Molecular vapor deposition of organosilanes

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Molecular Vapor Deposition of Organosilanes

By

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Abstract

Current strategies for low temperature bonding (<300 C) and 3D integration employ polymer interfaces (1-3 um) with low thermal conductivity which can result in poor heat transfer between bonded elements. The introduction of thinner interfaces to improve heat transfer is desirable; however, deposition of thin polymer films (<100 nm) for bonding applications can lead to reduced film uniformity and negatively affect bonding strength. Self-assembled monolayer (SAM) chemistries provide a potential solution and can yield nanometer control of the interfacial layer thickness without a significant effect on surface roughness. Siloxanes are one available option to realize these nanometer thin reactive layers. Due to their propensity to crosslink and form multilayers, careful control of the reaction conditions is required. Considering this, we have evaluated the molecular vapor deposition of siloxane precursors to generate molecular layers with reactive end-groups for potential use in bonding applications. Film stability, morphology, thickness, and composition were monitored after deposition using atomic force microscopy, ellipsometry and x-ray photoelectron spectroscopy.
Introduction

1.1 Three Dimensional Integration

Processing techniques in device manufacturing are moving towards three-dimensional stacking approaches, or three-dimensional integration (3DI), instead of relying on two-dimensional layouts. There are several reasons to shift from 2D to 3D packing including increased efficiency and power, larger chip and interconnect density, and decreased delay time [1-3].

Previous 2D technologies relied on connecting components via wire bonds in horizontal arrays or in small stacks. Although these methods were successful in creating the necessary interconnects between components, the use of wire bonds limits efficiency and chip density due to the length of wire used in the bond. In 3D integration, the amount of space consumed by components is greatly reduced by vertically stacking and the formation of interconnects using through silicon vias (TSVs), seen in Figure 1[4]. There are several different methods to stacking the components and forming the TSVs including the via first and via last approaches[5].

Figure 1. 1A) 20 chip stack, 1B) X-Ray image of stack showing vertical interconnects[4].
1.2 Current Bonding Methods

One of the most crucial steps in 3D integration is the type of bonding used to form electrical interconnects and stack substrates. There are several different bonding techniques in use today, each with a variety of applications; their uses vary from mechanical support in temporary bonds to creating electrical connects in device fabrication. While these methods are currently employed, there are downfalls with each method allowing for further improvement on the bonding technique.

1.2.1 Wire Bonding

Prior to 3D integration, chip components were connected via wire bonds as shown in Figure 2. Wire bonding is the most common technique currently used to provide electrical interconnects[6]. Common techniques employ solder ball technology, where small copper balls are used to solder copper wires between each component. This method is time consuming and also has reliability issues[1].

Figure 2. Copper wire bonds [7]
While these bonds create successful interconnects, the length of the bonds leads to lower efficiency and less power through dissipation out of the wires. The bond length cannot be shortened because, if decreased too much, shorts can occur between wires[6]. Wire bonds also introduce problems with spacing and chip density as components can only be spaced to the limits of the wire bonds. This leads to a limitation in the amount of components that can be placed on one wafer[1].

1.2.2 Metal-Metal

The most common metal-to-metal bonds in 3D integration are the copper-to-copper bonds that are used to create TSV interconnects in wafer stacks. By forming interconnects through the stack instead of using long wire bonds, TSVs provide a more efficient electrical connect than wire bonding[3, 8]. They also allow more components to be stacked in the same area on a wafer and thus increase the chip density per wafer. Figure 3 shows a chip stack with copper TSV interconnects.

![Figure 3. Through Silicon Via [9]](image)

While these bonds do provide more efficient interconnects, they are created under high temperature (300-600°C) and pressure (100-800MPa)[9], which can lead to device
failure. Another issue is the mismatch in thermal expansion coefficients. Upon heating, the copper expands at a higher rate than the silicon that surrounds it. This can cause the TSVs to push out of the substrate or can lead to the silicon cracking. Improvement of these harsh conditions would produce a more efficient metal-to-metal bond with less potential damage to wafers.

1.2.3 Polymer

Polymer bonding, shown in Figure 4, is often used in MEMS applications for sealing devices and for temporary bonding. One common example of temporary bonding is the use of carrier wafers. The bond is only needed during the thinning process for support and is then later removed. Some of the more common polymers used for this application are BCB, photoresists, epoxies, and polyimides, among others[10]. These bonds are formed at lower temperature (<400°C), range in thickness from 1-100µm, and can be used with many different types of substrates[10]. Polymer bonds are not used for interconnects due to the insulating properties of the polymer, and are therefore used for mechanical stability and sealing.

Figure 4. SEM of polymer bond [11]
While these bonds are effective, there are downfalls. Due to the high coefficient of thermal expansion, the polymer expands when heated and can lead to shifting of the wafers during bonding, causing misalignment in the wafers[10]. The materials also have poor thermal conductivity that can cause excess heat build up and lead to device failure. Some polymeric materials also can break down at elevated temperature[10]. As with metal-to-metal bonding, a lower temperature bond would alleviate some of the problems associated with polymer bonding.

1.2.4 Hybrid Bonding

One of the newest bonding methods for 3D integration is hybrid bonding, which is a combination of both polymer and metal-to-metal bonding. This combination of bonding techniques allows for the electrical connection to be made via copper-copper bonding and provides additional mechanical stability through polymer bonds.

