A novel fabrication technique for three-dimensional nanostructures

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A NOVEL FABRICATION TECHNIQUE FOR
THREE-DIMENSIONAL NANOSTRUCTURES

by

Ravi Kiran Bonam

A Dissertation
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Abstract

Three dimensional micro- and nano-structures are commonly used in the field of Photonics, Optoelectronics, Sensors and Biological applications. Although numerous physical models are developed, a major challenge has been in their fabrication which is commonly limited to conventional layer-by-layer techniques. In this dissertation, a novel method for fabricating three dimensional structures using Electron Beam Lithography (EBL) will be presented.

Electron Beam Lithography is one of the most important tools used in the field of micro- and nano-fabrication. Ultra high resolution (< 10 nm), ability to pattern without the use of a mask, versatility and large intrinsic depth of focus are its primary advantages. Large depth of focus provides the capability to pattern thick layers of resist. This feature of EBL coupled with the deposition of multiple layers of resist has led to the ability to fabricate three dimensional structures. A thorough review of EBL, the proposed Multi-Layer Direct Write technique and other issues related to fabrication of three dimensional structures will be presented.

Resists are films sensitive to electromagnetic radiation dispersed in suitable solvents. Currently, resists are deposited on wafers using the process of spin-coating. Consecutive spin coating of resists requires the use of compatible solvents to prevent unwanted dissolution. Hansen Solubility Parameters (HSP) were used to determine compatible solvents and resist polymers were recast into them. Detailed solubility analysis of all commercially available electron beam resists is also presented. Other issues related to depositing multiple layers of resist are also discussed.

Polymeric three dimensional structures exposed to electron beam radiation have limited structural strength and during the process of development, fluid interaction with structures causes deformation. This has been observed in some cases of free standing nanostructures and Finite Element Modeling was employed to determine its bounds. Different models illustrating fluid flow and its interaction with structures
will presented and compared to experimental observations.
CHAPTER 1

Introduction

Numerous lithographic techniques have been proposed for fabricating three dimensional nanostructures with applications in photonics. Although there are many theoretical models developed, lithographic fabrication is an ongoing challenge. Photonics broadly refers to controlling the flow of light. It can be controlled by structures that can confine light in one, two or three dimensions. Waveguides, Cavities and Photonic crystals are a few structures that are used to confine light. Waveguides can confine light in two dimensions and are popularly used in Telecommunications (optical fibers) and Bio-medical applications (endoscopes). Waveguides and cavities can be used to make logic devices and switches [1] for optical data processing. More interesting applications are in field of photonic crystals, periodic arrays of dielectric media can be used to confine light in three dimensions. Controlling flow of light in three dimensions requires the ability to make three dimensional nanostructures. Other applications for nanostructures are in the field of meta-materials where the structural inhomogeneities define their optical properties, such as negative refractive index [2].

Photonic structures are also commonly observed in nature i.e. on butterfly wings, beetles, peacocks. The bright color from these animals is due to presence of hierarchical 3-D nanostructures with dimensions comparable to wavelength of light [3]. Inspired by these biological nanostructures, one of the most recent applications is in the field of chemical and biological sensing. It has been shown that varied optical responses occur when vapors of different chemicals interact with the nanostructures, especially with the ones on butterfly wings [4]. To further understand the underlying principles of gas and nanostructure interactions and their effects on optical responses, lithographic fabrication of the structures is required (more details in Appendix A).
A few techniques proposed by researchers for fabricating three-dimensional nanostructures are described as follows,

1. Aligned layer-by-layer UV or electron beam lithography [5, 6, 7] - This is the most basic and common technique used to fabricate three dimensional nanostructures. Each level is defined by a set processes which include, photo/electron-beam lithography, Etching and Deposition. The processes need to be setup individually and are repeated until the required structure is fabricated. Electron beam lithography or UV lithography define feature sizes. Deposition and Etching techniques are used to transfer patterned features into the substrate. A major disadvantage of this process is its slow and serial nature.

2. Interference lithography or Holographic lithography [8, 9, 10] - This technique employs the interference patterns between two or more light sources to form patterns in resist. The pattern would consist of periodic series of fringes which represent the intensity maxima and minima. The disadvantage of this process lies in the resolution of interference patterns and the depth of their focus which is limited to the wavelengths of light used.

3. Two-photon lithography [11] - This technique utilizes two photons of different wavelengths on transparent phase masks to generate 3D distributions of intensity near the surface of the mask. The photopolymer has to be sensitive to both the photons. A complex phase mask with subwavelength structures is required for this process.

4. Electron or Focused Ion beam induced deposition [12, 13, 14] - This technique utilizes the ability to selectively dissociate volatile precursor molecules under electron or ion beam radiation to deposit metals or other elements. The serial process of deposition makes this process slow. Bresin [14] et al. outlined a process which involves cooling precursors to cryogenic temperatures and using
electron beams with multiple energies to fabricate three dimensional structures. The depth of penetration of the beam is dependent on beam energy. Although this process improves the speed of fabrication, it requires special setup to cool the precursors.

5. Glancing angle deposition [15] - This technique utilizes Physical Vapor Deposition combined with substrate motion to create unique three-dimensional photonic crystals. Although, large area fabrication is possible using this technique it is unsuitable as a generic three-dimensional fabrication technique.

6. Nanoimprint lithography [16] - This technique utilizes a series of imprinting steps to create three-dimensional structures. It requires an imprint template and can reproduce only one level in a single exposure limiting throughput.

The aforementioned techniques require repetitive processing or special setups to fabricate three dimensional nanostructures which increases processing complexity and fabrication time. A few techniques are devised to fabricate specific types of structures. Scalability and throughput is very limited making them incapable to perform as large scale manufacturing techniques. A novel fabrication technique proposed in this work aims at addressing these issues.

Large intrinsic depth of focus and penetration depth of high energy electron beams (> 50 keV) (or other accelerated particle beams) is utilized to pattern thick layers of resist (> 500 nm) [17]. When a resist stack consisting of layers with varying contrast is patterned with a high energy electron beam, it is hypothesized that multiple resist layers can be addressed in a single exposure. Selective crosslinking or clearing of the resist layers in the stack after development will result in three dimensional structures. This document is divided into multiple chapters which outline various aspects of the proposed fabrication technique along with detailed results and analysis of related challenges.
Chapter 2 will describe Optical and Electron Beam Lithography. Detailed description of processes involved in Electron Beam Lithography will also be presented.

Chapter 3 will discuss details of the proposed lithographic technique for fabricating three dimensional nanostructures. Results obtained from implementing the proposed process on positive, negative resist stacks and factors effecting it will be presented. A novel proximity effect correction technique along with effects of focus on three dimensional structures will be presented. Applied Monte-Carlo simulations were used to simulate dose contours in resist and validated with experimental results.

In Chapter 4, materials involved and incompatibilities that occur in the process of depositing multiple layers of photoresist will be discussed. Hansen Solubility parameters were used to characterize solubility of commercially available electron beam resists. Resist polymers were recast into compatible solvents for coating layers consecutively. Effects of polymer molecular weight and factors affecting adhesion between layers will also be presented. Materials used to protect the three dimensional structures and their surface will also be discussed.

Chapter 5 describes metrology techniques used in this work to characterize resist thickness and obtain dimensions of fabricated structures. Ellipsometry was used to characterize resist thickness and Scanning Electron Microscopy (SEM) was used to image three dimensional structures fabricated in resist.

Chapter 6 discusses finite element modeling performed on tree structures to estimate deformation due to shear from fluid-structure interaction. Results from simulation models were compared to experimentally analyzed images.
2.1 Introduction

Lithography is a method of transferring patterns onto material. It is used as a low-cost manufacturing technique for printing features on large scale. Stone lithography was one of the earliest techniques to print on paper using ink. Lithography became popular with time and is commonly used for printing books and high volume texts. This technique was invented by Alois Senefelder in 1817 [18].

Similarly in the field of micro and nano-fabrication, lithography is the process of writing microscopic patterns on radiation (UV, EUV or Charged particle) sensitive polymer films called Photoresist (will be discussed in chapter 4). Resists are broadly classified into two types, Positive and Negative. Lithography plays a major part in manufacturing of integrated circuits because it is a major driver in defining device sizes in electronic circuits. Figure 2.1 illustrates the process of making patterns on resist films applied to silicon wafers using lithography. There are two different types of photoresists, positive and negative. In positive photoresists, the area exposed by radiation will readily dissolve in a solution called the Developer, leaving the unexposed areas covered with resist. In case of a negative photoresist, the unexposed areas will dissolve in the developer leaving the the exposed resist patterns on the wafer.

Lithography in the semiconductor industry can be broadly classified on their use of masks. A mask in general is considered to be an apparatus that can be used to selectively block a physical quantity. In optical lithography, masks have patterns that selectively block the passage of light. Masks are usually made of glass, transmissive for Ultra Violet, Deep Ultra-Violet radiation and reflective for Extreme Ultra Violet
radiation. The glass substrate contains a pattern that is to be repeated multiple times using photolithography process. Patterns on the mask are usually made of materials that absorb incident and scattered Ultra-Violet radiation.

1. Mask Lithography includes the use of Ultra Violet (UV - 436nm, 365nm), Deep UV (DUV - 248nm, 193nm), Extreme UV (13.5nm), Imprint etc.

2. Mask-less Lithography includes the use of Electron Beam, Ion Beam, Direct Laser, Probe tip etc. A few electron beam based massively parallel exposure tools are being pursued with programmable masks facilitate large area exposures[19, 20, 21].

Figures 2.2 and 2.3 illustrate a major difference between Mask and Maskless lithography. In Optical Lithography, Ultra-Violet radiation is incident on a mask which contains features to be transferred onto the resist. The features on the glass mask selectively allow transmission of UV radiation, thereby forming required patterns in resist.
Electron beam lithography uses a narrow beam of electrons whose position and dose (depends on dwell time) can be controlled by magnetic and electrostatic elements that allow the beam to raster on required areas.

Figure 2.2: Optical Lithography

Figure 2.3: Electron Beam Lithography

Figure 2.4 shows the process of lithography in conjunction with the design part for Mask and Maskless lithography cases. In the case of Mask lithography, layout designs are sent to a mask fabrication center. This step delays the process of lithography from several days to a few weeks, based on complexity of the pattern.
Figure 2.5 shows a few details involved in mask fabrication process. Mask substrate preparation may include cleaning and multi-layer deposition (in case of EUV masks). Post exposure processing includes etching pattern into mask substrate. The time delay and expenses involved in mask fabrication is a major disadvantage of Mask Lithography [22, 23].

In the case of Maskless lithography, the layout design is converted into appropriate format readable by the lithography tool and patterning process can commence at user’s discretion. The flexibility of editing layout designs and fast turn around time of the fabrication process are major advantages of Maskless Lithography. However, throughput of sequential patterning has always been a drawback.

Figure 2.4: Lithography Process
Figure 2.5: Mask Fabrication Process
2.2 Optical Lithography[24]

Currently, Optical lithography uses Deep Ultra-Violet light (193nm) for large scale manufacturing of electronic circuits. Miniaturization of devices is a major driver for advancement of electronic circuits and this has led the semiconductor industry to shift to light sources with shorter wavelength. Figure 2.6 shows a schematic of projection optical lithography. It consists of a light source with certain wavelength $\lambda$. The light from the source is used to image features on the mask which are focused on to the substrate using a set of lenses.

![Projection Optical Lithography Schematic](image)

**Figure 2.6:** Projection Optical Lithography Schematic

Light sources in optical lithography tool ranged from Mercury (Hg), noble gas discharge lamps with filters to excimer lasers. Lasers started gaining more popu-
larity as semiconductor industry’s need for higher resolution and higher throughput increased. Commonly used excimer lasers were, Krypton Flouride (KrF, 248nm) and Argon Flouride (ArF, 193nm). Extreme Ultra-Violet (EUV, 13.5nm) lithography utilizing a plasma source is still under development to continue scaling of semiconductor devices.

Optics involving UV and DUV light are transmissive as shown in figure 2.6. For a given process and wavelength of light used, equation 2.1 gives the minimum size of the feature that can be imaged or resolved and is termed as the Rayleigh resolution limit.

$$ Resolution(R) = k_1 \frac{\lambda}{n \sin(\theta)} $$  \hspace{1cm} (2.1)

The $n \sin(\theta)$ term in the equation is also called as numerical aperture (NA) and relates to optics used in the lithographic setup, where $n$ is the refractive index of the medium (air) and $\theta$ is the half-angle subtended by the objective lens. $k_1$ depends on the process and materials. Currently $k_1$ is 0.61 but can be smaller by stricter control of process parameters.

Based on equation 2.1, resolution can be improved by using smaller wavelengths of light, improving the process or increasing the numerical aperture. Hence, over the years wavelength of light used for patterning was reduced to improve resolution of lithography. The numerical aperture of the optics also has control on the resolution of the image. It can be increased by changing the refractive index of medium between objective lens and the wafer. Immersion lithography uses water as the medium and this increases the effective numerical aperture and there by enhances the resolution.

The distance between image plane and objective lens, Focus, is an important factor that determines the resolution and legibility of the image. There are tolerance limits for focus within which the image formed by the optics is still considered acceptable. This acceptable limit is called Depth of Focus (DOF) and is dependent
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<tbody>
<tr>
<td>436</td>
<td>443</td>
<td>605</td>
</tr>
<tr>
<td>365</td>
<td>371</td>
<td>506</td>
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<tr>
<td>248</td>
<td>252</td>
<td>344</td>
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<tr>
<td>193</td>
<td>196</td>
<td>268</td>
</tr>
<tr>
<td>13.5</td>
<td>13.7</td>
<td>18.75</td>
</tr>
</tbody>
</table>

Table 2.1: Optical Lithography - Wavelength dependent Resolution and Depth of Focus

on wavelength for a given optics setup. In the field of micro and nanolithography, constraints on the line widths are very stringent as defocus will significantly change the line width. The depth of focus for a given optical system is proportional to the fraction of wavelength and square of numerical aperture and is given by equation 2.2,

\[
\text{Depth of Focus (DOF)} = \pm k_2 \frac{\lambda}{(NA)^2}
\]  

(2.2)

\(k_2\) is a constant and is based on the tolerance required for the lithographic process. As values of focus change from optimum values, brightness of the image also reduces and is diffracted away from the center spot thereby changing the image profile.

Table 2.1 gives an overview of typical Resolution and Depth of Focus values with varying wavelengths of radiation at a given process(\(k_1 = 0.61\)) and 20% tolerance for peak intensity(\(k_2 = 0.5\)) and Numerical aperture(0.6). As seen from the table above, depth of focus reduces with wavelength of radiation and has adverse effects on performance of the lithographic process.
2.3 Electron Beam Lithography

Electron Beam Lithography (EBL) is a technique that uses a narrow beam of electrons to write patterns in resist materials. Unlike optical lithography, where a mask with features is illuminated with light, a narrow beam of electrons (due to their negative charge) are deflected by electrostatic and magnetic lenses to selectively pattern the resist. EBL is capable of having higher resolution than any other top-down lithographic technique.

Figure 2.7 illustrates a general schematic of an EBL tool.

Any of the following physical processes can cause electron emission from a conducting tip,

1. **Thermionic Emission** - In this process a metal is heated to a certain temperature at which electrons will attain sufficient energy to overcome the work function barrier and escape the surface.
2. **Photoemission** - When a photon with sufficient energy is incident on the surface of a metal, its interaction with electrons will cause transfer of energy and when the energy is greater than work function of the metal, electrons will escape from the surface.

3. **Field Emission or Cold Emission** - When a high voltage is applied between a cathode and an anode, the electric field lowers the potential barrier at the surface of the metal and electrons tunnel through the barrier and escape the surface.

4. A **combination of Thermionic and Field emission** is also used in some applications, as heating would assist in increasing the efficiency of the field emission process even at slightly lower electric fields.

For all these processes to produce a beam of electrons, a high acceleration voltage and vacuum are required. The distribution of electrons in a beam can be approximated by Gaussian functions. Three important properties of electron sources used in Gaussian beam tools are,

1. **Virtual source size (measured in nm)** - It determines the demagnification required to form a small spot on the image plane.

2. **Brightness of the source (measured in amperes/area/solid angle)** - This is analogous to intensity in Optical Lithography and is important factor that directly effects the throughput. EBL is limited in throughput partially because of limited source brightness due to space charge effects.

3. **Energy spread (measured in eV)** of emitted electrons effects the variation in velocity and trajectory of electrons which is one of the causes for aberrations.

Optics for electron beams are made of either electrostatic or magnetic lenses. The Rayleigh resolution for an electron beam changes with the acceleration voltage
and it is usually of the order of pico-meters. The major advantages of EBL over conventional optical lithography are,

1. Very high resolution (less than 10nm)
2. Maskless patterning
3. Large intrinsic depth of focus (dependent on acceleration voltage).
4. Versatile and well suited for research and prototyping applications

An important part of an EBL tool is a Blanker, which partially affects the throughput. It consists of two conducting parallel plates and when a voltage is applied between them, it deflects the beam from its original path such that it cannot expose the resist.

The disadvantage of this technology is its Throughput. Unlike optical lithography where the mask with features are flood exposed with light, in EBL a beam of electrons has to write patterns sequentially which is a major reason for its incapability to be used for large scale manufacturing.

Figure 2.8 shows a plot of variation of penetration depth [25, 26] of a beam of electrons in silicon with beam energy. At 100keV the beam penetrates about 60µm and the depth of penetration can be calculated using equation 2.3.

\[
R(\mu m) = 0.04 \frac{(kV)^{1.75}}{\rho(gm/cm^3)}
\]  

(2.3)

The basic parameters that determine the quality of EBL are,

1. **Spot Size (nm)** - It is the demagnified virtual source size and directly depends on the beam current and final aperture size.

2. **Beam step size (nm)** - It is distance between two pixels and is adjusted based on the spot size. The beam step size directly affects the LER (Line Edge
Figure 2.8: Electron penetration depth in Silicon with beam energy ($\rho = 2.4\text{gm/cm}^3$)

Roughness) which is an important parameter in the field of lithography. Figure 2.9 illustrates a square pattern made up by spots of definite sizes. For a straight line, the beam step size should be less than or equal to the spot size. Each spot in the figure represents an exel(exposure element) which is analogous to a pixel in electronic displays.

3. **Dose** ($\mu\text{C/cm}^2$) - It is a measure of the number of electrons required to write a pattern in resist, measured in micro-coulombs, $\mu\text{C}$. This value is resist and electron beam energy dependent.

4. **Dwell Time (seconds) or Frequency (Hz)** - The amount of dose delivered to the substrate can be changed by beam dwell time which directly translates into the tool’s capability to raster the beam. This is dependent on the operation frequency of the tool’s electronics.

The beam current, area dose, dwell time and the area over which dose is deliv-
Dose (\(\mu C/cm^2\)) = \(\frac{Beam\ Current(nA) \times Dwell\ Time(seconds)}{Area(cm^2)}\) \hspace{1cm} (2.4)

where dwell time can also be written as \(\frac{1}{tool\ frequency}\).

Figure 2.10a, b, c and d show contrast curves of Copolymer MMA:MAA (Methy methacrylate:Mehtacrylic Acid), PMMA (poly-methyl methacrylate) positive resists and NEB-31, HSQ (Hydrogen Silsesquioxane) negative resists when exposed to a 100keV electron beam. Contrast curves plot normalized thickness against dose and the following information about the resist can be inferred from the graphs,

1. Type of resist - Positive or Negative

2. Sensitivity - Dose-to-clear (positive resist) is minimum dose required to make the exposed pattern dissolvable in the developer. Dose-to-crosslink (negative resist) is minimum dose required to make a pattern insoluble in the developer.

3. Contrast - It is defined as the measure of non-linearity of the response of a
development process to the chemical contrast produced by the exposure. This is essential as it determines how small of an image modulation can be successfully converted into image in the resist. It is a measure of how well a feature printed in resist can be distinguished from its background (in this case is the substrate).

As dimensions of the pattern become smaller and are of the order of the spot size, dose required to pattern those features increases exponentially.

**Figure 2.10:** Contrast curves for electron beam resists - positive, a. Copolymer (MAA:MMA), b. PMMA (developed in MIBK:IPA (1:3)) and negative, c. NEB-31, d. HSQ (developed in TMAH(0.26N))
2.3.1 Proximity Effect

The Electron Beam is formed when electrons from the source are focused and accelerated through an electric field. The typical potential difference between emitter and anode can vary from 1keV to 100keV. The DeBroglie wavelength (equation 2.5) of the electron decreases with increasing accelerating voltage.

\[ \lambda(m) = \frac{h}{\sqrt{(2meV)}} \]  

(2.5)

where \( h \) is Planck's constant in SI units, \( m \) is mass of the particle, in this case is mass of an electron, \( e \) is charge of the particle, \( V \) is acceleration voltage.

At a 100keV the wavelength of the electron is about 10 picometers. When the primary beam interacts with the substrate, scattering events (small and large angle) cause the beam to broaden and lose energy. Proximity effect [27] in EBL is the undesired influence of electrons due to scattering in resist and substrate. The range of electron scattering changes with beam energy. There are many physical processes that occur when electron beam interacts with the substrate coated with resist. The most important factor that needs to be considered in the case of EBL is **Scattering**. From figure 2.8 in previous section, a 100keV beam has a penetration depth of 60\( \mu m \).

Consider the electron beam as a collection of particles accelerated towards the substrate, which can also be visualized as an arrangement of atoms. Classically, when an accelerated particle collides with another particle there can be elastic or inelastic collisions based on exchange of energy in the process. Figure 2.11 illustrates the classical picture of an electron beam interaction with the substrate and resist, which are also shown at atomic scale.

