Self-forming diffusion barrier layer in Cu–Mn alloy metallization

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Advancement of semiconductor devices requires the realization of an ultrathin diffusion barrier layer between Cu interconnect and insulating layers. The present work investigated the possibility of the self-forming barrier layer in Cu–Mn alloy thin films deposited directly on SiO_2. After annealing at 450 °C for 30 min, a Mn containing amorphous oxide layer of 3–4 nm in thickness was formed uniformly at the interface. Residual Mn atoms were removed to form a surface oxide layer, leading to a drastic resistivity decrease of the film. No interdiffusion was detected between Cu and SiO_2 within the detection limit of x-ray energy dispersive spectroscopy. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1993759]

Cu metallization has been used as an interconnect material for advanced semiconductor devices. A typical interconnect structure is composed of $Cu/Ta/TaN/SiO_2$. The double layers of Ta/TaN are called a barrier layer as a single entity and are necessary to prevent interdiffusion between Cu and Si atoms. Since the barrier layer has a poor electrical conductivity, its thickness should be reduced as much as possible while maintaining a good diffusion barrier property and a good adhesion strength with neighboring layers. However, the barrier layer formation has become increasingly difficult as the technology node is reduced from 90 to 65 and to 45 nm. An alternative to the conventional barrier process is a "self-forming" barrier process. This process involves with the deposition of a Cu alloy thin film directly on SiO_2, followed by heat treatment to migrate the alloying element to the alloy/SiO_2 interface and to form a thin barrier layer via reaction with SiO_2.

Previous researchers investigated this possibility, using a strong oxide former, such as Mg and Al, as an alloying element in Cu. After heat treatment, a thin oxide layer was formed on the film surface and acted as a self-passivation layer.[1–3] These elements also showed a better adhesion of the alloy film to SiO_2 than pure Cu, implying the formation of an interface oxide phase. The sequence and kinetics of interface reaction were investigated by Frederick *et al.* for Cu–Mg alloys.[4–6] They reported the formation of a uniform MgO layer of 20 nm thick at the interface after heating to 600 °C. Although the MgO layer could be considered as a self-forming barrier, the thickness of 20 nm does not satisfy the requirement for the future technology node, i.e., 5 nm for a technology node of 45 nm. Moreover, the MgO formation accompanied the reduction of SiO_2 and freed Si atoms to diffuse into the Cu layer. This had led to increase in interconnect resistivity. Meanwhile, Barmak *et al.* examined the effects of other elements (Mg, Ti, In, Sn, Al, Ag, Co, Nb, B, Ir, and W) on resistivity before and after annealing at 400 °C for 5 h.[7] Among these elements, Ag and B were acceptable in terms of resistivity by properly controlling their concentrations. However, the major purpose of their work was to investigate the effects of alloying elements on the microstructure. No information was provided for the interface reaction

with SiO_2. Thus far, a proper alloying element has not been reported for the realization of the self-forming barrier process.

In the present work, we chose Mn as an alloying element because of the following favorable points over Mg and Al. The driving force for oxide formation at the interface can be assessed with the heat of formation and, more accurately, with the standard free energy of oxide formation, $\Delta G°$. The $\Delta G°$ parameter of Mn oxide is slightly larger than that of SiO_2, so that the reduction reaction of SiO_2 is not expected as was the case for Mg and Al. Moreover, the impurity diffusivity of Mn in Cu is faster than the self-diffusivity of Cu by an order of magnitude at 450 °C.[8,9] Thus, Mn atoms are expected to migrate to the interface and to form a stable oxide before noticeable reaction occurs between Cu and Si. More importantly, this work also shed a light, for the time in this field, on the activity coefficient, γ, of alloying elements in Cu. The activity coefficient is a measure of chemical interaction between solute and solvent atoms in a solid solution alloy. The activity coefficient of Mn in Cu is larger than 1,[10] while that of Mg and Al in Cu is less than 1.[11,12] This indicates that Mn can be easily expelled from Cu when a more favorable reaction can take place with an adjacent material, such as SiO_2. In contrast, Mg and Al tend to remain in Cu because of their strong chemical interaction with Cu. If Mn is expelled completely from the original Cu–Mn alloy, interconnect resistivity can be reduced to the level of pure Cu.

