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Self-forming Mn-based diffusion barriers on low-k substrates

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In this work, we report on a self-forming barrier process in Cu–Mn alloys. Cu–Mn alloy films were directly deposited onto low-k substrates by co-sputtering and then subjected to an annealing treatment at various temperatures. X-ray diffraction patterns obtained for the Cu–Mn alloys showed Cu(111), Cu(200), and Cu(220) peaks, while transmission electron microscopy images revealed that a uniform Mn-based interlayer self-formed at the Cu–Mn/low-k interface after annealing. In order to evaluate the barrier properties of the Mn-based interlayer, thermal stability measurements were carried out with the low-k dielectrics. The Cu–Mn alloy showed improved thermal stability when compared to a pure Cu reference sample. The chemical composition of the self-formed interlayers on the low-k substrates was ultimately investigated by X-ray photoelectron spectroscopy analysis. Our results show that the composition of the self-formed interlayers depends on the oxide and carbon concentrations in the low-k material. © 2014 The Japan Society of Applied Physics

1. Introduction

As the width of Cu wires is reduced to the sub-micron scale in ultralarge-scale integrated (ULSI) devices, large resistance–capacitance (RC) delays become a critical issue.1–4) Below a dimension of 20 nm, the electrical conductivity of a Cu metal wire is lower than that of bulk Cu due to increased electron scattering. In addition to the dimensional effects of the Cu interconnect, the conductive diffusion barrier, which is adopted to prevent Cu atoms from penetrating into the dielectric trenches, also contributes to the total electrical resistance (R) of the interconnect line. The technique currently used in the industry, which utilizes a Ta/TaN stack produced by physical vapor deposition (PVD), is reaching its limit as a copper diffusion barrier in advanced back-end of the line (BEOL) interconnect technology.3–7) Various methods have been reported to reduce the electrical resistance of the Cu interconnect by fabricating a thin barrier layer.8–13) One such technique involves the preparation of thin barrier layers in Cu alloy films through annealing at elevated temperature.12–19) These layers are formed after the segregation of the metallic solutes and their subsequent reaction with the underlying oxide dielectric layers. Eventually, the layers act as a barrier, adhesion promoter, reliability enhancer, and oxidation retardant. However, two major problems have prevented the widespread adoption of this method. Firstly, oxide formation serves to reduce the dielectric layer, which in turn leads to the migration of Si atoms to the Cu interconnect.20) Secondly, the alloying element that is not involved in the oxidation reaction tends to remain in the Cu interconnect.21) Both cases lead to a notable increase in the resistivity.

Recently, Koike et al. reported on the self-forming barrier process for Cu–Mn alloys.14) The reaction layer formed between the alloy film and the dielectric was only 3–4 nm thick after annealing at 450 °C for 30 min. Because of the large activity coefficient of Mn in Cu, any residual Mn present after annealing could be removed from the alloy film to form a surface oxide layer. As a result, a significant decrease in the film resistivity was observed. Furthermore, several transmission electron microscopy (TEM) studies have shown that thin (2–3 nm) Mn silicate layers act as effective barriers to Cu, O, and H2O diffusion. Promising electrical characteristics have also been reported from capacitance measurements performed on Cu interconnects.22,23) However, comparatively few studies have focused on the interfacial chemistry and thermal stability of the chemical species present at the Mn/low-k dielectric interface.

In the present study, we deposited Cu–Mn alloy films on various low-k substrates and investigated the properties of the Mn-based self-formed barriers at the interfaces between the alloy films and dielectric substrates. The microstructure and composition of the Mn-based self-formed barriers were examined after a copper reverse plating process via TEM and X-ray photoelectron spectroscopy (XPS), respectively. The electrical properties of the annealed Cu–Mn alloy films prepared on the dielectric substrates were also investigated. Based on the obtained results, an optimized fabrication process for the self-formation of a Mn-based interface layer is proposed.

