 (a)). It can be clearly seen that there is no damage layer on top of the EBID deposit (compare with Figure 5-7(a)). This indicated the sputter coated Ir/AuPd double layers can effectively retard the penetration of 30keV Ga⁺ ion into the deposit and thus help to avoid damage to the deposit. Higher magnification TEM image (Figure 5-12(c)) shows top interface between Ir coatings and deposit. The deposits consist of Pt nanocrystals with diameters in the range of 2-3 nm embedded in an amorphous matrix. No amorphisation of the sample was observed. High-resolution TEM analysis (Figure 5-12(d)) of the bottom interface between Si and deposit shows no ion beam damage either from FIB deposition or milling.
Figure 5-12. Ir/AuPd double protection layer for TEM sample preparation.

(a) Scanning electron micrograph of the Platinum materials deposited using electron beams with decreasing electron flux at high vacuum condition (image taken at a stage tilt at 52°); (b) Cross sectional TEM images of the single Pt deposit (indicated by arrow) show the effectiveness of the Ir/AuPd double protection layer. (c) HR-TEM view of the top interface between Pt and Ir/AuPd protective layer, and (d) bottom interface between Pt and Si substrate. The oxide layer is about 5nm thick.

B. Evaluation on large EBID Pt deposit on SrTiO$_3$ substrate

In order to reinforce the argument that there is no Si amorphisation underneath the deposit, an additional sample was prepared on substrate with no intrinsic oxide layer. The substrate is a 10×5×0.5 mm single side polished (100) single crystal SrTiO$_3$, with RMS surface roughness of 1.5 Å (Applied Technology Enterprises). The electron beam size was set as 11µm and deposition time was 30 minutes. Figure 5-13 (a) shows the SEM image of the disk-like Pt deposit and the diameter is about 11 µm. Figure 5-13(b) shows the cross-sectional TEM image of the deposit. The deposit shows a similar polycrystalline nanostructure and no damage layer was observed at the bottom interface. It should be
noted that a transient region was observed between the SrTiO$_3$ substrate and the bottom part of Pt deposit, which suggests the initial growth kinetics are different from those for the following deposit growth. The sizes of the Pt nanocrystallites are smaller than those of the nanocrystallites above this transient region and the density of the deposits seem to be lower as well (different contrast). This difference may be due to (i) differences between the material properties of the deposited materials and the substrate which lead to changes in secondary electron emissivity, and (ii) the intrinsic insulator property of the SrTiO$_3$ substrate, which will cause an increase in charge-induced SE emission$^{33,34}$. More work is needed to clarify this.

Figure 5-13. HRTEM on the interface between EBID deposit and SrTiO$_3$ substrate.

(a) Scanning electron micrograph of the disk-like Pt deposit grown on SrTiO$_3$ substrate; and (b) HR-TEM view of the bottom interface between Pt deposit and SrTiO$_3$ substrate.
5.4. Summary

In this chapter, two cross-sectional TEM sample preparation methods, “trench method” and “lift-out” method, and their relative advantages and disadvantages have been discussed. The “in-situ lift-out” cross-sectional TEM sample preparation procedure has been demonstrated by using a FEI FIB-SEM dual beam system attached with an omniprobe micromanipulation system.

The ion beam damage and artifacts during FIB-TEM sample preparation, particularly in electron-beam-induced deposits, including W and Pt-containing specimens have been investigated. TEM observations of the cross-sections of the deposits show that the damages appear in forms of amorphisation of both top surface of the deposits and the substrates. Protection techniques for cross-sectional TEM sample preparation of electron-beam-induced deposits by FIB are developed and evaluated. Sputter coated AuPd and Ir thin film were used reduce the damages generated by 30keV Ga⁺ ion beam during FIB imaging and deposition. The cross-sectional TEM analysis results show that the protection layers can be effectively avoid the ion beam damage to both EBID deposits and the Si substrate.
5.5. References


19 http://www.emitech.co.uk/.


Chapter 6

6. Structure of Pt-containing nanocomposites grown by electron beam induced deposition in high vacuum environment

6.1. Introduction

Gas-assisted electron beam induced deposition (EBID) is a promising maskless technique for nanofabrication at the nanoscale at the nanoscale. EBID is initiated by dissociation of gaseous precursor adsorbates by energetic electrons crossing a substrate surface, giving rise to deposition in the vicinity of an electron beam. To date, most work on the nanostructure of EBID-fabricated materials has focused on metal-containing materials. Typically, the deposits are nanocomposites consisting of metal crystallites (with diameters in the range of 1 to 10 nm) embedded in an amorphous matrix composed of reaction byproducts and impurities present at the substrate surface during EBID. Using organometallic precursors will typically result in low purity metal deposits and the high impurity content will degrade the conductivity of deposited metal, which is not preferable for the electrical applications for EBID, such as the site-specific nanocontact in interconnect. Except for the relative higher resistance (including contact resistance) of the EBID deposits, the widely scattered resistivity data in the literature as a function of electron beam current, energy, scanning parameters are intended to show a significant correlation between the nanostructures and resistivities of the metal-containing deposits. The physical properties and uniformity of the EBID deposited materials become increasingly important as the features approach nanometer size. A systematic investigation of the structural and chemical character of the metal-containing deposits is
necessary in order to understand how composition and nanostructure affect the electrical performance.

The height of EBID structures is generally at the nanometer or sub-micron scale, which is lower than or comparable to the penetration range of the energetic electrons typically used for EBID. As a consequence, while electron irradiation initiates EBID through the dissociation of adsorbates, it also serves to deposit energy into underlying EBID-grown material and can give rise to material modification during growth. Recently, we have reported the evolution of nanostructure of W-containing composite grown by a defocused electron beam with top-hat electron flux profile (i.e., with a constant intensity over a certain area, and zero intensity outside) in an environmental scanning electron microscope.\(^1\) Structural analysis based on transmission electron microscopy (TEM) has demonstrated that the WO\(_3\) grain size and the degree of deposit crystallinity increase with deposition time under conditions of fixed low electron flux. These changes correlate with the degree of electron energy deposition into the material during growth, indicating that electron beam induced modification of as-grown material is significant in controlling the nanostructure and functionality of materials fabricated by EBID.

In this chapter, a systematic study of the structure and composition of Pt-containing nanocomposite prepared in a high vacuum SEM instrument by using \((\text{CH}_3)_3\text{CH}_2\text{C}_5\text{H}_4\text{Pt}\) precursor was reported. The internal grain size and crystallinity of the deposits fabricated under various electron flux are characterized by cross-sectional TEM. In addition, specimens grown under a fixed electron flux followed by post-electron beam irradiation process for different time are also investigated. It has been further observed the intermixing of the nanocomposite with an amorphous oxide overlayer on a Si
substrate from both of the above set of specimens and demonstrates that these effects scale with energy density delivered to the material by the electrons used for deposition.

6.2. Experimental and simulation details

6.2.1. Electron-beam-induced deposition

EBID was performed using a Nova 600 Nanolab SEM/FIB dual beam system. The substrate was p-type Si (100), plasma cleaned right prior to growth to remove residual surface hydrocarbons\(^2\) inside the microscope without breaking the vacuum, yielding an approximately 5nm thick SiO\(_x\) overlayer. Trimethyl-methylcyclopentadienyl-platinum \(\text{[(CH}_3\text{)}_3\text{CH}_2\text{C}_2\text{H}_4\text{Pt]}\) was used as the EBID precursor. The base pressure prior to introduction of the precursor vapor was less than \(3.5\times10^{-4}\) Pa, and the steady state background pressure during EBID was approximately \(6.7\times10^{-3}\) Pa. The precursor crucible temperature was 45ºC. The precursor vapor was delivered using a capillary-style gas injection system. The distance between the bottom of the precursor injection needle and the sample surface was about 100 \(\mu\)m at 5 mm working distance. A detailed analysis of gas flow and the local pressure distribution near the sample surface can be found elsewhere.\(^3\) EBID was performed at room temperature, using a stationary electron beam with a top-hat electron flux profile and an energy and current of 20 keV and 2 nA, respectively. This approach eliminates complications caused by scanning (i.e., effects of pixel dwell and revisit times on EBID growth kinetics), and yields deposit geometries that can be modeled by simple, unambiguous Monte Carlo simulations of electron interactions with solids. In addition, using a defocused electron beam can lessen the effects of beam-induced impurity migration and heating.
The electron beam diameter was controlled by the objective lens current which was varied to control the electron beam diameter (and hence flux) used for EBID. Three sets of samples were prepared (see Table 6-1). The first sample (A0) was grown using a beam with a diameter of 11 μm, and a deposition time of 30 min. The second sample consists of four deposits (A1 to A4) each fabricated using a fixed growth time of 120 s and beam diameters of 850, 1410, 2020 and 2580 nm, respectively. The third sample consists of five deposits (B1 to B5) each fabricated using an electron beam with a diameter of 1100 nm, and a growth time of 60 s. Each of these deposits was subsequently irradiated by the 1100 nm beam in a high vacuum environment (in the absence of the EBID precursor) using an irradiation time of either 0, 120, 240, 480, or 960 s. Table 6-1 lists the electron flux and fluence delivered to each deposit during growth and post-growth processing.

EBID deposit cross-sections were prepared for TEM by a typical in situ lift-out method using a 30 keV Ga$^+$ focused ion beam (FIB) on a FEI Nova 600 Nanolab dual beam system. Ion beam damage$^{1,5,6}$ of the deposits was prevented by sputtering a 50nm Ir, and a 50nm AuPd layer onto the sample prior to cross-section preparation by the 30 keV Ga$^+$ beam. Specimen batches two and three were each milled into a single cross-section that contained all deposits comprising each batch. TEM analysis was performed in high vacuum using a JEOL 2010F microscope operated at 200 kV. Compositional depth profiling was performed using a PHI model P660 scanning Auger microscope with an in-situ, 3 keV Ar$^+$ ion source. Auger electron spectroscopy (AES) was performed using a beam energy, current and diameter of 10 keV, 1 μA and ~ 1μm, respectively. The Ar$^+$ sputter and Auger acquisition times were 30 and 48 s, respectively.
Table 6-1. Summary of EBID Pt-containing deposits.

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<th>Sample</th>
<th>d_{beam} (nm)</th>
<th>t (s)</th>
<th>t_p (s)</th>
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<th>Fluence (e/cm^2)</th>
<th>Height (nm)</th>
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Summary of deposits investigated in this study (d = diameter of the top-hat electron beam and of the top surface of the deposit, t = growth time, t_p = post-growth electron exposure time, T_o = thickness of the oxide between the deposit and the Si substrate).

6.2.2. Monte Carlo simulations

Electron energy deposition profiles were calculated using the continuous slowing down approximation using standard Monte Carlo simulations of electron-solid interactions,\textsuperscript{7-10} employing Mott elastic cross-sections\textsuperscript{8}, and a modified expression for the Bethe stopping power.\textsuperscript{10} The substrate was approximated by bulk Si (i.e., the SiO_x layer was ignored in the simulations), and the EBID-grown nanocomposite by 416 nm thick bulk Pt_xC_{(1-x)} with a Pt atomic fractions of 0, 0.2, 0.4 and 0.6. The densities for amorphous C and pure Pt were assumed to equal 2.2 g/cm^3 and 21.4 g/cm^3. Each simulation was performed using 10^5, 20 keV electrons.
6.3. Results

6.3.1. Deposit composition and nanostructure

Figure 6-1(a) shows a secondary electron image of an EBID deposit with a top diameter of 11 μm. The dark ring seen around the deposit is a thin film that typically surrounds structures grown by EBID. It is attributed primarily to EBID driven by backscattered electrons (BSEs) and the type II secondary electrons (generated by the escaping BSEs) emitted from the substrate during growth.11-14 Bright field TEM images of the deposit and the deposit-substrate interface are shown in Figure 6-1(b) and (c), respectively. The deposit is approximately 140 nm tall, and consists of nanocrystallites embedded in an amorphous matrix. The mean crystallite diameter is smaller than 5 nm. The crystallite packing density exhibits a slight increase with distance from the top surface (towards the Si substrate), and a relatively broad deposit-substrate interface indicative of intermixing between the nanocrystals and the amorphous oxide on the Si substrate.

Figure 6-1. Nanocomposite grown on SiOₓ/Si by electron beam induced deposition.

(a) Scanning electron micrograph taken using a sample tilt of 52°; (b) low-magnification cross-sectional TEM image; (c) high-magnification image of the interface between the nanocomposite and the substrate.

