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Formation of a manganese oxide barrier layer with thermal chemical vapor deposition for advanced large-scale integrated interconnect structure

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Advanced large-scale integrated interconnect structure faces a major challenge in forming a thin and conformal diffusion barrier layer. We deposited a Mn oxide layer by thermal chemical vapor deposition (CVD) on SiO_2 substrates and investigated deposition behavior and diffusion barrier property. A thin Mn oxide layer was formed with a uniform thickness of 2.6–10 nm depending on deposition temperature between 100 and 400 °C. Heat-treated samples of Cu/CVD-Mn oxide/SiO_2 indicated no interdiffusion at 400 °C for 100 h. The CVD of the Mn oxide layer was found to be an excellent barrier formation process. © *2008 American Institute of Physics*.
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Manufacturing technologies of microelectronics have been developed toward higher integration density with smaller design rules. Accordingly, a Cu interconnect structure is needed to shrink to a narrower line width and spacing. This requires the reduction of barrier layer thickness to prevent the increase of the effective resistivity of the copper lines.[1] However, the barrier layer formation with a physical vapor deposition (PVD) technique has become difficult as the technology node is reduced to 45 nm and beyond.

Self-formed barrier layer process using a Cu alloy is expected to be a solution for this problem. Koike and Wada[2] reported the self-formation of a diffusion barrier by direct deposition of a Cu–Mn seed layer on a tetraethylorthosilicate (TEOS)-SiO_2 substrate. The Mn oxide layer was self-formed at the interface by annealing at elevated temperatures and acted as an excellent barrier layer.[2–4] However, as in the case of the conventional barrier, PVD of the Cu–Mn seed layer will eventually encounter the difficulty in conformal deposition in narrow line trenches and via holes.

Chemical vapor deposition (CVD) has been known for its good step coverage and is a candidate technique for the formation of a thin conformal barrier layer, a Cu seed layer, and an entire Cu line. In order to take advantage of the excellent reliability of the Mn oxide diffusion barrier layer, Mn deposition with CVD is expected to be a very attractive process for an advanced technology node.

Up to date, only a few works have been reported for CVD-Mn layer. Wen-bin *et al.*[5] investigated the thermal decomposition behavior of methylcyclopentadienyl tricarbonyl manganese, $(MeCp)Mn(CO)_3$, with *in situ* mass spectrometry. They also reported that the deposition of a metallic Mn layer occurs with thermal CVD above 410 °C.[6] Although metallic manganese was obtained, the characterization of manganese film remains to be unclear. Maruyama and Osaki[7] reported the formation of a Mn oxide layer above 250 °C with metal organic CVD in air. However, no information was provided for the Mn oxide deposition behavior.

In this research, we performed thermal CVD of metal organic Mn precursor on a TEOS-SiO_2 substrate. The chemistry and structure of the deposited layer and its deposition behavior were investigated at various deposition temperatures and time. Diffusion barrier property of the Mn oxide film was also investigated by annealing at high temperature.

Substrates were *p*-type Si wafers having a plasma TEOS-SiO_2 of 100 nm in thickness. Bisethylcyclopentadienyl manganese, $(EtCp)_2Mn$, was used as a metal organic manganese precursor. The Mn precursor was vaporized and introduced into a hot-wall reaction chamber with H_2 carrier gas in the thermal-CVD process. After the CVD-Mn deposition, the sample was transferred without breaking vacuum to a load-lock chamber to deposit a Cu overlayer using a dc sputtering system at room temperature. A Cu overlayer was deposited because we wanted to protect the CVD-Mn layer from atmospheric reaction when the sample was taken out from the chamber.

A transmission electron microscope (TEM) attached with an X-ray energy dispersive spectrometer (EDS) was used to investigate the microstructure, thickness of the CVD-Mn layer, and chemical composition of the sample. X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical bonding states of the CVD-Mn layer.

Figure 1 shows cross-sectional TEM images of the as-deposited PVD-Cu/CVD-Mn/SiO_2 samples at 200, 400, and 500 °C for 30 min. Below 400 °C, a thin layer is formed on SiO_2. On the other hand, a thin layer and large particles are observed at 500 °C. From TEM-EDS results, the thin layer is consisted of Mn, O, and C, while the particle is consisted of Mn.

Figure 2 shows the XPS spectra of Mn $2p_{3/2}$ of CVD-Mn/SiO_2 samples deposited at 200 and 500 °C for 30 min. The peak position of Mn $2p_{3/2}$ of the sample deposited at 200 °C is 642.2 eV. The two peaks of Mn 2*p* of the sample deposited at 500 °C are observed at 639.2 and 640.4 eV. Previous works reported that a binding energy of Mn–O is 640–643 eV.[8] These results indicate that the thin uniform layer on SiO_2 is MnO_x and the particle observed above 500 °C is metallic Mn.

Figure 3 shows the thickness change of the MnO_x layer with substrate temperature up to 400 °C. The thickness increases gradually with increasing the substrate temperature.