Figure 2.12 illustrates a trajectory and physical processes that occur when an electron with sufficient kinetic energy interacts with the resist and substrate. The physical processes [28] include generation of,
1. **Backscattered Electrons (BS)** - BS1 electrons are a result of elastic collisions between electrons from primary beam and nucleus of atoms in resist or substrate. There is no energy loss in this interaction. BS2 electrons are a result of inelastic collisions where the electrons from the primary beam lose some of their energy to the substrate but have enough energy to eject from the surface after a few collision events.

2. **Secondary Electrons (SE)** - Secondary electrons are a result of high energy electrons (particularly from the primary beam) interacting with electron cloud surrounding the atoms of resist or substrate. SE1 electrons are generated due to the primary beam’s direct interaction with the electron cloud of atoms in the substrate or resist. SE2 electrons are generated as a result of scattered primary beam’s interaction with substrate or resist atoms. There is transfer of energy is both cases of secondary electron generation.
Numerous Monte-Carlo simulations [29, 30] have been designed over the years to model electron beam interactions with solids. Monte-Carlo simulation is an iterative technique based on deterministic physical models which can be used to integrate multiple trajectories and give a cumulative result. To estimate the trajectory of an electron as it interacts with the substrate, at each step the following parameters need to be calculated,

1. **Distance between scattering events** - can be calculated using elastic cross-section models

2. **Scattering angles** - Polar and Azimuthal

3. **Energy of electron lost at each interaction** - calculated using Bethe stopping power which is based on the density($gm/cm^3$) of the interacting solid.

CASINO, a Monte-Carlo simulator was used in this work to illustrate electron scattering.

Figures 2.13A and 2.14A show images of a 100keV electron beam interacting with Silicon and Figures 2.13B and 2.13B show images of 100keV electron beam interacting with PMMA(poly methyl methacrylate). As observed from the images, loss in primary beam energy is minimal in 20µm of the resist stack. As energy decreases resist sensitivity increases and it need to considered while patterning thick($>20µm$) layers of resist.

Proximity effect can be estimated by the following methods,

1. **Simulation** - Mathematical representation of incident beam, scattering of the beam are required to model and calculate exposure energy density profile. This would require knowledge of stack materials (density etc.) and processes involved in interaction.
2. **Experimental evaluation** - This requires analysis of patterned features on resist coated substrate. Scattering can be estimated by comparing printed pattern dimensions to the design and then apply corrections. Experimental evaluation of proximity effect is time consuming.

Scattering of electrons due to interaction with solids is the cause for Proximity Effect in EBL and can be categorized into two types,

1. **Forward Scattering** - As the electrons from primary beam start interacting with resist, a fraction of them will undergo small angle scattering events, which broadens the initial beam profile. The size of the spot formed by the beam can be broader at the bottom of the resist layer than at the top. Equation 2.6 [25, 26] gives an empirical relation between beam blur and beam voltage, resist thickness.
Figure 2.13: CASINO(version 3) generated images of a 100keV electron beam A. interaction with Silicon, B. interaction with PMMA

\[ D_f = 0.9 \left( \frac{R_f}{V_b} \right)^{1.5} \]  

(2.6)

where \( D_f \) is the beam blur in nanometers, \( R_f \) is the thickness of resist in nanometers, \( V_b \) is the beam voltage in kilo-volts.

Figure 2.15 illustrates beam blur due to forward scattering in resist(50nm) for a 100keV electron beam. The blue lines in the image are trajectories of electrons as they traverse through the resist and their spread can be approximated by a curve, highlighted in red. This curve is called a Gaussian and can be represented by the following mathematical relation.
Figure 2.14: CASINO(version 3) generated images of a 100keV electron beam A. interaction with Silicon, B. interaction with PMMA (both images are on same scale)

Figure 2.15: Electron Beam-substrate interaction - Forward Scatter with Gaussian fit (image generated using CASINO Monte-Carlo software)
\[ G(x) = k \cdot \exp \left( -\frac{x^2}{a^2} \right) \] (2.7)

where \( k \) is a constant, \( a \) is the width of the Gaussian curve at FWHM (full width half maximum) and \( x \) is a variable.

The major cause for beam blur in a resist is its density.

2. **Backscattering** - Primary electrons will continue to penetrate through the resist and into the substrate and as density of atoms (and their atomic number) is comparatively higher, they will undergo large angle scattering. Some of these scattered electrons may return back to the surface causing additional resist exposure at regions not intended by primary beam exposure. The range of scattering in this process depends on energy of the primary beam and substrate material properties.

Figure 2.15 illustrates backscatter trajectories for a 100keV beam and they are spread over a larger area, about 30\( \mu m \) radial distance. This contributes to major part of the proximity effect.

![Figure 2.16: Electron Beam - substrate interaction - Backscatter](image)

Figure 2.16: Electron Beam - substrate interaction - Backscatter (image generated using CASINO Monte-Carlo software)
Figures 2.15 and 2.16 show forward and backscatter distributions of electrons approximated by Gaussian curves of two different widths. Figure 2.15 represents distribution of small angle scattering experienced by electrons due to interaction with resist molecules. Figure 2.16 shows trajectories of electrons scattering from the substrate and ejecting out. These electrons also cause exposure in resist over a large area and are main contributors to the proximity effect. Figure 2.17 shows a plot of the energy density distribution of 100keV electron beam as it interacts with three different resists coated on silicon substrate. The energy density distribution plot, also known as Point Spread Function (PSF) was generated using Sceleton (Monte-Carlo simulator). Shown in the plot are symmetric halves of two Gaussian curves used to fit the simulated data. (more details on Sceleton in APPENDIX - Dose distribution - MATLAB simulation program code section)

![Energy Density Distribution](image)

**Figure 2.17:** Simulated Energy Density Profile - PMMA, NEB-31, HSQ on Silicon

Equation 2.8 is a linear combination of two Gaussian curves.
\( f(r) = C_f \exp \left( -\frac{r^2}{\alpha^2} \right) + C_b \exp \left( -\frac{r^2}{\beta^2} \right) \)  

(2.8)

where \( C_f \) and \( C_b \) are coefficients of forward and back scattering, \( r \) is radial distance, \( \alpha \) is the width of forward scatter Gaussian at FWHM and \( \beta \) is the width of the backscatter Gaussian at FWHM.

Equation 2.9 [27] most common double Gaussian equation used to approximate the energy density profile.

\[
f(r) = \frac{1}{\pi(1+\eta)} \left( \frac{1}{\alpha^2} \exp \left( -\frac{r^2}{\alpha^2} \right) + \frac{\eta}{\beta^2} \exp \left( -\frac{r^2}{\beta^2} \right) \right)
\]

(2.9)

where \( \eta \) is the ratio of dose contribution due to backscattered electrons to the dose contribution by incident electrons and those components are given by \( I_f \) and \( I_b \)

\[
\eta = \frac{I_b}{I_f}
\]

(2.10a)

\[
I_f = \int_0^{2\pi} \int_0^\infty C_f \exp \left( -\frac{r^2}{\alpha^2} \right) drd\phi
\]

(2.10b)

\[
I_b = \int_0^{2\pi} \int_0^\infty C_b \exp \left( -\frac{r^2}{\beta^2} \right) drd\phi
\]

(2.10c)

The energy deposited at any pixel \((x, y)\) is given by,

\[
E(x, y) = f(r) * d(x, y)
\]

(2.11)

where \( f(r) \) represents the energy density profile and \( d(x, y) \) is the dose delivered at \((x, y)\).

### 2.3.2 Proximity Effect Correction

Scattering of electrons in the resist and substrate causes exposure of resist in undesired areas and needs to be corrected in order to achieve good quality lithog-
raphy. As discussed in the previous section, proximity effect can be approximated using a double Gaussian expression. Mathematical operations can be applied to the expression to correct for this effect. There are numerous methods reported in literature [31, 32, 33, 34, 35, 36, 37, 38] to correct for this effect and following are a few of them,

1. **Background exposure (GHOST)** - This technique works by equalizing backscattered electron dose received by all points within the pattern.

2. **Shape Bias** - The dimensions of the pattern are adjusted to compensate for the proximity effect.

3. **Dose Modulation** - This technique is most popular and implemented on most of the EBL tools.

   Dose modulation is popular because dwell time is easier to control on the EBL tool rather than changing pattern dimensions, particularly for dense patterns. The aim is to determine the required dose for each pixel(exposure element) with good accuracy (within the limit of tool’s correction capability) while having a tolerable computation time.

   In the case of dose modulation, two techniques are reported in literature,

1. **Exact Dose Correction** by Kern [34] - In this technique the pattern data is transformed in a way to compensate for the effects of electron scattering. As shown in figure 2.18 the quotient of the operation $p(u, v)/e(u, v)$, where $p(u, v)$ and $e(u, v)$ are the fourier transforms of pattern $P(x, y)$ and PSF (point spread function) respectively, is the spatial frequency spectrum of the required charge density distribution $Q(x, y)$ which is obtained from the inverse fourier transform.

   If there are unexposed exels in pattern, their charge density is given by
\[ Q_F = \eta_e Q_P \quad (2.12) \]

where \( \eta_e \) is the backscattering ratio, and \( Q_P \) is the dose used for exposed exels.

![Diagram](image)

**Figure 2.18:** Dose Modulation - Exact Dose Correction

2. **Self-Consistent Dose correction** by Parikh [32] - Let \( Q_j \) is the dose applied to the \( j \)th pixel and total energy deposited a pixel \( i \) which is in proximity is given by,

\[ E_i = \sum_{j=1}^{N} R_{ij} Q_j \quad (2.13) \]

where \( R_{ij} \) represents the energy distribution profile for an electron beam of given energy, \( r_{ij} \) is the distance between exels \( i, j \), \( \sigma_f^2 \) is width of forward
scatter Gaussian and $\sigma_b^2$ is width of backward scatter Gaussian.

\[
R_{ij} = \frac{\Delta V_f}{t} \left( \frac{1}{\pi \sigma_f^2} \exp \left( -\frac{r_{ij}^2}{\sigma_f^2} \right) + \frac{\eta_f}{\pi \sigma_b^2} \exp \left( -\frac{r_{ij}^2}{\sigma_b^2} \right) \right) \quad (2.14)
\]

For each exposed pixel in the pattern we get $N$ equations which can be written in matrix form as,

\[
[E_i] = [R_{ij}] [Q_j]
\quad (2.15)
\]

The aim is to solve equation 3.4 so that all values of $N$ and $E$ are equal by changing values of $Q$.

Figure 2.19 shows a contact pad pattern being printed in PMMA (Poly Methyl Metha-acrylate) coated on a silicon wafer. As seen from results of the exposures, shape and dimensions of the pattern not corrected for proximity effect are very different from the design. A separate exposure with proximity effect correction applied shows pattern structure and dimensions identical to that of the design.
Figure 2.19: Proximity effect correction - Dose modulation
Electron Beam Lithography (EBL) is commonly used to write 2-D (two dimensional) patterns in resist coated on silicon wafers. In this section, a novel approach for making 3-D (three dimensional) structures using EBL will be discussed.

The two important factors that make this technique feasible are,

1. Penetration depth of the electron beam - As discussed in earlier section, it increases with beam energy and this increases the ability to pattern thick stacks of resist. Beam spread also reduces giving more control on critical dimensions. Exposure in resists is mainly dependent on secondary electrons [39] and they are generated along the path of the primary beam facilitating necessary chemical changes in thick (order of \( \mu m \)) resists.

2. Resist materials with different sensitivities and tones - Availability and ability to stack materials with sufficient dose contrast for a given beam energy. This makes it feasible to selectively address them using a high energy electron beam along the depth of the stack.

Figure 3.1 and 3.2 illustrate the process of making a free standing 3-D structure by stacking materials with different sensitivities. Wafers are coated with multiple layers of resist and dose is delivered selectively to achieve three dimensional periodicity.

In this work of fabricating 3-D structures, a 100 keV electron beam was used for patterning resist stacks.
Figure 3.1: Multi-Layer Direct Write - Negative stack

Figure 3.2: Multi-Layer Direct Write - Positive stack
3.1 Positive Resist Stack - Experiments and Analysis

This section discusses implementation of multi-layer direct write strategy on a positive resist stack and various structures fabricated in the process.

The positive stack process flow, as shown in figure 3.2, consists of a stack of alternating low/high sensitivity resists. In this case the low sensitivity resist is PMMA (Poly Methyl Metha Acrylate) 950K (polymer chain molecular weight) in Anisole (solvent, also called Methoxy Benzene) with a large area dose to clear of 650µC/cm². High sensitivity resist is a copolymer made of MMA:MAA (Methyl Metha Acrylate:Metha Acrylic Acid) in Ethyl Lactate. It has a large area dose-to-clear of 175µC/cm². The dose to clear values specified here are for 200nm thick resist and electron beam energy of 100 keV.

Figure 3.3a, b shows SEM images of 40 and 60 layers of distinct Copolymer/PMMA coatings. This shows that multiple layers of resist can be stacked together without being intermixed.

Figures 3.4a, b shows a top down image of the design file with relative dose assignments, where 1x represents dose to clear the complete stack (Copolymer/PMMA) and 0.3x represents dose to clear for Copolymer only and 0x represents areas where there is no exposure. Figures 3.4c, d show corresponding SEM images of structures formed due to exposing the designs on a Copolymer/PMMA stack.

Figure 3.5a shows design file for a tree structure with relative dose assignments and figure 3.5c shows corresponding cross-section SEM images of patterned 4 layer Copolymer/PMMA stack. Figure 3.5b shows design for a rod and hole structure with relative dose assignments and figure 3.5d shows corresponding cross-section SEM image of patterned 6 layer PMMA/Copolymer stack.

Figure 3.6 show 30, 40 and 60 layers of resist patterned using a similar pattern. These images show evident spread which is inherent to beam energy.

Figures 3.7 shows the effect of dose on lamella length for two different 12-layer
Figure 3.3: Positive(Copolymer/PMMA) resist stack A - 40 layers, B - 60 layers

stacks, $1.5\mu m$ and $1.68\mu m$. As lamella length increases from 300nm to 500nm, the
dose required to make a legible structure also increases. Similarly, figure 3.8 shows
the effect of dose for two different 12-layer stacks, $1.5\mu m$ and $1.68\mu m$. The thickness
of each of lamella , space between them is different and in both cases as dose increases
the resist at bottom of the stack clears, creating a more legible structure. Figure 3.9
shows a plot of dose variation with lamella length, and it can be observed that dose
slightly increases with lamella length.

Figure 3.10 shows a plot of dose variation with number of levels of the stack,
where each level represents one set of Copolymer (210 nm) and PMMA (70 nm) layers.
This plot shows absolute values for base and lamella doses. Base dose is the minimum
dose required to clear a given thickness of resist. It increases with number of levels
and this causes increased proximity effect, thereby lowering lamella dose as seen on
Figure 3.4: Tree structures with lamellae - a. CAD design file with dose assignments for tree structures c. SEM image of 22 layer resist stack (PMMA layer - 210nm, Copolymer layer - 70nm) patterned with 100keV electron beam in a single step; b. CAD design file with dose assignment for structures with ribs, d. SEM image of 12 layer resist stack (PMMA layer - 150nm, Copolymer layer - 60nm) patterned with 100keV electron beam in a single step; (L, T, S and M denote Lamella, Trunk, Space and Microrib respectively)

the lamella dose curve. Lamella dose was lowered to prevent breakage of structures. For the structure in discussion, base dose was used to pattern spaces between the structures and lamella dose was used for spaces between lamellae.

Figure 3.11 shows a plot of lamella dose fraction, which is ratio of lamella dose to base dose. The fraction decreases as number of levels are increased and this represents loss in the ability to control contrast between layers. In this work, it was noticed that using a 100 keV electron beam the ability to control dose for patterning three dimensional structures is completely lost for stacks with thickness greater than 3.5µm.

Figure 3.12a shows images of a patterned 12-layer Copolymer/PMMA (2200K)
stack where the thickness of PMMA lamellae is 50nm. Figure 3.12b shows a similar structure with thicker lamellae with better thickness uniformity. PMMA is synthesized in various molecular weights and in this work three variants were used, 495K, 950K and 2200K. For a given molecular weight of resist, there exists a critical thickness beyond which coating would be non-uniform and solvent diffusion occurs. At lamellae thicknesses of less than 50nm, solvents diffuse through 950K PMMA coatings. Diffusion coefficient and coating uniformity are highly dependent on molecular weight [40]. More detailed analysis on effect of molecular weight on diffusion is presented in Chapter 4.

Figure 3.13a, b show optical images of fabricated structures in 12-layer of alternating Copolymer/PMMA stack. This shows that the technique is scalable for
Figure 3.6: A - Positive(Copolymer(150nm)/PMMA(60nm)) resist stack patterned with 100keV A - 30 layers 1500μC/cm², B - 40 layers at 2000μC/cm², C - 40 layers at 3000μC/cm², D - 60 layers at 4000μC/cm².

large area manufacturing. The nominal time required for fabricating the structures is 2min/mm² and is dependent on beam current and resist sensitivity.
Figure 3.7: Positive(Copolymer/PMMA) resist stack analysis - Lamella length vs. Stack thickness at best dose
Figure 3.8: Positive(Copolymer/PMMA) resist stack analysis - Stack thickness vs. Dose at 400nm lamella length
Figure 3.9: Dose variation for six level Copolymer(210nm)/PMMA(70nm) stacks with variable lamella length
Figure 3.10: Positive stack dose plot for copolymer (210 nm) and PMMA (70 nm)
Figure 3.11: Positive stack lamella dose fraction for copolymer (210 nm) and PMMA (70 nm)
Figure 3.12: Copolymer/PMMA($M_w=2200K$) 12-layer stack with, a - 50nm thick lamellae, b - 70nm thick lamellae
Figure 3.13: Optical image of fabricated structures, A - $2 \times 2 \text{mm}^2$, B - $12 \times 12 \text{mm}^2$

area
3.2 Negative Resist Stack - Experiments and Analysis

Although there are solubility issues with coating multiple negative resists, similar structures can be formed by using the same process shown in figure 3.1 if they possess sufficient dose contrast. Due to solvent incompatibility between commercially available negative resist materials, they were re-cast into compatible solvents. Chapter 4 will discuss material compatibility issues in detail.

Figure 3.14 shows contrast curves for negative resists, mAaN and HSQ processed in Tetramethyl Ammonium Hydroxide(TMAH) at two different temperatures, 18C and 50C. The difference in contrast can be used to make three-dimensional nanostructures. Figure 3.15 and Figure 3.16a shows images of three dimensional structures fabricated using a negative resist stack. The resists were re-cast into compatible solvents before the spin-coating process. Figure 3.16b shows an image of a combination of positive/negative stack where the empty tunnel space is cleared positive resist and crosslinked negative resist forms the layer above it. Due to multiple factors (discussed in chapter 4, listed on Table 4.6) spin-coating of more than three resist layers consecutively was not feasible.
Figure 3.14: Contrast curves for maN and HSQ (at various developer temperatures) - Developer sin 0.26N TMAH
Figure 3.15: Negative resist stack images, a - SU-8 on NEB, b - maN on HSQ
Figure 3.16: Multi-layer process implemented on Negative resist stack images (HSQ/ma-N) and Negative/Positive resist (HSQ/Copolymer)
3.3 Dose distribution - Simulation and Experiments

Due to scattering of the electron beam as it interacts with material, uniform dose distribution can only be maintained to a certain stack thickness. This limits the capability of maintaining critical dimensions along the height of a three-dimensional structure. The dose contrast available between different resist layers in a given multilayer stack is also an important factor to be considered.

For a given energy of incident electrons on a substrate, as depth increases it is expected that energy density (measured in $eV/cm^3$) decreases. This is mainly due to scattering and other physical process such as generation of x-rays. Inelastic scattering caused small angle deflections in the electron trajectories causing the primary beam to spread. Dose (measured in $\mu C/cm^2$) required to pattern resist at a given beam energy is the number of electrons required to caused necessary a chemical change. As stack thickness increases, beam spread is evident and the dose delivered along the primary path of the beam decreases. Hence, to pattern thick layers of resist higher incident doses are required.

To precisely determine the effect of beam spread on dose delivered to resist, monte-carlo simulations were used to generate energy density distributions as a function of stack depth. Sceleton (Monte-Carlo simulator) was used to simulate interaction between high energy electrons and resist. The output of the simulation consists of energy density values as a function of depth and radial distance from the point of injection. Although, the program’s output file contains data as a function of depth and radial distance a special program had to be developed to visualize the simulated data.

Data generated by simulations performed using Sceleton were used to estimate the trends of energy density variation in resist stack as a function of depth and lateral spread. At constant energy, interaction of electrons with resist or substrate does not vary and hence, dose required is also constant for a certain thickness (about 10$\mu$m in
PMMA as shown in Figure 2.14). Hence, delivered charge per unit area or dose is a major factor in patterning thick layers of resist. (more details on data obtained from Skeleton simulations is available in Appendix B)

Even though there are multiple secondary processes such as backscatter contributing to exposure, it is assumed in this work that most of the exposure (for thicknesses considered in this work) is due to primary beam’s interaction with resist and variation of energy density (eV/cm³) is proportional to the variation of flux or dose (µC/cm²). This assumption is based on scattering events which are major factors for energy loss/deposition in the process of electron-material interaction at any given plane along the electron beam’s interaction path in the material. Hence, in a given area as energy loss increases, scattering also increases causing beam spread.