![Hybrid bond schematic](image)

Figure 5. Hybrid bond schematic

The bond is created by spin coating a polymer, such as polyimide, over the surface of a wafer. The surface of the wafer has raised copper structures that will later be used to form TSVs. These structures are usually on the order of 100 nm [12-15]. The polymer coats the entire surface and fills the voids caused by the protruding copper structures, and
creates a planar surface. This wafer is then brought into contact with another wafer that has received the same treatment. The wafers are heated and both the polymer films and the copper form bonds across the interface.

Although this method is an improvement on methods that use strictly metal-to-metal or polymer films, it can be improved. One of the most apparent problems is that the polymer film covers the entire surface of the substrate, including the copper surfaces that will be used to form the electrical interconnect. This could ultimately lead to interference in the electrical connection created across the copper interface and ultimately failure. Another downfall of the technique is that it still incorporates a thick polymer film between the wafers leading to thermal conductivity issues. A method is needed that addresses and eliminates these problems.

1.3 Interfacial Crosslinking

Interfacial crosslinking is a technique that tries to address the problems associated with polymer films such as excessive heating, electrical interference, and wafer shifting, but also addresses the problems seen in metal-to-metal bonding such as device failure due to high bonding temperature and pressure. This technique replaces the thick polymer film, usually greater than 50 nm, with a molecular thin film, 10-50 Å, capable of forming interfacial bonds across substrates at low temperature (>150°C).

The ideal film characteristics for this application are uniformity across the surface, the ability to form a strong bond with the wafer surface, and the ability to form bonds across the interface. The film must also be capable of being deposited and forming
interfacial bonds at low temperature. Ideally, both deposition and bonding would occur below 150°C. Bonding in this temperature range would eliminate device failure due to increased temperature and prevent materials from undergoing large expansions while heating.

By introducing thin films for bonding, we hope to facilitate the formation of copper bonds at lower temperatures, while maintaining the mechanical stability provided by polymer bonding.

1.4 Organosilanes

The class of molecule chosen for this research is organosilanes. Their basic structure is shown in Figure 6, and makes them ideal for this application due to the functionalities found on each end of the molecules.

![Figure 6. Basic Organosilane Structure](image)

One end of the molecule has two to three anchoring groups that can form a covalent bond with a metal oxide substrate, shown in Figure 7, and the other end has a functional group capable of reacting with other molecules to form bonds. By applying these molecules on substrates, a bond can be formed across the interface through a reaction in the functional groups while the other end is anchored to the surface.
Organosilanes are commercially available with many different types of functional
groups including, but not limited to, amines, epoxides, thiols, and isocyanates. This
variety of reactive groups yields an array of bonding possibilities

In addition to their wide range of functional groups, organosilanes were chosen
because they are known to readily react with metal oxides, including silicon, and form
covalent bonds with the surface via a dehydration reaction shown in Figure 7. Table 1
lists the organosilanes that were chosen for this research, along with additional silanes
with potential use for this application (reagents used in this project are marked with an
asterisk).

<table>
<thead>
<tr>
<th>Reagent Name</th>
<th>Chemical Formula</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-Aminopropyltrimethoxysilane (APTMS)</td>
<td>C₆H₁₃NO₃Si</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>4-Aminobutyltrithoxysilane</td>
<td>C₁₀H₂₂NO₃Si</td>
<td></td>
</tr>
<tr>
<td>3-Aminopropyltriethoxysilane</td>
<td>C₉H₂₂NO₃Si</td>
<td></td>
</tr>
<tr>
<td>Bis(3-(triethoxysilyl)propyl)disulfide</td>
<td>C₁₈H₴₂O₆S₂Si₂</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Butenyltrithoxysilane</td>
<td>C₁₀H₂₂O₃Si</td>
<td></td>
</tr>
<tr>
<td>3-Butenyltrimethoxysilane</td>
<td>C₇H₁₄Si</td>
<td></td>
</tr>
<tr>
<td>Organosilane</td>
<td>Molecular Formula</td>
<td></td>
</tr>
<tr>
<td>-------------------------------------------------</td>
<td>-------------------</td>
<td></td>
</tr>
<tr>
<td>10-undecenyltrimethoxysilane</td>
<td>C_{14}H_{30}O_{3}Si</td>
<td></td>
</tr>
<tr>
<td>10-(carbomethoxy)decyltrimethoxysilane</td>
<td>C_{14}H_{32}O_{3}Si</td>
<td></td>
</tr>
<tr>
<td>2-(carbomethoxy)ethyltrimethoxysilane</td>
<td>C_{7}H_{16}O_{5}Si</td>
<td></td>
</tr>
<tr>
<td>2,2-dimethoxy-1-thia-2-silacyclopentane</td>
<td>C_{5}H_{12}O_{2}SSi</td>
<td></td>
</tr>
<tr>
<td>(3-glycidoxypropyl)methyltriethoxysilane</td>
<td>C_{11}H_{24}O_{4}Si</td>
<td></td>
</tr>
<tr>
<td>(3-glycidoxypropyl)dimethylethoxysilane (GPDES)</td>
<td>C_{10}H_{22}O_{3}Si</td>
<td></td>
</tr>
<tr>
<td>(3-glycidoxypropyl)triethoxysilane</td>
<td>C_{12}H_{26}O_{4}Si</td>
<td></td>
</tr>
<tr>
<td>(3-glycidoxypropyl)trimethoxysilane</td>
<td>C_{10}H_{20}O_{5}Si</td>
<td></td>
</tr>
<tr>
<td>5,6-epoxyethyltrimethoxysilane</td>
<td>C_{12}H_{26}O_{4}Si</td>
<td></td>
</tr>
<tr>
<td>2-(3,4-epoxycyclohexyl)-ethyltrimethoxysilane</td>
<td>C_{11}H_{22}O_{3}Si</td>
<td></td>
</tr>
<tr>
<td>6-azidosulfonylhexyltrimethoxysilane</td>
<td>C_{12}H_{22}N_{3}O_{3}Si</td>
<td></td>
</tr>
<tr>
<td>Tris(3-trimethoxysilylpropyl)isocyanurate</td>
<td>C_{21}H_{45}N_{3}O_{12}Si_{3}</td>
<td></td>
</tr>
</tbody>
</table>
There were several criteria used to identify which reagents would be suitable including functional group, vapor pressure, and molecular length. Organosilanes were chosen that had functional groups that could be capable of reacting at low temperature (<150°C). One of the main concerns with this method is whether the end groups remain reactive after deposition.

