Correlation of Surface and Film Chemistry with Mechanical Properties in Interconnects

Ying Zhou*,§, Guanghai Xu§, Tracey Scherban§, Jihperng Leu¶, Grant Kloster¶
and Chih-I Wu¶

§Materials Technology Laboratories, Logic Technology Development, Intel Corporation,
Hillsboro, OR 97124, USA
¶Components Research, Logic Technology Development, Intel Corporation,
Hillsboro, OR 97124, USA

Abstract. As the industry moves towards using low k dielectrics in advanced interconnects, interfacial adhesion and film mechanical properties play increasingly important roles in yield and reliability. Improving these mechanical properties requires a better understanding of the surface, interface and film chemistry. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) was used to examine the surface molecular structure of organosilicate and organic polymer based low k interlayer dielectrics (ILDs). Strong correlations were established between surface group functionality, reactivity of the TiN precursors with the ILDs during Atomic Layer Deposition (ALD), and adhesion between the copper barrier and the ILDs. Hydrogen plasma treatment significantly changed the surface chemical structure of the polymer ILD through hydrogenation. Correspondingly, degradation of barrier/polymer adhesion and thermal stability was observed. For the organosilicate ILD, the modulation of film chemistry, primarily the siloxane structures, corresponds with modulus, hardness, cohesive strength and dielectric constant change. The mechanisms of such a correlation will be discussed.

INTRODUCTION

Integrating low k dielectric materials in advanced interconnects poses unprecedented challenges due to significant differences in film material properties between SiO₂ and low k dielectrics. To provide value added information for the materials integration, there is an increasing need to enhance collaboration between different disciplines of materials characterization. For example, the film bulk chemistry has a significant impact on dielectric constant, modulus, hardness and cohesive strength. Additionally, the surface chemistry influences the surface wetting properties, interface adhesion, and surface reactivity. A molecular-level understanding of low k dielectrics is required to enable the integration of these materials with the complex interactions found in semiconductor manufacturing processes.

Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) [1] is a promising technique for the characterization of interconnects. This technique applies a sub-nanosecond pulse of ions bombarding the surface, ejecting ions from the surface of the material of interest. TOF-SIMS is one of the most surface sensitive analysis techniques, because the majority of the ions are generated from the top 5-10Å. Due to the very low dose of incoming ions used in “static” mode, molecular fragments can be detected. The combination of surface sensitivity and molecular specificity provides powerful insight to the surface functional groups. By adding a second ion beam with substantially higher current for depth profiling, TOF-SIMS also can provide the elemental distribution gradient in the film. The depth profile complements bulk chemical analysis techniques such as FTIR and solid state NMR.

In this work, we will discuss the impact of film and surface chemistry on atomic layer deposition (ALD) nucleation activity, barrier/ILD interfacial adhesion, and ILD mechanical properties. An organosilicate and a polymer are discussed as examples of two distinctly different ILD materials. The results clearly demonstrate the need for a greater understanding of material surface and film chemistries as the complexity of interconnects continues to increase.

EXPERIMENTAL

Time of Secondary Ion mass spectra were collected on a Cameca ION-TOF 300mm spectrometer. The
analysis ion beam was a 25keV Ga beam with a 600ps pulse width @ 1pA current. The mass resolution was >10,000 at 100 amu with a reflectron type analyzer. The depth profile was accomplished with a pulsed Cs ion beam at 1KeV@10nA rastering larger than analysis areas between the analysis cycles. Temperature dependent TOF-SIMS was carried out in a sample preparation chamber with a vacuum of 1E-7 torr.

FTIR data were collected on a Nicolet Magna-IR 860 spectrometer (32 scans averaged, 4 cm⁻¹ resolution), using transmission mode. In order to reduce effects due to film thickness variations, peak area ratios are reported using the Si-O peak area as a denominator in all cases.

The interfacial adhesion was obtained with a 4-point bend method described elsewhere [2]. Hardness and elastic modulus data were collected using an MTS NanoXP nanoindenter with a Berkovich diamond tip. Fifteen indents, spaced at 100 µm, were made on each sample. Samples were loaded in continuous stiffness mode. The hardness and modulus were calculated using a contact depth range of 200-400 nm for hardness and 50-150 nm for modulus to avoid substrate interactions. A Poisson’s ratio of 0.25 was assumed.

RESULTS AND DISCUSSION

(1) Surface Chemistry on Atomic Layer Deposition (ALD) Activity

While the adhesion of Cu barrier to ILD is controlled by many parameters [3], the initial reactivity between the barrier precursor and ILD during atomic layer deposition can shed some light on the bonding information of the metals to the ILD. We have examined the ALD activity on two representative low k ILDs: a CVD organosilicate and a polymer. Figure 1 shows a positive ion mass spectrum of the CVD organosilicate. The spectrum resembles that of siloxanes [4]. The dominant fragments are Si and SiCH₃. In addition, di- and tri-methyl silane fragments Si(CH₃)₂ and Si(CH₃)₃ are presented as well, indicating various bonding configuration of Si. This was confirmed by solid state NMR. At higher mass range (Figure 2), siloxane polymer fragments are prominent.