Based on the aforementioned assumption energy density distribution (also called as point spread function) as a function of radial distance from the point of incidence was extracted along height of the stack. A minimum energy density of 1eV/cm³ was used as cutoff limit to determine radial distance value as a function of depth. Mathematical functions were fit to data obtained from the simulations to approximate the dose and spread as functions of depth. Equations 3.1, 3.2 were obtained from mathematical fits to the simulated data sets. Figure B.13a, b shows dose and spread data from Skeleton along with fits from mathematical expressions 3.1, 3.2 respectively.

\[
D_1(x) = D_c * a_1 * e^{b_1*x} \tag{3.1}
\]

\[
D_2 = D_1(x) * a_2 * y^{b_2} \tag{3.2}
\]

where, \(D_1(x)\) is the on-axis (along beam’s primary path) dose as a function of depth, \(D_c\) is the incident dose at the surface, \(a_1=2.581\times10^7\) and \(b_1=-0.000612\) are fitting constants, \(x\) is depth. \(D_2(y)\) is radial dose spread as a function of depth,
\( a_2 = 4.604 \times 10^{-5},
\)  \( b_2 = 1.836 \) are fitting constants, \( y \) is lateral spread. The aforementioned fitting constants pertain to a 100keV electron beam interacting with a 10 \( \mu \)m thick resist stack.

![Mathematical fit to experimental data for Dose and Spread as a function of depth](image)

**Figure 3.17:** Mathematical fit to experimental data for Dose and Spread as a function of depth

Figure 3.11 shows an experimentally measured plot of variation of dose contrast between Copolymer and PMMA layers for a 100keV electron beam with number of levels (thickness). As thickness of stack increases, dose to clear increases leading to increased effect of spreading causing loss of dose distribution control for a given beam energy.

From equations 3.1 and 3.2, for a given incident dose, effective dose variations can be visualized along depth and radial distance for a given stack thickness. Figure 3.18 shows dose contours generated from a simulation program in MATLAB (see
Appendix B for simulation program) for a 100keV electron beam interacting with a 6µm thick PMMA stack at various incident doses (white text on images). Although, dose values in the images are for a given area, the simulated images pertain to a single layer of the area extending in and out of the image. The values of incident dose on the images refer to $D_c$ for equation 3.1. Each image shows variation of delivered charge per unit area (dose) as a function of depth (y-axis) and width (x-axis). As depth increases, the dose delivered decreases prompting increased incident dose to pattern thick layers of resist. Due to minimal change in beam energy (as shown in Figure 2.14) for the range of resist thickness (6µm) considered in this work, change in sensitivity due to beam energy can be neglected.

800µC/cm² is nominal dose-to-clear for PMMA in MIBK:IPA(1:3) mixture. As dose increases from 1000µC/cm² to 5000µC/cm², the nominal dose-to-clear is transferred deeper into the stack making it soluble in the developer and this is represented by red color in the images. Figure 3.19 shows SEM images of a 6µm thick PMMA stack exposed to a 100keV electron beam, developed in MIBK:IPA(1:3) mixture. The contrast between exposed and unexposed areas can be observed from 500µC/cm² to 2000µC/cm². Beyond 2000µC/cm², proximity effect causes loss in contrast that was visible at lower doses. At about 3500µC/cm², the nominal dose-to-clear is transferred to the bottom of the 6µm stack but there is a finite amount of dose that spreads laterally. This is an intrinsic effect of electron beam resist interaction and increases with depth.

Figure 3.20 shows electron beams of three different energies (100keV, 150keV, 200keV) interacting with a 6µm stack. For a higher beam energy lateral dose spread is comparatively lower at a given depth. This enables better dose control while patterning thick resist stacks. Figure 3.21 shows dose contours for 100, 150 and 200keV electron beams in a 10µm stack.

Figure 3.22 shows a simulation generated image of 100keV, 150keV and 200keV
Figure 3.18: Simulated Dose contour of a 100keV electron beam in PMMA

electron beams interacting with a 60 layer Copolymer/PMMA stack. (Appendix B shows more detailed dose distribution results - Dose Distribution section, Effect of Dose section)

Figure 3.23 shows a plot comparing simulation and experimental results of 100keV electron beam spread in PMMA. It should be noted that beam spread comparison for SEM and simulated images was made based on maximum values. In the experiment, 500 nm wide lines were patterned with multiple passes (combination of multiple spots) and for equal comparison of beam spread between SEM and simulated images, the nominal value of line width was subtracted from measured value of line width from SEM images.

Figure 3.24 shows a plot comparing experimental and simulation results of penetration depth of a 100keV electron beam in PMMA. The results from the simulation
model are in good agreement with experimentally obtained values. Experimental and simulated comparison of beam penetration depth and spread are based on maximum values obtained at dose-to-clear for PMMA (800\(\mu\)C/cm\(^2\)). It can be noticed in figure 3.24, at 3000\(\mu\)C/cm\(^2\) there is change in the trend of increase in penetration depth. This can be explained from simulated dose contours in figure 3.18. As dose increases, penetration depth (on beam’s normal incident path) increases but, for a given beam energy as electrons in the beam traverse through material multiple scattering events spread the beam laterally reducing the beam’s influence along its primary path. This phenomenon causes inflection in beam’s penetration depth as seen in figure 3.24.
**Figure 3.20:** Dose contours for 100, 150 and 200keV electron beams in 6μm PMMA stacks - all dose scales are in μC/cm²
Figure 3.21: Dose contours for 100, 150 and 200keV electron beams in 10μm PMMA stacks - all dose scales are in μC/cm²
Figure 3.22: Simulated image resulting from the convolution of applied dose and Copolymer/PMMA contrast curves for 100, 150 and 200keV electron beams in 6μm Copolymer/PMMA stacks
Figure 3.23: Beam Spread vs Dose for a 100keV electron beam - Simulation and Experiment
Figure 3.24: Beam Depth (on normal incident path) vs Dose for a 100keV electron beam - Simulation and Experiment
3.4 Effect of Focus on Lithography

Multi-Layer Electron Beam Lithography is flexible, scalable and well suited for large area (>1mm$^2$) fabrication. Focus is a major factor that effects quality of lithographic fabrication involving electromagnetic or charged particle radiation. Optimum focus on wafer plane is necessary to maintain dimensions of patterns close to the designed values. The effect of focus is equally prominent in the multi-layer direct write technique for three dimensional structures as it tends to move the dose distribution envelope. Figure 3.25 illustrates the difference between the positive and negative focus offset. The area under the dotted lines pertains to the dose distribution, which can be shifted by applying an offset to measured height.

![Figure 3.25: Focus offset diagram](image)

Figures 3.26 shows the effect focus of on a 12-layer Copolymer/PMMA positive resist stack at an optimum dose-to-clear of 800µC/cm$^2$. On analyzing dimensions
of the trunk of the structures, it can be noticed that as focus changes from positive to negative the lateral dimensions of the trunk shrink. This relates to the dose distribution and its uniformity. Figure 3.27 shows images of Copolymer/PMMA stack at three different doses. As the dose increases, the effects of change in focus also increase. (more details in Appendix B - Effect of Focus section)

![Figure 3.26: Effect of focus at 800 μC/cm² on Copolymer/PMMA stack](image)

Analyzing the images infers delicate interplay between focus and dose. A positive focus offset delivers uniform dose distribution at slightly lower doses and negative focus offset requires a higher dose to clear for a given stack thickness. There is a finite extent to which focus adjustments can be made to deliver uniform dose. (Appendix B shows more results on effect of focus on lithography)
Figure 3.27: Effect of focus for 800 μC/cm², 825 μC/cm², 850 μC/cm² on Copolymer/PMMA stack (all images are on same scale)
3.5 Proximity Effect Correction

Proximity effect is undesired exposure contribution of scattered electrons or other charged particles in resist and substrate. The range of this effect increases with beam energy and needs to be corrected for maintaining dimensional uniformity across the patterned area. It is well known and documented in the field of electron beam lithography and many correction approaches are available[31, 32, 33, 34, 38]. It is more prominent in high energy (>30keV) systems due to large beam penetration and scattering. Figure 3.28 shows a flow chart for processing pattern design files for electron beam exposure with proximity effect correction. Figure 3.29 illustrates cross-section of a uniform pattern on a single resist layer. A plot of corresponding dose level against position is also shown with dose profiles for corrected and un-corrected pattern. As parts of the resist beyond "A" and "B" are not patterned, reduced proximity effect at the edges leads to dose (green curve) below threshold($D_t$), as shown in the plot. Proximity effect correction increases effective dose (blue curve) at the edges to compensate for reduced dose.

The following process flow was applied in this work to emulate Multi-layer proximity effect correction,

1. Read design file and identify number of layers.

2. Input nominal dose-to-clear(positive resist) or dose-to-crosslink(negative resist) values. Example - Dose-to-clear for PMMA - 650 $\mu$C/cm$^2$ and Copolymer(MMA:MAA) - 175 $\mu$C/cm$^2$

3. Identify largest dose value and calculate relative dose factors.

   Example - PMMA dose factor - 1, Copolymer relative dose factor - 0.26.

4. Assign relative dose factors to corresponding layers and separate them.
5. Perform Proximity Effect Correction (PEC) on all layers with corresponding relative dose factors.

Example - perform individual PEC on PMMA and Copolymer layers.

6. Assign calculated dose factors to all layers.

7. Merge layers with assigned dose factor data.

8. Write converted design file.

Figure 3.30 shows a flow chart of the proposed proximity effect correction module.

Figure 3.31 illustrates multiple layers of resist on a wafer along with their respective threshold doses in the plot. Due to multiple dose thresholds the new strategy proposed here aims at assigning proximity effect corrected doses to the different layers in the same design file.
Figure 3.29: Proximity Effect Correction for large area (> 250\(\mu\)m) patterns on a single resist layer

Figure 3.32 highlights different areas on the resist stack and corresponding SEM images of corrected and uncorrected patterns. For the uncorrected set of images, structures at the edges of the patterned area (highlighted in blue and green) are not developed completely compared to structures at the center (highlighted in red). The aforementioned Proximity Effect Correction flow chart was applied to the design file improving developed profile of structures at the edges to maintain uniformity of structure shapes and dimensions in the patterned area.

In general, the modified proximity effect correction technique should consider the variable dose thresholds as a function of position. The single layer ”Exact Dose Correction[32]” (refer section 2.3.2) technique corrects for proximity effect by solving for equal energy (E) based on the point spread function over patterned area (R) by changing dose values (Q).
\[ [E_i] = [R_{ij}] [Q_j] \] (3.3)

where \( i \) and \( j \) are pixel positions.

This can be modified for the multi-layer process as follows where threshold for each patterned pixel is based on its position and layer,

\[ [E_i(l)] = [R_{ij}(l)] [Q_j] \] (3.4)

where \( l \) is layer number.
Figure 3.31: Proximity Effect Correction strategy for large area (> 250μm) patterns on multiple resist layers

3.6 Summary

Three dimensional fabrication technique presented in this work is a function of the following,

1. Penetration depth of a high energy particle beams or any type of electromagnetic radiation,

2. Inter-layer dose contrast,

3. Resist Tone (Positive or Negative)

By changing the aforementioned parameters most periodic three dimensional nanostructures can be fabricated. Proximity correction technique is required for uniform dose delivery over a large area and a commonly utilized single layer correction technique is modified to accommodate multiple layers of resist along with their respective thresholds.
Figure 3.32: Proximity Effect Corrected pattern
CHAPTER 4
Materials

4.1 Introduction

Resists are broadly classified into two types, Positive and Negative. Positive resists unexposed to radiation (UV or electron beam) have very low solubility in the developer but when exposed to the right amount of radiation or dose-to-clear, their solubility increases. Negative resists unexposed to radiation are completely soluble in the developer but when exposed to radiation or dose-to-crosslink, it becomes insoluble in the developer.

In optical lithography, the ability to continue shrinking the size of the devices is dependent on radiation of wavelength (Rayleigh resolution) used and also on the resist’s capability to be imaged at higher resolutions. A lot of research is underway to make resists faster and increasing their capability of being imaged at higher resolutions (<10nm)[41].

Resists are solutions composed of two main parts,

1. The solute part consists of radiation sensitive polymer and other additives on which the microscopic patterns can be formed. It compromises 1-5 wt% of the resist solution.

2. The solvent is a volatile liquid that vaporizes when resist is spin coated on the wafer. It compromises 90-95% of the resist solution.

There are many factors that should be considered while choosing a solvent for the resist polymer and few of them are,

1. **Solubility** - It determines how well the solute is dispersed in the solvent, which directly effects the coating uniformity and shelf life.
2. **Boiling point, Melting point and Flash point** - The flash point determines how fast the solvent evaporates in the process of spin coating which also effects the uniformity of the film.

3. **Viscosity** - It affects the ability of the solvent to spread in the process of spin coating. Solvent with low viscosity are suitable for spin coating applications.

4. **Environmental Health and Safety concerns**

   A major requirement of Multi-Layer direct write technique lies in the feasibility of coating multiple layers of resist with different sensitivities consecutively. The following issues need to be considered to make a multi-layer coating of different resist materials using spin coating process for fabricating three dimensional nanostructures,

   1. **Solvents** - They act as carriers for the resist polymers. Consecutive spin coating of different resist materials to produce a multi-layer stack requires non-interacting solvents, where solvent of one resist does not dissolve the other or vice versa.

   2. **Coating Uniformity and Adhesion** - Surface functionalization to make resist layers polar or non-polar might be required to enhance adhesion between adjacent resist layers.

   3. **Solvent Diffusion and Polymer intermixing** - For a given polymer chain molecular weight of the resist, there exists a critical thickness below which intermingling of adjacent resist layers occur. This causes loss in dose contrast thereby making the technique incapable of fabricating three dimensional structures. The critical thickness of Copolymer (60K) and PMMA (950K) were estimated at about 100nm and 45nm.
4. **Dose contrast** - For a given process, materials coated consecutively should have different sensitivities to electron beam radiation for achieving three dimensional structures.

5. **Developer** - A common developer is required for maintaining the dose contrast and to have a clean development.

6. **Chemical amplification** - This is a common process that occurs in negative resist materials. Exposure to radiation causes generation of acid ($H^+$) which leads to crosslinking of the polymer making it insoluble in developers. The generated acid can diffuse through the film and it can cause the effective thickness of fabricated structures to change. Experimental analysis is required to check for this effect if chemically amplified resist are used in this technique.

The following section will review basics of solubility and the Hansen Solubility model which was used in this research to identify mutually exclusive solvents and common developers.

### 4.2 Solubility

#### 4.2.1 Introduction

Mutually exclusive solvents are necessary for coating multiple layers of resist consecutively. Although commercially available resist polymers are soluble in numerous solvents, they are not necessarily non-interacting. The process of recasting resists into suitable solvents requires insight into parameters effecting solubility.

Solubility is the ability of a solvent to dissolve a solute and the degree of solubility is a measure of the amount of solute that can be dissolved in a given amount of solvent. The dissolution of a solute in a solvent can provide important information about the solute’s chemical properties. Molecular forces in solute and solvent hold the molecules together and their strength defines the solute/solvent’s state i.e. solid,
liquid or gas. The intramolecular cohesive forces are due to solute-solute, solvent-solvent interactions. To form a homogenous solution the intramolecular forces should be overcome by intermolecular cohesive forces (solvent-solute) which arise when the solute is dissolved in the solvent.

Figure 4.1 is a graphical illustration of a solute and a solvent with cohesive energies $E_1$ and $E_2$ respectively. When energy $E_1$ and $E_2$ is given to the solute and solvent respectively, the molecules will acquire enough energy to overcome the cohesive intramolecular forces between them. When the solute is dissolved in the solvent, there would be energy due to interactions between the solute and solvent.

![Figure 4.1: Solvent, Solute and Solution - cohesive energy](image)

For solute to spontaneously dissolve in the solvent, the cohesive energy due to solvent-solute interactions ($E_3$) should be greater than or equal to the cohesive energy due to solvent-solvent ($E_1$) and solute-solute ($E_2$) interactions.

### 4.2.2 Theory

For a given state of matter the molecules will have internal energy $U$ and energy due to ambient pressure and temperature. At any given instance, the internal energy (dU) of a system is equal to the sum of heat added to the system (dQ) and work done by the system (dW) as shown in equation 4.1a. The sum of internal energy and energy provided by surroundings is called as Enthalpy, given by the equation 4.1b.
Entropy \( (S) \) is the measure of randomness of a system and the difference between enthalpy and entropy is free energy of the system available for work and is termed as Gibbs free energy \( (G) \). Gibbs free energy, from equations 4.1c where temperature \( T \) is in Kelvin, decreases for all spontaneous changes and is minimum at thermodynamic equilibrium.

\[
\begin{align*}
\frac{dU}{dT} &= dQ - dW \\
H &= U + PV \\
G &= H - TS
\end{align*}
\] (4.1a, 4.1b, 4.1c)

In terms of thermodynamics, for a solute to spontaneously dissolve in a solvent the free energy of the system (solution) should be less than the combined free energies of solvent and solute\([42]\). Higher free energy difference implies higher spontaneity in solubility. The cohesive energy density can be calculated using the heat of vaporization, which is the energy required to vaporize a liquid. At this point, the molecules attain enough energy to overcome intramolecular forces and move out of their spheres of influence. The cohesive energy density of a material can be calculated by the equation 4.2,

\[
C = \frac{\Delta H - RT}{V_m}
\] (4.2)

Joel Hildebrand proposed quantification of solubility [43, 44, 45] and square root of cohesive energy density was termed as Hildebrand solubility parameter \((Mpa^{1/2})\) as shown in equation 4.3.

\[
\delta = \sqrt{c} = \left[ \frac{\Delta H - RT}{V_m} \right]^{1/2}
\] (4.3)

Table 4.1 gives tabulated values of the Hildebrand Solubility parameter. From
the table it would be expected that solvents with similar Hildebrand solubility parameters will have similar solubility properties. For example, Acetone and Diacetone alcohol have similar Hildebrand solubility parameters and would be expected to have similar degree of solubility for a given material.

Figure 4.2 shows a plot of degree of swelling of a Linseed oil film against Hildebrand Solubility parameter ($\delta$).

Highlighted in red are two solvents Chloroform and Trichloroethylene with similar Hildebrand Solubility Parameter (around 19) and marked in blue is the degree of swelling for the solvents. This shows severe discrepancy in the technique because liquids with similar cohesive energy densities should have similar solubility characteristics. The reason for this inconsistency is due to the fact that the addends of cohesive energy densities are different. If the component differences are taken into account and quantified, the prediction of solubility can become more accurate. To include component differences into solubility theory, the different types of interactions contributing to cohesive energy should be considered.

1. Dispersion forces - These forces are due to the random movement of electron cloud surrounding the molecule. The fluctuations in the electron cloud
distributions cause electrical dipoles to be created constantly. These random
polarity changes induce complementary polarities in proximity molecules caus-
ing temporary attraction between each other. These induced attractions are
called London dispersion forces or induced dipole-induced dipole forces. The de-
gree of attraction between the temporary dipoles is related to the surface area.
This type of interaction is most common in molecules with straight chains.

Figure 4.3 shows electron cloud distribution images (time-averaged) of two Io-
dine molecules which are far apart. When the molecules are in proximity to each
other (second set of images), the partial negative and positive charges ($\delta^+, \delta^-$)
formed due to polar fluctuations cause attraction between the molecules.

2. Polar forces - These forces are similar to dispersion forces but are stronger.
Some atomic elements form ionic bonds where they attract electrons from their
donors and this causes permanent imbalance in the electron density. The imbal-
ance makes the molecule polar and its polarity is related to its atomic composi-
tion, geometry and its size. The molecules with opposite polarities attract each other and this interaction is called *Keesom interaction or dipole-dipole forces*.

Figures 4.4 and 4.5 show two different types of interactions contributing to the Polar forces. Figure 4.4 shows two Hydrogen Chloride molecules with partial charges, $\delta^+$ and $\delta^-$, on Hydrogen and Chlorine atoms respectively. The molecules are bound by a covalent bond and high electronegativity difference between the atoms forms a permanent partial charge on the atoms leading to a permanent dipole. When the atoms are in proximity to each other, the partial negative charge on Chlorine atoms attracts the Hydrogen atom of another molecule which has a partial positive charge.

Figure 4.5 shows a Hydrogen Chloride molecule and an Oxygen molecule’s electron cloud image. When both the molecules are far apart, the electron cloud distribution on the oxygen molecule is uniform. The second set of images show the case when they are in proximity to each other. The permanent dipole on Hydrogen Chloride molecule changes the electron cloud distribution in the Oxygen molecule and induces polarity. This causes interaction between both
Figure 4.4: Polar forces - Keesom Interaction

Figure 4.5: Polar forces - Debye Interaction

3. **Hydrogen bond forces** - These forces are a special case of dipole-dipole in-
teraction because it occurs in molecules where a hydrogen atom is attached to Oxygen, Nitrogen or Flourine atoms. In such cases a partial positive charge is formed on the hydrogen atom which is capable of exerting considerable attraction on electrons in other molecules forming a protonic bridge which is stronger than other dipole interactions. This is stronger than other vanderwaals interactions, plays a significant role in solubility and hence is considered independently.

The best example for hydrogen bonding is between water molecules. Figure 4.6 shows interaction between two water molecules. Partial charge on Hydrogen atom of one molecule and Oxygen atom of another molecule causes attraction between them and thus forming a hydrogen bond.

![Hydrogen bond](image)

**Figure 4.6:** Hydrogen bond forces

The inconsistency shown in Figure 4.2 is due hydrogen and polar bonding parameters. Linseed oil film belongs to the family of hydrocarbons and mostly has dispersion forces between its molecules. Solvents like Chloroethylenes, Ketones have high polar and hydrogen bonding between their molecules but solvents like Chloroform, Alkanes have a high dispersion bonding which is the reason for higher solubility or swelling of the oil film. Even though the cumulative cohesive energy density of sol-
vents is same, the differences in component forces and in this case primarily hydrogen bonding explains the observed differences.

4.2.3 Hansen Solubility Model

Hansen Solubility model is a widely accepted three component model developed by Charles M. Hansen in 1966. This model divides the Hildebrand Solubility Parameter into three different parts taking into account the dispersion component ($\delta_d$), polar component ($\delta_p$) and hydrogen bonding component ($\delta_h$). As discussed in the previous section, cohesive energy ($E$) between molecules is due to the presence of van der Waals attractive forces and is the sum of three component energy terms as shown in equation 4.5.

$$E = E_D + E_P + E_H$$ \hspace{1cm} (4.4)

where $E_D$ corresponds to energy due to dispersion component, $E_P$ corresponds to polar component and $E_H$ corresponds to hydrogen bonding component.