Figure 6-2 shows AES depth profiles obtained from a deposit grown under the same conditions as the one shown in Figure 6-1. The deposit contains Pt, C, N and traces
of O. The composition is relatively uniform through to the interfacial region after the top surface is sputtered away. The profile at the interface exhibits elevated O content, and a broad transition region within which the Pt and C concentrations decrease and the Si concentration increases. Accounting for the relative sensitivities of the AES peaks, the atomic composition in the middle of the EBID nanocomposite is 68 at.% Pt, 18% C, 5% N, 2% O. The Si signal (7 at.%) is possibly attributable to the background noise coming from the Si substrate during AES analysis. The size of the Ar ion beam is larger than that of the deposit, resulting in the Si signal from outside of the deposits. O is also present in the form of gaseous impurities (e.g., H₂O, O₂) in the dual beam chamber, as is N (e.g. N₂). C comprises about 35 at.% of the precursor molecule [(CH₃)₃CH₅C₅H₄Pt]. The reduced C content (18 at.%) measured in the deposit indicates C removal during EBID, possibly in the form of volatile species such as CH₄, and CO.
Figure 6-2. Auger depth of profiles.

Auger depth profiles of a nanocomposite grown under the same conditions as the sample shown in Figure 6-1. Auger spectra were acquired using a beam energy and current of 10 keV and 1µA.

Figure 6-3 shows four deposits fabricated using a fixed growth time of 120 s, and beam diameters of 850, 1410, 2020 and 2580 nm. The deposit height decreases with increasing electron beam diameter due to the corresponding decrease in electron flux. Figure 6-4(a)-(d) shows high-resolution cross-sectional TEM images taken from the center of each of the deposits shown in Figure 6-3. The nanocomposites consist of crystallites with a mean diameter of less than 5 nm, embedded in an amorphous matrix. The degree of crystallinity is seen to increase with the electron flux used for EBID. Figure 6-5 shows SAD patterns corresponding to the deposits shown in Figure 6-3 and Figure 6-4. The SAD patterns are consistent with face-centered cubic (fcc) Pt with a lattice constant of $a = 3.92\text{Å}$ (JCPDS file No. 4-802$^{15}$, do not show any evidence of a preferred growth direction, and show that the both the deposit crystallinity and grain size increase with electron flux. The latter is illustrated more clearly in Figure 6-6 which shows normalized, radially averaged intensity profiles of the first two rings of each SAD pattern. The widths of the first and second rings (corresponding to the (111) and (200) reflection planes) decrease and the intensity of the second ring increases with electron flux.
Figure 6-3. Scanning electron micrograph of deposits grown on a SiOx/Si substrate.

Each deposit was grown for 120 s using a beam energy and current of 20 keV and 2 nA, respectively. The deposit top diameters (from left to right) are 850, 1410, 2020 and 2580 nm. The deposit heights are 1190, 440, 220 and 140 nm, respectively. Images were taken using a sample tilt of 52°.

Figure 6-4. High-resolution cross-sectional TEM images of the deposits.

Images (a) to (d) correspond to deposits A1 to A4, respectively.
Figure 6-5. Selected-area diffraction patterns.

Images (a) to (d) correspond to deposits A1 to A4, respectively.

Figure 6-6. Intensity profiles of the diffraction rings.

Intensity profiles of the first two rings of each of the diffraction patterns shown in Figure 6-5 normalized to the intensity of the first ring (corresponding to the (111) reflection plane).

6.3.2. Intermixing of the deposit and the substrate
Figure 6-7 shows a cross-sectional TEM image of a SiOₓ/Si substrate taken from the TEM sample shown in Figure 6-3. The image was taken far away from the deposits and shows an amorphous oxide layer with a thickness of ~ 5.4 nm. Figure 6-8 shows images of the interface between each of the four EBID deposits and the SiOₓ-Si substrate. The thickness of the SiOₓ layer decreases systematically from ~2.5 nm (deposit A1, highest electron flux (2.2×10¹⁸ cm⁻²s⁻¹) used for EBID) to 1.6 nm (deposit A4, lowest electron flux (2.4×10¹⁷ cm⁻²s⁻¹)), as is summarized in Table 6-1.

Figure 6-9 shows five deposits each fabricated using a fixed growth time of 60 s, and a beam diameter of 1100nm. After EBID, deposits B1 to B5 were irradiated by an electron beam, in high vacuum, for 0, 2, 4, 8, and 16 minutes, respectively. Figure 6-10 shows high-resolution cross-sectional TEM images of the interface between the deposits and the SiOₓ-Si substrate. The thickness of the SiOₓ layer decreases systematically from ~3.8 nm (deposit B1, no post-growth electron irradiation) to 1.2 nm (deposit B5, 16 minute post-growth electron irradiation). The results show that the degree of intermixing scales with electron beam irradiation time in a high vacuum environment.
Figure 6-7. High-resolution cross-sectional TEM image of SiOₓ/Si substrate.

It shows the amorphous oxide overlayer (thickness ≈ 5.4 nm) far away from the deposits shown in Figure 6-3.

Figure 6-8. HRTEM images of the interface between the substrate and deposits.
Images (a) to (d) correspond to deposits A1 to A4 (shown in Figure 6-3), respectively. The SiO$_x$ thickness in images (a) to (d) is 2.5±0.1 nm, 2.2±0.1 nm, 1.9±0.1 nm, and 1.6±0.1 nm, respectively.

Figure 6-9. SEM of deposits grown on a SiO$_x$/Si substrate.

Each deposit was grown for 60 s using a beam energy and current of 20 keV and 2 nA, respectively. The deposits B1 to B5 were subsequently irradiated by an electron beam in high vacuum for 0, 2, 4, 8, and 16 minutes, respectively. The average height is 412.4±9.4 nm. (image were taken using a sample tilt of 52°)
Figure 6-10. HRTEM images of the interface between the substrate and the deposits.

Images (a) to (e) correspond to deposits #B1 to #B5, respectively. The thicknesses of the interfacial amorphous layer is 3.83±0.10 nm, 2.89±0.09 nm, 2.31±0.14nm, 1.67±0.09 nm and 1.14±0.09 nm, respectively.
Figure 6-11. Depth-resolved total electron energy deposition profiles for Pt$_x$C$_{(1-x)}$.

The solid-vacuum interface is at $z = 0$ and the Pt$_x$C$_{(1-x)}$-Si interface at $z = 416$ nm. The Pt atomic fractions ($x$) is 0, 0.2, 0.4 and 0.6, respectively. $\frac{dE}{dz}$ is the mean energy deposited per incident electron per unit depth. (Accelerating voltage = 20 keV, $10^5$ electrons per simulation).

6.3.3. Monte Carlo simulations

Figure 6-11 shows depth-resolved total electron energy deposition profiles calculated for Pt$_x$C$_{(1-x)}$ films on Si using Pt atomic fractions of 0, 0.2, 0.4 and 0.6, where $\frac{dE}{dz}$ is the mean energy deposited into the solid per incident electron per unit depth ($z$). The film thickness is 416 nm (i.e., the same as the mean height of deposits B1-B5, see Table 6-1). The profiles show that a significant amount of energy is deposited at the deposit-substrate interface for all 4 film compositions (the atomic fraction of Pt in EBID-grown films is typically on the order of 15 % and can be increased by post-growth processing treatments$^{17-20}$).
The results in Figure 6-11 are representative of the energy deposition behavior occurring during EBID of the structures shown in Figure 6-4 and Figure 6-5. The dE/dz profiles show that the energy deposition (per electron rate per unit depth) in a Pt/C deposit and the total energy deposited into Pt/C (E_{Pt/C}) both increase with Pt/C deposit thickness. Similarly, the total energy deposited into Pt/C deposit normalized to the total energy deposited into Si substrate also increases with Pt/C deposit thickness. The dE/dz profiles also reveals that the energy deposition per electron rate per unit volume (which is proportional to dE/dz) at every z-coordinate in a Pt/C deposit increase with Pt/C deposit thickness. The results show that the extent of electron beam induced material modification occurring during EBID is expected to increase with increasing electron flux (current density), which correlates with the increasing grain size and crystallinity seen in Figure 6-4.

6.4. Discussions

6.4.1. Nanostructure evolution during growth

The observed changes in crystallinity and grain size with electron flux are similar to the results from WO₃ deposits using WF₆ as precursor gas.¹ In that system, the degree of crystallinity and the WO₃ grain size were shown to increase with growth time (i.e., electron fluence), and the observed changes in nanostructure were interpreted in terms of the electron energy density deposited into the material during growth.¹ This interpretation requires some explanation. The height of deposits grown by EBID is generally at the micron or submicron scale, which is lower than or comparable to the penetration range (R) of the energetic electrons typically used for EBID and can be approximated by:²¹
\[ R = \frac{27.6AE_L^{\frac{5}{3}}}{\rho Z^{\frac{1}{9}}} \]  

(6.1)

where \( A \) is atomic weight (g/mol), \( E_L \) is beam energy (keV), \( \rho \) is density (g/cm\(^3\)) and \( Z \) is atomic number. Consequently, while electron irradiation initiates EBID through the dissociation of precursor adsorbates, it also serves to deposit energy into underlying EBID-grown material (see, for example, the electron energy deposition profiles shown in Figure 6-11), causes modification of electron sensitive materials, and responsible for the changes in WO\(_3\) nanostructure reported in reference\(^1\). Qualitatively the same behavior was observed in deposits comprised of metallic (Pt) crystallites in an amorphous matrix fabricated using Pt(PF\(_3\))\(_4\) precursor, indicating that the observed behavior may be a universal characteristic of granular nanocomposites grown by EBID. In that case, the amorphous matrix consists of mainly phosphorus, the partially dissociated precursor molecules, the corresponding fragments and ligands, as well as trace of hydrocarbon molecules. The changes in crystallinity with beam diameter reported here are consistent with this prior work. The similar results from two different EBID-grown nanocomposite materials systems: 1) metal oxide particles in an amorphous matrix, and 2) metal particles in an amorphous matrix indicate that the factors such as electron flux, energy deposited into deposits are likely important in EBID-grown materials in general.

### 6.4.2. Intermixing of the deposit and the substrate

The results from the intermixing study are summarized in Table 6-1 and show that:

i) The extent of intermixing (in terms of oxide thickness reduction) increases with electron fluence used to post-process samples B1-B5.
ii) The extent of intermixing increases with increasing electron beam diameter (i.e., decreasing electron flux) used to grow samples A1-A4.

iii) Intermixing is most pronounced in sample A0 which was grown using the lowest electron flux and fluence, but the longest time of all the samples investigated.

If local heating (which is proportional to flux) were responsible for the observed intermixing, the sample with the lowest flux (A0) would have the least intermixing. In fact, the opposite is observed: the intermixing is most pronounced in the specimen with lowest flux. This result indicates that electron beam induced heating plays a minor role; instead, the observed changes in nanostructure are rate-limited by mass transport inside the solid. The increasing extent of intermixing with decreasing electron flux used to grow samples A1-A4 can also partially attribute to the protection of underneath oxide by as-deposited Pt layer from irradiation by the following incoming electrons during the dissociation process.

The data from B1-B5 indicate that that intermixing is driven by electron irradiation throughout the entire deposit and the deposit-substrate interface, as per the energy deposition profiles shown in Figure 6-11. However, it should be noted that analogous mass transport behavior has been studied in a range of material systems, including SiO2, and is typically assisted by internal electric fields generated by localized excess charge that accumulates during electron irradiation.22-24 Field-enhanced migration likely plays a role in the intermixing reported here because the amorphous matrix and the oxide are both insulating, and the deposits can sustain internal electric fields.
6.5. Summary

EBID Pt-containing deposits were prepared using a defocused electron beam. Auger depth profile analysis shows the deposit consist mainly Pt (68%) and C (18%). Cross-sectional TEM analysis demonstrated that Pt grain size and crystallinity increase with both electron flux and post-EBID electron exposure time. The intermixing of the deposits and the substrate (i.e. oxide layer) are observed specimens grown using different electron flux and the degree of intermixing is a function of the growth parameters used for EBID. The intermixing effect is also observed at the interface for deposits grown under identical growth conditions but different post-electron irradiation time. The results show that the degree of intermixing scales with electron beam irradiation time in a high vacuum environment. Both the experimental and simulation results indicate the above effects scale with energy density delivered to the material by the electrons used to induce deposition. Furthermore, our results indicate that electron beam induced material modification plays a significant role in the functionality of EBID-fabricated materials. Hence, the effects discussed in this paper can potentially be used to control the nanostructure and functionality of EBID-fabricated materials.
6.6. References

Chapter 7

7. EBID W-containing deposit from WF$_6$ in ESEM

7.1 Introduction

The vast majority of the EBID literature is concerned with gas injection system (GIS)-based gas delivery into a high vacuum SEM chamber. A small number of papers have shown some very compelling advantages of Environmental scanning electron microscopy (ESEM) beam chemistry (as mentioned in previous chapter). Hence, ESEM beam chemistry is explored in parallel (from the nanostructure viewpoint) and compared to high vacuum EBID. ESEM was used to fabricate tungsten-containing nanostructures from WF$_6$ by electron beam induced deposition (EBID). The deposition time and the diameter of a stationary electron beam were varied to achieve accurate control over electron flux and fluence. EBID growth kinetics were characterized by measurements of vertical and volume growth rates, and illustrate that low flux, stationary electron beams can be used to eliminate complex growth kinetics caused by adsorbate depletion and by the scanning of electron beams during EBID. Such simplifications are highly desirable in basic, quantitative studies of EBID. However, the experiments also revealed complications caused by changes in electron emissivity occurring during EBID, and by electron emission from deposit sidewalls. High-resolution transmission electron microscopy (TEM), electron-energy-loss spectroscopy, and energy dispersive x-ray spectroscopy were used to characterize deposit nanostructure and composition. Deposits fabricated by ESEM using WF$_6$ precursor were found to consist of tungsten trioxide (WO$_3$) nanocrystallites embedded in an amorphous matrix. Oxide formation is attributed to the presence of residual oxidizers detected in the ESEM chamber by mass
spectrometry. Under conditions of low, fixed electron flux, the degree of deposit crystallinity and WO₃ grain size were found to increase with deposition time. These changes in nanostructure are ascribed to electron beam induced modification of the deposits occurring during EBID.