In contrast to the spectrum of an oxide (Figure 3) which shows dominant SiOH signal, the SiOH ion intensity is substantially weaker than SiCH₃ in the spectrum of the CVD organosilicate (Figure 1), indicating the majority of the Si on the surface is terminated by CH₃ with little oxide exposed. Due to the lack of polar functional groups like SiOH on the surface, the organosilicate film is hydrophobic. When the surface was exposed to ALD TiN precursor

![Figure 1. A positive ion mass spectrum of the CVD organosilicate in the low mass range.](image1)

![Figure 2. A positive ion mass spectrum of the CVD organosilicate in the high mass range.](image2)

![Figure 3. A positive ion mass spectrum of an oxide.](image3)
sensitivity of ppm for Ti, the Ti signal was relatively weak as shown in Figure 4. In contrast, TiCl$_4$/NH$_3$ reacted readily on an oxide, generating 50Å TiN with the same number of deposition cycles, as is shown in Figure 5. This difference can be summarized by the following equations:

\[
\begin{align*}
\text{TiCl}_4 + \text{Si-OH} & \rightarrow \text{Cl}_x\text{Ti-O-Si} + \text{HCl} \quad (1) \\
\text{TiCl}_4 + \text{Si-CH}_3 & \rightarrow \text{No reaction} \quad (2)
\end{align*}
\]

Si-CH$_3$ does not react with TiCl$_4$ like SiOH, as C-H bond is covalent and significantly more stable than O-H bond in the SiOH.

For the polymer ILD, the positive ion mass spectrum shows fragmentation patterns that can be summarized with a formula C$_m$H$_n$, where m/n ratio is substantially less than 1 (Figure 6). For example, the dominant peaks for fragments containing 4 carbon atoms are C$_4$H$_2$ (50amu) and C$_4$H$_3$(51amu), rather than the alkane peaks of C$_4$H$_7$(55amu) and C$_4$H$_9$(57amu). In the higher mass range, polymer fragments with the general formula C$_n$H$_{(1-3)}$ dominate the spectrum. The fragmentation pattern observed on the polymer ILD is representative of aromatic polymers [4].

Some siloxane related fragments were observed in the TOF-SIMS spectrum as well (Figure 6). However, XPS detected less than 1at% Si on the surface. Therefore, these species will not have measurable impact on the surface chemistry and will not be discussed further.

Unlike the CVD organosilicate, a significant amount of Ti nucleation on the polymer ILD film without any surface modification was observed during ALD of TiN (Figure 7). In this case, the nucleation...
mechanism is different from the one depicted in equation (1). Instead, the likely reaction pathway between TiCl$_4$ and the polymer is through coordination of d orbitals of Ti with the π electrons of the aromatic rings. Coordination of d orbitals with π electrons is a fairly common mechanism for forming organometallics between transition metals and aromatics. A textbook example is Cr(η$_6^-$-C$_6$H$_6$)$_2$ in which all six π electrons are shared with the metal(Cr) [6].

![Figure 7. A positive ion mass spectrum of ALD TiN on the polymer ILD.](image)

(2) Adhesion between barrier and polymer ILD

The examples discussed in section (1) illustrate that surface chemistry plays a key role in initial deposition and bonding of the barrier to ILDs. The bonding strength between barrier and the ILD is also directly reflected in the adhesion strength. The model of interaction between Ti and the aromatic polymer appears to be applicable to CVD barriers as well. 4-point bend measured that the adhesion between a CVD Ti based barrier and the polymer was in the range of 40 J/m$^2$ (Figure 8), substantially higher than that on SiO$_2$. The film remained intact through various torture tests including thermal anneal and CMP. However, the barrier on H$_2$ plasma pretreated polymer showed measurable adhesion degradation, reducing adhesion strength from 40 J/m$^2$ to 20 J/m$^2$ (Figure 8).

The mechanism of this adhesion degradation can be explained by the chemical structure change induced by H$_2$ plasma as shown in Figure 9. For various fragment lengths, the dominant peaks shifted from C$_n$H$_{13}$ to C$_4$H$_7$ upon H$_2$ plasma treatment. This shift indicates increased H content in the hydrocarbon.

![Figure 8. Adhesion between Cu barrier and the polymer ILD.](image)

![Figure 9. A positive ion mass spectrum of H$_2$ plasma treated polymer ILD.](image)

![Figure 10. Reaction pathways of aromatics during hydrogenation.](image)

There are many possible hydrogenation pathways, such as hydrogenating aromatics into cyclic alkanes/alkenes, opening rings into linear alkanes/alkenes, and fragmenting longer carbon chains (hydrogenolysis) as depicted in figure 10. While it is not possible to separate these reaction pathways unambiguously from the mass spectra, the data conclusively show that H$_2$ plasma reduced the surface aromatic structures.
The change of film chemistry has several potential consequences. First, the reactivity between the metals and alkanes is substantially lower. We can use ALD of TiN on the CVD organosilicate as an example. The CH3 in Si-CH3 is fairly stable in terms of reactivity toward metals, similar to that of CH3 in alkanes CH2-(CH2)n-CH3. Elevated reaction temperature or plasma condition would be needed to initiate the bonding formation. Second, the transition metal bonding with the aromatic ring π electrons that existed on untreated polymer is changed to sigma bonding with alkanes, reducing the coordination number of C to Ti. In addition, hydrogenation could reduce crosslinking in the polymer film by breaking some of the bonds (hydrogenolysis), thereby degrading cohesive strength of the ILD in the modified region. The combination of all these effects might explain the degraded adhesion between the barrier and the polymer upon H2 plasma treatment.