The Hildebrand Solubility parameter ($\delta$) is given by,

$$\delta^2 = \frac{E}{V_m} = \frac{E_D}{V_m} + \frac{E_P}{V_m} + \frac{E_H}{V_m}$$ \hspace{1cm} (4.5)

Equation 4.6 shows the relation of Hildebrand parameter ($\delta$) to the three different Hansen solubility parameters,

$$\delta = \sqrt{\delta_d^2 + \delta_p^2 + \delta_h^2}$$ \hspace{1cm} (4.6)

The Hansen Solubility parameters (HSP) are used to make up three dimensional (3-D) space where solvents are represented as a point with coordinate ($\delta_d, \delta_p, \delta_h$) and polymers as spheres with a center coordinate and interaction radius (R). Figure 4.7 shows an illustration of Hansen space with Dispersion, Polar and Hydrogen bonding...
components as the three axes.

Alkane and straight chain hydrocarbons have zero polar and hydrogen components. For polar molecules, the dispersion force for a particular liquid is calculated using the homomorph method [48]. The homomorph of a polar molecule is the nonpolar molecule most closely resembling it in size. For example, n-hexane is the homomorph of n-hexanol, where the dispersion component of n-hexanol is very close to n-hexane. The Hildebrand value for the nonpolar homomorph, in this case n-hexane (which is entirely due to dispersion forces) is assigned to the the polar molecule, n-hexanol as its dispersion component value. This value is subtracted from the Hildebrand value of n-hexanol and the remainder represents the Polar interaction of the molecule. Through trial and experiment this value was separated into Polar and Hydrogen bonding components best reflecting the empirical evidence.

Table 4.2 shows Hansen Solubility parameters for a few solvents along with their Hildebrand parameter ($\delta$) which was already discussed in the previous section. We can see from the table that benzene and chloroform have same Hildebrand solubility parameter, but their Polar and Hydrogen bonding components differ a lot, which
<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta_d$</th>
<th>$\delta_p$</th>
<th>$\delta_h$</th>
<th>$\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>15.5</td>
<td>10.4</td>
<td>7</td>
<td>19.7</td>
</tr>
<tr>
<td>Diacetone Alcohol</td>
<td>15.8</td>
<td>8.2</td>
<td>10.8</td>
<td>20</td>
</tr>
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<td>Benzene</td>
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<td>0</td>
<td>2</td>
<td>18.7</td>
</tr>
<tr>
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<td>17.4</td>
<td>3.1</td>
<td>5.7</td>
<td>18.7</td>
</tr>
<tr>
<td>Toluene</td>
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<td>1.4</td>
<td>2</td>
<td>18.3</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>14.9</td>
<td>0</td>
<td>0</td>
<td>14.9</td>
</tr>
<tr>
<td>Water</td>
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<td>16</td>
<td>42.3</td>
<td>48.0</td>
</tr>
<tr>
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<td>8.8</td>
<td>19.4</td>
<td>26.2</td>
</tr>
<tr>
<td>Trichloroethylene</td>
<td>18</td>
<td>3.1</td>
<td>5.3</td>
<td>18.7</td>
</tr>
<tr>
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<td>1</td>
<td>3.1</td>
<td>18.2</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>15.5</td>
<td>5.3</td>
<td>7.2</td>
<td>18.2</td>
</tr>
</tbody>
</table>

Table 4.2: Hansen Solubility Parameters (in SI units, $MPa^{1/2}$) [48]

accounts for the differences in their properties.

Similarity between two solvents or degree of solubility of a polymer in a solvent can be determined by calculating distance between them in Hansen space. Equation 4.7 is used to calculate the HSP distance,

$$D = \sqrt{4(\delta_d^a - \delta_d^b)^2 + (\delta_p^a - \delta_p^b)^2 + (\delta_h^a - \delta_h^b)^2}$$  \hspace{1cm} (4.7)

Where $\delta_d^a, \delta_p^a, \delta_h^a$ are the Hansen Solubility parameters (HSP) of a solvent or polymer and $\delta_d^b, \delta_p^b, \delta_h^b$ are HSP of a solvent. Smaller value of D would mean greater similarity of solvents or higher solubility of the polymer in that solvent. The factor ”4” of the first term in the equation doubles the dispersion component and creates spherical plots.

In HSP space, solvents are represented as points and polymers are spheres with a center coordinate and interaction radius (R). The solvents with relative distance less than the interaction radius can dissolve the polymer. In terms of free energy, surface of the sphere represents zero free energy of mixing and the area inside the sphere corresponds to negative free energy and hence solvents inside or at the boundary of the sphere dissolve the polymer spontaneously.
Figure 4.8 (axes are measured in MPa$^{1/2}$) shows two polymers represented as spheres and a few solvents as points in Hansen space. Figures 4.9a, b, c (axes are measured in MPa$^{1/2}$) show two dimensional projections of the 3-D plot. The 2 − $D$ plots show differences between the polymers 1 and 2 along with compatible solvents.

Polymer 1 (NEB-31 - negative electron beam resist) has $\delta_d = 14.4$, $\delta_p = 11.3$, $\delta_h = 14.5$ which is center of the sphere with interaction radius $R = 13.4$ and Polymer 2 (SU-8 - negative resist) sphere has a center given by $\delta_d = 18.4$, $\delta_p = 10.1$, $\delta_h = 7.4$ with an interaction radius $R = 8.5$. The HSP values of polymers are generated by fitting spheres to data obtained from solubility analysis discussed in the next section.
4.2.4 Hansen Solubility Parameters - Experiment

To estimate properties of unknown polymers, spheres are fit around experimentally determined solubility data. Resists with a nominal thickness of 200nm were coated on silicon wafers and exposed to various solvents. Thickness measurements were made using an Ellipsometer to confirm visual inspection following assignment of scores. After suitable solvents were identified, resist polymers were recast (evaporate original solvent and mix in desired solvents) and tested for the solvent’s ability of clearly dissolve the polymer. About 50 solvents were used in this work to estimate the Hansen Solubility parameters for electron beam resist polymers and are listed in Table 4.3. The polymer under consideration is ma-N, a Novolac based negative...
electron beam resist. Solubility data for a other commercially available electron beam resists are available in the Appendix C.

A minimum of two soluble solvents and one insoluble solvent is needed to estimate the HSP of the polymer. The accuracy of the fit increases with more solvents. The "Score" column is a value assigned based on experimental evaluation of solubility. A solubility scale of 6 was used and "1" would mean that the solvent completely dissolves the polymer, "6" would mean insoluble and "3" would mean partial solubility. A larger scale will increase the accuracy of the fit, but a scale of "6" is sufficient for this work. The "RED" is the Relative Energy Difference which is the ratio of distance from polymer spheres center to the solvent to the radius of the polymer sphere. If the RED number is less than 1, solubility of the polymer in a given solvent is thermodynamically possible and if it is greater than 1 the polymer tends to be insoluble.

A Sphere was fit around the data in table 4.3 which yielded the Hansen Solubility parameters of the negative electron beam resist polymer, \( \delta_d = 17.02 \), \( \delta_p = 10.42 \), \( \delta_h = 14.4 \) and an interaction radius \( R = 13.6 \). The accuracy of the fit was 97%. A licensed software from Hansen-Solbility.com, HSPiP, was used to perform data fits and generate the Hansen Solubility parameters.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \delta_d )</th>
<th>( \delta_p )</th>
<th>( \delta_h )</th>
<th>Score</th>
<th>RED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>15.5</td>
<td>10.4</td>
<td>7</td>
<td>1</td>
<td>0.587</td>
</tr>
<tr>
<td>Anisole</td>
<td>17.8</td>
<td>4.4</td>
<td>6.9</td>
<td>1</td>
<td>0.714</td>
</tr>
<tr>
<td>Benzyl Alcohol</td>
<td>18.4</td>
<td>6.3</td>
<td>13.7</td>
<td>1</td>
<td>0.367</td>
</tr>
<tr>
<td>2-Butanol</td>
<td>15.8</td>
<td>5.7</td>
<td>14.5</td>
<td>1</td>
<td>0.39</td>
</tr>
<tr>
<td>t-Butyl Acetate</td>
<td>15</td>
<td>3.7</td>
<td>6</td>
<td>1</td>
<td>0.843</td>
</tr>
</tbody>
</table>

Continued on next page
Table 4.3 – continued from previous page

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( \delta_d )</th>
<th>( \delta_p )</th>
<th>( \delta_b )</th>
<th>Score</th>
<th>RED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroacetaldehyde Diethyl Acetal</td>
<td>16.0</td>
<td>6.2</td>
<td>4.4</td>
<td>3</td>
<td>0.810</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>19</td>
<td>4.3</td>
<td>2</td>
<td>3</td>
<td>1.055</td>
</tr>
<tr>
<td>1-Chloronaphthalene</td>
<td>20.5</td>
<td>4.9</td>
<td>2.5</td>
<td>1</td>
<td>1.089</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>16.8</td>
<td>0</td>
<td>0.2</td>
<td>6</td>
<td>1.292</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>17.4</td>
<td>4.1</td>
<td>13.5</td>
<td>1</td>
<td>0.471</td>
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<tr>
<td>Cyclopentanone</td>
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<td>11.9</td>
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<td>1</td>
<td>0.696</td>
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<tr>
<td>Decane</td>
<td>15.7</td>
<td>0</td>
<td>0</td>
<td>6</td>
<td>1.318</td>
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<tr>
<td>Dipropylene Glycol</td>
<td>16.5</td>
<td>10.6</td>
<td>17.7</td>
<td>1</td>
<td>0.254</td>
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<tr>
<td>Ethanol</td>
<td>15.8</td>
<td>8.8</td>
<td>19.4</td>
<td>1</td>
<td>0.425</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>15.8</td>
<td>5.3</td>
<td>7.2</td>
<td>1</td>
<td>0.672</td>
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<tr>
<td>Ethyl Lactate</td>
<td>16</td>
<td>7.6</td>
<td>12.5</td>
<td>1</td>
<td>0.291</td>
</tr>
<tr>
<td>Ethyl Tert-Butyl Ether</td>
<td>14.7</td>
<td>3.6</td>
<td>4.6</td>
<td>1</td>
<td>0.939</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>17</td>
<td>11</td>
<td>26</td>
<td>1</td>
<td>0.852</td>
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<tr>
<td>Hexane</td>
<td>14.9</td>
<td>0</td>
<td>0</td>
<td>6</td>
<td>1.34</td>
</tr>
<tr>
<td>Hexamethyl disoboxane(OS-10)</td>
<td>12.6</td>
<td>2</td>
<td>0</td>
<td>6</td>
<td>1.385</td>
</tr>
<tr>
<td>Isobutyl Alcohol</td>
<td>15.1</td>
<td>5.7</td>
<td>15.9</td>
<td>1</td>
<td>0.460</td>
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<tr>
<td>Lactonitrile</td>
<td>16.1</td>
<td>16.8</td>
<td>21.2</td>
<td>1</td>
<td>0.697</td>
</tr>
<tr>
<td>Methyl Ethyl Ketone (MEK)</td>
<td>16</td>
<td>9</td>
<td>5.1</td>
<td>1</td>
<td>0.706</td>
</tr>
<tr>
<td>Methyl Isobutyl Ketone (MIBK)</td>
<td>15.3</td>
<td>6.1</td>
<td>4.1</td>
<td>1</td>
<td>0.857</td>
</tr>
<tr>
<td>N-Methyl-2-Pyrrolidone (NMP)</td>
<td>18</td>
<td>12.3</td>
<td>7.2</td>
<td>1</td>
<td>0.564</td>
</tr>
<tr>
<td>2-Methyl naphthalene</td>
<td>19.4</td>
<td>1.9</td>
<td>3.3</td>
<td>3</td>
<td>1.084</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>20</td>
<td>10.6</td>
<td>3.1</td>
<td>1</td>
<td>0.937</td>
</tr>
<tr>
<td>Nitroethane</td>
<td>16</td>
<td>15.5</td>
<td>4.5</td>
<td>1</td>
<td>0.830</td>
</tr>
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Continued on next page
Table 4.3 – continued from previous page

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\delta_d$</th>
<th>$\delta_p$</th>
<th>$\delta_h$</th>
<th>Score</th>
<th>RED</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octamethyltrisiloxane (OS-20)</td>
<td>12.2</td>
<td>1.8</td>
<td>0</td>
<td>6</td>
<td>1.42</td>
</tr>
<tr>
<td>Phenyl Acetylene</td>
<td>18.8</td>
<td>2.8</td>
<td>4</td>
<td>1</td>
<td>0.981</td>
</tr>
<tr>
<td>2-Propanol (IPA)</td>
<td>15.8</td>
<td>6.1</td>
<td>16.4</td>
<td>1</td>
<td>0.392</td>
</tr>
<tr>
<td>Propylene Glycol</td>
<td>16.8</td>
<td>10.4</td>
<td>21.3</td>
<td>1</td>
<td>0.507</td>
</tr>
<tr>
<td>Propylene Glycol Monomethyl Ether Acetate (PGMEA)</td>
<td>15.6</td>
<td>5.6</td>
<td>9.8</td>
<td>1</td>
<td>0.531</td>
</tr>
<tr>
<td>1,1,2,2-Tetrachloroethane</td>
<td>18.8</td>
<td>5.1</td>
<td>5.3</td>
<td>1</td>
<td>0.816</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>18.3</td>
<td>5.7</td>
<td>0</td>
<td>3</td>
<td>1.127</td>
</tr>
<tr>
<td>Tetrahydronaphthalene</td>
<td>19.6</td>
<td>2</td>
<td>2.9</td>
<td>1</td>
<td>1.112</td>
</tr>
<tr>
<td>Toluene</td>
<td>18</td>
<td>1.4</td>
<td>2</td>
<td>3</td>
<td>1.134</td>
</tr>
<tr>
<td>Trans-Crotononitrile</td>
<td>16.4</td>
<td>18.8</td>
<td>5.5</td>
<td>1</td>
<td>0.901</td>
</tr>
<tr>
<td>Trans-Decahydonaphthalene</td>
<td>18</td>
<td>0</td>
<td>0</td>
<td>6</td>
<td>1.312</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>18.4</td>
<td>2.6</td>
<td>2.3</td>
<td>3</td>
<td>1.085</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>17.8</td>
<td>1</td>
<td>3.1</td>
<td>3</td>
<td>1.076</td>
</tr>
</tbody>
</table>

Similarly solubility parameters for a few negative e-beam resists were determined (see Appendix C for solubility data). Figures 4.10, 4.11 show two three dimensional plots of different negative and positive resists which were evaluated in this study using solvents in table 4.3. Tables 4.4 and 4.5 show HSP values for different negative and positive electron beam resists obtained from repeating the experimental solubility procedure. The plots and tables show differences in solubilities of the resist, from which suitable solvents with necessary compatibility can be selected making it possible to coat the multi-layer stack necessary for fabricating the 3-D structures.

The positive electron beam resists evaluated in this research are as follows,
### Table 4.4: Negative E-Beam resist HSP values

<table>
<thead>
<tr>
<th>Resist</th>
<th>$\delta_d$</th>
<th>$\delta_p$</th>
<th>$\delta_h$</th>
<th>Radius (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSQ (Dow Corning)</td>
<td>14.4</td>
<td>6.0</td>
<td>5.8</td>
<td>11</td>
</tr>
<tr>
<td>NEB-31 (Sumitomo)</td>
<td>15.8</td>
<td>10.6</td>
<td>14.2</td>
<td>12.1</td>
</tr>
<tr>
<td>ma-N (Microresist)</td>
<td>19.4</td>
<td>10.3</td>
<td>15.9</td>
<td>15.1</td>
</tr>
<tr>
<td>SU-8 (Microchem)</td>
<td>18.4</td>
<td>8.1</td>
<td>7.3</td>
<td>7.3</td>
</tr>
<tr>
<td>TEBN-1 (Tokuyama)</td>
<td>16.2</td>
<td>6.9</td>
<td>8.6</td>
<td>13.3</td>
</tr>
<tr>
<td>Polystyrene (Pressure Chemical)</td>
<td>17.7</td>
<td>7.9</td>
<td>2.9</td>
<td>8.5</td>
</tr>
</tbody>
</table>

### Table 4.5: Positive E-Beam resist HSP values

<table>
<thead>
<tr>
<th>Resist</th>
<th>$\delta_d$</th>
<th>$\delta_p$</th>
<th>$\delta_h$</th>
<th>Radius (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA 950K (Microchem)</td>
<td>16.2</td>
<td>20.7</td>
<td>11.3</td>
<td>11.4</td>
</tr>
<tr>
<td>ZEP 520A (Zeon)</td>
<td>15.7</td>
<td>19.6</td>
<td>10.6</td>
<td>11.4</td>
</tr>
<tr>
<td>Copolymer MAA:MMA (Microchem)</td>
<td>15.9</td>
<td>15.3</td>
<td>10.7</td>
<td>8.1</td>
</tr>
</tbody>
</table>

### Figure 4.10: Negative electron beam resists in Hansen Space

1. Poly Methyl Methacrylate (PMMA) - It is a chain scission positive electron beam resist and is available in different molecular weights. Electron beam exposure of the polymer causes chain scission, breaking links of the long polymer chain. The exposed areas have a higher dissolution rate in developer solution compared to the unexposed areas, making it selectively patternable. PMMA
dissolves easily in a non-polar, aromatic solvents such as Anisole and Chlorobenzene. Figure 4.12 shows an illustration of a Methyl Methacrylate monomer. In the process of polymerization, these monomers link together forming long chain polymers. The molecular weight of each chain depends on the number of monomer links. In this work PMMA 495000, 950000 and 2200000 were used in the positive stack with Copolymer.

2. **Copolymer (Methyl Methacrylate: Methacrylic Acid) P(MMA:MAA)**

   - It is also a chain scission positive electron beam resist and has a molecular weight of 60,000. The dose required to expose this polymer is lower than PMMA. Due to the difference in chemistry, this polymer is soluble in polar solvent like ethanol, ethyl lactate etc. This makes it readily usable with PMMA for multi-layer coating process. Figure 4.13 shows an illustration of a Methyl Methacrylate: Methacrylic acid co-monomer.

The following negative e-beam resists were evaluated for their ability to work
with each other for fabricating three dimensional structures.

1. SU-8 - It is a chemically amplified, epoxy based negative resist used commonly
in Photolithography (i-line). It has a dose-to-crosslink of about $5 - 10 \mu C/cm^2$ for a 100keV electron beam. This resist is commonly developed in Propylene Glycol Monomethyl Ether Acetate (PGMEA) but can also be developed in other non-aqueous solvents.

2. **KMPR** - It is also a chemically amplified resist and has similar dose-to-crosslink as SU-8, about $5 - 10 \mu C/cm^2$ for a 100keV electron beam. This resist develops in aqueous developers such as Tetra Methyl Ammonium Hydroxide (TMAH).

3. **NEB-31** - It is a polyvinyl phenol based, chemically amplified resist and has a comparatively more dose to crosslink, $30 \mu C/cm^2$ for a 100keV electron beam. It develops in aqueous basic developers and also in a few non-polar solvents. Figure 4.14 shows an illustration of a Poly Vinyl Phenol monomer.

![Poly Vinyl Phenol monomer](image)

**Figure 4.14:** Poly Vinyl Phenol monomer

4. **HSQ** - Unlike other resists which are carbon based, Hydrogen Silsesquioxane (HSQ) contains silicon. Electron beam radiation breaks the Si-H bonds and the
cubic silsesquioxane molecules form an Si-O network [49]. This resist develops in aqueous base developers. Figure 4.15 shows an illustration of a Hydrogen Silsesquioxane monomer. Unlike usual polymers where each monomer unit is covalently bonded in the process of polymerization, HSQ molecules are bonded though hydrogen bonding. This makes it highly unstable and has low shelf life compared to other resists. The high resolution of this material is due to its low molecular weight.

Figure 4.15: Hydrogen Silsesquioxane monomer

5. **ma-N** - It is a novolac based non-amplified resist and consists of an azide based photoactive compound. On exposure to electron beam or UV radiation it assists in crosslinking the novolac making it insoluble in aqueous developers. Figure 4.16 shows an illustration of a Novolac monomer. The -R and -OH side groups assist in solubility and adhesion.

6. **Polystyrene** - The structure of this molecule is similar to Polyvinylphenol or novolac, but without the functional groups. This makes it soluble in aro-
matic solvents but is insoluble in aqueous developers. The dose-to-crosslink of this polymer changes with molecular weight i.e. higher molecular weight molecules would have lower dose to crosslink. The difference in solubility between Polyvinyl Phenol/Novolac and Polystyrene makes this polymer a viable candidate for multi-layer coatings. Figure 4.17 shows an illustration of a Polystyrene monomer. Figure 4.18 shows contrast curve for different molecular weight of Polystyrene. The poor contrast of the material can be attributed to the molecular weight distribution[50]. Figure 4.19a, b shows SEM images of maN/Polystyrene and NEB/Polystyrene multilayer coatings. The resist polymers were cast into compatible solvents before the spin coating process, maN, NEB in 2-Butanol and Polystyrene in Tetrachlorethylene.

Varying photoactive compound concentration in these polymer can change the dose-to-crosslink for these polymers.

Figure 4.20 shows an HSP plot of NEB-31 and SU-8 spheres with different
Figure 4.17: Polystyrene monomer

Polystyrene

Figure 4.18: Polystyrene Contrast Curve for different Molecular weights - Developed in PGMEA

solvents. Three regions on the plot are highlighted and they indicate appropriate solvents and a common developer. NEB-31 and SU-8 polymers were recast into 2-
Butanol and Tetrachloroethylene respectively. Propylene Glycol Monomethyl Ether Acetate (PGMEA) was used as common developer for both the polymers. Although the polymers could be coated consecutively, acid generated due to exposure diffuses through to the adjacent layers causing unwanted exposure.