### 7.2 Experimental methods

A field emission gun (FEG) environmental scanning electron microscope (ESEM) with a magnetic immersion lens electron column was used for deposition. The electron beam energy ($E$) was fixed at 20 keV. The electron probe current ($I_p$), measured in high vacuum using a Faraday cup, can be varied from a few pA to several nA. Tungsten hexafluoride (WF₆) was used as the EBID precursor and the chamber pressure during deposition was fixed at 100 mTorr. All experiments were performed at room temperature. A detailed description of the ESEM system and parameters used for EBID can be found in experimental setup chapter.

To study the effects of electron flux and fluence on the nanostructure and composition of materials fabricated by EBID, two sets of experiments were performed. First, the electron beam diameter was varied by changing the excitation of the objective lens, yielding accurate control over the electron flux at the substrate surface. All other microscope parameters were unchanged. In a second experiment, the objective lens current was fixed so as to produce a broad beam (diameter $\approx$ 1.3 µm) with a top-hat electron flux profile, and the deposition time was varied to control the electron fluence used for EBID. All EBID was performed using a stationary electron beam, eliminating ambiguities arising from EBID growth kinetics caused by changes in pixel overlap and pixel dwell and re-visit times.
7.2.1 Electron beam size dependent deposition

The substrate was a small section cut from a commercial n-type GaAs (100) wafer. Before deposition, the GaAs substrates were first annealed at 110°C in air for about 2 hours, then placed into the ESEM chamber and plasma cleaned with an Evactron 25 De-Contaminator [XEI Scientific, Inc] (0.4 Torr of air, 13 Watts, 1 hour) so as to volatilize residual hydrocarbons on the substrate surface and inside the vacuum chamber. The structures were deposited near the corner of the GaAs substrate, which served as a fiducial in locating the deposits during subsequent SEM imaging and focused ion beam (FIB)-TEM sample preparation. EBID was performed using a beam energy of 20 keV, and beam currents of 0.726 nA and 2.9 nA.

Prior to EBID, the working distance was set to 6 mm and the electron beam was focused onto the sample surface. Then, test structures were deposited as a function of the change in objective lens excitation current, and the deposit diameters were measured. The dependence of beam diameter on lens excitation was obtained, and used to classify the extent of beam defocus into four categories, referred to here as “defocus 4”, “8”, “12” and “16”.

7.2.2 Time dependent deposition

The substrate was a small section cut from a commercial p-type Si (100) wafer. Before deposition, the Si substrate was placed into the ESEM chamber and plasma cleaned (0.4 Torr of air, 13 Watts, 12 hours). EBID was performed using a beam energy of 20 keV, and a beam current of 371pA. The defocus condition was set to “defocus 12” and the deposition time was varied from 4 to 32 minutes.
7.2.3 Analytical techniques

The topographies and dimensions of the as-deposited W structures were first characterized by using high-resolution scanning electron microscopy (SEM). Then, the samples were coated with the sputtered Au-Pd protective layer and cross-sectional TEM samples were prepared using an FEI Nova 600 Nanolab FIB/SEM dual-beam system. The deposit nanostructures were examined using a JEOL 2010F high-resolution TEM. Chemical information was obtained by energy-dispersive x-ray spectroscopy (EDS), electron energy-loss spectroscopy (EELS) and electron diffraction analysis.

7.3 Results and Discussions

7.3.1 Growth kinetics

Figure 7-1(a) and (b) shows images of deposits fabricated using electron beam defocus conditions “4”, “8”, “12” and “16” (left to right, respectively). Figure 7-1(b) shows that the deposit height decreases with increasing electron beam diameter. The decrease in vertical growth rate corresponds to the change in electron flux caused by increasing the area irradiated by a fixed current electron beam. It should be noted that there is a thin halo surrounding each nominal W deposit, as indicated by the arrows in Figure 7-1(c). This halo is attributed to EBID driven by backscattered electrons (BSEs) and type 2 secondary electrons generated by the escaping BSEs, and primary electrons scattered by gas molecules above the sample surface (known in ESEM literature as the “electron skirt”1-4).
Figure 7-1. Scanning electron micrographs of deposits on a GaAs substrate.

(a) The four deposits indicated by black arrows were each grown for 2 minutes. The deposit tip diameter (from left to right) was approximately 295, 591, 850, and 1108 nm. Beam current and energy were fixed at 2.9 nA and 20 keV, respectively. The two small tips (indicated by white arrows) on either side of the deposits were each deposited using a focused electron beam and a deposition time of ~10 seconds; b) an image taken using a sample tilt of 52°; c) an image of a FIB cross-section of the sample.
Figure 7-2(a) shows the average vertical growth rate plotted as a function of incident electron flux for deposits grown using electron beam currents of 0.726 nA and 2.9 nA. Since the precursor pressure was fixed (at ~100 mTorr), growth rate on precursor pressure can be ignored. The average vertical growth rate, calculated by dividing the height of each deposit in Figure 7-1 by the deposition time (2 min), increased with electron flux at both beam currents. This increase is ascribed primarily to an increase in the electron emission current (from a growing deposit) occurring during EBID. The increase results from the fact that the deposit material properties are different from that of the substrate. In the present case, the BSE yield decreases with the height of a deposit grown on GaAs, as is shown (using a Monte Carlo simulation) in Appendix I. It should be noted that, as is indicated in Figure 7-2(a), focused electron beams give rise to very high vertical growth rates. This is attributed to the fact that the SE yield is a function of deposit shape. Highly defocused beams have approximately top-hat electron flux profiles, yielding deposits with flat top surfaces. Conversely, a focused beam has a Gaussian electron flux profile, leading to conical deposits with high SE emissivity, such as those indicated by the white arrows in Figure 7-1(a) and seen clearly in Figure 7-1(b). The high SE emissivity contributed to the high vertical growth rates of 39.2 and 64 nm/s at beam currents of 0.726 and 2.9 nA, respectively.

Figure 7-2(b) shows the average volume growth rate per unit beam current plotted as a function of incident electron flux for deposits grown using electron beam currents of 0.726 nA and 2.9 nA. For volume calculations, the deposit shapes were approximated by truncated cones with top and bottom diameters obtained from images such as those shown in Figure 7-1. In the case of top-hat-shaped deposits made using defocused
electron beams, the volume growth rate per unit beam current was approximately constant at each beam current, indicating the absence of significant adsorbate depletion effects (i.e., “reaction rate limited” growth kinetics). However, the volume growth rates differed by ~16% at the two beam currents (~8.4 × 10^5 nm^{-3}s^{-1}nA^{-1} at 0.726 nA, and ~7.2 × 10^5 nm^{-3}s^{-1}nA^{-1} at 2.9 nA), indicating a measurable adsorbate depletion effect at the higher beam current. The difference of 16% is, however, deemed too insignificant to merit further discussion of this discrepancy between the two datasets, particularly given that the data is limited to 2 beam currents. It should be noted, however, that within each dataset the volume growth rate per unit beam current decreased by ~20% when the electron beam was focused, despite the fact that the electron emission current increased (during EBID, due to efficient SE emission from the sidewalls of pillar-shaped deposits). This growth rate decrease indicates significant adsorbate depletion in the case of a focused electron beam (i.e., “mass transport limited” growth kinetics).

Figure 7-3(a) shows four deposits fabricated using a fixed electron flux (beam current = 371 pA) but different deposition times. It can be seen that the diameter of the deposit increased slightly with increasing deposition time (D_{4\text{ min}} = 1.35 \mu m, D_{32\text{ min}} = 1.65 \mu m). This lateral broadening effect has been described by other researchers and is attributed to electron emission from deposit sidewalls during growth.

Figure 7-4(a) shows the height and volume of the deposits in Figure 7-3, plotted as a function of growth time. Both the height and volume increase with increasing deposition time and the volume grows faster than the height. This is consistent with the above interpretation of the growth kinetics because the rate of change of the slope of the height profile is caused only by the change in electron emissivity from the top surface of
Figure 7-2. Growth rate plotted as function of electron flux.

Growth rate plotted as function of the incident electron flux for deposits grown using beam currents of 0.726 nA and 2.9 nA and a beam energy of 20 keV. (a) Vertical growth rate (also shown are the growth rates (of 39.2 and 64 nm/s) of pillars grown using focused electron beams). (b) Volume growth rate per unit beam current. The electron irradiation area was calculated using the flat top diameters of the W deposits seen clearly in Figure 7-1. In the case of a focused electron beam, the beam diameter was approximated to be 5 nm.
Figure 7-3. Scanning electron micrographs of deposits grown on a Si substrate.

a) Deposits grown for 4, 8, 16, and 32 minutes. The beam current and energy were fixed at 371 pA and 20 keV, respectively. b) Image taken using a sample tilt of 52°. c) Secondary electron image of a FIB cross-section of the sample.

the deposit. Conversely, the rate of change of the slope of the volume profile is also contributed to an increase in electron emissivity from the deposit sidewalls, hence the greater change in volume growth rate with time.
Figure 7-4. Heights and volumes and their corresponding growth rate.

(a) Heights and volumes of the deposits shown in Figure 7-3. (b) Corresponding average volume and vertical growth rates plotted as a function of the incident electron flux. The electron irradiation area used in the flux calculation was calculated using the top diameters of the deposits seen clearly in Figure 7-3.
The effects of EBID growth time on the growth kinetics are illustrated by Figure 7-4(b), showing the average deposit vertical and volume growth rates plotted for exposure times of 4, 8, 16 and 32 minutes (using an electron flux of $2.3 \times 10^{17} \text{cm}^{-2} \text{s}^{-1}$). Both the vertical growth rate and the volume growth rate increase with increasing electron fluence. Direct comparison of our measured growth rates to experimental data in the literature is not very meaningful because the growth rates are affected by parameters such as precursor pressure, desorption time, dissociation cross-section, electron flux and deposit geometry, many of which are either not known, or not specified by published papers. However, for completeness, Table 7-1 lists some reported vertical growth rates and estimated electron fluxes used for EBID of materials such as carbon,\textsuperscript{11,12} platinum,\textsuperscript{13-15} tungsten,\textsuperscript{16-18} cobalt\textsuperscript{19} and rhodium.\textsuperscript{20} These deposits were grown using stationary focused or defocused electron beams by high vacuum SEM or environmental SEM. The growth rates span 3 orders of magnitude due to the wide variety of EBID precursors and experimental conditions.

The high complexity of EBID growth kinetics\textsuperscript{5,6} makes simplifying experimental conditions highly desirable in basic EBID studies. Our results show that defocused, low flux, stationary electron beams can be used to eliminate complications caused by adsorbate depletion and scanned electron beams. However, the results also show that care must nevertheless be exercised due to complications arising from (i) differences between the material properties of the deposit and the substrate which lead to changes in electron emissivity during EBID, and (ii) complications caused by electron emission from deposit sidewalls, which affect volume growth rates.
Table 7-1. Vertical growth rate of the EBID deposits at different electron flux.

<table>
<thead>
<tr>
<th>Deposits</th>
<th>Precursor</th>
<th>Pressure (mTorr)</th>
<th>Beam energy (keV)</th>
<th>Beam current (pA)</th>
<th>Estimated electron flux (cm$^2$s$^{-1}$)</th>
<th>Growth rate (nm/s)</th>
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<tr>
<td>C</td>
<td>C$<em>{22}$H$</em>{46}$</td>
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<td>20</td>
<td>100pA</td>
<td>$6.3 \times 10^{18}$</td>
<td>21</td>
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<tr>
<td>C</td>
<td>C$<em>{14}$H$</em>{10}$</td>
<td>1</td>
<td>15</td>
<td>100pA</td>
<td>$8.0 \times 10^{18}$</td>
<td>10</td>
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<tr>
<td>Pt</td>
<td>C$_5$H$_3$Pt(CH$_3$)$_3$</td>
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<td>15</td>
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<td>$3.4 \times 10^{18}$</td>
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<td>W</td>
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<tr>
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7.3.2 Deposit nanostructures and composition

Figure 7-5 shows bright field TEM images of FIB cross-sections of the deposits shown in Figure 7-1. Nanocrystallites can be seen clearly in the higher magnification TEM image shown in Figure 7-6. The spacing between the fringes was measured at ~3.75 Å and 2.645 Å, which is in good agreement with the lattice spacing of the (200) and (220) planes of cubic tungsten trioxide.