Another consideration in selecting which organosilanes to investigate was their vapor pressure as the film will be deposited in the vapor phase. Currently the most common deposition technique is in the liquid phase. This often results in non-uniform films[16], as seen if Figure 8, which shows a film formed by immersing a silicon substrate into 50µl of (3-glycidoxypropyl)dimethylethoxysilane in hexane. Because interfacial crosslinking relies on a thin, uniform silane coating, liquid phase deposition is not ideal. The large non-uniform surface would limit contact area for bonding and lead to voids.

![Figure 8. 5x5um image of (3-glycidoxypropyl)dimethylethoxysilane deposited in hexane](image)

Organosilanes have been known to deposit in monolayer films when water is absent[16], which is why Molecular Vapor Deposition, MVD, is the deposition technique chosen in this research. Molecules with higher vapor pressure would be difficult to get
into vapor phase and make MVD films difficult to deposit. Those molecules with lower vapor pressures are much more suited to the MVD process.

Lastly, the length of the molecule was considered. Many organosilanes are too short to be considered for this method; the organosilane molecules must be able to form bonds across two substrates. To increase the chance of cross-linking, molecules greater than six angstroms in chain length were chosen. The vapor pressure and chain length criteria facilitate uniform MVD coating and the likelihood of the molecules to form interfacial bonds at low temperatures.

In a previous study by Krauter et. al., organosilane films were used to bond silicon substrates [17]. Bipodalsilanes with disulfide functionalities, shown in Figure 9, were deposited in liquid phase onto 4” silicon wafers.

![Figure 9. Bipodalsilanes used for bonding[17]](image)

The wafers were successfully bonded at 150ºC, as depicted in Figure 10; however, the films were light sensitive, causing the bonds to be unstable. In this research, we investigate organosilanes that are more stable and have potential to be used in bonding applications. Several reagents are identified as viable candidates and some chosen for further study.
1.4.1 Crosslinking Mechanisms of Chosen Organosilanes

The available reagents listed in Table 1 can be paired in several different arrangements to yield an array of bonding possibilities. For each functional group that has been chosen for further study in this research, at least one reaction mechanism is outlined in detail including the reactive groups participating in the reaction, the type of reaction, and the resulting products of the reaction.

1.4.1.1 2,2-dimethoxy-1-thia-2-silacyclopentane

Thiols are S-H functional groups that are chemically related to alcohols; however, thiols are usually more reactive. Thiols are known to react with alkylhalides, alkenes, and other thiols. Disulfide bonds are one common type of thiol linkage. One way they are formed is through the bonding of two thiol functional groups. This reaction occurs in the presence of oxygen at low temperature and releases water as the byproduct. The disulfide linkage is one of the most important reactions in protein formation; for instance,
Disulfide bridges made by the amino acid cysteine help to stabilize and retain the tertiary structure of folded proteins. Although other forces help to maintain structure, the disulfide linkage is the strongest, making it vital to protein structure and function.

Because this linkage occurs naturally in biology and at low temperatures, it is a viable candidate for use as an intermolecular crosslinker. One of the molecules selected for use in this application is 2,2-dimethoxy-1-thia-2-silacyclopentane, shown below.

Upon binding with the silicon surface via the silane group, the ringed structure is opened yielding a thiol reactive group. Deposition of this reagent onto two surfaces would allow the formation of a disulfide bond across the substrates via a condensation reaction. This bond can be formed via an oxidation reaction, shown in Figure 9, or through a radical reaction.

$$\begin{align*}
R\text{--SH} + \text{HS--R} & \rightarrow R\text{--S--S--R} + 2\text{H}^+ + 2\text{e}^- \\
\end{align*}$$

Figure 12. Disulfide bond formation

1.4.1.2 3-Aminotrimethoxy silane

Amines are a group of molecules characterized by a functional group with nitrogen as the central atom. The nitrogen can either be primary, secondary, or tertiary as
shown below, and are known to react with several different functional groups including ketons, aldehydes, acrylates, and epoxide.

\[
\begin{align*}
\text{Tertiary:} & & \text{Secondary:} & & \text{Primary:} \\
R_N & & R_N & & R_N \\
& & R & & H \\
H & & & & H
\end{align*}
\]

Figure 13. Classification of Amines

In this work, we choose to focus on the reaction between the amine, 3-aminopropyltrimethoxysilane (APTMS), Figure 14, and the epoxide, 3-glycidoxypropyldiethoxysilane (GPDES), Figure 18, to realize inter-substrate bonds.

