Interdiffusions and Reactions in Cu/TiN/Ti/Thermal SiO₂ and Cu/TiN/Ti/Hydrogen Silsesquioxane Multilayer Structures

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The continuous down-scaling of device dimensions in integrated circuits produces several problems for circuit operation, such as the rapid increase of interconnect resistance-capacitance (RC) delay. To reduce the RC delay, copper will substitute for aluminum to be the new conduction material because of its lower electrical resistivity; on the other hand, replacement of SiO₂ with low dielectric constant (\(k < 3.9\)) materials as the intermetal dielectrics is also indispensable. Hydrogen silsesquioxane (HSQ) produced by a spin-on method has been one of the promising new dielectric materials because of its good local planarity and excellent gap filling ability. It is based on caged oligomers with the general formula of \(\text{HSiO}_{(2)}\text{SiO}_{2}\). The caged oligomers are interlinked to form a porous network structure during a suitable curing process, and the dielectric constant of cured HSQ could be down to about 2.7.

There are two major drawbacks when copper is used as the interconnection metal. First, copper lacks adhesion to SiO₂ or most insulating materials. Second, copper is a fast diffusion species in Si, as well as in SiO₂. Because of the porous characteristics of HSQ films and many other low dielectric constant materials, it is foreseeable that copper will diffuse rapidly into HSQ or other porous low-\(k\) materials. Our latest research work is on interfacial reactions of Cu/HSQ deposited on silicon indicates that the Cu layer was transformed to copper oxides after vacuum annealing at elevated temperatures. The oxidation of Cu shall be related with the decomposition of HSQ at high temperatures, as well as the expedient Cu diffusion process due to the porous structure of HSQ.

Therefore, in order to integrate copper with low-\(k\) dielectric materials, it is necessary to implement an adhesion promoter plus a diffusion barrier between copper and dielectric layers. Good adhesion promoter requires not only mechanical bonding but also some chemical interactions with copper and dielectric materials. Titanium-based materials are the most frequently used adhesion promoter layer because of the excellent chemical reactivity of titanium. As for diffusion barrier, TiN is the most popular barrier for Al metallization and has been studied as diffusion barriers for the copper directly contacting with silicon, as well as for copper on SiO₂.

In this study, we investigate the thermal reactions of the multilayer structures, Cu/TiN/Ti/SiO₂ (thermally grown)/(Si) and Cu/TiN/Ti/HSQ/(Si). The symbol (Si) represents the single-crystalline silicon substrate. The samples were fabricated and then annealed in vacuum from 400 to 800°C. The material characteristics of these samples were analyzed using various analysis methods and the interdiffusion/reaction behaviors of the multilayer stacks are discussed.

**Experimental**

Phosphorus-doped n-type silicon (100) wafers were used as the substrates in this study. The wafers were degreased in organic baths and chemically etched with dilute HF solution (HF:H₂O = 1:20) to remove native oxide. The HSQ films, 600 nm in thickness, were fabricated by spin coating Dow Corning Flowable Oxide (FOx-15) on the clean silicon wafers. After spin coating, the samples were baked at 200°C for 2 min and cured at 400°C in N₂ atmosphere. The curing temperature is selected to make sure that HSQ transforms to an appropriate network structure. Thermal SiO₂ 450 nm thick was grown by oxidizing Si wafers in dry oxygen at 1050°C. Ti and TiN layers were deposited by radio frequency (rf) sputtering from a Ti metal (99.95% purity) target and at a negative substrate bias 100 V. The sputtering atmosphere for Ti and TiN were pure Ar, and 80% Ar + 20% N₂ mixture, respectively. Copper films were prepared by sputtering a Cu metal (99.99% purity) target, at a dc power of 100 W and a negative substrate bias 100 V. The thicknesses of Ti, TiN, and Cu films are 10, 50, and 180 nm, respectively. The two groups of samples, Cu/TiN/Ti/SiO₂/(Si) and Cu/TiN/Ti/HSQ/(Si), were annealed in vacuum (together with Ti foils to reduce residual oxygen) at temperatures ranging from 400 to 800°C, with an interval of 100°C, at 2 × 10⁻² Torr for 1 h.