A new combination of negative resist polymers were identified from this study and their Hansen solubility plots are shown in 4.21. From these plots, Tetrachloroethylene was chosen as a solvent for Polystyrene and 2-Butanol for maN and NEB. After casting the polymers in respective solvents a 4-layer distinct coating is shown in Figure 4.19.

From this work, it can be inferred that with four compatible positive and negative resists most periodic three dimensional structure can be fabricated. An ideal solubility plot for the four resist polymers is shown in Figure 4.22. Commercially available negative resists have one or more compatibility issues for multi-layer coating and table 4.6 summarizes all the observed anomalies.
(Appendix C has detailed solubility data for all electron beam resists analyzed in this work.)

Figure 4.20: HSP plot for NEB and SU-8
Figure 4.21: HSP plot for compatible negative e-beam resist - maN, NEB-31, Polystyrene

Figure 4.22: Ideal HSP resist solubility plot
4.2.5 Solvent Diffusion

Figure 4.23 shows an illustration of polymers and their molecular weights. Positive resists typically contain polymers of high molecular weights (100K to 1M) and negative resists have polymers of lower molecular weight (1000 to 10K). Figure 4.24 shows variation of dissolution rate with molecular weight of polymers and effect of radiation exposure[40]. When positive resists are exposed with adequate dose, links of polymer chains are broken, decreasing the effective molecular weight thereby increasing the dissolution rate as shown in figure 4.24a (as illustrated by arrow). Similarly 4.24b illustrates a similar plot for negative resists, where exposure to radiation causes polymer chains to crosslink and increase molecular weight thereby decreasing the dissolution rate (as illustrated by arrow).

Figure 4.25 illustrates a multi-layer process where two resists R1 and R2 are coated consecutively on a silicon wafer. After coating resist R2 on R1 the solvent from resist R2 can diffuse into R1 causing the polymers to intermingle. The diffusion is dependent on molecular weight and thickness of R1. For a given molecular weight of the polymer, there exists a critical thickness limit below which solvents can diffuse causing polymer chains to intermix. Figure 4.26 shows an SEM image of Copolymer/PMMA stack with intermixed layers making the process incapable of making three dimensional structures.
Figure 4.23: Illustration of polymer chains
Figure 4.24: Variation of dissolution rate with molecular weight, a - positive resist, b - negative resist
Figure 4.25: Illustration of polymer intermixing
Figure 4.26: SEM image - intermixed resist layers
<table>
<thead>
<tr>
<th>Negative resist</th>
<th>SU-8</th>
<th>NEB-31</th>
<th>HSQ</th>
<th>ma-N</th>
<th>KMPR</th>
</tr>
</thead>
<tbody>
<tr>
<td>SU-8</td>
<td>NA</td>
<td>LDC, AD</td>
<td>NUC, DI</td>
<td>HDC, AD</td>
<td>NCS, NDC</td>
</tr>
<tr>
<td>NEB-31</td>
<td>LDC, AD</td>
<td>NA</td>
<td>NUC</td>
<td>NCS</td>
<td>NCS, LDC, AD</td>
</tr>
<tr>
<td>HSQ</td>
<td>NUC, DI</td>
<td>NUC</td>
<td>NA</td>
<td>NUC, NDC</td>
<td>HDC, NUC</td>
</tr>
<tr>
<td>ma-N</td>
<td>HDC, AD</td>
<td>NCS, AD</td>
<td>NUC, NDC</td>
<td>NA</td>
<td>NCS, AD</td>
</tr>
<tr>
<td>KMPR</td>
<td>NCS, NDC</td>
<td>NCS, LDC, AD</td>
<td>HDC, NUC</td>
<td>NCS, HDC, AD</td>
<td>NA</td>
</tr>
</tbody>
</table>

Table 4.6: Negative resist compatibility information

NA - Not Applicable
LDC - Low dose contrast
AD - Acid Diffusion
NUC - Non-Uniform Coating
HDC - High Dose Contrast
NCS - No Common Solvent
NDC - No Dose Contrast
DI - Developer Incompatibility
4.3 Structure Protection and Surface Functionalization

A few three dimensional structures fabricated in this research are inspired from biological organisms, particular morpho butterflies. The optical activity from the structures is well known and their unique interactions with chemical and biological agents make them viable to be used in sensing applications. Inertness of the structures to different interacting analytes is an important factor that effects the sensing mechanism. Chemical reaction of vapors or gasses with the structures can alter response of the structure permanently causing the sensor to lose its property. It can also cause the sensor to give erroneous results. Hence, the materials used to make the nanostructures should be impervious to the vapors.

The following processes can be considered to increase tolerance of the structures to chemical and biological agents,

1. The polymeric structures formed by multi-layer technique can be crosslinked to increase their resistance to solvent and vapors using electron beam, photon or gamma radiation. The structures formed with positive resist materials are more vulnerable to vapor attack as residual dose breaks some of the polymer chains in the structures. Structures formed out of negative resist materials are already crosslinked by the electron beam in multi-layer patterning process.

2. Liquid or gas phase deposition techniques can be used to fill the patterned structures with vapor resistant materials. This technique uses the patterned structures as a mold. Conformality of the coating is a major concern that should be considered in selecting a technique.

3. Use a capping layer over the polymeric structures - With a controlled process, volatile silanes can be used to form atomic layers on top of the patterned structures. They form highly inert Si-O network and due to vapor phase nature of the deposition technique a conformal coating can be achieved.
Figure 4.28a shows SEM image of APTMS coated tree structure before exposure to solvents. Three different samples with the tree structures coated with APTMS were exposed to Acetone, Toluene and Ethanol as shown in figures 4.28b, c, d. The monolayer of Si-O formed from APTMS vapor on surface of the structures protects them from being dissolved by solvents.

Figure 4.27: 3-Aminopropyl Trimethoxysilane (APTMS)
Figure 4.28: APTMS coated tree structures a. Bare structure before solvent exposure and after exposed to b. Acetone c. Toluene d. Ethanol
4.4 Adhesion

In the process of multi-layer coating adhesion between adjacent layers is important. Adhesion between inter-layers is dependent on bonding between molecules of the two layers. This is similar to bonding between solvent-solute molecules in a solution. Polymers with similar chemistries form entanglements at polymer-polymer interfaces and this can be explained by presence of receptor groups which act as adhesion sites[51, 52, 53]. Figure 4.29 shows an illustration of two layer resist coating with receptor groups, X and Y. Adhesion can be enhanced by increasing receptor group density in the polymer coatings, using polymers with similar chemistries or using adhesion promoters.

![Figure 4.29: Illustration of adhesive groups in polymers](image)

In the case of PMMA/Copolymer(MMA:MAA) stacks, half part of both the monomers is similar as shown in Figure 4.30A and they act as adhesion sites due to dispersion bonding. In Copolymer, the Metha-acrylic Acid(MAA) part assists in dissolution in polar solvents such as Esters and Alcohols. Similarly, Figure 4.30B shows monomers for a three negative resists where the common molecules contribute...
Similarly, changing polarity of surfaces using mono-layers of volatile siloxanes can help in adhesion. Hexamethyl disilizane (HMDS) is commonly used as an adhesion promoter due to the presence of methyl groups which have better bonding properties with novolac based resists. Other materials such as Amino Propyl Trimethoxy silane (APTMS) can be used where the amine groups increase polarity of the surface and enhance adhesion. Figure 4.31 shows an illustration of HMDS process where hydrophilic surface of a bare silicon wafer is changed to hydrophobic.

### 4.5 Nanocomposites

Nanocomposites in resist materials are generally used to enhance the mechanical strength, etch resistance, dissolution inhibition [54, 55, 56]. Some of the aforementioned properties can be utilized in multilayer resist stacks. For the structures presented in this study mechanical strength is an important factor to be considered.
and a major motivation behind considering addition of nanoparticles to resists was to analyze any changes in mechanical strength. Apart from mechanical strength, incorporation of nanoparticles can be used as a tool to selectively etch them and create porous polymeric structures. The voids created after their removal from resist polymers will also increase surface area. Figure 4.32 show a few SEM images of 12-layer tree structures of Copolymer/PMMA stack with nanoparticles dispersed in them. Although the addition of nanoparticles seemed to strengthen the structures, the dose required for patterning increased. Figure 4.34 shows comparison of doses for bare six level structures along with structures with nanoparticles (SiO₂, TiO₂, Al₂O₃) incorporated in them. Base dose for the 12-layer structures is higher compared to bare structures due to reduced dissolution rate of resist with nanoparticles.

Nanoparticles (15mg) were obtained in the form of a powder and dispersed in Ethanol (25ml) or Toluene (25ml). A clear solution was formed and mixed with the resist solution followed by ultrasonic agitation to enhance dispersion. Figure 4.33
shows Transmission Electron Microscope (TEM) images of nanoparticles used in this work.

Although mechanical strength of structures increased due to incorporation of nanoparticles to the resists, it also increased the effective density of the material. Increase in density is similar to increase in molecular weight and in case of positive resists this requires more dose than nominal values compared to lower molecular weights due to increased number of chain scissions per area. Addition of nanoparticles can add some functionality to the structures and other studies can be done on effect of atomic number of nanoparticles in causing exposure in resist. Higher atomic number of particles can increase secondary electron yield and can cause reduction in high doses required to pattern the resist as observed in evaluated cases in this work.

Figure 4.32: 12-layer tree structures with a. Alumina nanoparticles in PMMA b. Silica nanoparticles in PMMA c. d. Titania nanoparticles in PMMA
4.6 Summary

Solubility study performed in this work was based on the assumption that coating multiple resist layers is limited by availability of non-interacting solvents. Apart
from information on solvents, Hansen solubility analysis on commercially available resists proved useful in identifying the underlying issues that need to be considered in the process of multi-layer resist coatings to facilitate fabrication of three dimensional nanostructures. The identified issues are summarized as follows,

1. **Solubility** - This is a major issue dependent on the spin-coating technique. Other deposition techniques without the use of solvents can be applied, such as Chemical Vapor Deposition (CVD) would reduce the burden of solubility analysis. As mentioned in the ”Adhesion” section, slight changes to monomers can greatly change solubility properties and still retain adhesion properties.

2. **Inter-layer Dose Contrast** - It is an important factor that facilitates fabricating three dimensional structures using this technique. Experimental analysis is required and should be done for various solvents which can be considered as developers for the multiple-resist stacks. The critical dose and contrast are effected by different solvents. Sufficient dose contrast in the normal dose region (Figure 3.11) is required to selectively address individual layers of resist in a multiple resist stack.

3. **Polymer Molecular Weight** - This factor is important in determining minimum resolution, thickness and solvent diffusion while deposition using a spin coating technique. There is a critical relation between coating uniformity, thickness and polymer molecular weight. It has been observed in this work that for a given thickness of coating, increasing polymer molecular weight causes reduced coating uniformity.

4. **Inter-layer Adhesion** - Adhesion between multiple layers of resist is an important factor to be considered while depositing multiple layers of resist. It is dependent on the cohesive forces between molecules and can be increased by adding adhesion sites or utilizing common molecules between resist polymers.
5. **Acid Diffusion** - Chemically Amplified Resists (CAR) are commonly used in photolithography for increasing quantum efficiency (number of acids generated per absorbed photon). The generated acid diffused through the polymer and causes necessary chemical changes. This property is not desired in a multi-layer resist stack because it can cause unwanted crosslinking/changes in adjacent resist layers.
Tree structure filled in flowable oxide (HSQ)
CHAPTER 5
Metrology

5.1 Introduction

Ellipsometry and Electron Microscopy were used to characterize thickness of the resist films and dimensions of fabricated structures. Silicon wafers were cleaned with Acetone and Iso-propyl Alcohol. Resist was coated on 3-inch, p-doped Silicon (100) wafers using a Brewer Science 200CBX spin coater. Detailed characterization of thickness of resist layers is important as lamella thickness and spacing between them directly effects optical response of the Photonic structures. The following tools were used in this research,

1. Spectroscopic Ellipsometry - J.A. Woollam Variable Angle Spectroscopic Ellipsometer (VASE) RC2


5.2 Ellipsometry

5.2.1 Introduction

Ellipsometry is a non-destructive optical technique which measures the change in polarization of light when it interacts with matter. Spectroscopic ellipsometry uses a range of wavelengths of light, UV(Ultra Violet)-Visible-IR(Infra Red). This technique is commonly used to measure thickness, roughness of thin films(a few hundred nanometers thick). The films can be absorbing or transparent over the wavelengths of light but need to be on a transparent or opaque substrate to generate contrast. The change in polarization of reflected light is sensitive to,

1. Layer Thickness
2. Optical constants (n, k)

3. Surface Roughness

4. Composition

5. Optical anisotropy

Figure 5.1 shows process involved with ellipsometry. The data measured from an ellipsometer does not directly yield any meaningful information, but needs to be interpreted using physical models which approximate the interaction of light with materials. Measured data is compared and fit to the designed model by fitting variable parameters.

*Figure 5.1: Ellipsometry - Process Flowchart*

Typically ellipsometers measure *change in polarization* of light to a known polarized state i.e. a polarizer is used at the source to induce certain polarization between
the p- and s- planes and after it reflects off the sample the change is measured. An ellipsometer measures two values \((\psi, \Delta)\) that express the ratio of amplitudes and phase difference between p- and s- components. The amplitude ratio \(\psi\) is characterized by refractive index \(n\), and \(\Delta\) represents light absorption which is described by the extinction coefficient \(k\). Figure 5.2 shows a brief illustration of linearly polarized light interacting with the resist and substrate. The reflected light is elliptically polarized and change in polarization is dependent on the material properties.

![Ellipsometry - Basic Principle](image)

**Figure 5.2: Ellipsometry - Basic Principle**

Figure 5.3 illustrates the different optical elements present in the ellipsometry configuration used for measurement in this research and details of the elements are as follows [57, 58],

1. **Light source** - Usually a broadband source with radiation from Ultra-Violet (UV) to Visible to Infra Red (IR). The source for this research was a combination of Xenon arc lamp, which has a wavelength range of 250nm – 900nm, a Quartz-Tungsten-Halogen (QTH) lamp which assists in the IR region 990nm – 1700nm.
2. **Polarizer** - This optical element is generally placed in front of the light source to extract linearly polarized light from unpolarized light. In general the polarizers are prisms made up of calcite crystals, Quartz or $MgF_2$ based on the wavelength range. Wire grid polarizers are used for the IR region.

3. **Compensator** - It is usually placed in front of the detector after the sample and is used to convert linear polarization to circular polarization and vice versa. It is usually a birefringent crystal, $MgF_2$ or Mica. If the compensator is rotated along the light path axis, relative phase difference will vary and thus phase control is possible.

4. **Analyzer** - It has the same functionality as the polarizer and usually placed in between a compensator and the detector. The analyzer is rotated at a certain frequency and as light from the sample passes through it, intensity at the detector varies as a sine wave with frequency of the rotating analyzer.

5. **Detector** - It is a Photo-Multiplier Tube (PMT) or Silicon(Si) or PbS(Lead Sulphide) solid state detector. The intensity of light is converted into a voltage and can be read out as an electrical signal.

### 5.2.2 Experimental Data and Modelling

Usually photoresists are organic materials which are transparent in the visible and near-IR region when they are a few hundred nanometers thick. For thickness analysis, a Cauchy model was used along with a layer to account for interfacial oxide on Silicon wafers. Figure 5.4 shows the model used to estimate the $(n, k)$ values of photoresist material. After measurements are taken from the ellipsometer, estimated data from model is fit to the experimental data with thickness and Cauchy coefficients as fitting parameters. (Appendix D provides more details on various models used in Ellipsometry)
Figure 5.3: Ellipsometry - Optical Elements

Figure 5.4: Ellipsometry model - Photoresist on Silicon wafer

Figure 5.5 shows an image from the software CompleteEASE, which was used to fit experimental data to the data generated from the model. It shows three layers,

1. Substrate - In this research Silicon wafers with thickness of (380µm) and pre-tabulated bulk optical values of (n, k) were used.
2. Layer 1 - Silicon wafers have a layer of interfacial oxide which is accounted for in this layer. It is usually about $1 - 2\, \text{nm}$ thick. Pre-tabulated values of silicon dioxide were also used.

3. Layer 2 - This layer corresponds to the photoresist coated on the silicon wafer. To model this material, we use cauchy dispersion model to fit data generated from the model to experimental data by varying model parameters. (for more information on models, see Appendix D)

Figure 5.6 shows the measured $\Psi$ and $\Delta$ values along with data generated from the model.

![Figure 5.5: Cauchy model for PMMA](image)

Table 5.1 shows Cauchy parameters derived from best fit of model generated data to experimental data for different positive photoresists used in this research.

<table>
<thead>
<tr>
<th>Resist</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA 950K (Microchem)</td>
<td>1.475</td>
<td>0.00438</td>
<td>0.00003</td>
</tr>
<tr>
<td>ZEP 520A (Zeon)</td>
<td>1.545</td>
<td>0.00578</td>
<td>0.00028</td>
</tr>
<tr>
<td>Copolymer MAA:MMA (Microchem)</td>
<td>1.478</td>
<td>0.00439</td>
<td>0.00003</td>
</tr>
</tbody>
</table>

**Table 5.1:** Positive E-Beam resist Cauchy coefficients
Table 5.2 shows Cauchy parameters derived from best fit of model generated data to experimental data for different negative photoresists used in this research.

<table>
<thead>
<tr>
<th>Resist</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HSQ (Dow Corning)</td>
<td>1.394</td>
<td>0.00419</td>
<td>0</td>
</tr>
<tr>
<td>NEB-31 (Sumitomo)</td>
<td>1.558</td>
<td>0.00604</td>
<td>0.00051</td>
</tr>
<tr>
<td>ma-N (Microresist)</td>
<td>1.614</td>
<td>0.00422</td>
<td>0.0013</td>
</tr>
<tr>
<td>SU-8 (Microchem)</td>
<td>1.572</td>
<td>0.00831</td>
<td>0.00044</td>
</tr>
<tr>
<td>TEBN-1 (Tokuyama)</td>
<td>1.607</td>
<td>0.00281</td>
<td>0.00088</td>
</tr>
<tr>
<td>Polystyrene (Pressure Chemical)</td>
<td>1.573</td>
<td>0.00244</td>
<td>0.00083</td>
</tr>
</tbody>
</table>

Table 5.2: Negative E-Beam resist Cauchy coefficients

ZEP is a positive electron beam resist and is sensitive to UV-Visible radiation. This can be observed as peaks in measured $\Psi$ and $\Delta$ parameters. Figures 5.7 and 5.8 show measured data along with modeled data using a Cauchy model to estimate the thickness of the film. The modeled data is a good fit to the measured data. Also, shown in figures 5.9 and 5.10 is the same data relating to ZEP photoresist with a Sellmeier model to estimate thickness of the resist film. It shows a better fit in terms of the Mean Squared Error (MSE), where MSE for Cauchy model is 7.78 and for Sellmeier model is 5.9 which reduces the error in thickness measurement by 0.01nm.

Resist thickness on silicon wafers can be controlled by the adjusting spin speed...
on the coater. The thickness of resist on coated wafers is verified using an ellipsometer and the change of thickness as a function of spin speed gives a spin speed curve. This data can be used to control thickness of structures along the height of stack. Figures 5.11, 5.12, 5.13 shows spin speed curves for Copolymer(MMA:MAA) EL6 and PMMA 950 A2. Figure 5.14 shows thickness variation of Copolymer and PMMA layers coated on silicon wafers.
**Figure 5.9:** Sellmeier model for ZEP

<table>
<thead>
<tr>
<th>Layer Commands:</th>
<th>Add Delete Grade Save Parameterize</th>
</tr>
</thead>
<tbody>
<tr>
<td>Include Surface Roughness = OFF</td>
<td></td>
</tr>
<tr>
<td>Layer # 2 = <strong>Sellmeier</strong> Thickness # 2 = 566.67 nm (fit)</td>
<td></td>
</tr>
<tr>
<td>Amp. = <strong>0.546</strong> Center En. = <strong>0.18115</strong> IR Pole Amp. = <strong>0.00548</strong></td>
<td></td>
</tr>
<tr>
<td>Einf = <strong>1.843</strong></td>
<td></td>
</tr>
<tr>
<td>Layer # 1 = <strong>INTR_JAW</strong> Thickness # 1 = <strong>4.34 nm</strong> (fit)</td>
<td></td>
</tr>
<tr>
<td>Substrate = <strong>SI_JAW</strong></td>
<td></td>
</tr>
<tr>
<td>Angle Offset = <strong>0.000</strong></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 5.10:** Psi and Del - Measured and Sellmeier Model for ZEP
Figure 5.11: Copolymer and PMMA spin speed curve on Silicon

Figure 5.12: Copolymer spin speed curve on PMMA
Figure 5.13: PMMA spin speed curve on Copolymer
Figure 5.14: Copolymer and PMMA resist uniformity on silicon
5.3 Electron Microscopy

5.3.1 Introduction [28]

Electron Microscopy is one of the most common techniques used for metrology to analyze post-processed wafers. This technique uses a narrow beam (of the order of nanometers) of accelerated electrons to probe samples. As the electrons interact with materials on the sample a variety of physical processes occur from which useful information can be extracted. Unlike Ellipsometry, this technique is invasive and a part of the processed sample needs to be cleaved for performing metrology.