The reaction between APTMS and GPDES is shown in Figure 15.

Amines also have the ability to react with acrylate functional groups. This class of molecule is characterized by the presence of an ester and vinyl group, as seen in Figure 16.
A nucleophile, in this case the amine in the APTMS molecule, attacks the double bond and can lead to addition products or even a negatively charged carbon atom (depending on the electron withdrawing characteristic of the substituent groups). One example is ethyl cyanoacrylate; here an amine attack leads to a carbanion which initiates an anionic polymerization reaction (Figure 14).

1.4.1.3 GPDES

Epoxides are characterized by three atom, ringed structure consisting of two carbons and an oxygen, also known as a three-membered cyclic ether. This functionality can be seen in the GPDES molecule, shown in Figure 18. Epoxides are particularly reactive due to the strain that exists in the ring. They are often used in reactions alkenes, amines, and hydrohalic acids. Here we are interested in their reaction with amines.
Due to the ring strain, the epoxide ring is easily opened in the presence of a nucleophile such as the amine on the APTMS molecule. The lone pair on the nitrogen attacks the least substituted carbon causing the ring to open. Proton exchange yields an alcohol on the negatively charged oxygen (previously shown in Figure 15).

1.5 Surface Initiated Polymerization

To realize successful interfacial crosslinking, one needs to overcome wafer bow[18] and unless extremely smooth surfaces are used, the separation distance between the wafers may cause issues with bonding. In addition, the substrates may have raised structures that lead to reduced surface area for bonding. On possible solution to form a more compliant surface with adhesive properties is to use surface initiated polymerization (SIP). SIP is a polymerization method that allows the film to grow from the surface in a bottom-up fashion either in liquid or in gas-phase. We intend to investigate gas-phase SIP where we use MVD organosilanes as initiators. As organosilanes primarily bind to silicon areas, this approach could allow spatial control of the SIP process and result in uniform polymerization in selected areas. If the polymer grows strictly from the MVD film, the polymer can for instance fill voids between copper structures and result in an adhesive film flush with copper vias.
The SIP process we are interested in pursuing for bonding, uses 2-ethylcyanoacrylate (Figure 19). This is a gas-phase polymerization approach used to reveal latent fingerprints and has also been used by Ericson to build up polymers on nanotextured surfaces[19].

![2-ethylcyanoacrylate molecule](image)

**Figure 19. 2-ethylcyanoacrylate molecule**

In fingerprint detection, 2-ethylcyanoacrylate polymerization is initiated from various nucleophiles present in biological materials, such as amines, left on surfaces and reacts via the mechanism shown in Figure 20, which shows a previously activated molecule continuing the polymerization process. Deposition can take place at ~50°C, and within minutes controlled deposition of >100 nm polymer films can be realized. Using this same process, we have investigated 2-ethylcyanoacrylate film deposition on APTMS monolayers, where the amine at the surface of the thin film acts as a polymerization initiator.

![Polymerization Mechanism of 2-Ethylcyanoacrylate](image)

**Figure 20. Polymerization Mechanism of 2-Ethylcyanoacrylate**
1.6 MVD

There has been extensive research done on organosilane deposition in the liquid phase. This approach is successful for introducing chemical groups on an interface, however the resulting surface coatings are often non-uniform and realizing monolayer coverage is an issue. In this work we focus on molecular vapor deposition (MVD) of organosilanes, and investigate the ability of MVD to deposit monolayer thin coatings in a controlled manner. Of key interest, is the investigation of the effects of deposition time and temperature on the film’s coating.

From an engineering aspect, we are interested in MVD on a full wafer scale. Thus, initial screening of reaction conditions was performed on smaller samples and, once deposition was optimized, we investigated MVD on 4” and 8” wafers.

1.7 Ellipsometry

The thickness of organosilane films was determined using variable angle spectroscopic ellipsometry (VASE). This analysis technique utilizes a polarized light beam that is reflected of a substrate. When the light hits the sample, the interaction causes the light beam to change polarization. The light beam, now with a slightly different polarization, is reflected from the surface and is collected in a detector. The change is the light’s polarization is then used to determine thickness and optical properties of the substrate. The interaction of the light with films and coatings on top of a thicker substrate allow extraction of film thickness. Ellipsometry can also be used to determine optical
properties of substrate such as dielectric functions or refractive indices. The technique is non destructive and capable of measuring thickness on the order of angstroms[20].

A typical ellipsometer is composed of a light source, polarizer, stage, and detector and is depicted in Figure 21[20].

![Figure 21. Schematic of Ellipsometer](image)

After the data is collected, optical models are used to fit the data to gain information on parameters such as film thickness or optical constants. The model is built so that the theoretical spectra matches the spectra of the data collected with an error of less than one. It is critical to realize that although a good fit to data may be achieved, several different variables may be manipulated, which can return inaccurate data if care is not taken to validate the results[20].

Ellipsometry is also used in this research for area mapping. To do this, the sample is mounted on a movable stage that allows measurements to be taken across the entire surface of the sample using an automated stepper program. Area mapping was used to
investigate deposition on 4” wafer samples. Similar as for single measurements, once all
measurements are complete, each data point is modeled to generate a surface map
showing the thickness variation across the wafer.

