Effects of Dielectric-Layer Composition on Growth of Self-Formed Ti-Rich Barrier Layers in Cu(1 at% Ti)/Low-k Samples

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In our previous studies, Ti atoms in Cu(Ti) alloy films were found to segregate at the film surface and the interface between Cu(Ti) alloy films and dielectric layers after annealing in Ar atmosphere at elevated temperatures. Such self-formed Ti-rich interface layers can act as a diffusion barrier layer. This technique was called “self-formation of the diffusion barrier,” which is attractive for the fabrication of ultra-large scale integrated interconnects. In the present study, we investigated the growth of Ti-rich barrier layers in Cu(Ti)/dielectric-layer samples with a low Ti content (1 at%) after annealing in ultra high vacuum (UHV). Ti atoms were found to segregate only to the Cu(Ti)/dielectric-layer interface under annealing in UHV. The microstructures were analyzed by transmission electron microscopy and Rutherford backscattering spectrometry, and correlated with the electrical properties of the Cu(Ti) films. It was concluded that Ti-rich interface layers were formed in all the Cu(Ti)/dielectric-layer samples. The Ti-rich interface layers were identified to consist of TiC or TiSi in addition to Ti oxides. The growth of the Ti-rich interface layers consisting of TiC was faster than those consisting of TiSi. Similarly, the resistivities of Cu(Ti)/dielectric-layer samples in which the TiC formation was observed were quickly reduced and those in which the TiSi formation was observed were gradually reduced. Compositions of the self-formed Ti-rich interface layers were concluded to be determined by the C concentration in the dielectric layers rather than by the enthalpy of formation. The growth of the self-formed Ti-rich interface layers consisting of TiC may be controlled by C diffusion in the Ti-rich interface layer. The composition of the dielectric layers was concluded to play an important role on the growth of the Ti-rich interface layers.

1. Introduction

In ultra-large scale integrated devices, large resistance-capacitance (RC) delay and poor device reliability are critical issues,1) and to reduce the RC delay development of low dielectric interlayers and passivation materials is mandatory.2,3) One of the primary factors for the increase in electrical resistivity of nano-scale Cu wires is the existence of barrier layers which prevent the intermixing of the Cu wires with the surrounding dielectric materials. The resistivity increases due to the barrier layers becoming significantly large with respect to the reduced in-line widths of the Cu wires.4,5) Thus, a fabrication technique to prepare nano-scale Cu wires with ultra thin barrier layers should be developed. To prepare such thin barrier layers in Cu alloy films, new fabrication techniques to form the barrier layers by annealing the Cu alloy films at elevated temperatures were extensively studied.6–11) This technique is conventionally called “self-formation of the barrier layer,” and application of this technique to the fabrication process of Cu interconnects is attractive.

We recently succeeded in forming Ti-rich barrier layers using Cu(Ti) alloy films prepared on SiO2/Si substrates after annealing at 400°C.12–14) In our previous study,15) seven dielectric layers such as low-k1(SiO2-Cy), low-k2, low-k3, low-k4, SiCO, SiCN and SiO2 layers were prepared and thin Ti-rich diffusion barrier layers were found to be formed at the interface between the Cu(Ti) films and the dielectric-layer/Si substrates after annealing at elevated temperatures. The Ti-rich interface layers formed in the Cu(10 at% Ti) alloy films deposited on the dielectric layers after annealing at 500 and 600°C consisted of crystalline TiC or TiSi in addition to amorphous Ti oxides. The primary factor to control composition of the self-formed Ti-rich interface layers was found to be the C concentration in the dielectric layers rather than enthalpy of formation of the Ti compounds (TiC and TiSi).

In the present study, we investigated the growth of Ti-rich interface layers in Cu(Ti)/dielectric-layer samples with a low Ti content (1 at%) after annealing in ultra high vacuum (UHV). Ti atoms were found to segregate only to the Cu(Ti)/dielectric-layer interface under annealing in UHV. The microstructures were analyzed by transmission electron microscopy (TEM) and Rutherford backscattering spectrometry (RBS), and correlated with the electrical properties of the Cu(Ti) films. Based on our present results, the growth of the Ti-rich interface layers in the annealed Cu(Ti)/ dielectric-layer samples is discussed.

