Copper Interconnects Grown by Electrochemical Displacing the Prepatterned SiC Barrier Thin Film
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The process of fabricating Cu layers by displacement reaction is demonstrated. SiC was used and displaced in the chemical reaction to form copper films. SiC was also adopted to improve the adhesion between the copper and the dielectric layer. The effects of the process recipe on the structure and reliability of the Cu lines were studied. The obtained average electrical resistivity of the Cu films was 2.04 μΩ-cm after thermal annealing and it was 2.32 μΩ-cm for samples grown from a less-oxygen-containing solution.

For future ultralarge scale integration (ULSI), the ever-decreasing lateral dimensions of contacts and via holes will require new development in metallization technology. Consequently, copper has been chosen as an alternative selection for interconnects with a lower resistivity, better mechanical properties, and a better electromigration resistance as compared to aluminum.1,2 For Cu metallization, an efficient diffusion barrier is required to prevent Cu atoms from penetrating into dielectrics or Si substrates. Refractory metals and their nitrides have been used and thoroughly investigated for interconnection applications. These materials are promising as diffusion barriers because of their good thermal stability at elevated temperatures.3 Several methods have been proposed for Cu deposition on these diffusion barriers, e.g., physical vapor deposition (PVD),4,5 chemical vapor deposition (CVD),6,7 and electrochemical deposition (ECD).8,9 Recently, displacement technique for Cu metallization was proposed as an ECD technique and is attractive in microelectronics and semiconductor industries because of its low processing temperature, high step coverage, high selectivity, and low cost.10

In this study, a low-cost selective plating technique without etching copper layers was investigated. This technique is simple and compatible to current VLSI fabrication technology. It is believed that this patterned plating technique has great potential for future applications in ULSI multilevel technology. The quality of the deposited Cu film, such as the electrical resistance and crystal grain orientation were evaluated by means of sheet resistance measurement and X-ray diffraction analysis.

Experimental
The fabrication flow for Cu in displacing the prepatterned SiC layer is shown in Fig. 1. A 150 nm thin SiO2 layer was first grown on a 6 in. Si(100) wafer, and a 150 nm Si3N4 layer was then deposited by low-pressure chemical vapor deposition (LPCVD) at 780°C. After depositing the insulators, 300 nm SiC layer were deposited on the Si3N4 layer by high-density plasma-chemical vapor deposition (HDP-CVD). Finally, interconnects were defined ahead on the SiC film by photolithography and dry etching process. Displacing the SiC by Cu was carried out by immersing the samples in our aqueous reaction bath at the room temperature for 3-10 min. The reaction solution contained cupric sulfate (CuSO4) at a concentration of 4 g/L and 1% buffered oxide etchant (BOE) which was a NH4F/HF mixture with a volume ratio of 10:1. Both were diluted and well mixed in a Teflon beaker with deionized (DI) water of 99%. In our experiments, Cu deposited selectively on the patterned SiC wires and then formed interconnects directly. The characteristics of the Cu wires were investigated by scanning electron microscope (SEM) and X-ray diffraction (XRD) spectroscopy. Energy dispersive X-ray spectroscopy (EDS) was used to analyze surface elements. The four-point probe was also used to measure the sheet resistance of the deposited Cu. The resistivity was calculated from the sheet resistance and the observed thickness from SEM.

In this study, thermal annealing in H2 at 500°C for 50 min was utilized in an attempt to reduce the resistance of our Cu interconnects. Another process flow of the oxygen-removing process is shown in Fig. 2. The oxygen-removing process was also used in the preparation of our reaction bath to decrease the obtained electrical resistivity of our samples. In this process, the solution was boiled in a loosely sealed Teflon beaker at 100°C for 30 min and then cooled to room temperature for reactions. It was expected that the amount of oxygen resolved in the water would be reduced and thus in the as-deposited Cu from the later reaction.

Results and Discussion

Our reaction bath was composed of DI water, BOE, and CuSO4 to displace SiC with Cu. Such a recipe is supposed to be compatible with the current fabrication technology. The F− ions released from BOE will break the SiC bonds. The F− and Si ions will produce SiF6 2− which is soluble in water. In the meantime, the Cu2+ ions from CuSO4 will reduce to be Cu atoms and deposit on the SiC layer.