1.8 XPS

Chemical characterization of the MVD films was performed using X-Ray Photon
Spectroscopy (XPS). In this method, an X-ray impinges upon the surface of the sample
and ejects an electron from the outer orbital of the atom [21]. It is an extremely surface
sensitive technique with a detection limit of parts per thousand. The penetration depth of
the X-ray is on the order of 1-2 nm and has a spot size of 400µm. Since, each element
has characteristic orbital binding energies, this allow identification of chemical species
present on the substrate surface. The released electron identifies not only the element
that it came from, but also yields information about the chemical state of the atom.

The components of an XPS system, are shown in Figure 22, and include an X-ray
source, an ultra high vacuum system, an analyzer, and a detector.

Figure 22. Schematic of XPS system [21]
Once the electrons are ejected from the surface, they enter an analyzer to separate the electrons based on kinetic energy. Once passing through the analyzer, the electrons are collected on a target. The number of electrons with a specific energy correlates to the intensity of the peak in the spectra. The intensity of the peaks can be used to determine the concentration of an element within a sample. This is done by integrating the area under each peak and determining the ratios of the elements.

Aside from determining the concentrations and ratios of elements present, it is also possible to determine the chemical states of the elements in the sample by using peak fitting software. Often a peak for a specific element is composed of atoms with different chemical composition. An example of this is seen in Figure 23[22].

![Figure 23](image)

*Figure 23. Example of XPS spectra containing peaks from multiple atomic states [22]*

Each peak corresponds to a different chemical state present, which causes a slight shift in binding energy. Peaks that shift to higher binding energy are typically more oxidized, while peaks that shift to lower energy are reduced. Reference peak tables
provide information on the binding energy of specific elements/compounds and the amount of various components can be determined by integrating the fitted peaks.

In this research, most of the XPS analysis was focused on identifying what elements were present in the samples and what chemical states they were in. For most of the organosilanes used, there are specific identifying elements, such as nitrogen, that could easily be identified to confirm MVD was successful.

1.9 AFM

Film uniformity and surface roughness were determined using atomic force microscopy (AFM). AFM is a surface sensitive technique that can provide information regarding topography, elasticity, and electrical conductivity of samples. For the scope of this research, AFM was used in tapping mode to study the surface topography and roughness characteristics of MVD films. AFM relies on raster scanning a sharp tip is brought near the surface of a sample. The tip interacts with forces created by the surface atoms and is deflected. This deflection is then measured and the height of the sample determined.

The AFM, in its most simple components, shown in Figure 24, consists of a sharp tip mounted on a cantilever, which is used to probe the surface, a piezoelectric stack, which is used to control the motion of the tip, and a power source.
The tip is extremely sharp and often made of silicon or silicon nitride. A sharper tip will provide higher resolution imaging due to its ability to interact with crevices or small particles. A less sharp tip would not be able to discriminate between these features and they would be lost in the image. Ideally, the tip should be the size of the radius of one atom. This results in the smallest possible area of interaction between tip and surface[24].

The tip is mounted on a thin, silicon cantilever usually around 100µm long. While the tip is responsible for the actual interaction with the surface, the cantilever is used to register the forces occurring during the interaction. The cantilever is flexible and moves up and down in response to the forces affecting the tip from the surface. A laser is used to vibrate the cantilever in tapping mode. The cantilever has a naturally occurring frequency at which it vibrates. As the tip interacts with the surface molecules, the forces cause this frequency to change. When this occurs, the feedback system adjusts the
voltage on the tip to bring the cantilever back to equilibrium. This is a constantly occurring adjustment, which leads to the height measurement of the sample.

The piezoelectric stack is an integral part of the feedback mechanism and is responsible for the x, y, and z movements of the cantilever. The feedback mechanism along with the response of the tip and cantilever allow the AFM to track surface features.

1.10 Cu Applications

As mentioned earlier, copper is used to form through silicon vias that provide electrical connections in a 3D chip stack. We aim for site-specific MVD/SIP on silicon areas surrounding copper and thus we need to investigate deposition of organosilanes on copper and patterned copper/silicon substrates. Ideally, the deposition would take place only on the silicon surfaces while the copper surfaces would be left free for metallic copper-copper bonding.

MVD conditions that give monolayer coatings on silicon, was used for copper. Early on it was noted that copper reacts readily with organosilanes, presumably through copper oxide. In order to protect copper from oxidation and to reduce the risk of silanization, a thiol-alkane monolayer was used. Alkanethiols are known to form well ordered, tightly packed self-assembled monolayers (SAMs) on coinage metals, such as copper and gold. In a study by Tan et al, a six carbon and twelve carbon length alkanethiol were deposited onto copper substrates and confirmed to prevent oxidation of the copper surface. The SAMs could later be removed by heating the substrates to 250°C[25]. In this work, we
investigate whether alkanethiol-SAMs could protect the copper from being modified with organosilanes, in addition to preventing oxidation.

**Materials and Methods**

2.1 Piranha cleaning

Silicon substrates prepared by immersion into Piranaha solution (3:1, \( \text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 \)) for five minutes and rinsed in deionized water (20 x 5mL) to remove any organic material from the surface and blown dry under a stream of \( \text{N}_2 \) gas.

2.2 Molecular Vapor Deposition of Organosilane Thin Films

Deposition conditions (time, temperature) were varied to determine the effect on the films’ uniformity and morphology. From this data, silanes can be chosen as viable candidates for use in interfacial crosslinking applications and their deposition optimized for bonding. All samples were analyzed using variable angle ellipsometry, XPS and AFM before and after film deposition.