2. Experimental Procedures

Low-k/Si, SiCO/Si and SiCN/Si substrates were used for deposition of Cu(Ti) alloy films. Four types of low-k(SiO2-Cy)/Si substrates (which were named here as low-k1–low-k4) were prepared (Table 1). The dielectric layers were grown on (100)-oriented Si wafers using conventional plasma chemical vapor deposition methods. For comparison, th-SiO2/Si substrates (the SiO2 layer was grown on the Si substrate by oxidation) were also grown. The dielectric constants, thicknesses and concentrations of C, O and Si of all the layers grown are summarized in Table 1. Prior to film deposition, the substrates were ultrasonically cleaned with acetone and isopropyl alcohol. The Cu(Ti) alloy films were deposited onto these substrates in a radio frequency magne-
3.1 Ti segregation at the interface between Cu(Ti) films and dielectric layers

In order to investigate the self-formation of the Ti-rich interface layers in Cu(1 at% Ti)/dielectric-layer samples, elemental depth profiles in the samples were obtained by RBS. Figure 1(a) shows the RBS spectrum profiles of the as-deposited Cu(1 at% Ti)/dielectric-layer samples. Before annealing, the Ti edge around channel 230 was detected and the constant intensity continued to the Cu edge around channel 250 in the RBS profile. This indicates that the as-deposited Cu(Ti) film formed a single Cu-Ti solid solution. After annealing at 400°C for 2 hours, Ti peaks around channel 230 were detected in all the samples, indicating Ti segregation at the Cu(Ti)/dielectric-layer interface. Surface segregation of Ti atoms was not observed. Similarly, after annealing at 600°C for 2 hours, Ti segregation was observed only at the Cu(Ti)/dielectric-layer interface. The Ti peak intensity was higher than that found in the samples that were annealed at 400°C. This suggests that the reaction of Ti atoms with the dielectric materials at 600°C was stronger than that at 400°C.

In the previous study, Ti segregation was to occur at the Cu(Ti)/dielectric-layer interface and the Cu(Ti) surface after annealing at Ar atmosphere. In the present study, Ti segregation was observed only at the interface after annealing in UHV. This indicated that the Ti atoms in the Cu(Ti) alloy films diffused only to the interface and reacted with dielectric layers, resulting in the formation of the Ti-rich interface layers.

3.2 Characterization of the self-formed Ti-rich interface layers

The self-formed Ti-rich interface layers were characterized by cross-sectional TEM observation and by a selected area diffraction (SAD) analysis. Figure 2(a) shows a cross-sectional TEM bright field image of the Cu(Ti)/low-k1 samples after annealing at 400°C for 24 hours. An electron incident beam with 200 kV acceleration voltage that was almost parallel to the (110) orientation of the Si substrate was used. An about 40 nm-thick Ti-rich interface layer was formed at the Cu(Ti)/low-k1 interface. A SAD image obtained around the Ti-rich interface layer in the same sample is shown in Fig. 2(b). The many small diffraction points indicate that fine polycrystalline grains were formed in the Ti-rich interface layer. The diffraction points were in good agreement with the diffraction-ring pattern of TiC, indicating that fine TiC polycrystalline grains were formed. Similarly, about 5 nm-thick Ti-rich interface layer was formed at the interface in the Cu(Ti)/SiCO samples after annealing at 400°C for 5 hours (Fig. 2(c)). The many diffraction points observed in Fig. 2(d) were in good agreement with the diffraction-ring pattern of TiC. On the other hand, a very thin Ti-rich interface layer was formed at the interface in the Cu(Ti)/SiO2 samples after annealing at 400°C for 24 hours (Fig. 2(e)). In a SAD image, weak diffraction points were observed in addition to strong diffraction points indicating Cu. The weak diffraction points were in good agreement with the diffraction-ring pattern of TiSi (Fig. 2(f)). Any deviation from the lattice constants of the stoichiometric TiC or TiSi compound was not clear in the present SAD analysis.