Experiments were performed as follows. Alloy films of Cu–7.9 at. % Mn were deposited directly on SiO_2 substrates to a thickness of 163 nm by simultaneous sputtering of Cu (99.9999%) and Mn (99.98%) targets. Substrates were n-type Si wafers having a plasma TEOS oxide of 100 nm in thickness. Distance between the targets and the substrate was ~20 cm. The substrate was rotated during deposition in order to obtain a homogeneous concentration of the alloy film. No intentional heating or cooling of the substrates was done during deposition. Base pressure of the sputter chamber was 2×10^{-6} Pa. Working pressure was 0.3 Pa. Sputter power was controlled to obtain a stable maximum deposition rate of 0.23 nm/s for Cu and a stable minimum deposition rate of 0.02 nm/s for Mn. These deposition rates determined the alloy concentration used in this work. The samples were then annealed in a separate annealing furnace having a base pressure of 5×10^{-3} Pa. Annealing was performed in a mixed gas atmosphere of Ar+3%H_2 at various temperatures up to

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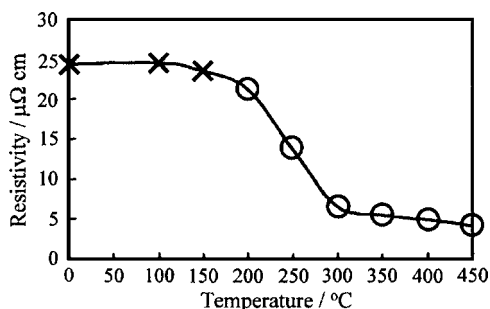
FIG. 1. Resistivity change of the Cu–Mn film after annealing at various temperatures. Cross marks represent delamination by tape test, while circle marks represent no delamination by tape test.

FIG. 2. Auger electron spectra after annealing at 450 °C for 30 min; Si (B.G.) indicates that the Si AES intensity is in a background level.

450 °C for 30 min. Some samples were annealed at 450 °C for 5 h. Tape test was performed before and after annealing, ten times for each sample. Since adhesion is generally poor between pure Cu and SiO_2, tape test could be used as a quick screening test to examine the occurrence of interface reaction between the Cu–Mn alloy layer and the SiO_2 layer. Resistivity was measured with a standard four-point probe apparatus at room temperature after annealing. Finite size factors for four-point measurements[13] were taken into account to obtain accurate resistivity values. Concentration profile along the thickness direction was measured by Auger electron spectroscopy (AES). Microstructure was investigated by observing cross-sectional images with a transmission electron microscope (TEM). TEM samples were prepared by bonding two samples face to face using epoxy, followed by mechanical thinning and ion-beam thinning to perforation. Chemical composition of each layer was measured with an x-ray energy dispersive spectrometer (EDS) attached to the TEM.

Figure 1 shows the temperature dependence of resistivity after annealing at various temperatures for 30 min. Symbols in the figure indicate the results of the tape test. Circles represent no peeling off of the Cu–Mn film from the SiO_2 substrate. Cross marks represent peeling off of the film from the substrate. The as-deposited film exhibits poor adhesion with the substrate and indicates a high resistivity of $\sim 24.4\ \mu\Omega$ cm. With increasing temperature to 150 °C, resistivity values remain nearly constant and adhesion is poor, indicating no interface reaction. With increasing temperature to 200 °C and above, a rapid resistivity reduction is observed and a good adhesion is obtained. This result suggests the occurrence of interface reaction and the reduction of the Mn content from the Cu–Mn alloy layer. The lowest resistivity of 3.17 $\mu\Omega$ cm was obtained after annealing at 450 °C for 5 h. It should be mentioned that a Mn oxide layer of 3 nm thick is formed on the film surface, as shown next. Without the surface layer of the Mn oxide, the actual resistivity of the annealed film is expected to be lower than the measured value.