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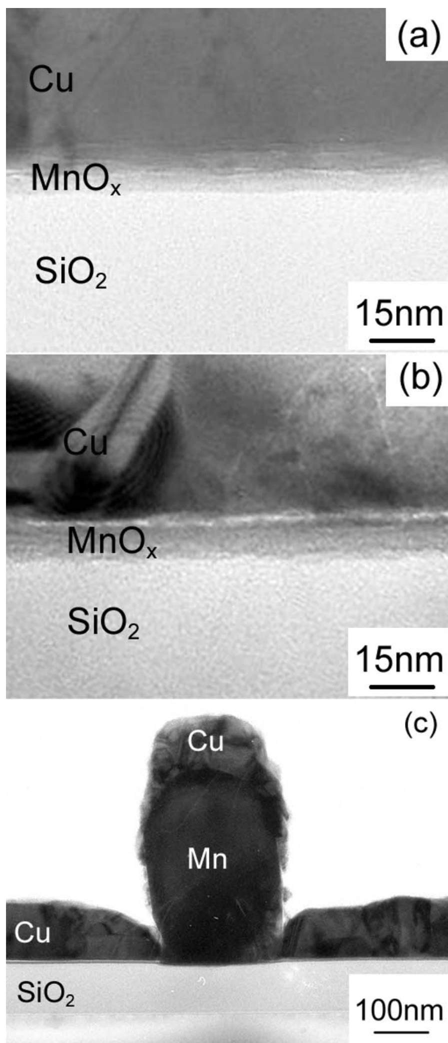

FIG. 1. Cross-sectional TEM images of as-deposited PVD-Cu/CVD-Mn/TEOS at deposition temperatures of (a) 200, (b) 400, and (c) 500 °C.

It should be noted that the thickness of the Mn oxide layer is in the range 2.6–10 nm, including the required thickness values in the ITRS road map. When the data are plotted in an Arrhenius fashion, an activation energy of 17.7 kJ/mol is obtained.

Figure 4 shows the thickness of the MnO_x film as a function of reaction time at 200 °C. A thin and uniform

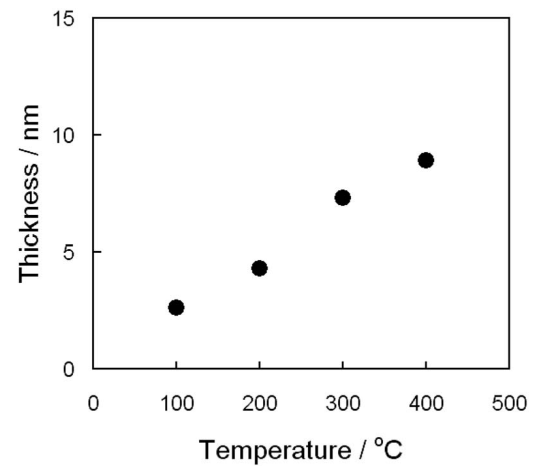

FIG. 3. Thickness change of the MnO_x layer with substrate temperature.

MnO_x film can be formed on SiO_2 after reaction time of only 1 min. Although the thickness of the MnO_x film is slightly increased with reaction time within the first 5 min, there is no notable growth of the MnO_x film with increasing reaction time in this condition.

Figure 5 shows cross-sectional TEM images and EDS results of the PVD-Cu/CVD-MnO_x/SiO_2 sample in the as-deposited condition and after annealing at 400 °C for 100 h in vacuum of better than 1.0×10^{-5} Pa. The MnO_x film was deposited at 100 °C for 30 min. A thin continuous MnO_x layer is observed at the interface between Cu and SiO_2 layers in the as-deposited sample. The MnO_x layer does not show a characteristic diffraction contrast of a crystalline structure. Thus, the CVD-MnO_x layer is considered to be an amorphous structure. After annealing, the MnO_x layer remains to be a thin amorphous structure. The EDS results confirm no Cu diffusion into the SiO_2 layer after annealing. The results clearly indicated that the CVD-MnO_x is thermally stable and acts as a good diffusion barrier.

In the present work, the CVD-Mn layer deposited below 400 °C was a thin and continuous MnO_x layer. On the other hand, the CVD-Mn layer deposited at 500 °C was metallic Mn particles in addition to the thin continuous MnO_x layer. These results indicate that the $(EtCp)_2Mn$ is thermally decomposed above 500 °C to deposit metallic Mn. Similar results were reported by Wen-bin *et al.*[5] They investigated the

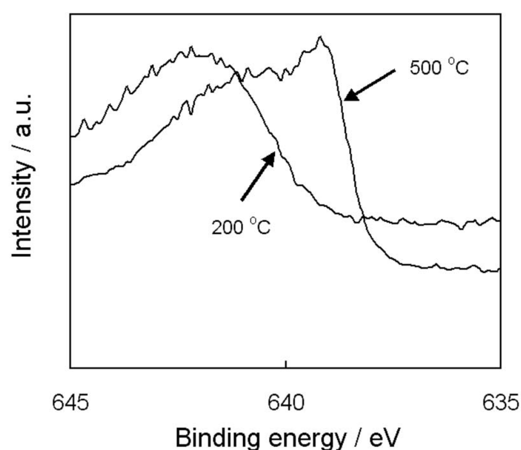

FIG. 2. XPS spectra of Mn $2p_{3/2}$ in CVD-Mn/TEOS deposited at 200 and 500 °C for 30 min.