An amorphous layer with a thickness of ~5 nm is present at the interface between the bottom of the deposit and the single crystal GaAs substrate. Figure 7-7(a) shows EDS spectra collected from the bulk EBID deposit, the interfacial amorphous layer, and the GaAs substrate. The spectra reveal that the amorphous layer contains Ga, As, O, W, and traces of carbon. No obvious F peak was observed in the x-ray spectra. In order to verify the absence of F, electron energy loss spectroscopy (EELS) was used to investigate the composition of the amorphous layer. Figure 7-7(b) shows the energy loss spectrum.
(ranging from 425 to 900 eV) taken from the amorphous layer in diffraction mode using a GIF200 spectrometer attached to a JEOL 2010F high-resolution TEM. The energy loss near edge structure around 532 eV corresponds to the oxygen K ionization edge. No obvious fluorine K ionization edge (685 eV) was observed and thus it is concluded that the concentration of F inside the amorphous layer was below the EELS detectability limit (of <1%). The amorphous layer likely formed during plasma cleaning of the GaAs substrate.

It is known that a reduction reaction between WF$_6$ and GaAs will take place at room temperature,$^{21-23}$

$$WF_6(g) + 2Ga(s) \rightarrow W(s) + 2GaF_3(s)$$

TEM analysis (not shown here) of a control GaAs specimen that was placed inside the ESEM chamber during EBID, but not exposed to electrons showed that this amorphous layer still exist. In addition, another cross-sectional TEM sample of virgin GaAs that was not exposed to either WF$_6$, the plasma, nor electrons was prepared and the TEM analysis showed that no obvious amorphous layer was present. All of these results, combined with the EDS analysis in Figure 7-7, indicate that the amorphous layer formed during oxygen plasma cleaning.
Figure 7-5. TEM images of cross-sections of the deposits (grown on GaAs).

Figure 7-6. High-resolution TEM image of the deposit-substrate interface.

Image corresponds to the “defocus 8” deposit on (100) GaAs. The deposit consists of 5-10 nm nanocrystallites embedded in an amorphous matrix. The nanocrystallite interplanar spacings and an amorphous interfacial layer are shown on the image.
Figure 7-7. EDS and EELS analysis.

(a) EDS spectra showing the composition of the deposit, interfacial amorphous layer, and substrate shown in Figure 7-6. The amorphous layer contains Ga, As, O and a trace of carbon. (b) The EELS spectrum of the amorphous layer, which shows that it contains oxygen, but does not contain fluorine.
Figure 7-8 shows cross-sectional TEM images of the deposits shown in Figure 7-3, and selected area diffraction (SAD) patterns taken from the center of each deposit. The deposits consist of nanocrystals with diameters in the range of 2-5 nm embedded in an amorphous matrix. The mean areas of the crystallites seen in Figure 7-8 are summarized in Table 7-2. Both the images and diffraction patterns indicate an increase in deposit crystallinity and grain size with growth time. A clear trend is seen in the selected area diffraction (SAD) patterns. At one extreme, the SAD pattern from the 4 minute deposit (inset of Figure 7-8(a)) is very hazy, with only the first few diffraction rings resolved. Conversely, the SAD pattern from the 32 minute deposit (inset of Figure 7-8 (d)), exhibits twelve sharp, distinct rings, indicating a higher degree of crystallinity and larger grain size.

A typical x-ray spectrum of the deposited material is shown in Figure 7-9, indicating that the deposits contain O, W and traces of C (Cu peaks seen in the spectrum originate from a Cu grid used to mount the sample). The presence of O and C, which are not present in the precursor molecule, can be accounted for by mass spectroscopy of the precursor. Figure 7-10 shows a mass spectrum of the gas present in the ESEM chamber during EBID. The spectral range of 0 to 50 u contains peaks that can not be assigned\textsuperscript{24} to WF\textsubscript{6} or its constituents, and have been assigned species containing O, C, H, N and F. The peak at 85u is tentatively assigned to SiF\textsubscript{3}\textsuperscript{+}, which likely originates from reactions\textsuperscript{31,32} between F-containing species and SiO\textsubscript{x}/Si substrate in the ESEM chamber. All peaks above 85 u were assigned\textsuperscript{24} to the WF\textsubscript{6} fragments as indicated in Figure 7-10(WF\textsubscript{6}\textsuperscript{+} itself is beyond the range of the mass spectrometer used in this work). The observed oxidization of W crystallites is
Figure 7-8. Bright field TEM image of the deposits.

Images (a)-(d) correspond to 4, 8, 16 and 32 min deposits on Si substrate, respectively, shown in Figure 7-3. Insets: selected area diffraction (SAD) patterns taken from the center of each deposit.

Table 7-2. Dimensions of the deposits and nanocrystallites.

<table>
<thead>
<tr>
<th>t (min)</th>
<th>h (nm)</th>
<th>d_t, d_b (nm)</th>
<th>A (nm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>64</td>
<td>1211,1220</td>
<td>10.2±0.6</td>
</tr>
<tr>
<td>8</td>
<td>132</td>
<td>1193,1344</td>
<td>16.1±1.9</td>
</tr>
<tr>
<td>16</td>
<td>288</td>
<td>1252,1500</td>
<td>21.7±2.9</td>
</tr>
<tr>
<td>32</td>
<td>678</td>
<td>1253,1747</td>
<td>25.1±2.2</td>
</tr>
</tbody>
</table>

[t = deposition time, h = height, d_t and d_b = top and base diameter respectively, A = mean crystallite area].

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Figure 7-9. A representative energy dispersive x-ray spectrum of the deposit.

Figure 7-10. Mass Spectrum in ESEM deposition chamber.

Mass spectrum showing low atomic number impurities in the gas used for EBID (all species shown are singly ionized unless indicated otherwise; in cases of multi-assignments, the most probable species is listed on top; n = 182, 183, 184, 186)
therefore attributed to the presence residual gases in the ESEM chamber, such as oxygen and water vapor.

According to the equilibrium phase diagrams of elemental tungsten and its alloys, the nanocrystallites can be pure tungsten, tungsten carbide and tungsten oxide. Table 7-3 lists some crystallographic data for possible equilibrium phases. To determine the phase of the crystallites, the diffraction patterns were indexed and the interplanar spacings corresponding to the sharp diffraction rings were measured. The data are consistent with the typical body-centered cubic structure of WO₃ with a lattice constant of a=7.521Å (shown in Table 7-4). The lattice images of the WO₃ nanocrystallites throughout the deposit are all consistent with this phase as well, although oriented with different zone axes parallel to the electron beam. No evidence was seen in the diffraction patterns of a preferred growth direction, but further work is needed to determine this unambiguously.

To explain the changes in deposit nanostructure seen in Figure 7-8, Monte Carlo simulations of electron energy deposition into the sample at different stages of WO₃ growth were performed. The substrate was approximated by bulk Si (i.e., the 5 nm oxide layer was ignored), and the EBID-grown material by bulk WO₃. Figure 7-11 shows plots of dE/dz, the mean energy (E) deposited per incident electron per unit depth (z), as a function of z for WO₃ thicknesses in the range of 0 to 800 nm. The dE/dz profiles show that the energy deposition rate per unit volume (which is proportional to dE/dz) at every z-coordinate in WO₃ and the total energy deposited into WO₃ (Eₚ₃) both increase with WO₃ thickness, over the range of thicknesses studied in this work. This is illustrated more clearly by the inset of Figure 7-11, showing the total energy deposited into the top 11 nm
of WO₃ (E₁₁) and into the whole WO₃ overlayer (EₗW₃), both plotted as a function of WO₃ thickness.

The results in Figure 7-11 are representative of the energy deposition behavior occurring during EBID of the structures shown in Figure 7-8. Hence, the extent of electron beam induced material modification occurring during EBID is expected to increase with deposition time, which correlates with the increasing grain size and crystallinity seen in Figure 7-8. The relative significance of the energy deposition rate and total energy deposited into a unit volume of EBID-grown material remain unclear, however, and are the subject of ongoing investigation. Similarly, discrimination between possible mechanisms behind the observed changes in nanostructure (including decomposition of EBID reaction products other than WO₃, charging, diffusion and drift of mobile species through the deposit, formation and desorption of volatile products such as CO, and electron beam induced heating) requires further work.
Table 7-3. Possible equilibrium phases of tungsten and its alloys.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Type</th>
<th>Space group</th>
<th>Lattice constant (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α W</td>
<td>Body-centered cubic$^{27}$</td>
<td>Im3m (229)</td>
<td>a=3.159</td>
</tr>
<tr>
<td>β W</td>
<td>Cubic$^{27}$</td>
<td>Pm3n (223)</td>
<td>a=5.05</td>
</tr>
<tr>
<td>WC</td>
<td>Hexagonal$^{27}$</td>
<td>P6m2 (187)</td>
<td>a=2.906; c=2.836</td>
</tr>
<tr>
<td>W$_2$C</td>
<td>Hexagonal$^{27}$</td>
<td>P31m (162)</td>
<td>a=5.190; c=4.724</td>
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<tr>
<td>αW$_2$C</td>
<td>Hexagonal$^{27}$</td>
<td>P3m1 (164)</td>
<td>a=2.997; c=4.727</td>
</tr>
<tr>
<td>W$_3$C</td>
<td>Body-centered cubic$^{27}$</td>
<td>Pm3n (223)</td>
<td>a=5.033</td>
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<tr>
<td>WO$_2$</td>
<td>Monoclinic$^{27}$</td>
<td>P2$_1$/c (14)</td>
<td>a=5.563; b=4.896; c=5.563; β=120.7°</td>
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<tr>
<td>WO$_3$</td>
<td>Monoclinic$^{27}$</td>
<td>P2$_1$/n (14)</td>
<td>a=7.301; b=7.538; c=7.689; β=90.9°</td>
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<tr>
<td>WO$_3$</td>
<td>Monoclinic$^{27}$</td>
<td>P2$_1$/n (14)</td>
<td>a=5.261; b=5.128; c=7.650, β=92.1°</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>Hexagonal$^{27}$</td>
<td>P6/mmm (191)</td>
<td>a=7.298; c=7.798</td>
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<tr>
<td>WO$_3$</td>
<td>Triclinic$^{28}$</td>
<td>P1-C$_1$ (2)</td>
<td>a=7.30; b=7.52; c=3.84; α=88.5°; β=90.6°; γ=90.6°</td>
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<tr>
<td>WO$_3$</td>
<td>Cubic$^{29}$</td>
<td>Pm3m (221)</td>
<td>a=3.78</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>Body-centered cubic$^{30}$</td>
<td>Im3m (229)</td>
<td>a=7.52</td>
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Table 7-4. Measured and reported d-spacings values for bcc WO$_3$.

<table>
<thead>
<tr>
<th>$d_{hkl}$ Å (measured)</th>
<th>$hkl$</th>
<th>$d_{hkl}$ Å (reported)</th>
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<tr>
<td>3.7730</td>
<td>200</td>
<td>3.7605</td>
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<tr>
<td>2.6252</td>
<td>220</td>
<td>2.6591</td>
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<tr>
<td>2.1701</td>
<td>222</td>
<td>2.1711</td>
</tr>
<tr>
<td>1.8693</td>
<td>400</td>
<td>1.8802</td>
</tr>
<tr>
<td>1.6711</td>
<td>420</td>
<td>1.6817</td>
</tr>
<tr>
<td>1.5213</td>
<td>422</td>
<td>1.5352</td>
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<tr>
<td>1.3195</td>
<td>440</td>
<td>1.3295</td>
</tr>
<tr>
<td>1.2493</td>
<td>600, 442</td>
<td>1.2535</td>
</tr>
<tr>
<td>1.2187</td>
<td>611, 532</td>
<td>1.2201</td>
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<td>1.1923</td>
<td>620</td>
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<td>1.0798</td>
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<td>1.0441</td>
<td>640</td>
<td>1.0430</td>
</tr>
<tr>
<td>1.0029</td>
<td>642</td>
<td>1.0050</td>
</tr>
</tbody>
</table>
Figure 7-11. Electron energy deposition profiles in deposits.

Depth-resolved total electron energy deposition profiles in bulk Si, and in multilayers consisting of a WO$_3$ overlayer on bulk Si, calculated for WO$_3$ thicknesses in the range of 0.1 to 0.8 μm. The solid-vacuum interface is at $z = 0$. WO$_3$-Si interfaces are indicated by vertical lines. $dE/dz$ is the mean energy deposited per incident electron per unit depth. Inset: Total amount of energy deposited into the top 11 nm and into the WO$_3$ overlayer ($E_{11}$ and $E_{WO3}$, respectively) plotted as a function of WO$_3$ thickness [accelerating voltage = 20 keV, $10^5$ electrons per simulation].
7.4 Summary

Tungsten-containing nanostructures were fabricated on GaAs and Si substrates by ESEM EBID using WF$_6$ precursor and electron beams with Gaussian and top-hat flux profiles. The growth kinetics of deposits made using well controlled electron flux and fluence were investigated. In the case of electron flux, the vertical growth rate increases gradually with increasing electron flux. A constant average volume growth rate per unit beam current indicates the absence of significant adsorbate depletion effects in our experiments. In the case of electron fluence, both the vertical and volume growth rate increases with incident electron fluence. TEM and electron diffraction analysis showed that the as-deposited structures consist of 2–5 nm WO$_3$ nanocrystallites embedded in an amorphous matrix. The nanostructure of the tungsten trioxide deposits revealed an increase in the degree of crystallity of the amorphous materials between the oxide nanocrystallites as a function of electron irradiation time. The increase in crystallinity correlates with an increase in energy deposition into the substrate during EBID.
7.5 References


"NIST Database (webbook.nist.gov/chemistry/form-ser.html)."