The following information of a sample can be extracted from electron microscopy based on the analyzed signal,

1. Topography

2. Morphology

3. Composition

4. Crystallographic Information

5.3.2 Theory

When an energetic electron beam interacts with the substrate a number of signals are generated based on different physical processes. The signals can be divided into two parts,

1. Electron signals - Backscattered electrons, Secondary electrons, Transmitted electrons (when sample thickness is of the order of 10 – 100nm), Auger electrons

2. Photon signals - X-rays, Bremsstrahlung, Cathodoluminescence.

Figure 5.15 shows the different signals generated when a high energy electron beam interacts with a solid sample. Also shown is an interaction volume to which the electrons are confined to and this changes with energy of the primary beam.
The Backscattered and Secondary electrons are used to generate images of the samples being probed. These images are analyzed using softwares to extract thickness information based on contrast difference between materials.

1. **Backscattered electrons** - They are generated due to elastic collisions between electrons from primary beam (1keV - 10keV) and atoms of the substrate. This scattering results in very small or no change in energy of the scattered electrons. These electrons can be classified into two types $BSE_I$, $BSE_{II}$ as shown in figure 5.16. $BSE_I$ are a result of primary beam undergoing elastic collisions in the first instance of its interaction with the substrate. $BSE_{II}$ are electrons which traverse through the substrate and lose some energy before exiting the substrate as show in figure 5.16. As they traverse through the substrate and lose energy, it can result in generation of secondary electrons.

These electrons can be detected by a solid state backscatter detector which is
usually a p-n junction which can have a positive or negative bias to adjust the image contrast. The signal at this detector combines both $BSE_I$ and $BSE_{II}$ to produce an image. The number of backscattered electrons are dependent on the atomic number ($Z$) of the substrate being probed. A material with higher $Z$ will generate more backscattered electrons compared to lower $Z$ from which information regarding composition can be extracted. Figure 5.17 shows a backscattered electron image of a Bismuth rich particle. Part of the image that is bright represents Bismuth whose atomic number, $Z=83$. Contrast in the image as discussed above is due to the difference in elemental compositions of the particle.

2. **Secondary electrons** - They are generated as part of the inelastic interactions of the primary beam with the electrons of atoms in the substrate. These electrons have energies less than $50\text{eV}$ and have a mean free path of few tens of
nanometers. These electrons can be divided into three categories, $SE_I$, $SE_{II}$, $SE_{III}$ as shown in figure 5.16. $SE_I$ are generated when the primary beam loses energy through an inelastic collision as it interacts with atoms at the surface. $SE_{II}$ are generated by $BSE_{II}$ as they emit out of the substrate. $SE_{III}$ are generated when backscattered electrons hit the pole piece which is a metal thereby generating secondary electrons.

The Secondary electron images are formed by a combination of $SE_I$, $SE_{II}$ and $SE_{III}$, although most of the signal is from the sample being probed. Most of the microscopes are equipped with an Everhart-Thornley detector which has a positively biased Faraday cage. This cage attracts most of the low energy electrons which contribute to the secondary electron signal. The images generated from this signal reveal information related to surface topography and morphology of the substrate. The secondary electron images are more visually interesting with rich surface details and are commonly used for quantitative analysis of dimensions such as thickness, width, height etc. Figure 5.18 shows a secondary electron image of the same particles as in figure 5.17. As discussed above, a lot of information regarding surface topography can be observed in the image.

Secondary electron images are routinely used for critical dimension (CD) analysis. As the structures fabricated in this research are used in the field of photonics, variation in dimensions effects the optical response of the structures. A major part in metrology is study of variations in dimensions of the structures. In this work the structures fabricated were used as optical sensors and required a variation of less than 5%. Multiple images analyzed to estimate mean and standard deviations of the dimensions of different parts of the structures.

A tree structure fabricated in a 12-layer Copolymer/PMMA stack was used for CD analysis. Figure 5.20 shows an SEM image with measurements made at all the six lamellae. The nominal coating thickness of PMMA layers was 55 nm as measured by
ellipsometry. Multiple images of the structure were analyzed and their thicknesses are plotted as shown in figure 5.19. Similarly, the space between lamellae, lamella length and ridge thickness were also measured for the same structure as shown in figures
5.22, 5.24, 5.26 and figures 5.21, 5.23 and 5.25 show plots of analyzed dimensions respectively. Nominal coating thickness of copolymer layer that forms space between lamellae was 152 nm. Width of lamellae per design was 500 nm and ridges was 75 nm.

The results shown from this work demonstrate less than 5% variation in thickness achievable by the process of spin coating. State-of-the-art spin coating equipment can achieve a minimum thickness variation of 1% over 300mm wafers. Because SEM imaging used an electron beam to generate an image, it causes structure deformation due to inherent dose delivered in the process of imaging. This should be considered and sufficient care should be taken while performing imaging over the structures.

High quality secondary electron images can be obtained by integrating multiple high rate scan images compared to slower scan rates. Slower scan rate has higher beam dwell time on samples causing physical damage which can deform structures.

![Lamella thickness analysis plot](image)

**Figure 5.19:** Lamella thickness analysis plot
Figure 5.20: Lamella thickness analysis - SEM

Figure 5.21: Space between lamellae analysis plot
Figure 5.22: Space thickness between lamellae - SEM

Figure 5.23: Lamella length analysis plot
Figure 5.24: Lamella length analysis - SEM

Figure 5.25: Ridge length analysis plot
Figure 5.26: Ridge length analysis - SEM
CHAPTER 6  
Finite Element Modelling

6.1 Introduction

In the past [5] three dimensional nanostructures were fabricated in a layer-by-layer fashion. Use of multiple process steps facilitates the use of metals and other elements with good structural properties. The technique elaborated in this research is developed for use with radiation (electron and photon) sensitive polymers, which have a limited range of structural properties. Estimation of structural deformation due to body load and fluid-structure interaction is important to determine feasibility of realizing and maintaining dimensions close to design, especially in free-standing three dimensional structures.

This chapter describes a model to estimate deformation in one of the structures manufacturable using this technique. Three dimensional nanostructures have a lot of importance in the field of photonics and sensors. Optical response from the nanostructures is strongly dependent on their dimensions. The fabrication process discussed in this research involves the following steps,


2. Electron beam exposure to pattern all multiple layers in a single step.

3. Development - This is a critical step in the process as it defines the structure by dissolving away the exposed(positive resist) or unexposed(negative resist). The developer is usually a liquid and its interaction with the developed structure can also cause deformations while it is being driven out.

Estimation of body load using mechanical properties (Young’s modulus, density etc.) can help determine static deformation in structures. This estimation can help in
optimizing structure designs. Fluid-Structure interaction while development can be estimated by solving Navier-Stokes equations. Pressure applied on the developer/rinse fluid from blow dry guns can be approximated to fluid velocity.

COMSOL multiphysics is a finite element modelling (FEM) software used to create theoretical models for the three dimensional structures. It uses arbitrary Lagrangian-Eulerian technique to simulate the dynamics of deforming geometry and moving boundaries. Although the fabrication process is feasible, mechanical properties (Young’s modulus etc.) of the material are important to fabricate the structure.

This chapter discusses details related to structural and fluid-structure interaction modelling of a three dimensional nanostructure.

6.2 Model Definition[60]

The bio-inspired photonic structures were used as test structures to model fluid-structure interaction.

Poly Methyl-Methacrylate(PMMA) was the material used to fabricate these structures. This material was supplied by Microchem and the materials properties for the polymer were used from Lucite. It is a positive resist and a mixture of Methyl Iso-Butyl Ketone(MIBK) and Isoproply Alcohol(IPA)was used for development and IPA was used to rinse the developed structure. IPA was blown out and evaporated using a nitrogen blow dry gun.

When the multi-layer coating of polymers is exposed to electron beam radiation, apart from primary areas residual dose is delivered to the unintended areas, which are the structures themselves. Mechanical properties of the polymer should be approximated by taking into account the residual dose delivered. In this model, the residual dose is considered to effect the polymers in their linear elastic limit allowing a proportional approximation. Hence, young’s modulus decreases with increasing dose linearly within the limit.
The young’s modulus of PMMA used for this model is \( E = 10 \text{kPa} \) with a density of \( \rho = 1190 \text{kg/m}^3 \). IPA is considered in the fluid-structure interaction model, with a density of \( \rho = 786 \text{kg/m}^3 \) and dynamic viscosity of \( \eta = 2.4 \text{mPa} - \text{s} \).

### 6.2.1 Fluid Flow

Fluid flow between the structures and lamella is described by the Navier-Stokes equations which are derived from Newton’s second law, conservation of momentum. This model considers that the fluids are incompressible which makes their density constant. The following equation describes flow of an incompressible fluid with laminar flow,

\[
\rho \frac{\partial \vec{u}}{\partial t} = -\nabla P + \rho \vec{g} + \eta \nabla^2 \vec{u}
\]  

(6.1)

where \( \nu \) is the kinematic viscosity, \( u \) is the velocity of the fluid in \( x \) direction, \( P \) is the pressure and \( \rho \) of the fluid density. This is a vector equation and will have two more sets to account for \( y \) and \( z \) directions in three dimensions.

From equation, 6.1, \( \frac{\partial \vec{u}}{\partial t} \) is the acceleration produced in the fluid and is equal to the sum of pressure gradient \( -\nabla P \), gravity \( \rho \vec{g} \), and the flow \( \eta \nu \nabla^2 \vec{u} \) which is in the direction of increasing velocity gradient.

When the wafer is removed from the developer, the developer is in a steady state i.e. initial velocity is zero. Pressure applied on the fluid (due to nitrogen) is considered constant. Fluid flow increases rapidly, reaches its peak and gradually reaches a steady state value. The equation governing velocity of fluid inflow \( (U_{in}) \) is given by the following [60],

\[
U_{in} = \frac{U.t^2}{\sqrt{(0.04 - t^2)^2 + (0.1t)^2}}
\]  

(6.2)
\[ q = \frac{1}{2} \rho v^2 \]  

(6.3)

where \( U \) is the velocity measured from the dynamic pressure equation 6.3, pressure measured from nitrogen gun is 2 psi over an area of \( 2 \times 2 \text{mm}^2 \), \( q \) is dynamic pressure in pascals, \( \rho \) is fluid density in \( \text{kg/m}^3 \), \( v \) is fluid velocity in \( \text{m/s} \).

Fluid flow Equation 6.2 is a general equation used to approximate velocity of fluid flow due to applied pressure. The outflow boundary condition is set to zero to create a pressure gradient and rest of the boundaries are set to static i.e. are not effected by fluid flow. Fluid flow calculated from the dynamic pressure equation 6.3 is applied in equation 6.2 and \( U_m \) is plotted on Figure 6.1. This information was used in the model to perform the simulation. The maximum fluid velocity was around \( 25 \mu \text{m/s} \) and had a steady state at \( 10 \mu \text{m/s} \).

![Fluid velocity graph](image)

**Figure 6.1:** Fluid Flow - Calculated from Dynamic Pressure Equation

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6.2.2 Structural Mechanics

PMMA considered in this model has its mechanical properties in its linear elastic regime. The force (per unit volume) experienced by the structure is due to fluid flow, which is a combination of pressure and viscous forces and is given by the following equation (in vector and tensor forms),

\[
F = -P + \eta \nabla^2 \vec{u} \tag{6.4a}
\]

\[
F_T = -n.(-pI + \eta(\nabla u + (\nabla u)^T)) \tag{6.4b}
\]

where the \( P \) or \(-pI\) represent pressure forces and \( \eta \nabla^2 \vec{u} \) or \( \eta(\nabla u + (\nabla u)^T) \) represent the viscous forces.

Arbitrary Lagrangian-Eulerian Formulation (ALE)[61, 62] - The partial differential equations are usually formulated either in a spatial coordinate system where the coordinate axes are fixed in space or material coordinate system fixes to the material in its reference configuration and follows the material as it deforms. The spatial coordinate system is referred to as the Eulerian formulation and latter is a Lagrangian formulation.

\[
\epsilon = \frac{1}{2}(\nabla u + \nabla u^T) \tag{6.5}
\]

Pure Eulerian formulation cannot handle moving domain boundaries because physical quantities are referred to fixed points in space while the set of spatial points inside the domain boundaries changes with time. Hence Eulerian equations should be rewritten to describe all physical quantities as functions of mesh coordinates instead of spatial coordinates. This results in an arbitrary Lagrangian-Eulerian method, which combines best features of both theories by allowing moving boundaries without the need for the mesh movement to follow the material. Because of the moving computational mesh greater distortions of the continuum can be handled than would be
allowed by a purely Lagrangian method, with more resolution than a purely Eulerian approach.

### 6.2.3 Fluid Structure Interaction [63]

Figures 6.2, 6.3 show simulated fluid flow and its interaction with two dimensional structures. The drag caused by fluid and limited mechanical strength of materials can cause deformation in structures.

![Figure 6.2: Fluid Structure Interaction - 2D simulation with Displacement and velocity field](image)

Figure 6.4 shows an image of the simulation space with three dimensional structure and direction of fluid flow. Figure 6.5 shows simulated fluid structure interactions results for six-level three dimensional structures with lamellae of different width (50, 60, 70 and 80nm). The maximum z-displacement is observed for 50nm lamella structures due to relatively low mechanical strength. Figure 6.6 shows six-level structures with ribs between lamellae. The ribs act as support for lamellae and prevent bending due to drag from fluid flow.

Figure 6.7 shows a plot of maximum z-displacement of lamellae due to fluid flow.
Figure 6.3: Fluid Structure Interaction - 2D simulation of structure with Ridge and Lamellae

for structures with and without ribs. It can be clearly noticed from the graph that presence of ribs limits lamella deformation. Figure 6.8A, B shows SEM images of six level Copolymer/PMMA structures without ribs and bent lamellae due to fluid flow. It should also be noted that deformation increases with length of lamellae i.e. greater in the 500nm case. Figure 6.8C, D shows structures with ribs that were processed under similar conditions as structures in figure 6.8A, B. The reduced deformation can be attributed to the ribs. This agrees with results from the simulation model as shown in Figure 6.9. Figure 6.10 shows a plot comparing experimental and simulated values of maximum z-displacement.
Figure 6.4: Three-dimensional six level lamellae structure with ribs and fluid flow
Figure 6.5: Three-dimensional six level lamellae structures, A - 50nm, B - 60nm, C - 70nm and D - 80nm thick lamellae
Figure 6.6: Three-dimensional six level lamellae structures with ribs, A - 50nm, B - 60nm, C - 70nm and D - 80nm thick lamellae
Figure 6.7: Vertical displacement (max.) vs. Lamella thickness of three-dimensional structures with and without ribs - Simulation
Figure 6.8: Patterned six level Copolymer/PMMA stack with variable lamella length without ribs, A - 300nm length, B - 500nm length, with ribs C - 300nm, D - 500nm
Figure 6.9: Fluid structure interaction simulation variable lamella length without ribs, A - 300nm length, B - 500nm length, with ribs C - 300nm, D - 500nm
Figure 6.10: Fluid structure interaction simulation vs. experiment
A novel fabrication technique has been presented in this research study with potential applications in the field of photonics, optical sensors, MEMS devices, nano-biology etc. Electron Beam Lithography (100keV) was used to perform experiments and validate the hypothesis of using the intrinsic depth of focus of high energy particle beams to address multiple resist layers in a given stack. The extents of using a 100keV electron beam tool were presented and images generated from simulation models were experimentally validated. The simulation models were used to estimate effects of using higher beam energies which demonstrated lower beam spread.

Solubility of commercially available resists was studied in detail which provided valuable insights into issues that need to be considered while coating multiple resist layers. Three dimensional Hansen solubility plots were used to identify compatible solvents. This study also led to identification of compatible resist polymers for a plausible negative resist stack. Issues related to resist adhesion and enhancing structural strength of polymeric structures using nanocomposites is also presented.

Finite Element modelling was performed on three-dimensional structures fabricated using this technique. Results from simulation models were compared to experimental observations. Other nanoscale effects such as surface tension, direction of applied pressure can be used to enhance the predictions of the simulation model.

Major advantages of this process over current state-of-the-art fabrication techniques include,

1. Fast fabrication time which enhances throughput,

2. Ability to make large area complex three dimensional nanostructures with minimal processing
Future directions include development of,

1. Novel materials with non-interacting chemistries

2. Better techniques to deposit multiple layers of electron beam sensitive materials

3. Techniques to functionalize three dimensional structures for various applications

4. Molding methods for fabricating structures of different materials

Figure 7.1 illustrates the use of different resist materials for fabricating complex three-dimensional structures with applications in photonics.

![Figure 7.1: Two three dimensional structures and corresponding resist stacks(SEM images reproduced with permission of authors [7, 64)](image)

In this work, the intrinsic depth of focus of the electron beam was used to create chemical changes in resist that caused a selective solubility gradient. Similarly,
index of refraction, glass transition temperatures, electronic properties etc. can be modified by electron beam irradiation and in this case are proven to be addressable in all the three dimensions. Polymeric materials with different dose contrast and ability to be transformed between conducting, semiconducting and insulating states open the prospect of intrinsically aligned polymer electronics that can be fabricated with a single exposure step.

Beam based lithography is frequently criticized for relatively slow throughput due to serial nature of the process. This process combines multiple exposures into a single exposure and thereby provides a significant gain in effective throughput.
References


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Basics of Structural Color

Electromagnetic radiation can be mapped out into a spectrum based on the frequency or wavelength. It is considered to have dual nature, i.e. wave and particle, to describe a variety of physical processes. Human vision is sensitive to the electromagnetic radiation within the visible region over a wavelength range of 400-700nm. Color perceived by human vision is due to the difference in frequency of radiation in the visible region. White light from sun and other artificial sources contain a range of frequencies from Ultra-violet to Infra-red, which includes the visible region. When white light interacts with matter a range of physical processes can occur which can be observed by analyzing the reflected and/or transmitted light.

Different materials have different colors due to selective absorption or reflection of particular wavelengths from incident white light. When matter is illuminated with white light, color is seen due to reflection of specific wavelengths of light and it can be classified into two major types.

1. **Pigment color** is due to the exchange of energy between incident light and material where most of the wavelengths are absorbed and a few are reflected which gives characteristic color to the material.

2. **Structural Color** is due to physical interaction of light with the spatial inhomogeneity of the material. In this case incident light does not necessarily lose energy to generate color.

When dimensions of structures are of the order of the wavelength of incident radiation, color of the structures can occur due to several physical processes. Struc-
natural color is commonly observed in nature and it can be explained by the following physical processes[65],

1. Thin-film Interference
2. Multilayer Interference
3. Diffraction
4. Scattering
5. Photonic Crystals

**Thin-film Interference**

Interference can be explained using wave theory of electromagnetic nature of light. It can be termed as interaction of two or more light waves yielding a resultant irradiance which deviates from the sum of the component irradiances [66].

Harmonic waves can be described using an amplitude, sine or cosine function, wave vector and frequency.

\[
E_1(x, t) = A_1 \sin(\kappa_1 x - \omega t + \epsilon_1) \tag{A.1}
\]

\[
E_2(x, t) = A_2 \sin(\kappa_2 x - \omega t + \epsilon_2) \tag{A.2}
\]

where \(A_1, A_2\) is the amplitude, \(\kappa_1, \kappa_2\) are wave numbers and \(\omega\) is the frequency and \(\epsilon_1, \epsilon_2\) are initial phases.

Based on superposition principle of waves, when waves and (1) and (2) interact and the resultant wave would have the following intensity,

\[
I = I_1 + I_2 + I_{12} \tag{A.3}
\]
where,

\[ I_1 = \langle E_1^2 \rangle \]  \hspace{1cm} (A.4)  
\[ I_2 = \langle E_2^2 \rangle \]  \hspace{1cm} (A.5)  
\[ I_{12} = 2 \langle E_1, E_2 \rangle \]  \hspace{1cm} (A.6)  

Equation (6) is the interference term and this varies in value with phase difference between the two waves which is given by,

\[ \delta = (\kappa_1 x - \kappa_2 x + \epsilon_1 - \epsilon_2) \]  \hspace{1cm} (A.7)  

The intensity of the interference term is given by,

\[ I_{12} = 2 \sqrt{I_1 I_2} \cos \delta \]  \hspace{1cm} (A.8)  

Based on phase difference between the two waves the value of interference term can range from constructive interference, \( I_{\text{max}} \), to destructive interference, \( I_{\text{min}} \), given by

\[ I_{\text{max}} = I_1 + I_2 + 2 \sqrt{I_1 I_2} \]  \hspace{1cm} (A.9)  
\[ I_{\text{min}} = I_1 + I_2 - 2 \sqrt{I_1 I_2} \]  \hspace{1cm} (A.10)  

Figure A.1 illustrates interaction of light with a thin-film interface. Glass has higher refractive index than air and when an incident ray reflects from air-glass interface there will be a 180° phase shift (equivalent to a shift by half a wavelength) induced in all the wavelengths of light. At the glass-air interface a part of the light will be reflected without any induced phase shift.

Figure A.2 shows interaction of white light with a 125nm thick film with refrac-
tive index greater than 1. At every interface, part of the incident light will be reflected and in this case there would be two sets of reflections at air-film (Reflection-1) and film-air (Reflection-2) interfaces. At the air-film interface, the light from Reflection-1 (all wavelengths) will undergo a phase shift of $180^\circ$ or $\lambda/2$. A part of the light trans-
mits through the film and reflects at the second interface i.e. film-air. The reflected light at this interface does not undergo any phase shift but the extra path traversed by it through the film (250 nm) causes an inherent phase shift. The wavelengths of light in Reflection-1 (air-film) and Reflection-2 in phase with each other will cause constructive interference leading to spectral color from the film. Because the phase shift is induced due to the extra path traveled by light through the film, color of light reflected from the film can be controlled by the thickness of the film and angle of incidence.

From figure A.2 the film thickness (125 nm) should correspond to an induced phase shift of 250 nm. Reflection-1 will have all the wavelengths shifted by $\lambda/2$ and Reflection-2 will have an induced phase shift of 250 nm, constructive interference will occur for wavelengths at 500 nm which is in the green region of the visible spectrum.