2.2.1 3-Aminopropyltrimethoxysilane

3-aminotrimethoxysilane (APTMS) is widely used, and gas-phase derivatization of various surfaces with this silane has been demonstrated [26-29]; therefore, it was used for initial screening of MVD conditions. From these studies, starting points for the other selected silanes were obtained. Preliminary studies showed that by incubating a sample with 40\( \mu \)l of ATPMS at 60°C in atmospheric pressure there is enough APTMS in the
vapor phase to effectively deposit approximately one monolayer on the substrate surface. These reaction conditions were the starting point for additional studies.

After piranha cleaning, 2 cm x 2cm samples were placed in a reaction chamber, 0.507L, with 40µl APTMS at 60°C at atmospheric pressure. The reaction time was varied from 1 to 24 hours to determine the effects of deposition time on APTES surface modification. Samples were also prepared 110°C to study the effect on higher temperature deposition.

2.2.2 (3-glycidoxypropyl)dimethylethoxysilane

Deposition of (3-glycidoxypropyl)dimethylethoxysilane (GPDMS) was performed following the same experimental setup as APTMS using both 60°C and 110°C for deposition temperatures. Deposition time was varied from 1-24 hours and the deposition was carried out under atmospheric pressure in identical reaction chambers.

2.2.3 2,2-dimethoxy-1-thia-2-silacyclopentane

DH-TSC is a very volatile compound with a low vapor pressure capable of room temperature deposition, but heating is required to initiate covalent bonding of the silicon groups on the organosilane molecule to the silicon surface. Without this heating, the bonds will not form as effectively and the film will not be securely anchored to the substrate. For this reason, 60°C was chosen for the deposition temperature to ensure the film was bound to the silicon surface. The reaction was done at atmospheric pressure from 1-24 hr.
2.2.4 Epoxycyclohexyl-ethyltrimethoxysilane

The ECH-ES molecule consists of an epoxide ring, as the GPDMS, but is on a six membered carbon ring. Because the molecule is large, it was determined that getting it to the vapor phase would more difficult and deposition was done at 110ºC. Again, the reaction was carried out at atmospheric pressure and the time was varied from 1 – 24 hours.

2.2.5 Tris(3-trimethoxysilylpropyl)isocyanurate

Tris(3-trimethoxysilylpropyl)isocyanurate molecule is very viscous. Due to this property, it was determined that getting the molecule into the vapor phase would be difficult and deposition was done at 110ºC. Deposition time was varied from 1-24hr and carried out at atmospheric pressure.

2.3 SIP of 2-Ethylcyanoacrylate

In addition to MVD films of organosilanes, polymer films of 2-ethylcyanoacrylate were also investigated. 2-ethylcyanoacrylate films were grown on an existing APTMS films, as the amine group acts as the initiator for the growth of the polymer film. Films was deposited by exposing an APTMS film, deposited as previously described in 2.2.1, to 50µl 2-ethylcyanoacrylate in a reaction chamber at 60ºC for 15 minutes. The characteristics of these films were analyzed using the same methods as the organosilane MVD films.

2.4 Ellipsometric Analysis of MVD Organosilane Films
Directly before and after MVD deposition, samples were analyzed using variable angle spectroscopic ellipsometry (VASE) to determine the film thickness. The samples were measured using a wavelength range of 250nm-1800nm at 55-65 degrees, with 2.5 degree increments. The thickness data was obtained using a thermal oxide model for silicon and was determined by subtracting the baseline thickness of the piranha cleaned silicon from the thickness obtained post deposition.

VASE was also used to investigate the deposition of APTMS on 4” wafers to determine the effects on the films in larger scale deposition. Films were deposited as described before, but a larger reaction chamber was used, 4.5L. Although the surface area of the wafer is much larger, the amount of silane was not increased because the volume of silane saturated the reaction chamber.

After the deposition of the APTMS film, a 2-ethylcyanoacrylate film was deposited. For this set of experiments, the volume of 2-ethylcyanoacrylate was increased to 300µl, to ensure the chamber was saturated.

2.5 XPS Analysis of Organosilane Thin Films

After determining the thickness of the films, XPS was used to characterize the elemental components of the film and confirm the deposition. For each sample, a survey scan (0eV- 1300eV) was taken along with high resolution of characteristic regions to identify specific atomic peaks in the spectra. These peaks include C (280-295eV), O (525-540eV), Si (95-110eV), S (156-172eV), and N (390-410eV). A Piranha cleaned silicon control was also included for each film.
2.6 AFM Analysis of Organosilane Thin Films

After film characterization, AFM was used to assess the affect of the film on the surface roughness of the silicon substrate and to determine the affects of changing deposition conditions on the films. A Veeco Dimension 3100 Scanning Probing Microscope was used in tapping mode. Scans of 10µm×10µm and 5µm×5µm were taken for each sample. Scans were also taken of a Piranha cleaned silicon control sample for reference.

The AFM is a very useful tool in characterizing both the thickness and uniformity of the films. The sensitivity of the tip allows the topography and continuity of the film to be determined. It also can reveal whether the thickness value found using ellipsometry is due to one continuous film, or if the thickness is an average value from island growths on the surface of the substrate. This sensitivity allows changes in the film due to different deposition conditions to be detected and ultimately optimize the deposition conditions.