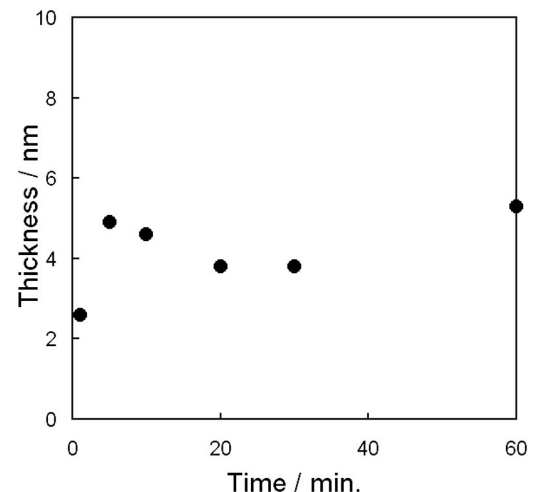

FIG. 4. Thickness of MnO_x as a function of reaction time at 200 °C.

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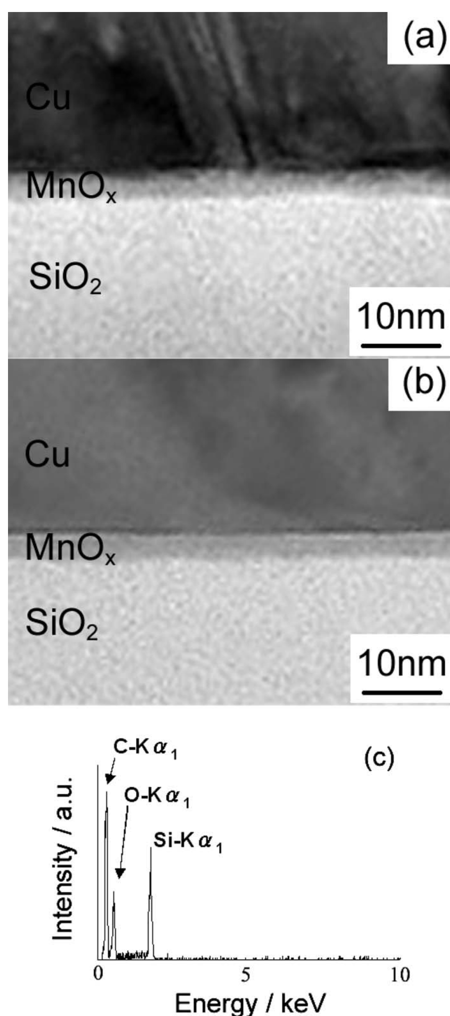

FIG. 5. Cross-sectional TEM images of PVD-Cu/MnO_x/TEOS sample deposited at 100 °C (a) before annealing, (b) after annealing, and (c) EDS spectra of the SiO_2 layer of the annealed sample.

CVD of the $(MeCp)Mn(CO)_3$ precursor and showed that thermal decomposition occurs above 410 °C to deposit metallic Mn by the breaking of Mn–Cp bonding.[5] It is considered that the thermal decomposition of the $(EtCp)_2Mn$ precursor used in the present work also occurs by the breaking of the same Mn–Cp bonding.

Deposition behavior below 400 °C was drastically different from the behavior at 500 °C. Instead of metallic Mn particles at 500 °C, a thin layer of MnO_x was formed below 400 °C with an apparent activation energy of 17.7 kJ/mol. This value is much smaller than the reported dissociation energies of 212 and 308 kJ/mol for Mn–Cp bond,[9,10] suggesting the operation of an enhancing mechanism to dissociate Mn to form the MnO_x at low temperatures. An analogous enhanced mechanism can be found in the self-forming barrier process of MnO_x with PVD Cu–Mn films on SiO_2.[4] In this case, solid-state reaction between Mn and SiO_2 was enhanced by the capture of electrons from Mn atoms by oxygen ions leading to the formation of electric field across the barrier layer. It is possible that the similar enhanced reaction takes place in gas-solid reaction between the $(EtCp)_2Mn$ precursor and SiO_2. The details of the reaction mechanism are a subject of future research.

A thin Mn oxide layer was formed with thermal CVD above 100 °C and below 400 °C. The MnO_x layer was an amorphous having a uniform thickness of 2.6–10 nm depending on deposition temperature. Thin layer formation and particle deposition were observed at 500 °C. The thin MnO_x layer formed below 400 °C was found to be thermally stable and act as a good diffusion barrier layer after annealing at 400 °C for 100 h. The obtained results indicate that CVD-MnO_x process is a promising technique to form a conformal and reliable barrier layer for an advanced large-scale integrated interconnect structure.

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