The sheet resistance of all samples, before and after annealing, was measured with a four-point probe. Surface morphology of the samples was characterized using scanning electron microscopy (SEM, Philips XL-40FEG). The characteristic phases were identified using glancing incident angle X-ray diffraction (GIXRD, MacScience MXP18) with Cu Kα radiation at an incident angle of 2°. Compositional depth profile analysis was performed with Auger electron spectrometry (AES, VG AES-310D). Because of the overlapping of Ti(LMM) and N(KLL) Auger transition lines near 385 eV, the profiles labeled as Ti + N were deduced from the signal at 385 eV, and the profiles labeled as Ti were deduced from the signal at 420 eV.

**Results**

Sheet resistance measurements.—All samples before and after annealing were characterized with four-point probe sheet resistance measurements. The sheet resistance may represent the degree of mixing at the interfaces, as well as the structural and/or compositional change of the layers. Figure 1 gives the sheet resistances of both groups of samples as a function of annealing temperature. For
both systems, the sheet resistance decreased with increasing temperature after annealing at 400-600°C, and began to increase after annealing at 700°C. After annealing at 800°C, the surface color of the Cu/TiN/Ti/HSQ/(Si) sample changed from the metallic Cu color (reddish-yellow) to silver gray, in some regions. The fraction of the color-changed area is around 25%. A small sheet resistance value (~170 mΩ) was obtained from the Cu-color area, while a large sheet resistance value (~1900 mΩ) was measured by probing the gray area. The surface of the 800°C annealed Cu/TiN/Ti/SiO₂/(Si) sample also exhibited some gray dots. However, these dots were very tiny and scattered. The measured sheet resistance values were uniform (~133 mΩ in average) all over the SiO₂ sample. Details of the gray-area morphology can be seen from SEM micrographs presented in the next section.

Surface microstructures.—Figure 2 presents the SEM micrographs on the surfaces of the as-deposited Cu/TiN/Ti/SiO₂/(Si) and Cu/TiN/Ti/HSQ/(Si) samples. Small nodules appeared on the surfaces and each nodule may correspond to one or several Cu grains. Therefore, the as-deposited Cu grain size shall be equal to or smaller than the nodule size. Figure 3 shows the surfaces of the 700°C annealed SiO₂ and HSQ samples. After annealing, the Cu grain boundaries became clear for SEM observation because of the thermal etching effect (grain boundary grooving during heat treatment), and the Cu grains had grown in size (largest at 700°C).

For both systems, the surface morphology of the 700°C annealed sample did not change significantly from that of the 600°C annealed sample (except for the grain growth). The increase of sheet resistance upon annealing at 700°C is thus not associated with the morphology of Cu films, but related with the reactions occurred in the inner layers of the samples.

Figure 4 shows the surface morphologies of Cu/TiN/Ti/SiO₂/(Si) and Cu/TiN/Ti/HSQ/(Si) samples after annealing at 800°C. As mentioned in the previous section, the surfaces of both 800°C annealed samples consisted of Cu-color area and gray area. The morphologies of the Cu-color regions are shown in Fig. 4a and b. Microvoids were witnessed on the Cu-color surfaces of both samples but the voids are in more number and larger sizes for the Cu/TiN/Ti/HSQ/(Si) sample. Formation of microvoids had also been observed by Rha et al. for the Cu/TiN/Ti/SiO₂ structure after annealing at 650°C for 2 h in a H₂ + Ar atmosphere.