Similarly, crystalline phases in the Ti-rich interface layers in the other Cu(Ti)/dielectric-layer samples after annealing...
at 400°C in UHV were identified. From secondary ion mass spectrometry measurements of the annealed samples, penetration of O atoms at the Ti-rich interface layer was observed (data not shown), suggesting that Ti oxides should be also formed at the Ti-rich interface layers. However, the oxides could not be identified by SAD analysis since they were not crystalline. Figure 3 shows schematic illustrations of the microstructure of the Cu(Ti)/dielectric-layer samples after annealing at 400°C in UHV. In addition to formation of amorphous Ti oxides in the Ti-rich interface layers in all the samples, formation of TiC was observed in the Cu(Ti)/low-k1, Cu(Ti)/SiCO and Cu(Ti)/SiCN samples, while formation of TiSi was observed in the Cu(Ti)/SiO2 and Cu(Ti)/low-k4 samples after annealing at 400°C. This is consistent with the previous study.15

3.3 Growth of the self-formed Ti-rich interface layers
The reaction of Ti atoms in the alloy films with the dielectric layers was found to occur in the system containing more than three elements, and thus the self-formed Ti-rich
Interface layer was found to consist of more than two phases. The crystalline phase contained in the self-formed Ti-rich interface layers varied with dielectric layers. We investigated growth of the self-formed Ti-rich interface layers in the Cu(Ti)/low-k\textsubscript{1}, Cu(Ti)/SiCO and Cu(Ti)/SiO\textsubscript{2} samples after annealing at 400°C in UHV. The TiC formation was observed in the former two samples and the TiSi formation was observed in the last samples. Figure 4 shows thicknesses of the Ti-rich interface layers formed in the Cu(Ti)/low-k\textsubscript{1}, Cu(Ti)/SiCO and Cu(Ti)/SiO\textsubscript{2} samples as a function of annealing time. The thicknesses of the Ti-rich interface layers in the Cu(Ti)/low-k\textsubscript{1} samples increased with increasing annealing time and a thickness of about 40 nm was obtained after annealing for 24 hours. The thickness of the Ti-rich interface layers in the Cu(Ti)/low-k\textsubscript{1} samples was almost proportional to square root of annealing time. In general, growth of a layered compound in the thin films can be controlled by both diffusion and interfacial reaction. The thickness of the layered compound is proportional to square root of time for diffusion-controlled growth and is proportional to time for reaction-controlled growth. Thus, for the present case, the growth of the Ti-rich interface layers in the Cu(Ti)/low-k\textsubscript{1} samples after annealing at 400°C was concluded to be mainly controlled by diffusion. The growth of the Ti-rich interface layers was reduced after annealing times of more than 24 hours and a thickness was about 50 nm was found after annealing for 72 hours. This was caused by lack of a Ti source in the Cu(Ti) alloy films. This is consistent with the resistivity approaching a minimum for the Cu(Ti)/low-k\textsubscript{1} samples after annealing for 24 hours (data shown later). The growth of the Ti-rich interface layers reduced the Ti concentration in the Cu(Ti) alloy films, and electrical resistivity of the alloy films was reduced due to the decrease in the impurity scattering.
The growth of the Ti-rich interface layers of the annealed Cu(Ti)/SiO samples was slower than that of the annealed Cu(Ti)/low-k1 samples, although formation of TiC and amorphous Ti oxides in the Ti-rich interface layers was same. The growth of the Ti-rich interface layers of the annealed Cu(Ti)/SiO samples was much slower than that of the Cu(Ti)/low-k1 and Cu(Ti)/SiCO samples. These observations are in good agreement with the electrical resistivity results (data shown later): the lowest electrical resistivities were found in the annealed Cu(Ti)/low-k1 samples and the slower electrical resistivity decrease was found in the annealed Cu(Ti)/SiO samples. The thin layer thickness observed in the annealed Cu(Ti)/SiO samples should be less than the critical thickness that a reaction-controlled growth will change to a diffusion-controlled growth, and thus the growth may be controlled mainly by interface reaction.