Chapter 8

8. Resistivity and impurity carbon sp$^2$/sp$^3$ bond ratio measurements

8.1. Introduction

Previous experimental results indicated that the degradation of resistivity was caused mainly by the inclusion of C atoms. Although many progresses have been made on reduction of impurity incorporation using in-situ or ex-situ methods, less attention has been paid to the characterization and quantification of the nature of the amorphous carbonaceous species inside the deposits. Most characterization techniques for EBID deposits, including Auger electron microscopy (AES), energy dispersive spectroscopy (EDS), and secondary ion mass spectroscopy (SIMS) can not obtain the chemical bond information of the carbon impurities, which is very important for the electrical characteristics of the deposits. The minimum feature size of EBID deposits has approached into nanometer range, which gives a great challenge to the spatial resolution of the above techniques. A systematic evaluation is necessary in order to understand the relationship between the structural, chemical homogeneity and the resistivity of electron beam induced metal deposits. In this chapter, detailed electrical and microstructural characterizations of EBID tungsten deposits from W(CO)$_6$ were performed, and the relationship between deposition conditions and the degree of structural and chemical homogeneity as well as the resistivity of electron beam induced tungsten deposits were also investigated. In addition, the resistivity of Pt line deposits fabricated using Pt(PF$_3$)$_4$ in environmental SEM and (CH$_3$)$_3$CH$_2$C$_3$H$_4$Pt in standard SEM were also measured and compared. The cross-sectional TEM analysis was performed on these line deposits to evaluate the crystallinity.
8.2. Experimental Methods

EBID was performed using an FEI Nova 600 NanoLab FIB/SEM system. The substrate was 30nm Si₃N₄ membrane (SPI Supplies), plasma cleaned prior to EBID to remove residual surface hydrocarbons. Tungsten hexacarbonyl [W(CO)₆] was used as the EBID precursor. The base pressure of the vacuum chamber prior to introducing precursor gas was less than 5.0×10⁻⁷ Torr, and the stable precursor pressure during deposition experiments was approximately 5×10⁻⁶ Torr. All depositions were performed at room temperature with the electron beam energies of 5, 10, 15, 20, and 30keV and nominal beam current of 2.0 nA for all beam energies. The electron beam was set as line scan mode, and the beam dwell time was 3 µs. The beam raster dimension was fixed as 14µm long. Deposition time was set as 30 seconds for each deposit.

Following growth, the microstructure and the carbon sp²/sp³ bond ratio of the samples were examined in a JEOL 2010F transmission electron microscope (TEM) equipped with a Gatan GIF 200 electron energy loss spectrometer, operating at 0.5eV/channel for the collection of carbon K ionization edge spectra. After collecting the spectra, background and plural scattering were removed by using Gatan DigitalMicrograph software. The quantification analysis process can be found in the previous chapter of experimental setup.

In order to measure the resistivity, W lines were also deposited on SiO₂/Si wafer which had been pre-patterned with four-terminal Au electrodes (100 nm thick) using conventional lithography and wet-etching techniques. The deposition parameters are same as those for Si₃N₄ experiment, except that the deposition time was 10 minutes. The resistance of the deposits was measured at room temperature, using a four-point probe
KEITHLEY 4200-SCS Semiconductor Characterization System. The cross-section area of the W deposits was measured by SEM image of FIB cross-section on the deposit.

The resistivity of Pt-containing nanowires fabricated on substrate with pre-patterned with four-terminal Au electrodes using Pt(PF₃)₄ in environmental SEM and (CH₃)₃CH₅C₅H₄Pt in standard SEM were also measured and compared. For each set of experiment, a series of nanowires was deposited with the same total dose, and same total exposure time but with different doses per scan and corresponding total numbers of scans per line. As a result, the dwell and loop times scale linearly with the dose per scan. For the purpose of simplicity, line-scan time is used in the following text. For the nanowires made in standard SEM, the beam energy and current were 20 keV and 2 nA, respectively. The line-scan length was 20 μm and the line-scan time for was varied from 0.0233 ms to 512 ms. The total deposition time for each nanowire was 5 minutes. For the nanowires made in environmental standard SEM, the beam energy and current were 20 keV and 3 nA, respectively. The line-scan length was 20 μm and the line-scan time was varied from 1.68 ms to 233.3 ms. The total deposition time for each line deposit was 5 minutes. After resistivity measurement, the cross-sectional TEM analysis was performed on these line deposits to evaluate the crystallinity.

8.3. Results and Discussions

8.3.1. W-containing nanowire deposition

A SEM image of the as-deposited structure is given in Figure 8-1(a). At higher magnification in the TEM, it can be seen that the microstructure of the deposit comprises metal-rich particulates in an amorphous matrix of a lighter atomic number (Figure 8-1(b)). Figure 8-2 shows the as-recorded energy loss spectra at an energy resolution of about 1.5
eV for the FWHM of zero loss peaks. The nitrogen peak came from the substrate. It also verified the presence of carbonaceous species inside the deposits.

Figure 8-3(a) shows the collected carbon K-ionization edge with plural scattering background removed. The edge shape can be decomposed into four separate features representing energy loss processes associated with $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma^*$ transitions, a third peak associated with C-H bonds (transition from 1s to C-H anti-bonding orbital), and the transitions from the 1s state to the continuum. The bound state transitions can be fitted to Gaussian peaks centered 285, 287 and 292 eV respectively, as shown in Figure 8-3(b). The incorporation of C-H bond is due to the unintentional hydrocarbon contamination and residual water vapor present in the chamber. The carbon sp²/sp³ ratio (x) can be obtained from the shape of the carbon absorption edge. Quantitative analysis of the near edge structure requires a standard, and is based on comparing the ratio of the normalized $1s \rightarrow \pi^*$ to $1s \rightarrow \sigma^*$ transition peak integrals of the sample to that of the standard.

It should be noted that the full width at half maximum (FWHM) of the Gaussian peaks is about 5-10 eV (see Figure 8-3(b)) in order to obtain minimum residuals from the peak fittings. This value is larger than the energy resolution of electron energy loss spectrometer. Taking into consideration the spectrometer energy resolution, a new criteria for the peak-fitting is used to perform the following quantification process on the carbon energy loss near structures of the W-containing deposit grown at various beam energy. The three peak positions are fixed at 285 eV, 287 eV, and 292 eV, corresponding to the $1s \rightarrow \pi^*$, $1s \rightarrow \sigma^*$, and 1s to C-H anti-bonding orbital transition, respectively. The FWHM of each peak is fixed at 2 eV, which is the normal spectrometer energy resolution. The
residuals resulting from this peak fitting procedure represent some other electronic
transitions,\textsuperscript{15,16} which are not considered in this work.

To a good approximation, the ratio of the integrated areas under the Gaussian
peak $I_\pi$ ($1s \rightarrow \pi^*$) and the peak $I_\sigma$ ($1s \rightarrow \sigma^*$) is proportional to $N_\pi/N_\sigma$, the ratio of the
number of $\pi$ and $\sigma$ orbitals. $N_\pi/N_\sigma$ is $1/3$ for 100% sp$^2$ (sp$^2$ hybridization, three hybridized
orbitals form three equivalent $\sigma$ bonds and the rest unhybridized p orbital forms one $\pi$
bond) and $0/4$ for 100% sp$^3$ (sp$^3$ hybridization, four hybridized orbitals form four
equivalent $\sigma$ bonds, no $\pi$ bond) bonded carbon, the number fraction of sp$^2$ bonded atoms
(x) can be derived by the following equation\textsuperscript{2}

$$x = \frac{sp^2}{sp^2 + sp^3} = \frac{N_\pi}{N_\pi + (N_\sigma - 3N_\pi)/4} = \frac{4N_\sigma}{N_\pi + N_\sigma}$$  \hspace{1cm} (8.1)

$$\frac{N_\pi}{N_\sigma} = \frac{x}{4 - x}$$  \hspace{1cm} (8.2)

Where

$$\frac{N_\pi}{N_\sigma} = \frac{[I_\pi/I_\sigma]_{\text{unknown}}}{3[I_\pi/I_\sigma]_{\text{standard}}}$$  \hspace{1cm} (8.3)

Substituting Eq. (8.2) into Eq. (8.3), the following equation can be obtained

$$\frac{[I_\pi/I_\sigma]_{\text{unknown}}}{[I_\pi/I_\sigma]_{\text{standard}}} = \frac{3x}{4 - x}$$  \hspace{1cm} (8.4)

Where $x$ is the sp$^2$ bond fraction inside the sample, $I_\pi$ is the integrated intensity of $1s \rightarrow$
$\pi^*$ transition peak, $I_\sigma$ is the integrated intensity of $1s \rightarrow \sigma^*$ transition peak.
Figure 8-1. SEM and TEM of the EBID tungsten containing line deposits.

(a) Scanning electron micrograph of EBID tungsten containing lines deposited on 30 nm Si$_3$N$_4$ membrane using electron beam energy of 5, 10, 15, 20, and 30keV, (top to bottom) respectively and (b) High-resolution transmission electron micrograph of as-deposited W nanostructures.

Figure 8-2. Electron energy loss spectra of EBID tungsten containing line deposits.

Electron energy loss spectra of EBID tungsten containing lines deposited on 30 nm Si$_3$N$_4$ membrane using electron beam energy of 5, 10, 15, 20, and 30keV.
Figure 8-3. Gaussian peak fitting of carbon K-ionization edge.

(a) The C K-ionization edge obtained from EBID_W with background subtraction and plural scattering removal and (b) showing the ELNES fit obtained when using three Gaussian peaks centered at 285, 287, and 292 eV.
For this study, C\textsubscript{60} fullerene was chosen as the standard because it does not suffer from this preferential orientation effects and is close to 100% sp\textsuperscript{2} bonded due to its nearly pure character. This analysis technique was used to examine the carbon bond character as a function of deposition conditions.

An example of EBID W line structure was shown in Figure 8-4(a). The lines had Gaussian-type cross section with dimensions of about 200nm in both bottom width and height as shown in Figure 8-4(b). The dependence of measured resistivity and sp\textsuperscript{2}/sp\textsuperscript{3} ratio on deposition beam energy was plotted in Figure 8-5. With increasing electron beam energy, the resistivity of the as-deposited W increase from 2.0×10\textsuperscript{7} \(\mu\Omega\) cm to 1.2×10\textsuperscript{9} \(\mu\Omega\) cm, while the carbon sp\textsuperscript{2}/sp\textsuperscript{3} bond ratio decreases from 1 to 0.6. The increase of resistivity is attributed to the decreasing fraction of graphitic (sp\textsuperscript{2}) bonded carbon inside the deposits. It is possible that high energy irradiation causes the polymer hydrogen carbon bond scission. When a C-H bond is broken, the hydrogen atoms may combine in pairs to form hydrogen gas. The free radical will seek to stabilize itself by combining other radicals resulting increasing sp\textsuperscript{3} bond fraction at higher beam energy. Another possible explanation of the decreasing resistivity with decreasing primary beam energy is that the secondary electron yield will increase with decreasing incident beam energy. Higher secondary electron emission can cause an increase in dissociation of the adsorbed precursor molecules resulting in a higher metal content. In addition, this will also cause an increase in the secondary electron stimulated desorption rate of the molecule\textsuperscript{3} (including both partially dissociated precursor molecules and the corresponding fragments or ligands). Both of these two effects may cause a decrease in resistivity of the deposit while the primary electron beam energy decreases.
(a) Overview of the structure used to measure resistivity: four-point configuration after W deposition, Au electrodes on SiO$_2$/Si and (b) scanning electron micrograph of FIB cross-section on the as-deposited W line ($E_0=20$keV).

Figure 8-5. Resistivity and carbon sp$^2$/sp$^3$ ratio versus beam energy.

The variation of the carbon sp$^2$ to sp$^3$ bond ratio (■), for a series of as-deposited Tungsten lines on Si$_3$N$_4$ membrane, and the measured resistivity (□) as a function of deposition beam energy.