2.7 MVD of APTMS on Copper

After investigating the deposition of organsilanes and SIP films on silicon, deposition was studied on copper substrates. Understanding the deposition on copper is important given its abundant use in the semiconductor industry. The copper substrates used in this studied were received from CNSE CSR. The substrates were CMPed with a roughness of 0.72± 0.09nm, which is within industry standards. APTMS was chosen for the study due to its predictable and controllable deposition characteristics.
All samples were cleaned with glacial acetic acid by immersion for five minutes and blow dry with N$_2$. The samples were placed in the reaction chamber with 40µl of APTMS for 1hr at 60ºC at atmospheric pressure. These reaction conditions correspond to the conditions required to form a single monolayer APTMTS film on a silicon substrate. Deposition of APTMS on copper films was analyzed using AFM and XPS. These films were not analyzed using VASE as reliable, consistent models could not be built for the data.

2.8 Octadecanethiol Protection of Copper

In order for copper to successfully be used to make TSVs and other interconnects, the surface must be free of contamination and oxidation. Given the propensity of organosilanes to deposit on metal oxides, a method was needed to protect the copper from film deposition. To protect the copper from APTMS deposition, a monolayer of octadecanethiol was deposited on the copper surface. The Cu substrate was cleaned using glacial acetic acid as in the previous section and immersed in a 1mM solution of octadecanethiol in ethanol (EtOH) for 12hrs. The substrate was then washed with 3x20ml EtOH, sonicated for 5 minutes, and blown dry with N$_2$. Directly following the monolayer deposition, a film of APTMS was deposited on the Cu substrate as described previously (2.2.1). The samples were analyzed using AFM and XPS.

Results

3.1 Ellipsometric Analysis of MVD Organosilane and SIP Films
Deposition time and temperature of organosilanes were investigated to determine the effect on film morphology, uniformity, and coverage. Variable angle spectroscopic ellipsometry was used to determine the thickness of MVD deposited films. Figure 25 shows the thickness for each film along with the temperature of the deposition.

![Thickness of MVD Organosilane Films](image)

**Figure 25.** Ellipsometric thickness of MVD organosilanes

Thin films, between 0.5-2nm, were found for most organosilanes between 1-3hrs. Although the thickness data is consistent with the presence of one to two monolayers, the thickness may be from a uniform film or due to the average thickness of a non-uniform film, thus further investigation of the films’ characteristics is needed.

One of the interesting characteristics to note, are the film thicknesses over time of the salines. The APTMS, GPDES, and ECH-ES all show an increase of film thickness
over time, while Iso-NCO and DH-TSC seem to deposit an initial film and then remain constant over time. The difference in the growth patterns appears to be related to the number of anchoring groups present. Molecules with two anchoring groups appear to have self limiting growth, while those with three appear to continue growth with time.

3.2 XPS Analysis of MVD Organosilane and SIP Films

A ThermoScientific X-Ray Photon Spectrometer was used to characterize the elemental composition of the MVD and SIP films. Identification of the elements present in the films supports the ellipsometric thickness data and helps to confirm the presence of the organosilane film. Figure 26 contains high resolution, characteristic XPS scans for each film studied.

Figure 26. XPS scans of organosilane films

Figure 26a is a high resolution scan of the nitrogen region (392-410eV) for the APTMS film. From this scan, it is seen that there is a high concentration of nitrogen in
the film compared to the control, which is a piranha cleaned silicon sample, verifying the presence of an APTMS film.

Verification of the two molecules with epoxide rings was difficult as there were no obvious elements to investigate. In order to verify the presence of the films, scans were taken of the carbon region on several samples exposed at increasing deposition times. This should show an increase in carbon concentration with an increase in the deposition time. The carbon region (208-294eV) is shown in Figure 26b. As expected, there is an increasing amount of carbon on the surface of the sample correlating with an increase in MVD exposure time. Two separate carbon peaks can be seen which represent the different types of carbon in the film. The peak at 288eV represents the more oxidized carbon from the epoxide ring on the molecule. The second, larger peak at 286eV corresponds to the carbon chain in the molecule. The increasing carbon concentration over time and the presence of two distinct carbon peaks confirms the GPDMS film deposition.

This same behavior can be seen in Figure 26c which is also of the carbon region for the ECHTMS film. Like the GPDMS, there are two clear peaks corresponding to the two oxidation states of the carbon in the sample. Again, the higher binding energy represents the carbon in the epoxide ring and the lower energy is the alkane chain of the molecule.

In Figure 26d, the high-resolution sulfur region (158-172eV) is shown for the SH-SCP MVD film. The peak seen in both the control and the SH-SCP spectra is the result of the silicon 2s peak. The sulfur peak for the film is the second peak seen at 184eV.
which is not present in the control. The presence of this peak in the SH-SCP sample confirms successful film deposition.

The nitrogen region was used to confirm the deposition of tris(3-trimethoxysilylpropyl)isocyanurate. A very large nitrogen peak is seen for the film sample, while the peak is not present for the silicon control, confirming the film’s presence.

3.3 AFM Analysis of Organosilane and SIP Films

After confirming the organosilane film deposition, a Veeco 3100 Scanning Probe Microscope was used to assess the affect of the films on surface roughness of the silicon. The AFM images for the films are shown in Figure 27 and Table 2 shows the roughness of the films.