Figure 2 shows an AES concentration profile of the annealed sample at 450 °C for 30 min. The vertical axis represents the Auger electron intensity, corresponding to the relative concentration of the constituting elements. The horizontal axis represents the sputtering time, corresponding to the distance from the Cu–Mn film surface along the thickness direction. The as-deposited samples could not be investigated because a part of the film was peeled off during handling. The AES profile indicates strong intensity of Mn and O on the film surface, indicating the formation of Mn oxide
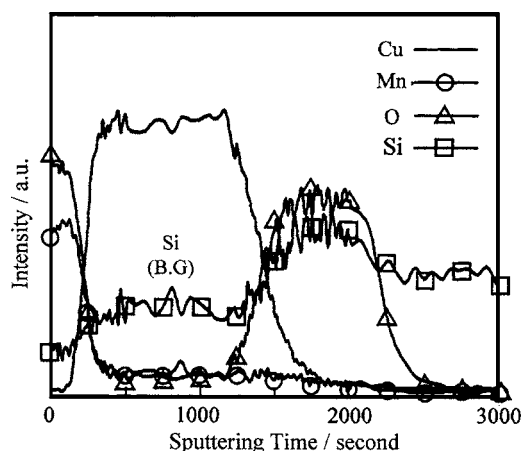
probably due to the presence of impurity oxygen in the annealing gas. The concentration of Si, O, and Mn in the Cu films was below the detection limit of AES. The indicated intensity profiles of these elements are of background level. Note that the background intensity of Si stays at a high level as indicated by B.G. When the differential peak of Mn was examined carefully, a weak Mn intensity can be seen in the interface region. However, sputtering rate seems to be too fast to capture a thin interface layer containing Mn in this figure. The presence of the interface layer can be seen clearly in the next TEM images.

Figure 3 shows cross-sectional TEM images of the annealed sample at 450 °C for 5 h. Figures 3(a) and 3(b) are the
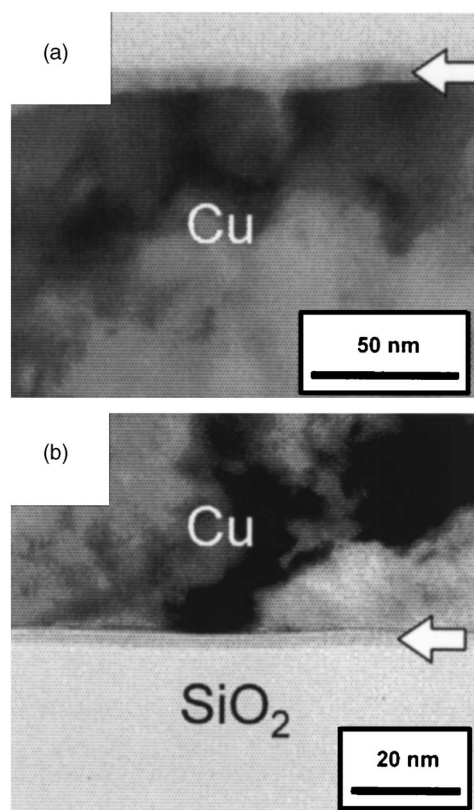