8.3.2. Pt-containing nanowire deposition

In order to study the effects of beam scanning speed on the resistivity of the EBID line deposits, the resistivity of Pt-containing line deposits fabricated Pt(PF$_3$)$_4$ in
environmental SEM and (CH$_3$)$_3$CH$_2$C$_5$H$_4$Pt in standard SEM were also measured and compared. Figure 8-6(a) shows one example of the Pt-line deposit across the four Au electrodes. Figure 8-6(b) and Figure 8-6(c) present the SEM images of the wires as they connect to the Au electrodes, which were taken at 45 degree to the sample surface to show the 3D geometry of the nanowires. In order to extract a contact resistance between the gold electrodes and the wires, both two-probe and four-probe measurements were performed, and the contact resistance was always immeasurably small as compared to the nanowire resistance.

The resistances of these nanowires were measured using four-point probe method described in previous chapter. The dimensions of the nanowire cross section were obtained by FIB sectioning. In order to avoid ion beam damage to nanowires, a 30-50 nm Ir thin film was sputter coated on the specimen before FIB cutting. Figure 8-7 shows the summary of the cross-sectional SEM images of theses nanowires made using an electron beam line scan time ranging from 0.42 to 233.3 ms. The nanowires had a Gaussian-type cross section as shown in Figure 8-7, which is an image of a cross section through the nanowire created by FIB milling. It can also be seen that the vertical growth rate of these nanowires increased abruptly, then reached a steady state with small fluctuation and eventually decreases quickly with increasing line-scan time (from fast to low scan speed), which indicated the transition from reaction-rate-limited growth regime to mass-transport-limited growth regime. During the EBID process, the molecule adsorption to the surface and the electron-impact dissociation occur simultaneously and compete with each other. For the fast scanning electron beam with a short dwell time, the electrons do not have enough time to dissociate the adsorbed molecules and the dissociation efficiency
as well as the growth rate is actually limited by the incident electron flux, as shown in Figure 8-9 (line-scan time from 0.42 to 1.68 ms). While the line-scan time increases, the corresponding dwell time per pixel also increases linearly, resulting in a higher growth rate. While the line-scan time keeps increasing, the growth rate starts decreasing, as shown in Figure 8-9 (line-scan time from 33.2 to 233.3 ms). This can be explained by the precursor depletion effect during the deposition process. For a relative slow scan beam (long dwell time), the area under the beam will quickly become depleted of mobile precursor molecules due to the high dose of the electrons. The supply of new molecules will have to come from outside the irradiated surface area as well as the vacuum chamber. So the growth rate is limited by the molecule transport rate and the deposition is in the mass-transport-limited (MTL) growth regime. What’s more, the deposit densification caused by electron irradiation\textsuperscript{14} during the deposition may also contribute the decrease in vertical growth rate. The middle region in Figure 8-9 is interesting and can be seen as an equilibrium state between dissociation and adsorption of the precursor molecules. The small fluctuation in the vertical growth rate is probably due to the experimental variations during the deposition process, such as local surface conditions, beam current variations, etc.
Figure 8-6. Pt-containing line deposit across Au electrodes.

(a) Top down view of the structure used to measure resistivity: four-point configuration after Pt-containing line deposition, Au electrodes on SiO$_2$/Si. Line deposit made using line scan time of 1.68 ms (b) and 116.7 ms (c), stage tilt=45°.
Figure 8-7. Cross-sectional SEM images of the Pt lines (Pt(PF₃)₄, ESEM).
Figure 8-8. Cross-sectional SEM images of the Pt lines ((CH₃)₃CH₂C₅H₄Pt, SEM).
Figure 8-9. Vertical growth rate versus line scan time.

The vertical growth rate of the cross-section of EBID Pt-containing nanowire (Pt(PF₃)₄, ESEM) and ((CH₃)₃C₃H₄Pt, SEM ) as a function of the scan time of the electron beam.

Figure 8-10. Resistivity versus line scan time.

Measured resistivity of EBID Pt lines deposits grown using Pt(PF₃)₄ in ESEM and (CH₃)₃CH₃C₃H₄Pt in dual beam system as a function of line scan time. Beam energy is fixed at 20 keV while the beam current is 2 nA and 3 nA for samples made in dual beam system and ESEM system respectively.
Similar analyses were also performed on the specimens prepared in SEM at high vacuum conditions using \((\text{CH}_3)_3\text{C}_5\text{H}_4\text{Pt}\) as precursor gas. Figure 8-8 shows the summary of the cross-sectional SEM images of these nanowires made using an electron beam line scan time ranging from 0.0256 to 512 ms. The corresponding growth rate was also plotted in Figure 8-9. One obvious difference between these two plots is that the growth rate of nanowires made in high vacuum conditions shows a transition from RRL regime to MTL regime. The absence of the steady regime is attributed to the relative low local precursor gas pressure \((6 \times 10^{-4} \text{ Pa})\) compared to the chamber pressure \((16 \text{ Pa})\) in ESEM system.

The as-measured resistivities of these nanowires as a function of the line scan time were plotted in Figure 8-10. It was found that the resistivity decreases rapidly with increasing line scan time, which is consistent with results from other metal line deposits\(^4\) in the literature. The deposition efficiency for the first two line deposits made under fast scanning electron beam in ESEM is relatively low, which results in either low metal content or discontinuous deposits. The as-measured resistivity is not accurate and has been taken out from the plot. Resistivity differences of about four orders of magnitude have been found. The resistivity measurements on the nanowires made using \((\text{CH}_3)_3\text{C}_5\text{H}_4\text{Pt}\) as precursor show a high resistivity of about 200 \(\Omega\) cm for a line scan time of 0.0256 ms and a low resistivity of about 25 \(\Omega\) cm for a line scan time of 512 ms.

The lowest resistivity of the nanowires measured reached about 2500 \(\mu\Omega\) cm, which is still 250 times higher than the resistivity of pure bulk platinum \((10.5 \mu\Omega\text{ cm})\). This resistivity difference was supposed to be due to microstructures and impurities in the nanowires. It was reported that the incorporation of phosphorus can be reduced by
heating substrates or introducing oxygen to oxidize the impurities during depositions.\textsuperscript{5} The improvement of the resistivity (reduction by factors of 1.6-9.9) by the post-deposition heating process in air has been demonstrated.\textsuperscript{6} Shrink of the deposits and decrease in their P content were observed.

The increase in resistivity with increasing line scan time can be explained via electron irradiation dose. From the cross-sectional SEM images of the deposits; the line widths can be assumed same value. The various line scan time determines the total electron dose per scan (fast scan results in a low electron irradiation dose). At low irradiation doses (low number of electrons per area), the deposits may contain more impurities (e.g., C or P), resulting from incomplete decomposition of the organometallic precursor and incorporation of the reaction fragments on the deposited metal films, which resulted in a higher resistivity. At higher irradiation doses the Pt-rich final deposit formed with lower resistivity. From the electron molecule interaction point of view, the behavior can be explained as follows: at low doses the reaction is electron limited and proceeds to the intermediate (incomplete decomposed molecule) product other than final product (pure metal). At high doses the reaction is molecule limited, i.e., each molecule undergoes a larger number of electron collisions while at the surface, which will dissociate the intermediate product into the final product by releasing more ligands and leaving purer tungsten.\textsuperscript{4}

Another interesting result is that the resistivity of nanowires made using Pt\((\text{PF}_3)_4\) in ESEM system is about four orders lower than that of nanowires made using \((\text{CH}_3)_3\text{CH}_2\text{C}_5\text{H}_4\text{Pt}\) in standard SEM system, which indicated Pt\((\text{PF}_3)_4\) is a promising candidate precursor used for EBID applications, such as site-specific electrical contacts and interconnects.
Except that the deposition conditions are different for the two sets of specimens, the major differences between them are the choice of precursor gas. The carbon-free precursor, Pt(PF$_3$)$_4$, is assumed to result in deposits with higher purity than the organometallic precursor, (CH$_3$)$_3$CHC$_5$H$_4$Pt. Although more intensive Pt peak was always registered in the energy dispersive x-ray (EDX) spectra from deposit from Pt(PF$_3$)$_4$, it is difficult to speculate on the exact quantities of the elements compared to the x-ray microanalysis spectra of these two deposits. Auger analysis was performed to measure the elemental concentrations among the deposits with larger sizes made by these two precursors. It turned out that the metal concentrations in the specimens were similar, around 50-60 at.%. For Pt(PF$_3$)$_4$, carbon contamination could be eliminated while incorporation of Phosphorus in the deposits were verified by both AES and EELS analysis. TEM analysis indicated that the as-fabricated materials generally had polycrystalline structure, with nanometer-size nanocrystals embedded in an amorphous matrix which likely has a stronger disorder. As a result, the electrical properties (e.g., resistivity) of the nanocomposite granular material not only depend on the metal purity, but also the nanostructures of the materials, such as the material crystallinity, metal grain size and grain packing density. Hence cross-sectional TEM investigations were performed on the nanowires to evaluate the crystallinity. Two nanowires (fast and slow scan) from each set of deposits were selected to compare the line scan effects on the nanostructure. For instance, cross-sectional TEM samples were made from two nanowires ((CH$_3$)$_3$CHC$_5$H$_4$Pt, SEM) grown at a line scan time of 0.512 and 512 ms and two nanowires (Pt(PF$_3$)$_4$, ESEM) grown at a line scan time of 1.68 and 116.7 ms. Figure 8-11 shows the low and high magnification cross-sectional transmission electron
micrographs and the corresponding selected-area diffraction pattern of the Pt nanowire using Pt(PF$_3$)$_4$ in ESEM with a line scan time of 1.68 ms and 116.7 ms, respectively. The cross-sectional position of the 1.68 ms line deposit was intentionally located on both the Au/Cr/SiO$_2$ and SiO$_2$ substrate in order to compare the bottom interfaces between the line deposits and substrate.

The deposit shows polycrystalline character and contains Pt nanocrystallites embedded in an amorphous matrix. Pronounced inhomogeneities are clearly visible in the as-grown material. Several distinct regions are labeled “A” to “D” in Figure 8-11(a). The width of region A is about 20nm which is several times larger than the diameter of the focused electron beam (which had Gaussian electron flux profile) and indicates the position of the intensity peak of the focused electron beam. Within region A, the Pt crystallite size and packing density increase with distance from the deposit top surface towards region C. This change correlates with the (cumulative) electron energy density deposited into the nanocomposite during growth. This vertical line shape region can also be seen in the cross-sectional SEM image (not shown here), except that it appears to be brighter instead of darker in TEM image because this region has a higher density of Pt nanocrystals resulting in a higher secondary electron yield.

Regions B and C were grown by electrons emitted from the deposit sidewalls, and electrons backscattered from the Si substrate, respectively. Hence, the electron flux responsible for the growth of regions B and C was lower than of region A, as was the electron energy density deposited into regions B and C during EBID. The contrast seen between regions A, B and C is caused primarily by differences in the packing density of the Pt nanocrystallites.
The interfacial region D located between the substrate and the EBID-grown material has a lower Pt crystallite density than the adjacent regions A and B, and was observed only in deposits grown using relatively high electron fluxes and fluences. It was not observed in analogous deposits grown using WF_{6} precursor, nor in deposits grown using Pt(PF_{3})_{4} and low electron flux and fluence. It is suggested that region D may be a consequence of the materials densification (i.e., volume shrinkage) of region A under the electron irradiation during the deposition process. Close inspection of the “dark vertical line” (Region A in Figure 8-11(a)) reveals that it’s surrounded by a bright outline that looks similar to region D. This appears to support our suggestion that region D is a consequence of electron beam processing and volume shrinkage of a surrounding region. In addition, there may be some Pt transport from region D to region A.

Figure 8-11(b) shows the high-resolution TEM view of the specimen where the deposits consist of nanocrystals with diameters in the range 3-5 nm embedded in an amorphous matrix. The corresponding SAD patterns, as shown in Figure 8-11(c), are consistent with face-centered cubic (fcc) Pt with a lattice constant of \(a=3.92\text{Å}\) (JCPDS file No. 4-802). Evaluation of the lattice planes yields the spacings \(d_{111}=0.23\text{ nm}\) and \(d_{200}=0.20\text{ nm}\), in good agreement with those of bulk platinum. The diffraction patterns do not show any evidence of a preferred growth direction.
Figure 8-11. TEM and SAD patterns for Pt nanowires grown in ESEM system.

(a)-(b) Low and high magnification cross-sectional transmission electron micrograph and (c) the corresponding selected-area diffraction pattern of the Pt nanowire with line scan time of 1.68 ms using Pt(PF₃)₄ in ESEM; (d)-(f) correspond to the nanowire grown with line scan time of 116.7 ms.
TEM image of the slow scan deposit (Figure 8-11(d)), however, shows a more uniform structure. The uniform Pt grains distribution indicates the electron beam has enough time to process the as-deposited materials during the deposition, which make the grain size saturated. Both its TEM image and SAD pattern show an increase in grain size and crystallinity. For instance, the size of the Pt nanocrystallites is about 5-8 nm, which is larger than that deposit made with fast scan speed. Compare to Figure 8-11(c), the SAD pattern shown in Figure 8-11(f) also shows polycrystalline diffraction rings, with the presence of much more bright spots, which indicates higher crystallinity and grain size, as shown in Figure 8-11(e). It’s interesting that the vertical line is absent from the slow scan deposit since the total primary electron fluence was similar at each scan speed (beam current and deposition time were both fixed). This suggests that the electron flux plays a role in nanostructure formation.