2. Experimental procedure

First, the low-k SiO2/Cy/Si substrates (denoted here as low-k 1–3) used for the deposition of the Cu–Mn alloy films were prepared (Table I). The dielectric layers were grown on the surface of n-type Si wafers using plasma chemical vapor deposition methods. The dielectric constants, thicknesses, and concentrations of Si, C, and O for all of the grown layers are summarized in Table I. Alloy films of Cu–Mn were deposited directly on the low-k substrates via the simultaneous sputtering of Cu (99.99%) and Mn (99.99%) targets; the distance between the targets and the substrate was ~5 cm.
and the substrate was rotated during the deposition to ensure uniform alloy film coverage. The substrate was heated to 150°C during the deposition to obtain an alloy film with low resistivity. The chamber was evacuated to 1.334 × 10⁻⁸ Pa as a base pressure, and a working pressure of 6.67 × 10⁻¹ Pa was maintained with Ar gas. The RF power densities were 1.38 and 0.91 W cm⁻² on the Cu and alloy targets, respectively. A deposition time of 5 min was employed; the resulting thickness of the Cu–Mn alloy thin films was approximately 50 nm. The composition of the Cu–Mn alloy films was Cu–7.6 at. % Mn. Following the deposition of the films, the samples were heat-treated in a separate annealing chamber under a base pressure of 4.00 × 10⁻¹ Pa. Annealing was performed in vacuum at various temperatures up to 400°C for 1 h. Analysis with high-resolution X-ray diffraction (XRD; Rigaku D/max-2500/pc, Cu Kα 1.54062 nm) was employed to examine the crystal structure of the deposited thin films. The film and self-formed interlayer thicknesses, both before and after annealing, were analyzed via TEM (JEOL JEM-2100F, operating voltage: 200 kV). A Cu reverse plating process was used to remove the top Cu film and expose the self-formed layer. This process ensured that the self-formed layer was intact and remained in its as-formed state for analysis. The chemical states of the self-formed layer were examined by XPS (Thermo Fisher) for analysis. The chemical states of the self-formed layer were intact and remained in its as-formed state for analysis.

The additive Mn atoms in the as-deposited specimens is referred to as the variation percentage of sheet resistance (ΔRₛ/Rs%); this may be expressed as follows:25,26)

\[
\frac{\Delta R_s}{R_s} = \frac{R_{s,after-annal} - R_{s,as-deposited}}{R_{s,as-deposited}} \times 100\%.
\]

Figure 2 shows the values of ΔRₛ/Rₛ% versus annealing temperature for the Cu–Mn alloy/low-k/Si samples. Cu diffuses quite rapidly in Si and forms Cu–Si compounds at a low temperature (near 200°C). This results in an increase in the Cu film sheet resistance.25 The variation percentage of the sheet resistance of the Cu–Mn alloy films decreased significantly after annealing due to grain growth and the segregation of Mn atoms at the film surfaces and Cu–Mn alloy/dielectric interfaces. This is consistent with the XRD findings displayed in Fig. 1. When compared to the annealed Cu–Mn alloy on low-k 1, the variation percentage of the sheet resistance of the annealed Cu–Mn alloy films on

Fig. 1. (Color online) XRD patterns of Cu–Mn alloy/low-k 1/Si samples annealed at various temperatures for 1 h.

Fig. 2. (Color online) Sheet resistance variations of Cu–Mn alloy/low-k/Si samples as a function of annealing temperature.

3. Results and discussion

Figure 1 shows the XRD patterns obtained for the Cu–7.6 at. % Mn alloy/low-k 1/Si samples annealed at different temperatures for 1 h. The intensity of the Cu(111), Cu(200), and Cu(220) peaks increases with increasing annealing temperature, indicating copper grain growth during the annealing process. The additive Mn atoms in the as-deposited Cu–Mn alloy/low-k 1/Si sample may have segregated to the Cu–Mn/low-k interface during annealing. Thus, no Cu–Mn intermetallic compound is detected. In addition, no other peak besides the Cu peak is observed for the Cu–Mn alloy deposited on the low-k 1 substrate after heat treatment. Under severe annealing conditions, a failed Cu barrier allows for the diffusion of a significant amount of Cu into the dielectric, leading to a detectable Cu₂Si peak.24 Heat treatment at 400°C for 1 h was likely not severe enough to induce the formation of the silicide. The Cu(111) peaks of the Cu–Mn alloy/low-k 1/Si samples annealed at temperatures above 300°C are significantly larger than those of the other specimens. Wong et al. reported that a strong Cu(111) reflection can lead to enhanced adhesion between the Cu seed layer and the diffusion barrier. With this in mind, Cu–Mn alloys that are formed after annealing above 300°C could benefit the performance of Cu interconnects.
low-\(k\) 1 and low-\(k\) 3 is dramatically lower. Such results indicate that the annealed Cu–Mn alloy/low-\(k\) 2 samples may still contain residual Mn or lattice defects that have not been completely eliminated. The trend of decreasing sheet resistance with increasing annealing temperature may be affected by the composition of the dielectric layer.