Figure 27. AFM images (5μm x 5μm) of organosilane films
<table>
<thead>
<tr>
<th>Organosilane</th>
<th>RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>APTMS</td>
<td>0.23± 0.07</td>
</tr>
<tr>
<td>GPDMS</td>
<td>0.28± 0.07</td>
</tr>
<tr>
<td>SH-SCP</td>
<td>0.34± 0.07</td>
</tr>
<tr>
<td>ECHTMS</td>
<td>0.97± 0.15</td>
</tr>
<tr>
<td>ISONCO</td>
<td>0.43± 0.15</td>
</tr>
<tr>
<td>Control</td>
<td>0.16± 0.04</td>
</tr>
</tbody>
</table>

Table 2. Roughness of organosilane films

From these images, it is seen that APTMS, GPDMS, and SH-SCP (Figure 27 a-c) form uniform films that have minimal affect of surface roughness. The films appear to cover the entire silicon surface uniformly, and the film thickness can be controlled by varying the reaction time and temperature. In these images, the APTMS and SH-SCP were deposited at 60ºC for 1hr and the GPDMS was deposited at 110ºC for 3hrs.

The IsoNCO and ECHTMS, Figure 27d and e, films exhibit island growth instead of uniform film formation. The IsoNCO and ECHTMS were deposited for 1hr at 110ºC. It is not clear whether there is an underlying monolayer film with islands growing from it or whether the islands are the only film growth. Further investigation is needed to determine the mode of growth. APTMS also exhibited island growth at increased deposition times and temperatures.

One factor contributing to the island like growth may be the number of anchoring groups on each molecule. As stated previously, those molecules that seem to have limited growth have only two anchoring groups, while those that show increased growth rate with increased deposition time have three anchoring groups. This additional anchoring group may allow the molecules to react more readily with themselves and form thicker films.
Although these films are not uniform films, they still have only a minimal effect on the surface roughness of the substrate. Due to their limited effect on surface roughness, these films may still be used for interfacial crosslinking applications.

3.4 Large Scale Deposition of APTMS and SIP films

After determining the optimal deposition conditions needed to achieve uniform thin films using APTMS, the deposition was investigated on 4” wafers. Figure 28 shows surface maps of a Piranha cleaned silicon wafer (a), an APTMS film (b), and 2-ethylcyanoacrylate film on APTMS (c).

![Surface map of 4” piranha cleaned silicon wafer](image)

Figure 28a. Surface map of 4” piranha cleaned silicon wafer
Figure 28b. Surface map of 4” silicon wafer after APTMS thin film deposition

The Piranha cleaned silicon substrate is uniform across the wafer’s surface, as seen in Figure 28a. With the addition of the APTMS film, 28b, the surface becomes
slightly non-uniform with a thicker film seen closer to the APTMS source. Next, the addition of the 2-ethylcyanoacrylate film, 28c, the film becomes noticeably non-uniform. The greatest thickness is seen on the edge of the wafer that was closest to the 2-ethylcyanoacrylate source. The film thickness gradually decreases as the distance for the source increases. Further research is needed in order to create a more uniform concentration of acrylate within the reaction chamber. If this can be achieved, a more uniform film may be realized.

3.7 XPS analysis of APTMS MVD on Cu

One of the most important aspects of using MVD of organosilanes is to be able to protect copper structures on the wafer from the deposition. To do this, octadecanethiol was used to coat the copper surface prior to MVD APTMS deposition and could later be removed by heating the substrate. Figure 29 shows the nitrogen spectra for a plain copper substrate, copper with an APTMS MVD film, and a copper substrate protected first by the alkanethiol then exposed to the APTMS vapor.
Figure 29. XPS spectrum of copper substrate with and without alkanethiol protection

The copper substrate with the APTMS film shows a very large nitrogen peak, while the sample protected by the octadecanethiol shows a much lower concentration comparable to the nitrogen levels on the control. These results show that the use of alkanethiol monolayers is a successful method for protecting copper surfaces from silane deposition. By doing this, films can be directly deposited onto the silicon regions, while leaving the copper regions, protected by the thiol film, to be bonded later.

Although there is a thiol film deposited on the copper, as Tan et. Al. showed, this film can be removed by heating the substrate to 250°C[25]. This will allow the copper to be protected from both oxidation and silane deposition and later be passivated by heating the substrate for bonding. These results are promising for the use of SIP films for interfacial crosslinking applications.
Conclusions

Three dimensional integration (3DI) is the latest advance in packaging technology. One of the most important aspects of implementing 3DI is developing new bonding methods to most efficiently create wafer stacks with through silicon via (TSV) interconnects. Interfacial crosslinking is one potential method that would facilitate copper-copper bonding to create TSVs while still providing mechanical stability using surface initiated polymerization (SIP) films on silicon regions.

In this research, deposition time and temperatures were investigated to determine effects on the films’ characteristics. Thin film deposition was achieved for several organosilane films, as well as SIP deposition of 2-ethylcyanoacrylate films. Films were analyzed using variable angle spectroscopic ellipsometry (VASE), X-ray photon spectroscopy (XPS), and atomic force microscopy (AFM). All depositions were verified via XPS and the morphology of the films was determined using AFM.

Organosilane thin film deposition was successful, with one to two monolayer films achieved by varying deposition times and temperatures. Films were relatively uniform with little to no effect on surface roughness.

Large scale deposition of APTMS and 2-ethylcyanoacrylate was investigated using VASE surface mapping. Analysis of films showed non-uniform deposition across the surface of the wafer with a thicker film occurring near the source and a thinner film forming farther away from the source. Further investigation is needed to achieve uniform film formation.

From this research, it can be determined that organosilanes and SIP films are viable reagents for use as interfacial crosslinkers. Further research is required to
determine optimal film characteristics and bonding conditions for future use in bonding applications. The introduction of interfacial crosslinking into 3DI could prevent damage and create more efficient chips.