It was expected that the bottom interface region is different from what has been seen on previous sample. This might be due to the charging issues since this portion of the line deposit is right on the insulating SiO₂ substrate. The formation of the interface region on different substrate (i.e., Au) verifies that this is not due to the reaction between Si substrate and the adsorbed precursor gas in the similar experiments performed on bared Si substrate. Ongoing studies of deposits grown using a range of precursors and substrates are being conducted to elucidate the mechanism behind the formation of this interfacial region.

Figure 8-12 shows the low and high magnification cross-sectional transmission electron micrographs and the corresponding selected-area diffraction pattern of the Pt nanowire using (CH₃)₃CH₃C₅H₄Pt under high vacuum condition in the SEM with
capillary gas injection system with a line scan time of 0.512 ms and 512 ms, respectively.

It can be seen that both the as-deposited nanowires consist of homogeneous distribution of the Pt nanocrystallites in the amorphous matrix. A slightly increase in grain size and crystallinity were observed from the slow scan nanowire, which was confirmed by the high-resolution TEM image and SAD patterns. This can be explained according to the preceding arguments.

Figure 8-12. TEM and SAD patterns for Pt nanowires grown in SEM system.

(a)-(b) Low and high magnification cross-sectional transmission electron micrograph and (c) the corresponding selected-area diffraction pattern of the Pt nanowire with line scan time of 0.512 ms using (CH₃)₃CH₂C₅H₄Pt in SEM; (d)-(f) correspond to the nanowire grown with line scan time of 512 ms.
Even though the nanostructure evolution is not significant for the high vacuum deposit, the differences in microstructure between them and the ESEM deposits still shed some light on tremendous difference in resistivity of these EBID nanowires. As I mentioned above, the Pt concentrations for both deposits are in the similar range value (50-60 at.%). The microstructures of the nanowires seem to play an important role in the electrical properties of the as-grown nanowires. TEM analysis (Figure 8-11 and Figure 8-12) shows that the nanowires consist of with a great volume fraction of metal nanocrystallites, where a metallic network may form. However, previous studies of the electron transport properties in such nanocomposites do not show metallic behavior even for the deposit with the lowest resistivity after heat annealing.\textsuperscript{10,11} The electron transport properties of the nanocomposite material is dependent on the conductance of the embedded metal nanocrystallites and the amorphous matrix. The giant drop in resistivity for nanowires shown in Figure 8-10 is attributed to the significant increase in the intergrain conductance (matrix) due to the higher packing density of the Pt nanocrystallites. In addition, the probability of the inter-grain tunneling occurring between the Pt nanocrystals embedded in the insulating matrix will increase dramatically. The electron mean free path is generally several nanometers,\textsuperscript{12,13} which is of the order of the metal grain size determined by high-resolution TEM image, suggesting the existence of the grain-boundary scattering within the nanowires. High degree crystallinity will also result in a decrease in structural defect, particularly with regard to grain boundaries between the single crystallites in the polycrystalline deposits, which can reduce the grain boundary scattering effect during the electron transport through the nanowire.
Furthermore, the coalescence of small Pt nanocrystals into large grains observed in Figure 8-11 will also contribute to the decrease of the resistivity.

8.4. Summary

In this chapter, the EBID metal-containing nanowires from various precursors were fabricated on top of a SiO$_2$ substrate in which Au electrodes were previously patterned by conventional lithography techniques. Their electrical resistivities were measured via standard four-point probe method. For deposits grown from W(CO)$_6$, analytical TEM and EELS analysis were used to gain insights into the impurity carbon chemical bonding-resistivity relationship of the deposits. With increasing electron beam energy, the resistivity of the as-deposited W increase from $2.0 \times 10^7$ $\mu\Omega$ cm to $1.2 \times 10^9$ $\mu\Omega$ cm, while the carbon sp$^2$/sp$^3$ bond ratio decreases from 1 to 0.6. The increase of resistivity is attributed to the decreasing fraction of graphitic (sp$^2$) bonded carbon inside the deposits.

As for the Pt-containing nanowires grown from (CH$_3$)$_3$CH$_2$C$_5$H$_4$Pt and Pt(PF$_3$)$_4$, resistivity measurements and the cross-sectional TEM analysis were performed. It has shown that the resistivity of the deposited material is dependent on the beam scanning conditions. Faster scanning gives higher vertical deposition rates, but the resulting material has higher resistivity. The measured resistivity ($\sim 10^4$ $\mu\Omega$ cm) from nanowire grown from Pt(PF$_3$)$_4$ is about four orders of magnitude smaller than that ($\sim 10^8$ $\mu\Omega$ cm) from those grown from (CH$_3$)$_3$CH$_2$C$_5$H$_4$Pt, which indicates this carbon-free precursor can be a good candidate for the application of low-resistance nanocontact and interconnects. The cross-sectional TEM analysis shows that the as-deposit materials have polycrystalline structures with nanometer-size nanocrystallites embedded in an
amorphous matrix. An increase in crystallinity and grain size of the deposited materials made using a slow scanning electron beam, which can be correlated to the decrease in the resistivity measured in the nanowire. TEM analysis also revealed that the nanowires formed by decomposition of Pt(PF₃)₄ have a higher degree of crystallinity and a larger size grain size compared to those by (CH₃)₃CH₅C₅H₄Pt.
8.5. References


7. Unpublished data


16. E. Sohmen and J. Fink, "Electron-energy-loss studies of Rb\textsubscript{x}C\textsubscript{60} and Rb\textsubscript{x}C\textsubscript{70} (x=0, 3, and 6)", Phys. Rev. B \textbf{47}, 14532 (1993)
Chapter 9

9. Conclusions and future directions

9.1 Conclusions

EBID structures were grown on bulk substrates from a variety of precursors including \((\text{CH}_3)_3\text{C}_5\text{H}_4\text{Pt}, \text{W(CO)}_6, \text{WF}_6 ,\text{and Pt(PF}_3)_4\) in either a high vacuum dual beam focused ion beam/scanning electron microscope (FIB/SEM) or an environmental scanning electron microscope (ESEM). The effects of deposition conditions on the growth kinetics, microstructure and composition of the grown materials, structural and chemical homogeneity of impurities inside the deposits as well as the resistivity are investigated.

EBID growth kinetics is affected by parameters such as precursor pressure, desorption time, dissociation cross-section, electron flux and deposit geometry, many of which are either not known, or not specified in published papers. In this work, low flux, stationary electron beams were used to eliminate complex growth kinetics caused by adsorbate depletion and by the scanning of electron beams during EBID. Such simplifications are highly desirable in basic, quantitative studies of EBID. The growth kinetics of deposits grown from WF\(_6\) precursor in ESEM using well controlled electron flux and fluence were investigated. In the case of electron flux, the vertical growth rate increases gradually with increasing electron flux. A constant average volume growth rate per unit beam current indicates the absence of significant adsorbate depletion effects in the experiments. In the case of electron fluence, both the vertical and volume growth rate increases with incident electron fluence. Experiment results show that care must be exercised due to complications arising from (i) differences between the material
properties of the deposit and the substrate that lead to changes in electron emissivity during EBID, and (ii) complications caused by electron emission from deposit sidewalls, which affect volume growth rates.

The ability to manipulate and process materials at the nanoscale with excellent reproducibility is important to the advancement of the nanotechnology field. Material grown by electron beam induced deposition (EBID) using (CH₃)₃CH₃C₅H₄Pt and WF₆ precursor show similar microstructures, metal oxide particles in an amorphous matrix, and metal particles in an amorphous matrix respectively. Changes in grain size and degree of crystallinity as function of EBID deposition conditions, e.g., electron flux and electron fluence, were observed. Specifically, material grown using (CH₃)₃CH₃C₅H₄Pt precursor consists of platinum nanocrystals embedded in an amorphous matrix. This nanocomposite is shown to intermix with the amorphous oxide on a Si substrate. The extent of intermixing scales with the electron beam fluence delivered to the material during EBID, and during post-growth electron beam irradiation in high vacuum (in the absence of the precursor). Dependencies on electron flux, fluence and electron exposure time indicate that beam-induced heating does not play a significant role in the observed intermixing between the crystallites and the amorphous oxide on a Si substrate, but rather that the process is electron-activated and rate limited by mass transport within the solid. Materials grown using WF₆ precursor consist of WO₃ nanocrystallites embedded in an amorphous matrix. The nanostructure of the tungsten trioxide deposits revealed an increase in the degree of crystallinity of the amorphous materials between the oxide nanocrystallites as a function of electron irradiation time. The increase in crystallinity correlates with an increase in energy deposition into the substrate during EBID,
indicating that electron beam induced modification of as-grown material is significant in controlling the nanostructure and functionality of materials fabricated by EBID. Our results show that the material nanostructure can be controlled by growth parameters that control the electron energy density delivered to the deposits during and after EBID. This is desirable because a key benefit of EBID is that it does not require bulk heating of the substrate.

EBID-grown materials from organometallic precursors are generally nanocomposites consisting of metal crystallites (with diameters in the range of 1 to 10 nm) embedded in an amorphous carbon-rich matrix composed of reaction byproducts and impurities present at the substrate surface during EBID. The chief impurities are carbon and oxygen, resulting from incomplete decomposition of the organometallic precursor and incorporation of the reaction fragments on the deposited metal-containing films. Deposits grown from W(CO)$_6$ precursor contain tungsten nanocrystals and hydrocarbon matrix. The chemical form of the impurity carbon, in term of $sp^2/sp^3$, was investigated by EELS. Experiment results show that the carbon $sp^2/sp^3$ bond ratio, as well as the resistivity of the deposits can be controlled by changing the deposition conditions, e.g., primary electron beam energy. With increasing electron beam energy, the resistivity of the as-deposited W increases while the carbon $sp^2/sp^3$ bond ratio decreases. The increase of resistivity is attributed to the decreasing fraction of graphitic ($sp^2$) bonded carbon inside the deposits.

Fundamental electrical property of the EBID-grown disorder material system (metal nanoparticles randomly distribute among amorphous matrix) does not depend on the composition solely, the metal grain size and packing density, the electron tunneling mode, electron-electron interaction, the inter-grain conductance, etc. will also influence the measured resistivity. Experiment results show that the average measured resistivity
(~10^4 \, \mu \Omega \cdot cm) from nanowires grown from Pt(PF_3)_4 is about four orders of magnitude smaller than that (~10^8 \, \mu \Omega \cdot cm) from those grown from (CH_3)_3CHC_5H_4Pt, even their metal purity are in similar range. Cross-sectional TEM analysis revealed that the nanowires formed by decomposition of Pt(PF_3)_4 have a higher degree of crystallinity and a larger size grain size and higher grain packing density compared to those formed by (CH_3)_3CHC_5H_4Pt, which can explain the giant drop in resistivity. Another important factor need to be taken into consideration is that the P-rich other than C-rich amorphous matrix for deposits grown from Pt(PF_3)_4 precursor. Further more, extent of electron beam induced material modification occurring during EBID are expected to increase with electron beam scanning speed for each set of line deposits, which correlates with the increasing grain size and crystallinity. All of the above results indicate the carbon-free precursor could be a good candidate for the fabrication of low-resistance nanocontact and interconnects and the electron beam induced material modification plays a significant role in the functionality of EBID-fabricated materials.

### 9.2 Future directions

Future work will include investigation of EBID grown metal-containing deposits in presence with environmental gases (such as H_2O, O_2, N_2O) to improve the noble metal purity and compare them with the deposits prepared in high vacuum environment. Quantifications of carbon sp^2/sp^3 ratio of W-containing deposits grown from W(CO)_6 precursor using defocused electron beam with constant beam energy as well as the corresponding accurate Monte Carlo simulations are needed to elucidate the relationship between the impurity carbon chemical bondings and the total energy delivered into the
deposits during deposition. Further investigation of the temperature-dependent electron transport properties of EBID Pt- and W-containing nanowires is needed to understand fundamental electron transport mechanism in this type of granular materials, which is critical for the future practical applications of EBID, such as nanocontacts and interconnects.
Appendices

Appendix I: Monte Carlo simulations

This Appendix documents Monte Carlo simulations performed using the package CASINO, modified to enable the extraction of depth-resolved primary electron energy deposition profiles. Each simulation was performed using $10^5$, 20 keV primary electrons. Densities of 7.16, 5.32 and 2.33 g/cm$^3$ were used for WO$_3$, GaAs and Si, respectively. Backscattered electron (BSE) yields ($\eta$) are calculated automatically by CASINO. Depth-resolved energy deposition profiles were obtained using the methodology described in reference$^1$.