The adhesion was degraded even more drastically at elevated temperatures on H2 plasma treated polymer. While the barrier/ILD interface remained intact after a 400C anneal on polymer films that were not exposed to plasma, delamination was observed on H2 plasma treated films. Temperature dependent TOF-SIMS (Figure 11) clearly detected that the ratio between aromatics and alkanes/alkene increased significantly upon annealing at 300C, moving toward the structure of an untreated film. The increased ratio indicates decomposition and desorption of the hydrogenated species, transforming the surface back to the original film structure. The reduced crosslinking, molecular weight, and bond strength between the C atoms likely account for the poorer thermal stability of the treated film. Further support for this model is found in the fact that delamination was reduced or eliminated by annealing the H2 plasma treated film to 200-400C prior to barrier deposition.

(3) The correlation between film chemistry of the organosilicates and mechanical properties

Generally, the parameters impacting dielectric constant and mechanical strength not only include chemical structure, but also porosity. Using the CVD organosilicate as an example, we have examined the relationship between the film chemistry and mechanical properties as well dielectric constant.

Figure 11. Impact of thermal anneal on H2 plasma treated polymer.

Figure 12. Correlation between hardness and SiCH3 in the CVD organosilicate.

Figure 13. Correlation between elastic modulus and SiCH3 in the CVD organosilicate.

Figures 12 and 13 show that the higher level of SiCH3 measured in FTIR directly correlates with lower modulus and hardness. Since the modulus
correlates linearly with cohesive strength for the CVD organosilicate [7], a higher SiCH$_3$ concentration correspondingly correlates to a lower cohesive strength. This is because that Si-CH$_3$ represents a terminal group as opposed to a bridging Si-O group. Therefore it does not contribute to the overall bond strength or cohesive strength. Replacement of Si-CH$_3$ by Si-O increases the crosslinking between Si atoms as an O atom connects between Si atoms, thus increasing the mechanical strength and film density as expected. However, the Si-O bond is more polar and also prone to moisture absorption, contributing to k increase at lower SiCH$_3$/SiO ratios as shown in Figure 14.

When the organosilicate is subjected to various chemical or beam treatments, chemistry changes of the film can be detected with TOF-SIMS depth profiling. Figure 15 shows a depth profile of the organosilicate post e-beam treatment with varying energy. C depletion through e-beam induced decomposition of Si-CH$_3$ structure was observed. The depth of the C depletion strongly depended on the beam energy. Consistent with the mechanism discussed above, modulus and hardness increased as the C reduced in the film (Table 1). However, the dielectric constant generally increases as well. Therefore, the challenge for low k organosilicate lies in improving mechanical properties without degrading the dielectric constant significantly.

Table 1. The impact of E-beam treatment on elastic modulus and hardness of the CVD organosilicate

<table>
<thead>
<tr>
<th>Treatment Conditions</th>
<th>Elastic Modulus (GPa)</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>9.9 ± 0.1</td>
<td>1.8 ± 0.1</td>
</tr>
<tr>
<td>UV-treated</td>
<td>8.5 ± 0.9</td>
<td>1.7 ± 0.1</td>
</tr>
<tr>
<td>e-beam treated 8 keV</td>
<td>22.8 ± 0.4</td>
<td>3.1 ± 0.1</td>
</tr>
<tr>
<td>e-beam treated 3 keV</td>
<td>12.8 ± 0.4</td>
<td>1.9 ± 0.1</td>
</tr>
</tbody>
</table>

CONCLUSIONS

We have demonstrated that the reactivity of TiCl$_3$/NH$_3$ with the ILDs strongly depends on the surface chemistry during ALD of TiN. Ti does not nucleate on the organosilicate with Si-CH$_3$ terminated surface unless it is converted to oxide. The reaction of TiCl$_4$ with aromatic polymers has a distinctly different reaction pathway, possibly through coordination of Ti with the π electrons in aromatics. H$_2$ plasma converted the aromatic structure into alkanes/alkenes, leading to degraded adhesion between barrier and polymer ILD and thermal stability. The mechanical properties of the organosilicate such as modulus, hardness and cohesive strength were found to strongly depend on the film chemistry. Converting SiCH$_3$ into oxides through various chemical or energetic beam treatment improves the mechanical strength generally at the expense of increasing dielectric constant. These results demonstrate the criticality of understanding interface and film chemistry during integration of low k ILDs in advanced interconnects.
REFERENCES