Figure 4c and d shows the typical morphologies of gray regions in the 800°C annealed Cu/TiN/Ti/SiO₂/(Si) and Cu/TiN/Ti/HSQ/(Si) samples, respectively. The gray regions are basically circular dots for both systems. The gray dots in the HSQ sample have sizes ranging from 300 to 1500 μm in diam and there may be several dots connected to a large patch. On the contrary, the sizes of gray dots in the SiO₂ sample range from 30 to 500 μm in diam and the dots are scattered distributed (~70 dots/cm²). It implies that the reaction is much more extensive in the HSQ sample than in the SiO₂ sample.

Inside the gray dots of the Cu/TiN/Ti/SiO₂/(Si) sample, a rectangular crystallite had developed at the dot center, while the gray dots in the Cu/TiN/Ti/HSQ/(Si) sample exhibit dendritic structures, radiating from the center. We had observed similar rectangular crystallites in the 800°C/30 min annealed Cu/TiB₂/(Si) structure, and similar dendritic structures were reported by Wang et al. in the 950°C/30 s annealed Cu/TiN/(Si) structure. The rectangular crystallites and the dendritic structures in Ref. 12 and 17 were both identified to be Cu₃Si phase and they originated from the reaction of Cu with the Si substrate. It is thus possible that the gray dots seen in the current study may also contain Cu₃Si and represent severe reactions of the top Cu layers with the Si substrates.

Phase analyses.—GIAXRD spectra of 2° glancing incident angle for both groups of samples, before and after annealing at 600-800°C,
are shown in Fig. 5. Figure 5a shows that the major phases were the same (Cu and TiN) for the as-deposited and 600-800°C annealed Cu/TiN/Ti/SiO₂/(Si) samples. Although there were scattered gray dots appeared on the 800°C annealed SiO₂ sample, the degree of reaction was not high enough to be detected by GIAXRD. For the Cu/TiN/Ti/HSQ/(Si) system, Fig. 5b, the major phases were also Cu and TiN for the as-deposited and 600, 700°C annealed samples. However, in addition to Cu and TiN, a Cu₃Si phase is shown in the 800°C spectrum. The Cu₃Si phase shall be connected with the reaction regions (the large gray dots and patches) of the 800°C annealed Cu/TiN/Ti/HSQ/(Si) sample.

**Compositional analyses.**—Figures 6 and 7 present the AES compositional depth profiles of both systems as deposited and after annealing at 700°C. Without using any standard sample, the atomic concentrations presented here are only semiquantitative. Figure 6 shows that after annealing at 700°C, the O profile had significantly extended into the Ti layer, and slightly into the TiN layer of the Cu/TiN/Ti/SiO₂/(Si) sample. As for the Cu/TiN/Ti/HSQ/(Si) system, Fig. 7 shows that the O profile of the 700°C annealed sample run through the whole TiN-Ti layers, and reached the Cu/TiN interface. The increase of sheet resistance for both systems after annealing at 700°C, therefore is attributed to the “oxygen incorporation” in the TiN-Ti layers, as revealed by the AES depth profiles.

Figure 8 shows the AES depth profiles obtained by probing the “Cu-color” regions of the 800°C annealed Cu/TiN/Ti/SiO₂/(Si) and Cu/TiN/Ti/HSQ/(Si) samples. For both samples, the oxygen concentrations in the TiN-Ti region are significantly high. This high oxygen content shall account for the high sheet resistance values in the Cu-color regions of the 800°C annealed samples. Figure 8b shows that the Cu profile had penetrated into the TiN layer in the 800°C annealed HSQ sample. In addition, the Ti, N, and O signals were
detected on the sample surfaces for both systems. This implies that the TiN layer (incorporated with oxygen) may be exposed to the surface within the microvoids (Fig. 4a and b), so that Ti, N, and O signals were detected on the surfaces.