Because the low-\(k\) samples contain different concentrations of C, Si, and O, the Mn-based interlayers in these samples may consist of different compounds. To more closely examine the Mn-based interlayers, cross-sectional TEM analysis was carried out for the Cu–Mn alloy/low-\(k\)/Si samples after annealing at 300 °C. Figures 3(a)–3(c) show cross-sectional TEM bright-field images of Cu–Mn alloy/low-\(k\) 1, Cu–Mn alloy/low-\(k\) 2, and Cu–Mn alloy/low-\(k\) 3 after annealing at 300 °C for 1 h, respectively. Mn-based interlayers with a thickness of approximately 2 and 3 nm appeared to form on the low-\(k\) 1/Si and low-\(k\) 3/Si substrates, respectively. An interlayer was not detected on the low-\(k\) 2/Si sample by TEM, indicating that the reaction of Mn atoms with low-\(k\) 2 was weaker than with the low-\(k\) 1 and low-\(k\) 3 substrates.

To examine the exact chemical composition of the self-formed barrier layer, we removed the top copper layer from the post-annealed samples by a copper reverse plating process to ensure that the self-formed layer was intact and in its as-formed state. Figures 4(a)–4(c) show the Mn 2p, C 1s, and Si 2p XPS spectra, respectively, of the bare self-formed layer on various low-\(k\) substrates. The Cu–Mn alloy/low-\(k\)/Si samples were annealed at 300 °C for 1 h and then immediately subjected to the copper stripping process. Different XPS spectra were obtained from these three samples. The Mn 2p XPS spectra obtained from the samples all show a peak at 642.0 eV, which is attributed to MnCO\(_3\) or MnSiO\(_3\) [Fig. 4(a)]. This suggests the possibility that two Mn compounds can contribute to the stoichiometry of the Mn-based interlayer. To determine the exact chemical composition of the interlayer, the binding energies of C 1s and Si 2p were investigated [Figs. 4(b) and 4(c)]. MnCO\(_3\) was identified in the C 1s XPS spectra around 286.6 eV, while MnSiO\(_3\) was detected in the Si 2p XPS spectra around 105 eV. According to the XPS findings, the Mn-based interlayer on the low-\(k\) 1 and low-\(k\) 3 substrates has a lower concentration of MnCO\(_3\) than what is observed on low-\(k\) 2. In addition, the Si binding energy for the Mn-based interlayer on the low-\(k\) 1 and low-\(k\) 3 substrates exhibits a larger shift from the Si–O bond (103.0 eV) to the MnSiO\(_3\) bond than what is observed for low-\(k\) 2. Additionally, the Mn-based interlayer on the low-\(k\) 2 substrate shows a larger peak at the MnCO\(_3\) position when compared to the interlayers on low-\(k\) 1 and low-\(k\) 3. As evident in the Si 2p spectra, the amount of shifting from the Si–O bond to the MnSiO\(_3\) bond is insignificant. This indicates that a greater proportion of the chemical composition of the Mn-based interlayer on the low-\(k\) 1 and low-\(k\) 3 samples was MnSiO\(_3\). In contrast, the Mn-based interlayer formed on low-\(k\) 2 consisted mostly of MnCO\(_3\). The formation energy of MnSiO\(_3\) was reported to be larger than that of other Mn compounds (Table II); therefore, the formation of MnSiO\(_3\) is energetically favorable. Note that MnSiO\(_3\) was formed on the low-\(k\) 1 and low-\(k\) 3 samples, while MnCO\(_3\) was formed on the low-\(k\) 2 substrate. Previously, Kohama et al. investigated the interaction between various dielectrics and Cu–Ti alloys. The researchers suggested that the composition of self-formed Ti compounds was determined by the C concentration of the dielectric rather than just the enthalpies of formation. Based on the results of this study, we believe that the C concentration in the low-\(k\) substrates plays an important role in determining the Mn compound present in the self-formed barrier. Based on the C concentration in the dielectric layers (Table I), MnCO\(_3\) would easily form on dielectric layers with a high C concentration. The Mn-based interlayers were formed by the reaction of the Mn atoms with the dielectric layers. Because of the lower formation energy of MnCO\(_3\), compared to MnSiO\(_3\), a weak reaction would be observed on the dielectric with a higher C concentration. This caused weak Mn segregation to the interface between the Cu–Mn alloy and the low-\(k\) samples with a high C concentration. As
a result, the large amount of C in the low-\(k\) 2 may reduce the diffusion rate of Mn in the alloy film. This slower diffusion rate may suppress the formation of the Mn-based interlayer as shown in Fig. 3.