3.4 Resistivity decrease as a function of annealing time

Electrical resistivity decreases with growth of the self-formed Ti-rich interface layers due to decreasing impurity scattering of Ti atoms in the alloy films. Figure 5 shows electrical resistivities of the Cu(Ti)/dielectric-layer samples after annealing at 400°C as a function of annealing time. The electrical resistivities of the as-deposited Cu(Ti) alloy films were reduced significantly after annealing, because the Ti atoms in the Cu(Ti) alloy films segregated at the Cu(Ti)/dielectric-layer interfaces after annealing at 400°C. There were two tendencies in the resistivity decrease as a function of annealing time. The resistivities of Cu(Ti)/low-k1, Cu(Ti)/low-k2, Cu(Ti)/SiCO and Cu(Ti)/SiCN samples were quickly reduced to about 5 μΩ⋅cm after annealing for 24 hours and any further significant decrease in resistivity was not observed as shown in Fig. 5(a). The resistivities of Cu(Ti)/SiO2 and Cu(Ti)/low-k4 samples were gradually reduced and continued to be reduced even after annealing for 24 hours as shown in Fig. 5(b). Such the difference of resistivity tendencies was in good agreement with the difference of Ti compound formation (TiSi or TiC) in the Ti-rich interface layers as shown in Fig. 3. The electrical resistivities of the samples where the TiC formation was observed were always lower than those of the annealed samples where the TiSi formation was observed. This suggests that growth of the Ti-rich interface layer consisting of TiC was faster than that consisting of TiSi. The electrical resistivities of Cu(Ti)/low-k1 samples were the lowest in the samples where the TiC formation was observed after annealing. This indicates that the reaction of Ti atoms with low-k1 films was the strongest.

3.5 Determining of Ti compound formation in the Ti-rich interface layers

The enthalpy (−ΔH) of TiC formation of 185 kJ/mol\(^{16}\) was reported to be larger than that of the TiSi formation of 142.8 kJ/mol\(^{17}\) and thus, the TiC formation was energetically favorable compared with the TiSi formation at the interface. However, this cannot explained the TiSi formation in the annealed Cu(Ti)/low-k4 samples. Although the value of −ΔH for TiN formation of 336 kJ/mol\(^{16}\) is larger than that of the TiC formation, TiC formation was observed in the annealed Cu(Ti)/SiCN samples. Thus, enthalpy of formation does not play an important role in the determining which Ti compound (TiC, TiSi or TiN) would be formed in the self-formed Ti-rich interface layers.

The growth of a single phase of TiC was reported to be controlled by C diffusion in TiC\(^{18}\) and that of TiSi is controlled by Si diffusion.\(^{19}\) The growth lengths at 400°C after 24 hours were estimated to be 5 × 10\(^{-6}\) nm and 59 nm for C in TiC and for Si in TiSi, respectively. Thus, the growth of TiC should be faster than that of TiC. This is not in good agreement with the present result that the growth of the Ti-rich interface layer consisting of TiSi was slower than that of TiC, although the Ti-rich interface layer did not consist of only one phase of either the TiC or TiSi layer.

As we mentioned in the previous study,\(^{15}\) the C concentration in the dielectric layers was believed to play an important role in determining compositions of the self-formed Ti-rich interface layers. Although the Si concentration in the low-k layers is similar, the C concentration of 14 at% in the low-k4 layer is lower than that in the low-k1 (17 at%). The C concentration of about 25 at% in the SiCO and SiCN layers is higher than those in the low-k layers, although the Si concentration is higher than those in the low-k layers. Based on the C concentration in the dielectric layers as listed in Table 1, crystalline TiC should form on the dielectric layers with a C concentration higher than 17 at%. This interpretation in addition to diffusion-controlled growth of the Ti-rich interface layers consisting of TiC and TiC growth controlled by C diffusion in TiC\(^{18}\) suggests that the growth of the self-formed Ti-rich interface layers consisting of TiC may be controlled by C diffusion in the Ti-rich interface layer.