**Diffraction**

Diffraction can also be explained by the wave theory of light. It refers to the bending of light when it interacts with an obstacle. There is no significant physical difference between Interference and Diffraction. The effects of Diffraction can be observed using a single slit as shown in figure A.3. When an incident wave interacts with the slit, we can broadly consider top and bottom of the slit as two different sources of radiation. The diffracted waves will cause constructive and destructive interference. The interference effects will show up as bright and dark regions and are called diffraction fringes. The effects of diffraction can be observed prominently for wavelengths of the order of the size of diffracting objects.

The effects of diffraction can be explained by two theories, Fresnel and Fraunhofer, based on the position of observation plane. Fresnel theory explains the near-field effects and Fraunhofer theory explains far-field effects. Figure A.4 illustrates the diffraction pattern of a single slit as a function of distance from the slit where, $z$ is
the distance of plane of observation from the slit, \(d\) is the width of the slit (square slit of length 100nm considered in this case), \(\lambda\) is the wavelength of incident light (600nm used for simulation). When the plane of observation is at a distance less than \(\frac{d}{\lambda}\), curvature of the spherical wavefronts cannot be ignored and this is called near-field. As the plane is taken farther away both the incident and diffracted light can be considered as plane waves and this is termed as far-field.

Figure A.4 shows diffraction fringes caused due interaction of light with a single slit. The bright pattern in the center is called the primary maxima or zeroth order of diffraction. The zeroth order is followed by two bright bands on either sides which are the first orders of diffraction with comparatively reduced intensity.

The intensity of diffracted waves in Fresnel zone is given by the following equation[67],

\[
I = \frac{I_0}{2} \left[ \left( C(\zeta) + \frac{1}{2} \right)^2 + \left( S(\zeta) + \frac{1}{2} \right)^2 \right] \tag{A.11}
\]
where,

\[ \zeta = \sqrt{\frac{k}{2z}}x \]  
\[ k = \frac{2\pi}{\lambda} \]

and \( C(\zeta), S(\zeta) \) are given by,

\[ C(\zeta) = \int_{0}^{\zeta} \cos \left( \frac{\pi t^2}{2} \right) dt \]
\[ S(\zeta) = \int_{0}^{\zeta} \sin \left( \frac{\pi t^2}{2} \right) dt \]

The intensity of light from Fraunhofer theory which applies to far-field effects
can be calculated using the following equation[66],

$$I(\theta) = I_0 \text{sinc}^2 \left( \frac{d \sin \theta}{\lambda} \right)$$  \hspace{1cm} (A.14)

where $\theta$ is the angle measured from optic axis, $d$ is width of the slit and $\lambda$ is wavelength of radiation.

Both theories indicate strong dependence of diffraction on wavelength of incident radiation and dimensions of the obstacle. From geometrical optics[66], we can find the angle at which different maxima occur i.e. destructive interference will occur

$$d \sin \theta_m = m \lambda$$  \hspace{1cm} (A.15)

where $d$ is the size of the slit and $\lambda$ is wavelength of radiation and $m$ is an integer indicating the order of diffraction. The primary maxima occurs at $\theta=0$ and the following maxima occur at intervals of $2\pi$. From equation A.15 it can be inferred that the angle of diffraction is proportional to the wavelength of radiation and hence longer wavelengths have higher angle of diffraction for a given order.

When white light interacts with obstacles in a periodic arrangement i.e. multiple equidistant slits or grating structures, based on the periodicity of the structures light is dispersed into its spectral components. Figure A.5 illustrates dispersion of white light into its component wavelengths when it interacts with the periodic structures in the grating. Figure A.6 shows diffraction of light due to multiple slits and it should also be observed that there is no wavelength dependence at the primary maxima. By tuning the spacing between the gratings or slits, the wavelength of reflected (diffraction grating case) or transmitted(multiple slit case) light can be changed and hence the color of light can be changed.
Scattering

When light, as an electromagnetic wave, interacts with a discrete or collection of particles, the electrons in the particles are perturbed due to the electric field of...
incident light. The perturbation results in separation of charge i.e., the electric field induces a dipole in the molecule. The oscillation induced dipole can be manifested as a source of EM radiation, which is observed as scattered light. Hence, scattering of light can be described as complex interaction between incident EM wave and the molecule or atom.

Scattering of light as it interacts with matter is commonly observed but, under certain conditions it can cause certain wavelengths to be more prominent than others causing bright color. Scattering of light from a particle or a collection of particles is influenced by any of the following factors,

1. Optical property of the medium which is usually given by its complex refractive index, \( n - ik \), where \( n \) is the refractive index and \( k \) is the absorption coefficient.

2. Wavelength of incident radiation, \( \lambda \)

3. Size of particle

Scattering can be explained by the following theories,

1. **Rayleigh Scattering** formulated for small(lesser than wavelength of light), dielectric(non-absorbing) spherical particles.

2. **Mie Scattering** is a general spherical scattering solution, absorbing or non-absorbing, without any particular particle size. It is mostly used to explain scattering effects for particles comparable or larger than wavelength of incident light.

The intensity of the scattered radiation from a single particle due to Rayleigh scattering is given by,

\[
I = I_0 \left( \frac{1 + \cos^2(\theta)}{2R^2} \right) \left( \frac{2\pi}{\lambda} \right)^4 \left( \frac{n^2 - 1}{n^2 + 2} \right)^2 \left( \frac{d}{2} \right)^6
\]  

(A.16)
where $I_0$ is the intensity of incident radiation, $R$ is distance between the particle and the observer, $\theta$ is the scattering angle, $n$ is refractive index of the particle and $d$ is its diameter[68].

It is evident from the equation that as ratio of wavelength of incident radiation to diameter of the particle decreases, the intensity of scattering increases and is inversely proportional to the fourth power of incident radiation’s wavelength. Hence, it is more effective for shorter wavelengths i.e. blue end of visible spectrum, which is the reason for the blue sky.

Rayleigh scattering fails to explain scattering when size of particles is comparable or larger than wavelength of incident radiation.

When particle size is larger or comparable to the wavelength of incident radiation, the interaction between them can be given by solving Maxwell’s equations. A Mie theory calculation will yield efficiency of scattering which relates cross-sectional area of scattering to the true geometrical cross-sectional area of the particle[69].

Let $r$ be radius of the particle and $k = \frac{2\pi}{\lambda}$. When light of intensity $I_0$ is incident on a sphere the scattered intensity is given by,
\[ I = I_0 \left( \frac{i_1 + i_2}{2k_2r^2} \right) \]  
\hspace{1cm} (A.17)

where \( i_1, i_2 \) refer to intensity of light vibrating perpendicular and parallel to the plane of incidence[70].

As seen in figures A.7 and A.8, according to Rayleigh, scattering of incident radiation is uniform in all directions. For larger particles, Mie theory explains that scattered radiation is concentrated along the angle of incidence.

Figure A.9 illustrates Rayleigh scattering when white light interacts with particles much smaller than the wavelength of light. As discussed earlier in this section shorter wavelengths, blue light, are scattered more than the longer wavelengths, red light in visible spectrum.

**Multilayer Interference**

Multilayer interference is an extended case of interference where multiple layers are stacked together to produce a cumulative effect. Under certain conditions the reflections from the stack would interfere constructively, resulting in a selective spectral
Figure A.9: Rayleigh Scattering - Color

response.

Figure A.10 shows a multilevel (each level is layer 1 and layer 2) stack of alternating layers with refractive indices, $n_a$ and $n_b$, physical thicknesses $d_a$ and $d_b$. The optical thickness of a material is given by,

$$\text{optical thickness(material a)} = \text{refractive index} (n_a) \times \text{physical thickness} (d_a)$$

For constructive interference to occur in a multilayer stack, the light reflecting from each of the layers should be in phase. The path traversed by each wavelet adds up to its initial phase and they can be adjusted by changing optical thickness of the layers in the multilayer stack. The thicknesses can be tuned to generate required optical response. The reflectance of a single interface is given by,

$$r^2 = \left(\frac{n_b - n_a}{n_b + n_a}\right)^2$$  \hspace{1cm} (A.18)

Based on the optical thicknesses of layers in the stack there can be two cases i.e. an ”ideal” stack where $n_a d_a = n_b d_b$ or ”non-ideal” stack where $n_a d_a \neq n_b d_b$ [71].

For an ”ideal” stack the reflectance maxima occur at the following wavelengths,
\begin{equation}
\lambda = 4n_a d_a, \frac{4n_a d_a}{3}, \frac{4n_a d_a}{5}, \ldots \text{etc.} \tag{A.19}
\end{equation}

and minima of zero reflectance occur at

\begin{equation}
\lambda = \infty, \frac{4n_a d_a}{2}, \frac{4n_a d_a}{4}, \ldots \text{etc.} \tag{A.20}
\end{equation}

When wavelengths under consideration are close to ”ideal” wavelength i.e., 
$\cos^2 \phi < r_2$, the reflectance of the stack is given by [72],

\begin{equation}
|R|^2 = \frac{1}{1 + \frac{4m^2(r^2 - \cos^2 \phi)}{r^2(1-m^2)^2}} \tag{A.21}
\end{equation}

where,

\begin{equation}
m = \left[ \frac{1 - \sqrt{\left(\frac{r^2 - \cos^2 \phi}{\sin^2 \phi}\right)} - r}{1 + \sqrt{\left(\frac{r^2 - \cos^2 \phi}{\sin^2 \phi}\right)}} \right]^p \tag{A.22}
\end{equation}

$\phi$ is defined the phase retardation for light of wavelength $\lambda$ as it traversing
through a single level of the stack and is given by (ideal stack \( \phi_a = \phi_b \)),

\[
\phi_a = \left( \frac{2\pi}{\lambda} \right) n_a d_a
\]  \hspace{1cm} (A.23)

Consider an ideal stack of \( n_a = 1.5, \ d_a = 100 \) and \( n_b = 1, \ d_b = 150 \). According to equations A.21, A.22 there should be a primary maxima at \( \lambda_{max} = 2 \times (n_a d_a + n_b d_b) \) followed by maxima at \( \lambda_{max}/3, \lambda_{max}/5 \) etc. Figure A.11 shows reflectance plot obtained from the ideal stack with different number of stacked layers. The reflectance increases with the number of layers.

![Ideal stack reflectance](image)

**Figure A.11:** Multi layer interference - Ideal stack\((n_a d_a = n_b d_b = 150nm)\) - (1-7)levels

In case of non-ideal stack where, \( n_a d_a \neq n_b d_b \), there are a few important facts to be noted[73],

1. The peak reflectance decreases.
2. The bandwidth of principal peak decreases.
3. Secondary maxima, which is absent in case of ideal stack, appears at \( \lambda_{max}/2 \).
Consider a non-ideal stack with $n_a = 1.5$, $d_a = 80$ and $n_b = 1$, $d_b = 180$. Figure A.12 shows reflectance plot for the aforementioned non-ideal stack with primary maxima at $\lambda_{\text{max}} = 2 \ast (n_a d_a + n_b d_b)$ followed by maxima at $\lambda_{\text{max}}/2$, $\lambda_{\text{max}}/3$, $\lambda_{\text{max}}/5$ etc. Comparing figures A.11, A.12, we can clearly see the decrease in reflectance and the secondary maxima as discussed above.

![Non ideal stack reflectance](image)

**Figure A.12:** Multi layer interference - Non-Ideal stack($n_a d_a = 120$, $n_b d_b = 180nm$) - (1-7)levels

**Photonic Crystals**

A crystal is a periodic arrangement of atoms or molecules. The pattern with which the atoms or molecules are repeated in space is the crystal lattice. In a photonic crystal, atoms and molecules are replaced with materials of different dielectric constants forming a continuous periodic dielectric function.

Photonic crystals modulate the flow of light (photons) as semiconductor crystals with electrons. Periodically arranged atoms in a semiconductor crystal form a periodic potential and propagation of electrons in the lattice is explained by the theory of quantum mechanics. Electrons propagate as waves, and waves that meet certain
criteria can travel through a periodic potential without scattering (although they will be scattered by defects and impurities). Importantly, the lattice can also prohibit the propagation of certain waves. There may be gaps in the energy band structure of the crystal, meaning that electrons are forbidden to propagate with certain energies in certain directions.

Similarly photonic crystals with low-loss periodic dielectric medium can be designed to allow light of certain wavelengths (light modes) to propagate through the crystal. We can design crystals with photonic band gaps, preventing light from propagating in certain directions with specified frequencies (i.e., a certain range of wavelengths, or colors of light).

The propagation of light through photonic crystals can be studied by applying and solving Maxwell’s equations for the geometries. Maxwell’s equations in SI units
are,

\[ \nabla \cdot \mathbf{D} = \rho \]  
(A.24a)

\[ \nabla \cdot \mathbf{B} = 0 \]  
(A.24b)

\[ \nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \]  
(A.24c)

\[ \nabla \times \mathbf{H} = \frac{\partial \mathbf{D}}{\partial t} + \mathbf{J} \]  
(A.24d)

Where \( \mathbf{D} \) is the electric displacement vector i.e. dielectric flux, \( \mathbf{B} \) is magnetic flux, \( \mathbf{E} \) and \( \mathbf{H} \) are electric and magnetic fields, \( \rho \) and \( \mathbf{J} \) are charge and current densities.

\( \mathbf{E}, \mathbf{H} \) and \( \mathbf{D}, \mathbf{B} \) are related by the following relations,

\[ \mathbf{D} = \varepsilon_0 \varepsilon \mathbf{E} + \mathbf{P} \]  
(A.25a)

\[ \mathbf{B} = \mu_0 \mu \mathbf{H} + \mathbf{M} \]  
(A.25b)

Where \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon \) is relative permittivity and \( \mu_0 \) is the permeability of free space, \( \mu \) is relative permeability. \( \mathbf{P} \) and \( \mathbf{M} \) are polarization and magnetization, related to electric and magnetic properties of a material can be expanded in a power series[74].

Assuming small electric fields, isotropic materials, index of refraction of the material is frequency independent and permittivity of the material is real and positive, the equations are further simplified and in radial coordinates can be written as,
\[ \nabla \cdot [\epsilon(r)E(r, t)] = 0 \quad (A.26a) \]
\[ \nabla \cdot H(r, t) = 0 \quad (A.26b) \]
\[ \nabla \times E(r, t) = -\mu_0 \frac{\partial H(r, t)}{\partial t} \quad (A.26c) \]
\[ \nabla \times H(r, t) = \epsilon_0 \epsilon(r) \frac{\partial E(r, t)}{\partial t} \quad (A.26d) \]

where \( D = \epsilon_0, \epsilon E \) and \( B = \mu_0, \mu(r)H, \mu(r) \) for most materials under consideration is close to unity.

E and H are complicated functions in space and time and Maxwell’s equations are linear, we can separate time dependence from spatial dependence by expanding the fields into a set of harmonic modes. Consider the following functions

\[ H(r, t) = H(r)e^{-i\omega t} \quad (A.27a) \]
\[ E(r, t) = E(r)e^{-i\omega t} \quad (A.27b) \]

To find equations governing mode profiles for a given frequency we need to insert equations A.28 into the modified Maxwell’s equations A.26a.
\[ \nabla \cdot \mathbf{H}(r) = 0 \]  
(A.28a)

\[ \nabla \cdot [\epsilon(r)\mathbf{E}(r)] = 0 \]  
(A.28b)

\[ \nabla \times \mathbf{E}(r) = i\omega\mu_0\mathbf{H}(r) \]  
(A.28c)

\[ \nabla \times \mathbf{H}(r) = -i\omega\epsilon_0\epsilon(r)\mathbf{E}(r) \]  
(A.28d)

Equations A.28 a, b in physical interpretation mean that there can be no point sources or sinks of displacement and magnetic fields in the medium. Equations A.28 c, d relate \( \mathbf{E}(r) \) to \( \mathbf{H}(r) \) and by eliminating either \( \mathbf{E}(r) \) or \( \mathbf{H}(r) \) using of them, we would get the following relations,

\[ \nabla \times \left( \frac{1}{\epsilon(r)} \nabla \times \mathbf{H}(r) \right) = \left( \frac{\omega}{c} \right)^2 \mathbf{H}(r) \]  
(A.29)

\[ \nabla \times \nabla \times \mathbf{E}(r) = \left( \frac{\omega}{c} \right)^2 \epsilon(r)\mathbf{E}(r) \]  
(A.30)

Equations A.29 and A.30 can be looked at as eigen value problems and solving them will give us allowed frequencies or modes. With this information we can determine optical properties of a photonic crystal and design them to required specifications.

It should be observed that equation A.29 has operators on one side of the equality but equation A.30 has operators on both sides. Hence, for mathematical convenience equation A.29 is used to calculate eigen modes and \( \mathbf{E}(r) \) can be determined from the following relation,
\[ E(r) = \left( \frac{i}{\omega \epsilon_0 \epsilon(r)} \right) \nabla \times H(r) \] 

(A.31)

Photonic Structures in Biology

A major part of motivation for this research lies in the challenge for fabricating the structures present on biological organisms such as butterflies, peacock feathers etc. The brilliant colors are due to the presence of highly ordered microscopic structures and their interaction with light.

Hierarchical nanostructures on butterfly wings are the primary cause for bright colors. Apart from exhibiting bright colors these structures have also shown variable responses to different types of gasses[4], which make them an interesting area of research. Figure A.14 shows a picture of morpho butterfly with SEM images of the nanostructures found on their wings. Figure A.15 shows reflectance, absorption and transmission over the visible wavelength region for different morpho butterflies. Figure A.16 shows presence of nanostructures from the SEM images of its feathers.

Figure A.17 illustrates a model of the structures found on the butterfly wings. The color produced from these structures is a combination of multi-layer interference, diffraction caused by the multiple levels of lamella and ridges respectively. The pigmentation underneath absorbs residual wavelengths to minimize scattering and enhance reflected light intensity. Optical response of the structures can be tuned by changing thickness of lamellae and air-gap between them.

The gaps between structures and lamellae facilitate air in the surroundings to interact with the surface of the structure. This interaction has been shown to effect the optical response of the structures and hence can be used as an atmospheric agent sensing apparatus. Figure A.18 shows an illustration of vapor molecules interacting with the structure and causing a change in the refractive index which ultimately effects the vapor response.
Figure A.14: Morpho butterfly - a) M. Sulkowskyi b) M. didius - SEM c) M. rhetenor - SEM d) M. Sulkowsyi-SEM images [75]
Figure A.15: Morpho butterfly reflectance plots, absorption and transmission - a) M. didius b) M. rhetenor c) M. adonis d) M. Sulkowsyi [76]
Figure A.16: Peacock [77]

Figure A.17: Butterfly Stack Model
Figure A.18: Butterfly Stack Model - Gas Interaction
APPENDIX B

Lithography

Figures B.1, B.2, B.3 show secondary electron images of free standing photonic structures made with a positive resist stack.

**Figure B.1:** A & B - Positive(Copolymer)/Negative(HSQ) resist stack - 2 layers, C - Positive(Copolymer/PMMA) resist stack - 2 layers, D - Positive resist stack - 4 layers

Figure B.4 shows images of ribs which act as support for longer lamellae and prevent bending due to shear from developer.
Figure B.2: A & B - Positive(Copolymer(210nm)/PMMA(70nm)) resist stack - 6 layers, C - Positive resist stack - 8 layers, D - Positive resist stack - 10 layers
Figure B.3: A - Positive(Copolymer(210nm)/PMMA(70nm)) resist stack - 16 layers, B - Positive resist stack - 20 layers, C - Positive resist stack - 22 layers, D - Positive resist stack - 24 layers
Figure B.4: Positive (Copolymer/PMMA) resist stack with ribs
Effect of Dose

This section shows images of increasing dose on thick resist stacks for a 100keV electron beam. It is interesting that increase in beam spread can be noticed from the difference in contrast between exposed and unexposed areas as incident dose increases.

Figure B.5: SEM images of PMMA (6µm) exposed to 100keV electron beam at various doses - Developed in MIBK:IPA(1:3)
Figure B.6: SEM images of PMMA (6μm) exposed to 100keV electron beam at various doses - Developed in MIBK:IPA(1:3)
Figure B.7: SEM images of PMMA (6μm) exposed to 100keV electron beam at various doses - Developed in MIBK:IPA(1:3)
Figure B.8: SEM images of Copolymer/PMMA(6μm) stack exposed to 100keV electron beam at various doses - Developed in MIBK:IPA(1:3)
Figure B.9: SEM images of Copolymer/PMMA(6μm) stack exposed to 100keV electron beam at various doses - Developed in MIBK:IPA(1:3)
Effect of Focus

This section shows images of the effect of focus on structure dimensions in a 12-layer Copolymer/PMMA stack. A positive value of focus represents the beam focused inside the substrate beyond the wafer and resist interface. A negative value of focus represents the beam focused above the resist layer.

![Figure B.10](image)

**Figure B.10:** Focus offset for 750, 775 and 800 $\mu$C/cm$^2$ at +7.5, +10 $\mu$m focus offsets
Figure B.11: Focus offset for 775 and 800 $\mu$C/cm$^2$ at +10, +12.5, +15, +17.5 $\mu$m focus offsets
Figure B.12: Focus offset for 750, 775 and 800 $\mu$C/cm$^2$ at -5, -10, -15 $\mu$m focus offsets
Dose distribution - MATLAB simulation program code

CASINO version 3 (http://www.gel.usherbrooke.ca/casino/) is a Monte-Carlo simulator of electron trajectories in solids and was used in this work to illustrate electron scattering. The following simulation parameters were used; Microscope and Simulation properties: Beam energy - 100keV, Number of electron trajectories - 10000, Beam radius - 20nm; Physical Models: Total and Partial Cross-sections - Rutherford (used due to the high energy of the beam), Effective Section Ionisation - Casnati, Ionisation Potential - Joy and Luo, Random number generator - Press et. al. [1986], Directing Cosin - Soum et.al. [1979], dE/dS Calculation - Joy and Luo [1989].