Leakage currents were measured using the MIS structure in order to better understand the effectiveness of the self-formed interlayer against Cu diffusion. The leakage current density results for the Cu–Mn alloy on various low-\(k\) substrates are shown in Fig. 5. Barrier formation was first induced at 300 °C for 1 h. Then, the Cu–Mn alloy/low-\(k\)/Si samples were thermally stressed from room temperature to 550 °C for 12 h. After thermal stressing, the leakage currents of the samples exhibited an immediate increase under a very low electric field. From Fig. 5, we can see that the leakage currents of the Cu–Mn alloy/low-\(k\) 2/Si samples increased drastically when the samples were thermally stressed at 450 °C for 12 h. In contrast, the Cu–Mn alloy/low-\(k\) 1/Si and Cu–Mn alloy/low-\(k\) 3/Si structures exhibited superior thermal stability after the barrier formation process. As revealed by the TEM and XPS analysis, the Cu–Mn alloy on the low-\(k\) 1 and low-\(k\) 3 substrates formed MnSiO\(_3\), which could act as a Cu diffusion barrier. Conversely, the Cu–Mn alloy on the low-\(k\) 2 substrate formed MnCO\(_3\) and exhibited poor thermal stability. This implies that MnCO\(_3\) cannot act as a Cu diffusion barrier. Meanwhile, the leakage current from the Cu–Mn alloy/low-\(k\) 3/Si structure annealed at 550 °C for 12 h is much less than the Cu–Mn alloy/low-\(k\) 1/Si structure annealed at 550 °C for 12 h. This difference is likely caused by the aforementioned variation in the interlayer thicknesses shown in Fig. 3 as well as the higher density of MnSiO\(_3\) in the Mn-based interlayer on the low-\(k\) 3. According to the XPS results in Fig. 4(a), the Mn-based interlayer on the low-\(k\) 3 has a larger concentration of MnSiO\(_3\) or MnCO\(_3\) compared to the Mn-based interlayer on the low-\(k\) 1. As shown in Fig. 4(b), the MnCO\(_3\) concentration of the Mn-based interlayer on the low-\(k\) 1 and low-\(k\) 3 are similar. In addition, the amount of the shift from the Si–O bond to the MnSiO\(_3\) bond is more drastic in the Mn-based interlayer on the low-\(k\) 3. These results indicate that the Mn-based interlayer on the low-\(k\) 3 has a higher concentration of MnSiO\(_3\). As mentioned earlier, due to the lower C concentration of the low-\(k\) 3, a larger part of the Mn-based interlayer on the low-\(k\) 3 was formed by MnSiO\(_3\) (which acts as a Cu diffusion barrier). Therefore, the Cu–Mn alloy/low-\(k\) 3/Si structure would have a better thermal stability than the Cu–Mn alloy/low-\(k\) 1/Si structure.

4. Conclusions

In this work, Mn-based self-formed barriers in Cu–Mn alloy films prepared on low-\(k\) substrates were investigated. The Mn-based self-formed barriers were formed at Cu–Mn alloy/low-\(k\) layer interfaces after a barrier formation process. XPS analysis was used to identify the constituent Mn compounds of the self-formed barrier. The Mn-based self-formed barrier on the low-\(k\) 1 and low-\(k\) 3 substrates consisted mainly of MnSiO\(_3\), while the barrier on the low-\(k\) 2 material consisted primarily of MnCO\(_3\). The composition of the self-formed Mn compounds after annealing was determined by analyzing the C compounds in the dielectrics as well as the enthalpy of formation of the Mn compounds. The ultrathin barrier on the low-\(k\) 1 and low-\(k\) 3 substrates was effective in preventing Cu diffusion and exhibited superior thermal stability when
compared to the self-formed barrier on the low-k 2 material. The leakage currents of the Cu–Mn alloy/low-k 1/Si and Cu–Mn alloy/low-k 3/Si samples, after a barrier formation process at 300 °C for 1 h, were lower compared to the Cu–Mn alloy/low-k 2/Si specimen subjected to the same barrier formation conditions. This indicates that MnCO3 does not act as a Cu diffusion barrier and that the chemical composition of the low-k material is an important consideration when selecting a dielectric for a self-forming barrier. The different reaction mechanisms and electrical properties of the Mn-based self-formed barriers on the various dielectrics could help in the realization of advanced Cu interconnects for the fabrication of ultrathin barrier layers in ULSI Si device applications.

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