When we probed the gray area of the 800°C annealed Cu/TiN/Ti/SiO₂/⁺Si and Cu/TiN/Ti/HSQ/⁺Si samples, the AES depth profiles showed severe intermixing of Cu, Ti, N, O, and Si signals all over the depth. The original multiplayer structures thus had disappeared in the gray area. The chemical composition on the selected regions marked by A, B, C, D in the SEM micrographs of Fig. 4c and d of the gray dots was further investigated by AES spot analysis (beam size = 300 nm in diam). The atomic concentrations (semi-quantitative) of Cu, Si, Ti + N, and O for each region are listed in Table I. Despite of the different morphologies, the center regions of gray dots, for both systems, are rich in Cu and Si. Away from the center, the Cu and Si concentrations decrease and the Ti + N concentration increases. The result indicates that the brightly contrasted materials, either rectangular crystallite or radiated dendritic structure, are compounds mainly consisting of Cu and Si. This compound is most likely Cu₂Si as revealed by the GIAXRD spectrum of the 800°C annealed Cu/TiN/Ti/HSQ/⁺Si sample. The Cu₂Si phase was not detected in the 800°C annealed Cu/TiN/Ti/SiO₂/⁺Si sample because the amount of the reaction product was too low to be observed.

**Discussion**

In our previous study on the thermal reactions of Cu/SiO₂ and Cu/HSQ systems,¹⁰ the sheet resistance of the Cu/HSQ sample began to increase after annealing at 500°C and the Cu layer was fully oxidized after annealing at 700°C. Therefore, the TiN/Ti layers are effective in improving the thermal stability of the Cu-HSQ system. The increase in sheet resistance of Cu/TiN/Ti/SiO₂/⁺Si and Cu/ TiN/Ti/HSQ/⁺Si systems after annealing at 700-800°C is a result of oxygen penetration into the TiN/Ti layers (see Fig. 6-8), which prevails over the effect of decreasing resistance by the grain growth or defect annihilation of the copper film.

It was reported that for the Ti/SiO₂,¹⁸ and Ti/HSQ¹⁹ systems, liberated oxygen atoms (from SiO₂ or HSQ) would diffuse into Ti during annealing and the final products were TiO and Ti₅Si₃. Although we did not observe the formation of TiO and Ti₅Si₃, the AES profiles (Fig. 6 to 8) clearly indicate the mixing of Ti with O, and possibly with Si as well, at the Ti/SiO₂ and Ti/HSQ interfaces after annealing at 700-800°C. These two phases may be too scarce to be detected because the thickness of the Ti layer is only 10 nm. By comparing the oxygen profiles in Fig. 6b and 7b, we also observed that the out-diffusion of oxygen proceeded further in the HSQ sample than in the SiO₂ sample. It is reasonable because HSQ is thermally unstable and undergoes redistribution reactions, which will produce some reactive intermediate products at temperatures higher than 350°C. Since the out-diffused oxygen atoms were also seen in the TiN layer, a barrier which is oxidation resistant, for example, TaN,²⁰ may be more satisfactory for the copper/low-k dielectrics integration.

After annealing at 800°C, although the Cu-color regions still preserved the multiplayer structures (see AES profiles, Fig. 8), microvoids were shown on the surfaces of both systems (Fig. 4a and b). These microvoids may be associated with the outgassing process.
structures upon annealing. As a result, the voids are in more number to the liberation of oxygen atoms, it was also reported that AES compositional depth profiles obtained from the Cu-color regions of the 800°C annealed (a) Cu/TiN/Ti/HSQ/(Si) and (b) Cu/TiN/Ti/HSQ/(Si) samples.

(i.e., liberation of oxygen) of the bottom dielectric layers. In addition to the liberation of oxygen atoms, it was also reported that significant out-diffusion of hydrogen exists for the barrier/HSQ structures upon annealing. As a result, the voids are in more number and larger sizes on the HSQ sample than on the SiO₂ sample. Furthermore, the penetration of Cu into TiN layer seen in the 800°C annealed Cu/TiN/Ti/HSQ/(Si) sample (Fig. 8b) also suggests that the outgassing process of HSQ may generate defects in the TiN layer, and those defects will facilitate the diffusion of Cu into TiN.