FIG. 3. Cross sectional TEM images after annealing at 450 °C for 30 min; (a) a magnified image near the Cu-SiO_2 interface region; (b) a magnified image near the Cu/SiO_2 interface region. Arrows indicate the location of the oxide layers.
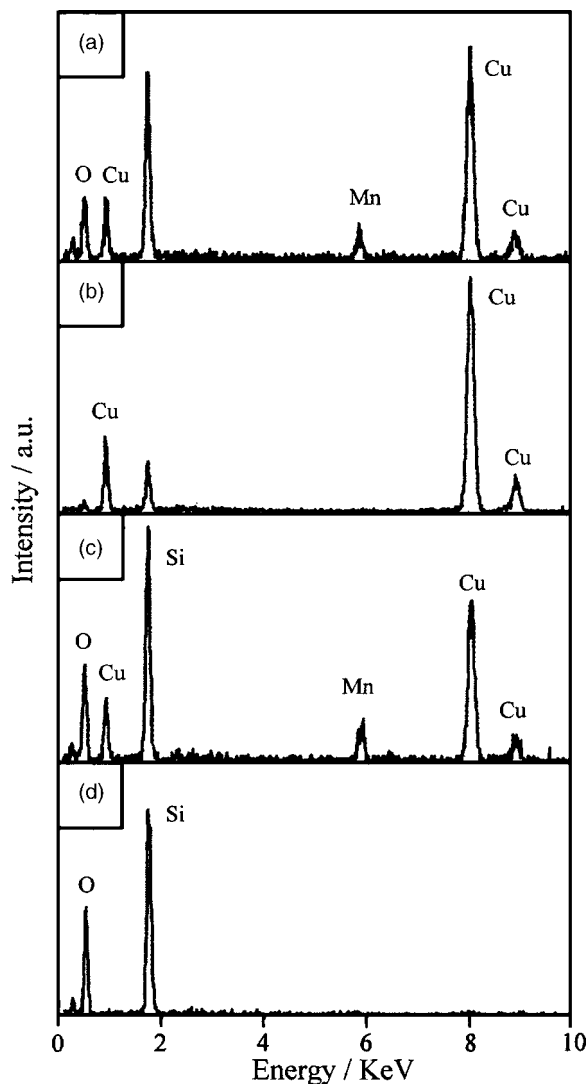
FIG. 4. EDS spectra after annealing at 450 °C for 30 min from (a) the surface layer; (b) the interior of the Cu film; (c) the interface layer; and (d) from the SiO$_2$ layer.

these points in mind, remarkable results are revealed in the EDS spectra. Figures 4(a)–4(c) show that Mn is observed in the surface and the interface layer, but not in the film interior. No segregation or precipitation was found at grain boundaries. This indicates that Mn atoms initially in the form of the Cu–Mn alloy have migrated during annealing to the surface and to the interface to form oxide layers leaving pure Cu behind. Although, exact concentration of the interface layer is not known at the moment, preliminary XPS data[14] indicate the formation of MnSi$_x$O$_y$.[15] Meanwhile, Fig. 4(d) shows only Si and O peaks, suggesting a good diffusion barrier property of the MnSi$_x$O$_y$ interface layer. Although EDS has a detection limit of no less than 0.1 at %, our separate measurements using a two-layer test structure indicate better leakage current and breakdown voltage in the Cu–Mn alloy than in the conventional Cu and a Ta barrier layer of 15 nm in thickness.[16]

The present results showed that Mn atoms in the Cu–Mn alloy film diffuse to the surface and the interface to form oxide. The interface oxide layer has an amorphous structure that is considered to be a favorable structure as a diffusion barrier layer. The thickness of this interface layer is uniform and is only 3–4 nm in thickness. These values are smaller than the target values of the barrier thickness for the technology node of 45 nm and beyond. The self-forming barrier process using the Cu–Mn alloy can serve as an alternative to atomic layer deposition[17] and self-assembled monolayer[18] approaches used for realizing nanometer thick diffusion barriers.

images of the surface and the interface regions of the Cu–Mn film, respectively. Both magnified images clearly show the formation of the surface and the interface layer having approximate thickness of 10 and 3 nm, respectively. The surface layer exhibits an inhomogeneous diffraction contrast, indicating the presence of a polycrystalline phase. On the other hand, the interface layer exhibits homogeneous contrast, indicating an amorphous phase. The EDS spectra taken with an electron probe of 1.7 nm in a nominal diameter are shown in Fig. 4(a) for the film surface, 4(b) for the film interior, 4(c) for the interface layer, and 4(d) for the SiO$_2$ layer. It is noted that a weak Si peak appears in all the spectra, even in the spectrum from the bonding epoxy layer (not shown here). This is due either to the excitation of the Si peak from the dead layer of the detector or to the contamination with Si atoms produced during ion milling and deposited on the entire surface of the sample. Thus, a weak Si peak should be neglected and not labeled in the figure. It is also noted that the size of the electron probe has a limitation so that the spectra from the thin surface and the interface layers exhibit other elements from their neighboring layers. Having

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