3.6 Dependence of electrical resistivities of Cu(Ti)/dielectric-layer samples on annealing temperature

Figure 6 shows electrical resistivities of Cu(Ti)/dielectric-layer samples after annealing for 2 hours at 400, 500 and 600°C. The electrical resistivities of the Cu(Ti)/low-k1 and
Cu(Ti)/low-k2 samples were linearly reduced with increasing annealing temperature. The reaction of Ti atoms with the low-k1 and low-k2 layers became strong with increasing annealing temperature. The electrical resistivities of the Cu(Ti)/SiCO and Cu(Ti)/SiCN samples were similarly reduced with increasing annealing temperature up to 500°C, but the resistivity decrease from 500°C to 600°C was smaller than those of the annealed Cu(Ti)/low-k1 and Cu(Ti)/low-k2 samples. Although the Ti-rich interface layers formed in the four samples was the same (TiC in addition to Ti oxides), the concentrations of C and Si in the low-k1 and low-k2 layers is different from those in the SiCO and SiCN layers (Table 1). Thus, the different tendencies of resistivity decrease with increasing annealing temperature may be determined by the C and/or Si concentration in the dielectric layers. This is similar to the result in which the formation of TiC or TiSi at the Ti-rich interface layers was determined by the C concentration in the dielectric layers.15)

The resistivity decrease for the annealed Cu(Ti)/low-k3 and Cu(Ti)/low-k4 samples from 400°C to 500°C was smaller than those of Cu(Ti)/low-k1 and Cu(Ti)/low-k2 samples. However, the resistivity decrease from 500°C to 600°C was larger. The small resistivity decrease from 400°C to 500°C in the annealed Cu(Ti)/low-k3 and Cu(Ti)/low-k4 samples could be explained by the slow growth of the Ti-rich interface layers consisting of TiSi. The electrical resistivity decrease with annealing temperature in the annealed Cu(Ti)/SiO2 samples was different from those in the annealed Cu(Ti)/low-k3 and Cu(Ti)/low-k4 samples.

Although the self-formed Ti-rich interface consisted of the same phases, the composition of SiO2 layers was different from that of low-k3 and low-k4 layers. Thus, the composition of the dielectric layers was concluded to play an important role in the growth of the Ti-rich interface layers.

4. Conclusions

The Cu(1 at%Ti) alloy films were deposited on the low-k1-4, SiCO, SiCN and SiO2 dielectric layers in order to understand growth of the Ti-rich interface layers after annealing at 400°C in UHV. Ti-rich layers were formed only at the Cu(Ti)/dielectric-layer interface in all the samples after annealing in UHV at 400, 500 and 600°C. The Ti-rich interface layers were identified to consist of TiC or TiSi in addition to Ti oxides. The TiC formation was observed when the dielectric layers were low-k1, low-k2, SiCO and SiCN, and TiSi formation was observed when the dielectric layers were low-k3, low-k4 and SiO2. The growth of the Ti-rich interface layers consisting of TiC was faster than that consisting of TiSi. The thickness of the Ti-rich interface layers in the Cu(Ti)/low-k1 samples was almost proportional to square root of annealing time, and thus the growth of the Ti-rich interface layers in the Cu(Ti)/low-k1 samples was concluded to be mainly controlled by diffusion. Electrical resistivities were reduced with increasing annealing time in all the samples. The resistivities of Cu(Ti)/dielectric-layer samples in which the formation of TiC was observed were quickly reduced and those in which the formation of TiSi was observed were gradually reduced. These observations are consistent with the growth tendencies of the Ti-rich interface layers. Compositions of the self-formed Ti-rich interface layers were concluded to be determined by C concentration in the dielectric layers rather than enthalpy of formation. The growth of the self-formed Ti-rich interface layers consisting of TiC may be controlled by C diffusion in the Ti-rich interface layer. The composition of the dielectric layers was concluded to play an important role on the growth of the Ti-rich interface layers.

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