The above redox reaction can be expressed by11,12

\[
\text{CuSO}_4 + \text{SiC} + 6\text{HF} + 3\text{H}_2\text{O} \rightarrow \text{H}_2\text{SiF}_6 + \text{H}_2\text{CO}_3 + \text{H}_2\text{SO}_4 + 3\text{H}_2 + \text{Cu}
\]

After the displacing deposition process, the resistances of copper lines were very high, because carbon and oxygen elements were mixed in Cu lines. Bonds of Cu-C or Cu-O were formed in the Cu lines. The Cu lines annealing in O2 at 500°C for 30 min was proposed to decrease concentration of carbon. At the same time, the Cu line oxidized. Figures 3a and b show the EDS spectrum of the Cu grown by the displacing reaction for 10 min with and without oxygen, respectively. The peaks of carbon and oxygen changed, although not obviously. The element weight of carbon decreased a little by the annealing in O2 at 500°C for 30 min. The Cu-C bond was broken by oxygen and carbon oxidized to CO2. At the same time, Cu easily oxidized and the weight of oxygen increased a little in the Cu lines. Table I shows the weight of every elements. Annealing in H2 at 500°C for 50 min reduced the concentration of oxygen in the copper layer. The resistivity of the Cu lines could be reduced after the films were annealed in H2 but carbon in the Cu lines may have been another reason for the higher the resistivity of the Cu lines. Figures 4a and b show that the surface morphologies of our samples originate with the layer structure of Cu/SiC/Si3N4/SiO2/Si after a 2 and 10 min displacement reaction at the room temperature, respectively. The residues between the Cu lines peeled off the SiC dielectric film during the displacing reaction. The loose packing of Cu grains and poor adhesion at the Cu/SiC interface caused hydrogen bubbles to form during contact displacement with the SiC films. These hydrogen bubbles deteriorated the adhesion of the Cu to the substrate.
underlying dielectrics and made the Cu surface rough. After reaction, the nominal 300 nm SiC changed to be a Cu layer of 455 nm thick. In our study, for the 0.7 μm wide SiC films, the reaction rates saturated after 15 min, which indicated the SiC layers was totally replaced. The texture structure of the Cu was also concerned in estimating the reliability of our Cu wires. Figure 5 shows the XRD spectrum of the displacement Cu. In this figure, the intensity of the (111) textured Cu is much higher than that oriented in (200). Because it was suggested that (111) textured Cu has a better performance to resist electromigration,13 it is believed that our displacement copper wires should be more reliable in conduction. Pull-off adhesion test sheet resistance measurements were carried out to evaluate the deposited copper film. The adhesion on SiC layer passed the tape-pulling test, and the adhesion strength measured by stud-pulling was 18.2 kg/cm².

In our study, the measured resistivity of our displacement copper film was 5-10 μΩ-cm which was higher than that of the Cu fabricated by sputtering. The annealing process after reaction and the oxygen-removing process before reaction were utilized to improve the electrical quality of our samples. Figures 4c and d show the surface morphologies of the displacement copper obtained with these two processes respectively. In the reaction solution, the Cu lines easily oxidized. H2O were produced by CuO with annealing in H2. H2O deteriorated the adhesion of the Cu to the underlying dielectrics. The surface of the Cu lines after the annealing in H2 rougher than the surface of the Cu lines by the oxygen-removing process. Both methods were found to improve the electrical quality significantly. Especially for the oxygen-removing process, without any thermal process required, the as-deposited Cu resistivity was only 2.12 μΩ-cm in average and even 1.98 μΩ-cm in minimum. In improving the resistance of our samples by annealing, the effect of the annealing time was also investigated. Figure 6 shows the resulting resistivity of the displacement copper as a function of the annealing time. As seen in this figure, the electrical resistivity of the

| Table I. The elements weight of Cu films grown by the displacing reaction for 10 min with and without oxygen annealing at 500°C for 30 min. |
|-----------------|---------------|-----------------|
| Element         | Without oxygen annealing | With oxygen annealing |
|                 | (wt %)         | (atom %)        | (wt %)         | (atom %)        |
| C K             | 1.31           | 6.05            | 0.97           | 4.40            |
| O K             | 2.96           | 10.23           | 4.05           | 13.80           |
| S K             | 0.37           | 0.64            | 0.48           | 0.81            |
| Cu L            | 95.36          | 83.08           | 94.50          | 81.00           |
| Totals          | 100.00         | 0               | 100.00         | 0               |
as-deposited copper before annealing is 5.61 $\mu$Ω-cm. In this experiment, the electrical resistivity of the copper decreased and dropped drastically to 2.04 $\mu$Ω-cm after 50 min of annealing. Such improvement can mainly be attributed to the defect reduction and recrystallization in the Cu grains. As compared to the results obtained with the oxygen-removal process, the annealing process would give a more uniform distribution of the obtained resistance for Cu. Nonetheless, the oxygen-removal process would give a very low resistance without any thermal treatment even though the treatment is able to largely reduce the resistance of Cu films.

Conclusions

In this study, we proposed a method to fabricate copper interconnects by displacing SiC with Cu. The electrical resistivity of the displacement copper film was lowered to 2.04 $\mu$Ω-cm by annealing in H$_2$ at 500°C for 50 min. With the help of oxygen-removing process in preparing the reaction solution, the electrical resistivity of the displacement copper film can also be improved.
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References