A. WO$_3$ on Si

Figure A-1(a) shows total energy deposition profiles calculated as a function of depth for bulk Si, and for multilayers consisting of a WO$_3$ overlayer on bulk Si, simulated for WO$_3$ thicknesses in the range of $10^2$ to $10^3$ nm. Figure A-1(b) shows the total energy deposited into the WO$_3$ overlayer ($E_{WO3}$), normalized to the total amount of energy deposited into bulk Si, and the BSE yield ($\eta$), both calculated as a function of WO$_3$ thickness. The plots show that the BSE yield and the energy (per primary electron) deposited into the WO$_3$ overlayer both increase with the thickness of the BSE overlayer. The BSE yield saturates at a WO$_3$ thickness of $\sim$800 nm. Hence, the BSE yield from the flat top surface of a WO$_3$ deposit grown using a defocused electron beam is expected to increase during EBID, until the deposit height exceeds 800 nm. Similarly, the amount of energy deposited into a WO$_3$ deposit (per unit deposition time) is expected to increases during growth (i.e., with deposition time).
Figure A-1. Total electron energy deposition profiles in Si and WO₃ overlayer on Si.

(a) Depth-resolved total electron energy deposition profiles in bulk Si, and in multilayers consisting of a WO₃ overlayer on bulk Si, calculated for the WO₃ thicknesses indicated. The solid-vacuum interface is at z = 0. Blue vertical lines show the location of the WO₃-Si interface corresponding to each energy deposition profile. dE/dz is the mean energy deposited per primary electron per unit depth, z. (b) Total energy deposited into the WO₃ overlayer (E₈O₃), normalized to the total amount of energy deposited into bulk Si (E₈), and the BSE yield (η), calculated as a function of WO₃ thickness.

Figure A-2 shows the mean energy deposited per primary electron into the top 2.7 nm of the WO₃ overlayer (E₈top) as a function of the overlayer thickness. E₈top is proportional to the energy deposition rate into the near-surface region of the deposit, which is in turn proportional to the generation rate of emitted SEs.²-⁴ The plot in Figure A-2 shows that E₈top (and hence the SE generation rate) increases with WO₃ thickness, until the thickness reaches ~1000 nm, at which point E₈top saturates. Hence, the SE yield from the flat top surface of a WO₃ deposit grown on Si using a defocused electron beam is expected to increase during EBID, until the deposit height reaches ~1000 nm. Similarly, the rate at which the electron beam modifies the near-surface region of the deposit is expected to increase with EBID time.
The curves in Figure A-1(a) show that the energy density deposited into the WO₃ overlayer increases with WO₃ thickness at every point (z) inside the WO₃ overlayer. Hence, the abovementioned increase in the rate of electron beam induced material modification with EBID time is expected at each point inside the WO₃ overlayer. It should be noted that since WO₃ is an insulator, the increase in SE yield with WO₃ height might be contributed to by the effects of sub-surface charging on the SE yield. Detailed discussions of these effects under ESEM conditions can be found in references.⁵-⁷

![Figure A-2. \(E_{\text{top}}/E_{100\text{nm}}\) as a function of the thickness of a WO₃ overlayer on bulk Si.](image)

\(E_{\text{top}}\) is the total energy deposited into the top 2.7 nm of WO₃ (per primary electron), and \(E_{100\text{nm}}\) is \(E_{\text{top}}\) in the case where the WO₃ thickness is 100 nm.

**B. WO₃ on GaAs**

An analogous Monte Carlo analysis was done for the case of a WO₃ overlayer on bulk GaAs. The results, shown in Figure A-3, illustrate that all of the conclusions drawn above (in the case of WO₃ on Si) are also applicable to this system, except that the BSE yield decreases with increasing WO₃ thickness. The SE yield is, however, expected to increase due to the corresponding increase in the energy deposition rate into the WO₃ SE
escape region (see Figure A-3(b)), and due to the effects of sub-surface charging on SE emission.\textsuperscript{5-7}

![Figure A-3](image)

Figure A-3. Normalized energy deposited into WO\(_3\) overlayer on GaAs.

(a) Total energy deposited into a WO\(_3\) overlayer (E\(_{W03}\)), normalized to the total amount of energy deposited into bulk GaAs (E\(_{GaAs}\)), and the BSE yield (\(\eta\)), calculated as a function of the thickness of a WO\(_3\) overlayer on bulk GaAs. (b) \([E_{top}/E_{100\,nm}]\) plotted as a function of the thickness of a WO\(_3\) overlayer on bulk GaAs, where \(E_{top}\) is the total energy deposited into the top 2.7 nm of WO\(_3\) (per primary electron), and \(E_{100\,nm}\) is \(E_{top}\) in the case where the WO\(_3\) thickness is 100 nm.
Appendix II: Mass spectral analysis of WF6 precursor

Residual gas analysis (RGA) of precursors in the ESEM chamber was performed using a differentially pumped RGA (Pfeiffer ThermoStar GSD 300 T, modified so as to eliminate the heated quartz capillary supplied with this unit). Neutral gas molecules are leaked into the RGA unit, where they are ionized using an electron source and analyzed using a Prisma Quadrupole mass spectrometer (QMS 200).

The molecular mass of tungsten hexafluoride (WF6) is approximately 299 amu, which is beyond the range of the mass spectrometer used in this work. Hence, it was only possible to analyze lower mass fragment ions that are generated when WF6 dissociates due to electron irradiation of the gas by the electron source inside the RGA. The reference mass spectrum of WF6 (taken from the NIST Mass spectral library) is shown in Figure A-4. The most intense peaks in the spectrum are for WF5+ and appear at m/z values of 277 (182WF5+), 278 (183WF5+), 279 (184WF5+) and 281 (186WF5+). Successive loss of F produces the lower intensity peaks clustered around 260, 241, 222, and 203 amu. Below m/z=200, much lower intensity peaks relating to smaller (and often doubly ionized) fragments are seen.

Analog mass spectra of WF6 were collected during EBID experiments at ESEM chamber pressures varying from 20 to 100 mTorr. A representative mass spectrum is displayed in Figure A-5 (this spectrum was recorded at 100 mTorr, but all of the peaks are also visible at lower chamber pressures). The inset shows the spectral range of 0 to 50 u, containing peaks that cannot be assigned to WF6 or its constituents. Assignments for these background peaks are provided in Table A-2.
Assignments for all of the WF$_6$ fragment peaks in the analog mass spectrum of Figure A-5 are shown in Table A-2. There are several notable differences from the reference spectrum. In particular, there are no WF$_5^{++}$ peaks (appearing around m/z=139 in the reference spectrum), and there is an unknown peak at m/z=85. The latter peak was tentatively assigned to SiF$_3^+$, possibly originating from a reaction between F$^-$ ions and silicon samples in the ESEM chamber or other chamber components.

The analog spectrum only provides information about the presence or absence of analyte gases in the ESEM chamber, and cannot be used for quantitative measurement of the concentrations of gases in a mixture. Concentration determination requires calibration of the detector response to different gases present in known concentrations in a calibration gas mixture. A calibration gas mixing system will be constructed in the future. The analog spectrum of Figure A-5 indicates that the peaks at m/z= 129, 131 and 184 (originating from $^{182}$WF$_4^{++}$, $^{186}$WF$_4^{++}$ and $^{184}$W$^{++}$) may be the best candidates for concentration measurements of WF$_6$. 
Figure A-4. Reference mass spectrum of WF$_6$.

Figure A-5. Analog mass spectrum of the ESEM chamber.

The total chamber pressure was ~100 mTorr. Note that the background level changes slightly because the spectrum was collected in several scans over mass ranges 50-100, 100-150 and 150-200.

Table A-1. Peak assignments for the analog mass spectrum.
<table>
<thead>
<tr>
<th>m/z</th>
<th>Fragment</th>
<th>m/z</th>
<th>Fragment</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>N⁺</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>O⁺</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>16</td>
<td>O⁺</td>
<td></td>
</tr>
<tr>
<td>17</td>
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</tr>
<tr>
<td>18</td>
<td>H₂O⁺</td>
<td>32</td>
<td>O₂⁺</td>
</tr>
<tr>
<td>19</td>
<td>F⁺</td>
<td>40</td>
<td>Ar⁺</td>
</tr>
<tr>
<td></td>
<td>32</td>
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<td>19</td>
</tr>
<tr>
<td>20</td>
<td>HF⁺</td>
<td>44</td>
<td>N₂O⁺</td>
</tr>
</tbody>
</table>

Table A-2. Assignments for the WF₆ fragment peaks in the analog mass spectrum.
Appendix III: Determination of convergent angle (α) and collection angle (β)

In TEM image mode, a magnified image of the specimen is present on the viewing screen and a diffraction pattern is present on the spectrometer objective plane. If there is no objective aperture inserted, the collection angle is very large (e.g., > 100 mrad). The exact value of β is not very important as the elemental quantification is rarely carried out under this configuration. However, the collection angle in TEM image mode with objective aperture inserted can be measured from the diffraction pattern of a known crystalline specimen (e.g., single crystalline silicon). Using Bragg’s law, the diffraction angle for the first order diffraction can be obtained

\[ \lambda = 2d \sin \theta \implies 2\theta_{b} \approx \lambda / d \quad (\theta \text{ is small}) \]  

(A.1)

where \(d\) is the lattice spacing (Å), \(\lambda\) is the wavelength (m) of the illumination electron beam in TEM. For single crystalline Si, \(d_{111} = 3.135\text{Å}\). \(\lambda\) can be calculated by considering relativistic mechanics. In this work, 200 keV TEM was used and the corresponding wavelength is equal to \(2.5\times10^{-12} \text{ m}\). The “first order” diffraction angle for Si (111) can be calculated.

\[ 2\theta_{b} = \frac{\lambda}{d} = \frac{2.5\times10^{-12} \text{ m}}{3.135\text{Å}} \approx 8 \text{ mrad} \]  

(A.2)

In Figure A-6, the corresponding collection angle (β) defined by the objective aperture is about 32 mrad. Depending on size of the inserted objective aperture, the corresponding EELS collection angle can be calculated and calibrated.
Figure A-6. Collection angle ($\beta$) in image mode.

(Left) Measurement of EELS collection angle ($\beta$) with objective aperture inserted. The dash circle indicates the objective aperture. (Right) The experimental SAD pattern of single crystalline Si taken at (100) zone axis is used to calculated the collection angle. The red dash circle denotes the objective aperture, and $g_1$ is the reciprocal vector for Si \{111\} plane.

The convergence angle ($\alpha$) in TEM image mode is generally very small (<3 mrad) during the parallel beam illumination. In diffraction mode, the objective plane of the spectrometer (the back focal plane of projector lens) contains a low magnification image of the specimen; a diffraction pattern can be seen on the viewing screen and the same pattern is in the plane of the spectrometer entrance aperture. Under these conditions, the collection angle is dependent on spectrometer entrance aperture. Similarly, the convergence angle and collection angle in diffraction mode can also be measured and calibrated using a standard crystal with known lattice parameter as shown in Figure A-7. The effective entrance collection angle can be calibrated using Bragg angle

$$\beta \approx \frac{d_{eff} \cdot 2\theta_g}{R}$$  \hspace{1cm} (A.3)
where the $R$ is the distance between the (000) spot and a known hkl spot. In this case, the known hkl spot is Si (111) spot. The effective entrance aperture diameter $d_{\text{eff}}$ at the recording plane is related to the actual diameter $d_{\text{actual}}$ by

$$d_{\text{eff}} = \frac{d_{\text{actual}} D}{D_A} \quad (A.4)$$

where $D$ is the distance between the projector crossover to the recording plane (negative film); $D_A$ is the distance between the crossover and the actual entrance aperture which is located underneath the exposure system. Furthermore, if the camera length ($L$) of the diffraction pattern visible on the microscope viewing screen is known ($2\theta_B = R/L$), then

$$\beta \approx \frac{D}{D_A} \frac{d_{\text{actual}}}{2L} \quad (A.5)$$

In this work, the diffraction pattern was taken using a camera length of 60 mm. In our JEOL 2010F TEM, the GIF 200 energy loss spectrometer was installed right under the camera chamber, without any other parts (e.g., Gatan CCD camera) between them. In this configuration, the distance between the projective lens crossover and the actual entrance aperture $D_A = 631 \, mm$; the distance between the projector lens crossover to the recording plane (negative film) $D = 431 \, mm$. For a 2 mm EELS entrance aperture, the collection angle $\beta \approx 11 \, mrad$. The collection angles $\beta$ for various camera lengths and entrance apertures are listed in Table A-3.
Table A-3. Collection angles $\beta$ for various camera lengths and entrance apertures.

<table>
<thead>
<tr>
<th>Camera length $L$(mm)</th>
<th>Entrance aperture diameter (mm)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.6</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>30</td>
<td>6.83</td>
<td>22.77</td>
<td>34.15</td>
</tr>
</tbody>
</table>
Figure A-7. Convergence angle ($\alpha$) and collection angle ($\beta$) in diffraction mode.

(a) Ray diagram in diffraction mode. The value of $\beta$ is determined by the effective diameter of the spectrometer entrance aperture ($d_{\text{eff}}$), projected into the diffraction pattern (From Ref. 8). (b) CBED pattern of Si. The dash circle indicates the EELS entrance aperture.
References