As noted, severe reactions in the samples. These gray dots have two characteristics: first, they were developed locally; second, they contained high Cu + Si contents at the center. These two characteristics are similar to the failure of Cu/HSQ metallization system with TiN barriers, where the formation of the failure dots was attributed to the interdiffusion of Cu and Si through some major defects in the TiN film. Mallikarjunan et al. reported that dielectric films exhibited significant leakage currents because there were "pinhole-like" defects in the dielectric layers. Therefore, when the defect in the TiN barrier and the defect in the SiO₂ or HSQ layer coincide to form a channel, Cu and/or Si (from the substrate) may diffuse expeditiously through the channel and react. The consequence is the formation of local failure dots (the gray dots) with abundant Cu and Si contents at the center. The center of each failure dot thus corresponds to the origin of the Cu/Si interdiffusion channel.

Similar to the microvoids, the gray failure dots are also larger in size and more in number for the HSQ sample. The porous and strong outgassing characters of HSQ may generate many defect channels so that the Cu-Si interdiffusion was facilitated. However, the characters of defects in the dielectric films, as well as in the barrier layer, are not clear yet at present. Further investigations shall be performed to elucidate this issue. From the above discussion, we may conclude that a diffusion barrier, which is thermally stable, resistant to oxidation and has a low density of defects, will be required for the successful implementation of Cu/low-k interconnection system.

Table I. AES spot compositional analysis on the gray dots of the 800°C annealed Cu/TiN/Ti/HSQ/(Si) samples. Positions of the analyzing regions are marked in Fig. 4c and d.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Position</th>
<th>Cu/TiN/Ti/HSQ/(Si)</th>
<th>Cu/TiN/Ti/HSQ/(Si)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A (center)</td>
<td>B (off-center)</td>
<td>C (center)</td>
</tr>
<tr>
<td>Cu (atom %)</td>
<td>43.5</td>
<td>21.9</td>
<td>41.1</td>
</tr>
<tr>
<td>Si (atom %)</td>
<td>25.9</td>
<td>13.0</td>
<td>41.2</td>
</tr>
<tr>
<td>Ti+N (atom %)</td>
<td>28.3</td>
<td>60.3</td>
<td>5.2</td>
</tr>
<tr>
<td>O (atom %)</td>
<td>2.3</td>
<td>4.8</td>
<td>12.5</td>
</tr>
</tbody>
</table>

Figure 8. AES compositional depth profiles obtained from the Cu-color regions of the 800°C annealed (a) Cu/TiN/Ti/HSO₂/(Si) and (b) Cu/TiN/Ti/HSQ/(Si) samples.

Conclusions

Thermal stabilities of Cu/TiN/Ti/SiO₂/(Si) and Cu/TiN/Ti/HSQ/(Si) multilayer structures were comparatively studied upon annealing at 400-800°C. The sheet resistance values of both systems decreased after annealing up to 600°C, and slightly increased after annealing at 700°C because of oxygen incorporation into the TiN-Ti layers. After annealing at 800°C, large gray failure dots formed on the HSQ sample surface and sheet resistance in the gray region increased substantially, while the sheet resistance of the SiO₂ sample only increased a little. Formation of the failure dots is attributed to the Cu-Si interdiffusion through the microstructural defects present in the dielectric layer, as well as in the barrier layer. The TiN-Ti layer therefore should be a sufficient barrier for preventing the Cu/HSQ interaction up to 600°C. However, a thin film, which is resistant to oxidation and has a low density of defects, will be a more robust diffusion barrier for the Cu/low-k interconnection system.

Acknowledgments

The authors acknowledge Dow Corning Taiwan, Inc., for providing the HSQ resin solution. Financial support for this work was provided by National Science Council of Taiwan, R.O.C., under contract no. NSC-89-2216-E-006-037.

National Cheng Kung University assisted in meeting the publication costs of this article.

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