Sceleton [78] is a Monte-Carlo program used in this work to generate statistical data resulting from electron-resist/substrate interaction. Elastic scattering is described by the Rutherford formula due to high energy of the incident beam. Energy dissipation due to inelastic scattering is expressed by Bethes energy loss formula in the continuously slowing down approximation (CSDA). The calculated radial energy density distribution, also called as a point spread function is written to a file to be used with proximity effect correction programs.

Mathematical functions were fit to data obtained from the simulations to approximate the dose and spread as functions of depth. The following functions were obtained from mathematical fits to simulated data sets and used to generate dose contours. The number of electrons used in the simulation were 10 million and minimum electron energy was 1eV. Figure B.13a, b shows dose and spread data from Sceleton along with fits from mathematical expressions B.1, B.2 respectively.

A stack thickness of 6µm and radial distance of 1µm were used to perform simulations.

\[ D_0(x) = D_c \ast a_1 \ast e^{b_1 \ast x} \] (B.1)
\[ D(y) = D_0(x) \times a_2 \times y^{b_2} \quad (B.2) \]

where, \( D_0(x) \) is dose as a function of depth, \( D_c \) is dose at the surface, \( a_1 = 2.581 \times 10^7 \) and \( b_1 = -0.000612 \) are fitting constants, \( x \) is depth. \( D(y) \) is dose as a function of lateral spread, \( a_2 = 4.604 \times 10^{-5}, \) \( b_2 = 1.836 \) are fitting constants, \( y \) is lateral spread.

Figure B.14 shows beam spread as a function of depth for three different beam energies.

![Figure B.13: Mathematical fit for Dose and Spread as a function of depth](image)
Figure B.14: Mathematical approximation of scleleton simulated data at 100, 150 and 200keV
Matlab m-code used for generating dose contours in PMMA is as follows,

```matlab
input_dose = input('enter dose'); % enter incident dose
stack_depth = 0:1:10000; % generate depth with 1nm mesh
spread_limit = 1:1:1000; % generate radial distance with 1nm mesh
for a = 1:length(input_dose)
dose_depth = [];
dose_depth = [input_dose*exp(-2e-4*stack_depth)]'; % calculate dose
% as a function of depth
spread = [4.6e-5 * power(stack_depth, 1.836)]'; % calculate radial % distance dose factor as a function of depth
im = [];
k = 1;
for i=1:length(dose_depth)
temp = [];
temp = dose_depth(i) * exp(-power(spread_limit/spread(i),2));% along depth of % stack calculate lateral dose values
for j=1:length(temp)
im(k, j) = temp(j);
end
k = k+1;
end
figure;
imagesc(im);
end
xlabel('Radial distance (nm)','fontsize',14); ylabel('Depth (nm)','fontsize',14); title('Dose
```
contour for 100keV’, ’fontsize’, 14);
Matlab m-code used for generating dose contour in PMMA/Copolymer stack is as follows,

```
p_dose = input('enter pmma dose'); % enter incident dose for PMMA
c_dose = input('enter copolymer dose'); % enter incident dose for Copolymer
levels = input('number of levels'); % enter number of levels
pmma = 70; % PMMA layer thickness
copolymer = 150; % Copolymer layer thickness
stack_depth = 1:1:(levels*(pmma+copolymer)); % calculate total stack thickness with 1nm mesh
spread_limit = 1:1:1000; % generate radial distance with 1nm mesh

p_im=[];
c_im=[];
im=[];
p_dose_depth = [];
c_dose_depth = [];

p_dose_depth = [p_dose*exp(-2e-4*stack_depth)]; % calculate % PMMA dose as a function of depth
p_spread = [4.6e-5 * power(stack_depth, 1.836)]; % calculate % radial distance dose factor for PMMA as a function of depth
p_im = [p_im ; p_dose_depth];

c_dose_depth = [c_dose*exp(-2e-4*stack_depth)]; % calculate
```

205
% Copolymer dose as a function of depth

c_spread = [4.6e-5 * power(stack_depth, 1.836)]'; % calculate
% radial distance dose factor for Copolymer as a function of depth

c_im = [c_im ; c_dose_depth];

k = 1;
for i=1:length(p_dose_depth)
    temp = [];
    temp = p_dose_depth(i) * exp(-power(spread_limit/p_spread(i),2)); % along depth
    of stack calculate lateral dose values for PMMA
    for j=1:length(temp)
        p_im(k, j) = temp(j);
    end
    k = k+1;
end

k = 1;
for i=1:length(c_dose_depth)
    temp = [];
    temp = c_dose_depth(i) * exp(-power(spread_limit/c_spread(i),2)); % along depth
    of stack calculate lateral dose values for copolymer
    for j=1:length(temp)
        c_im(k, j) = temp(j);
    end
    k = k+1;
end

im = p_im + circshift(p_im, [1, 2]);
figure;
imagesc(im);
[m, n] = size(im);
image = [];
level = 1;
pmma_flag = [];
copolymer_flag = [];
c = copolymer;
p = pmma;

%%%following section of code applies generated dose contour to Copolymer/PMMA stack%%%

for i = 1:1:m
if i == ((pmma+copolymer)*level)
level = level+1;
p = (pmma*level)+(copolymer*(level-1));
c = p + copolymer;
end
for j = 1:1:n
if (i/p <= 1)
pmma_flag(i) = i;
if im(i, j) >= 800
image(i, j) = 1;
else
image(i, j) = 0;
end
elseif (i/c <= 1)

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copolymers_flag(i) = i;
if im(i, j) >= 175
    image(i, j) = 1;
else
    image(i, j) = 0;
end
end
end
end
figure;
imagesc(image);
xlabel('Radial distance (nm)','fontsize',14);
ylabel('Depth (nm)','fontsize',14);
title('Copolymer/PMMA stack interaction - 100keV','fontsize', 14);
APPENDIX C

Solubility Data

This section contains solubility data tables for different electron beam resists that were experimentally analyzed in this work. Resists with a nominal thickness of 200nm were coated on silicon wafers and exposed to various solvents. A solubility scale of 6 was used where a score of ”1” would mean complete solubility, ”3” would mean partial solubility and ”6” would mean insolubility. Thickness measurements were made using an Ellipsometer to confirm visual inspection following assignment of scores. After suitable solvents were identified, resist polymers were recast and tested for the solvent’s ability of clearly dissolve the polymer.

Recasting procedure included evaporation of solvent from the original resist system as delivered by the manufacturer. This can be done by a steady centrifuge system or leaving the resist solution in a fume hood. Due to low flash point (< 30°C) of solvents the resist polymer remains after a few hours. The weight of polymer was measured using a micro-balance and added to compatible solvents identified using HSP analysis. Glass vials (25ml) were used to experimentally verify solubility and the solution was coated on silicon wafers to check coating uniformity.

It should be noted that this data pertains to solubility of thin polymers films and not bulk polymers. Although most of the data can be used to identify suitable solvents, actual solubility of bulk polymers might be different.

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<th>$\delta_d$</th>
<th>$\delta_p$</th>
<th>$\delta_h$</th>
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Table C.1: NEB-31(negative e-beam resist) solubility data

Continued on next page
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<td>0.896</td>
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<td>Chloroacetaldehyde Diethyl Acetal</td>
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Table C.2: SU-8(negative e-beam resist) solubility data

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<th>$\delta_h$</th>
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### Table C.3: TEBN - 1(negative e-beam resist) solubility data

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Table C.4: HSQ (negative e-beam resist) solubility data

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### Table C.5: KMPR (negative e-beam resist) solubility data

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Table C.6: Polystyrene (negative e-beam resist) solubility data

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### Table C.7: PMMA 950k (positive e-beam resist) solubility data

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Table C.8: ZEP 520A (positive e-beam resist) solubility data

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Table C.9: Copolymer MMA:MAA (positive e-beam resist) solubility data

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<th>δ_p</th>
<th>δ_h</th>
<th>Score</th>
<th>RED</th>
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<td>1,1,2,2-Tetrachloroethane</td>
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<td>5.1</td>
<td>5.3</td>
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APPENDIX D

Metrology

Ellipsometry - Theory

Light is a form of Transverse Electro-Magnetic (TEM) radiation with electric and magnetic components oscillating perpendicularly to each other. As most of the materials probed by ellipsometry are non-magnetic, changes in electric field component are only considered. Furthermore, the electric field $E$ can be represented by two components, $E_p$ relating to fields oscillating parallel to the direction of propagation and $E_s$ relating to fields oscillating perpendicular to the direction of propagation.

When electric field of the light waves are oriented in specific directions, such light is referred to as polarized light. The polarization state of light can be determined by phase difference between the p- and s- components of the electric field. Figures D.1, D.2, D.3 show three common forms of representation of light as a resultant of two components.

In case of linearly polarized light both p- and s- components have zero phase difference and a project of the components would be a straight line as shown in D.1. If the phase difference is 90° or $\frac{\pi}{2}$, the projection of the components would result in a circle. If the phase difference is any value other than 90° the projection would take the form of an ellipse as shown in figure D.3[66, 67]. Natural light is unpolarized i.e. the electric field components oscillate in random directions.

As mentioned earlier, ellipsometry measures the ratio of amplitude of p- and s- reflection components, represented by $r_p$ and $r_s$ respectively and the relative phase shift between them. $r_p$ and $r_s$ are defined by the ratios of reflected electric fields to incident electric fields. Equations D.1 show the values measured by ellipsometry. Figure D.4 shows an illustration of elliptically polarized light in p- and s- component
Figure D.1: Linearly polarized light

\[ E_p = A_p \cos(\nu t + \delta_p), \quad E_s = A_s \cos(\nu t + \delta_s) \]  
\[ (D.1a) \]

\[ r_p = \frac{E^r_p}{E^r_p}, \quad r_s = \frac{E^r_s}{E^r_s} \]  
\[ (D.1b) \]

\[ \rho = \frac{r_p}{r_s} = \tan(\psi) \exp(i \Delta) \]  
\[ (D.1c) \]

\[ \tan(\psi) = \frac{A^r_p/A^r_s}{A^i_p/A^i_s} \]  
\[ (D.1d) \]

\[ \Delta = (\delta^r_p - \delta^r_s) - (\delta^i_p - \delta^i_s) \]  
\[ (D.1e) \]
The use of linearly polarized light eliminates ($\delta_p^i - \delta_s^i$) as the initial phase difference between p- and s- components is zero. Rotating analyzer is used in most ellipsometers yields a sinusoidal wave whose intensity is dependent on the change in polarization of light.

Polarized light can be represented by Jones matrix and unpolarized or partially polarized light can be expressed using Stokes parameters and Mueller matrices. Jones matrix corresponding to light reflected by a sample is given by the equations D.2.

\[
S = \begin{bmatrix}
    r_p & 0 \\
    0 & r_s \\
\end{bmatrix}
\]  \hspace{1cm} (D.2a)

\[
\begin{bmatrix}
    E_{rp} \\
    E_{rs}
\end{bmatrix} = \begin{bmatrix}
    r_p & 0 \\
    0 & r_s
\end{bmatrix} \begin{bmatrix}
    E_{ip} \\
    E_{is}
\end{bmatrix}
\]  \hspace{1cm} (D.2b)
Elliptically polarized light

$\Delta = \delta_p - \delta_s = 45^\circ$

**Figure D.3:** Elliptically polarized light

Stokes parameters can be defined in several ways as shown in equation set D.3. $I_p$ and $I_s$ are light intensities in p- and s- components. $I_{+45^\circ}$ and $I_{-45^\circ}$ are linearly polarized light aligned at $+45^\circ$ and $-45^\circ$ and $I_R$ and $I_L$ are right and left circular polarized components. These parameters can also be determined by the $\Psi$ and $\Delta$ parameters measured using the ellipsometer as shown in the equations D.3.

\[
S_0 = I_p + I_s = 1 \quad \text{(D.3a)}
\]

\[
S_1 = I_p - I_s = -\cos 2\Psi \quad \text{(D.3b)}
\]

\[
S_2 = I_{+45^\circ} + I_{-45^\circ} = \sin 2\Psi \cos 2\Delta \quad \text{(D.3c)}
\]
Mueller matrices are used to represent partially polarized light. Resist materials are mostly transparent and non-absorbing except at UV-wavelengths. In this work spectroscopic ellipsometry is used in which the sample is probed with multiple wavelengths and hence, we can neglect the UV wavelengths for analysis.

**Models**

As shown in figure 5.1, a model has to be designed based on the properties of materials being probed. Materials can be broadly classified into three types or a combination of them based on their interaction with light and its wavelength,

1. Transparent
2. Reflective

3. Absorbing

For films whose thickness is of the order of hundreds of nanometers, part of the light is reflected and/or absorbed and/or transmitted and this is based on the refractive index \(n\) and absorption coefficient \(k\) of the material. The complex refractive index of a material is given by equation (D.4) which is also related to the complex dielectric constant, where \(\epsilon_1\) is the real part and \(\epsilon_2\) is the imaginary part. Parametric optical models correlate physical properties of the films to their interaction with light of different wavelengths. This dependence allows useful information to be extracted. To choose the appropriate model for analyzing measured data for a given material, knowledge of material’s properties (material preparation/deposition method, layers in the material) is required.

\[
N = n - ik, \quad N^2 = \epsilon = \epsilon_1 - i\epsilon_2 \tag{D.4}
\]

Dispersion relations describe the dependence of optical constants with wavelength of light. The parameters in these relations are adjusted to match the experimental data. Most of the bulk materials have tabulated values of refractive index \(n\) and absorption coefficient \(k\) and they can be directly used to model the interaction of light.

Transparent materials are often described using Cauchy, Sellmeier relationship in which absorption coefficient \(k\) and complex dielectric constant \(\epsilon_2\) are zero. For absorbing and partly-reflective films generalized oscillator models, Drude, Lorentz, Tauc-Lorentz, Cody-Lorentz are used which take the advantage of Kramers-Kronig relation to accurately describe dispersion of materials in both transparent and absorbing regions. Many different oscillator models have been proposed and they will be briefly described below. Kramers-Kronig consistency links the real and imaginary
optical constant, which means the shape of $n$ or $\epsilon_1$ is dependent on shape of $k$ or $\epsilon_2$ respectively. Modelling the absorption efficiently along with Kramers-Kronig relation can be used to determine the real part of dielectric constant ($\epsilon_1$).

Major difference between Tauc-Lorentz and Cody-Lorentz models lies in the absorption-onset region where photon energies are slightly greater than $E_g$ (band-gap). Cody-Lorentz model includes the Urbach absorption term as an explicit term in its approximation.

1. **Tabulated ($n$, $k$) or ($\epsilon_1$, $\epsilon_2$)** - Using material properties the refractive index ($n$) and absorption ($k$) or real part ($\epsilon_1$) and imaginary part of dielectric constant ($\epsilon_2$) can be estimated empirically. These values can be used to model the interaction of light (of different wavelengths) with the material and determine other physical parameters such as thickness, roughness etc.

2. **Cauchy model**[79] - Equation D.5 is most commonly used to model transparent, non-absorbing films. It is not valid for wavelengths in the IR region or UV region where some materials, especially photoresists, start absorbing light. It is not constrained by the Kramers-Kronig consistency and hence modelling of films in the absorbing spectrum of light can yield faulty results.

$$n(\lambda) = A_n + B_n \frac{\lambda}{\lambda^2} + C_n \frac{\lambda}{\lambda^4} \quad (D.5a)$$

$$\kappa = \kappa_{amp} e^{exp(E−bandedge)} \quad (D.5b)$$

where $A_n, B_n, C_n$ are Cauchy coefficients, variable fit parameters and $\lambda$ is the frequency of the light being used to probe the material. $\kappa$ is the extinction coefficient, used to model the absorption where $\kappa_{amp}$ is the amplitude and the exponent are fit parameters to determine the shape of the extinction coefficient dispersion.
3. **Sellmeier model** [80] - It can be used for a larger spectral range i.e., into the IR region for transparent films. It will maintain correct physical dispersion due to the enforcement of Kramers-Kronig relation. Hence it can model the absorption in the IR region with better accuracy compared to the Cauchy model. This model treats materials as a collection of atoms whose negative electron clouds are displaced by the positive nucleus due to oscillating electric fields from the light beam. It also assumes that atomic dipoles have no absorption and it is given by the equation D.6

\[
\epsilon(\lambda) = n^2 = 1 + \sum_{i=1}^{m} \frac{A_i \lambda^2}{\lambda^2 - \lambda_o^2}
\]  

(D.6)

where \(A_i\) is Sellmeier coefficient for each oscillator and \(\lambda_o\) is the resonant frequency at which the absorption is equal to zero. At the resonant frequency atomic dipoles’s oscillations show up as a peak in the real dielectric constant with zero absorption i.e., no broadening.

4. **Drude**[57] - This model takes into account the free electron transitions. In metals and semi-conductors the free carriers absorb light and cause changes in the dielectric function. This model is most commonly used to describe light absorption in metals.

In ellipsometry data analysis the following expression D.7 relates dielectric constant(\(\epsilon\)) to the energy of light being used to probe the material.

\[
\epsilon = \epsilon_\infty - \frac{A}{En^2 - i\Gamma En}
\]  

(D.7a)

\[
A = \epsilon_\infty E_p^2
\]  

(D.7b)
\[ E_p = \hbar \omega_p = \left( \frac{\hbar^2 e^2 N_f}{\epsilon_0 \epsilon_\infty m^*} \right)^{1/2} \]  
(D.7c)

\[ \Gamma = \hbar \gamma = \frac{\hbar e}{m^* \mu} \]  
(D.7d)

where \( \epsilon_\infty \) is the static dielectric constant of the material, \( E_p \) represents the plasma energy and \( \gamma \) is the broadening parameter, \( N_f \) is the number of free carriers per unit volume, \( m^* \) is the effective mass of the electron.

In terms of wavelength of incident radiation the relation between the complex dielectric constant is given by the following equation

\[ \tilde{\epsilon}(\lambda) = \epsilon_\infty - \frac{i4\pi\hbar^2}{\rho(\hbar \lambda + i\lambda^2 \tau)} \]  
(D.8)

where \( \tilde{\epsilon} \) is the complex dielectric constant of the material, \( \rho \) is the resistivity and \( \tau \) is the mean scattering time.

5. **Lorentz Oscillator model** [81, 57] - It is a classical model which considers a negatively charged electron is bound to a positively charged atomic nucleus. The binding between the electron and nucleus can be modeled as a spring. When light interacts with this model, the oscillating electric field will cause the electron to move along with the field. Equation D.9 represents lorentz oscillator model for approximating an absorbing material’s interaction with light.

\[ \epsilon = 1 + \frac{\epsilon^2 N_e}{\epsilon_0 m_e (\omega_0^2 - \omega^2) + i\Gamma \omega} \]  
(D.9)

As shown in equation D.9 the dielectric permittivity of the material is related to the number of electrons per unit volume \( N_e \), resonant frequency of the molecules \( \omega_0 \), \( \Gamma \) is the damping constant which is related to the force constant between
nucleus and electrons, $e$ is charge of an electron, $m_e$ is mass of the electron and $\omega$ is the frequency of light used to probe the material.

Multiple oscillators can be used to model a material and the following equation D.9 is commonly used for data analysis in ellipsometry.

$$\epsilon = 1 + \sum_j \frac{A_j}{En_0^2_j - En^2 + i\Gamma_j En}$$  \hspace{1cm} (D.10)

where $A_j$ is strength of the $j^{th}$ oscillator (amplitude) and $En$ is the incident photon energy and $En_0^2_j$ is the energy at resonant frequency, $\Gamma_j$ describes the broadening of the oscillator peak.

6. **Tauc-Lorentz oscillator model** [82, 57] - This model is employed to model dielectric functions of amorphous materials, transparent conductive oxides. Absorption in amorphous materials may be asymmetric and modeling them using the Lorentz model will lead to incorrect results. Tauc gap is often used to characterize optical properties of amorphous materials and as it defines the optical band gap in amorphous semiconductors. Equation D.11 gives relation between absorption and Tauc band gap.

$$\epsilon_2 = \frac{A_{tauc} (En - E_g)^2}{En^2}$$  \hspace{1cm} (D.11)

Hence modeling amorphous materials requires integration of Tauc gap with the Lorentz model. Multiplying D.9 with D.11 will give us the following equation which is only valid when $(En > E_g)$.

$$\epsilon_2 = \frac{A_{tauc} En_0 C(En - E_g)^2}{((En^2 - En_0^2)^2 + C^2 En^2) En}$$  \hspace{1cm} (D.12)

where $A$ is the amplitude of the oscillator, $C$ is the width of the oscillator at
half-maximum, $E_n$ is the energy of photons, $E_{n_0}$ is the energy at resonant frequency and $E_g$ is Tauc-gap.

From this $\epsilon_1$ can be determined using Kramers-Kronig consistency.

7. **Cody-Lorentz oscillator model** [83, 57] - It is also used to estimate properties of amorphous materials based on their interaction with light. The major difference between this and Tauc-Lorentz is how they model absorption energies slight larger the material’s energy gap. Both the models have their own absorption formulae as shown in D.11 and D.13.

$$\epsilon_2 = A_{cody} (E_n - E_g)^2$$  \hspace{1cm} (D.13)

The Cody-Lorentz model also includes an Urbach absorption term. In amorphous materials different transitions from valence states (localized or extended) to conduction states (localized or extended) cause a tail to show up in band diagrams and this relates to the Urbach term. It adds up the transition energy term, where absorption changes from Lorentzian to Cody, and the Urbach energy term where absorption changes from Cody to Urbach behavior.

Aforementioned models are some of the basic ones used to model most of the materials used in this research. There are numerous other models developed to approximate the interaction of light with materials.