Growth of Nano-sized Copper Seed Layer on TiN and TaSiN by New Non-toxic Electroless Plating

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ABSTRACT —**The purpose of this research is to explore the properties of a copper seed layer grown by electroless plating on TiN. We have developed a displacement layer made of amorphous silicon (a-Si) and copper contact displacement process to improve the island structure of copper activated layer which can then be grown directly on the surface of TiN. Furthermore, this research proposes glyoxylic acid as replacements to formaldehyde, which is commonly used at present as a reductant but regarded as a carcinogen, and is of high volatility. The copper seed layer has been grown by the electroless plating method on an activated surface of TiN, at the set temperature of 60 °C with the plating bath consisting of the copper source, complexing agent, stabilizer and surfactant. The existence of a copper seed layer provides not only the conduction layer, but also the copper nucleation layer, to help the growth of electroplated copper on the surface of TiN. Moreover, based on the results of the studies can lead us to grow a nano-sized Cu seed layer on the top of a TaSiN layer.**

I. INTRODUCTION

As the size of via/contact holes is scaled down to the sub-micron region, the step coverage problem appears, which leads to reliability problems when using aluminum to form the interconnection between different wiring layers. The poor step coverage in the sub-micron via/contact holes results in high current density and enhancement of electromigration. Copper is being considered to replace current Al metallization in ultralarge scale integrated (ULSI) technology because of lower resistivity, potentially higher resistance to electromigration and stress-induced voiding [1]. In comparison with other copper deposition techniques, electroplating is the most common technique for the filling of high aspect ratio trenches and vias in dual damascene technologies due to its high deposition rate, low processing temperature, good step coverage, good via/trench filling capability and low cost of tools and manufacture. However, electroplating of copper directly onto barrier layers has proven to be difficult. A conductive seed layer on the top of barrier layer is required. The objective of this study is to use the method of electroless plating to grow this seed layer.

Activation of a metal is necessary in order to pursue the autocatalytic reaction for the electroless plating of copper. The use of palladium is a well-known technique for treating a surface to initiate the autocatalytic reaction of copper. However, the presence of Pd reduces the stability of the electroless Cu plating bath and the formation of the CuPd alloy increases the resistivity of electroless Cu deposits [2]-[3]. After the activation step, copper is deposited by the technique of electroless plating. The use of formaldehyde as a reducing agent in the plating bath is well-known, but formaldehyde is a known carcinogen.

In view of the above considerations, we have developed a Cu contact displacement technique for activation on the top of TiN and TaSiN. We have also successfully used glyoxylic acid instead of formaldehyde as the reducing agent in the electroless Cu plating bath.

II. EXPERIMENTAL

In this study, substrates with the layers TiN/Ti/SiO_2/Si were used. A SiO_2 dielectric layer with a thickness of 5500 Å was deposited on a Si wafer using the thermal oxidation method before TiN/Ti deposition. Ti and TiN were deposited using a PRIMUS 2500^{TM} sputtering system manufactured by Materials Research Corporation (MRC). The thickness of the Ti and TiN layers were fixed to 400 Å respectively.

Prior to the introduction of the Cu electroless plating solution, the noncatalytic TiN surface was activated by immersion into an activation solution. The Cu contact displacement process described by Dubin *et al.* [4] was employed to activate the substrate surface. The aqueous copper contact solution (100 mL) used was comprised of 0.025 M of $CuSO_4 \cdot 5H_2O$, 1 M of HF and one drop (~16 mg) of Triton X-114 (surfactant).

After the activation step, the copper was deposited by the technique of electroless plating. Two kinds of plating baths were used. One contained 0.087 M of formaldehyde and the other contained 0.087 M of glyoxylic acid as the reducing agent. The total plating solution of 200 mL with pH = 12.5 (adjusted by tetramethylammonium hydroxide; TMAH) and temperature of 60 °C also consisted of copper sulfate (0.035 M) as a metal source, EDTA (ethylenediaminetetraacetic acid; 0.06 M) as the

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complexing agent, Triton X-114 (2 drops; ~ 32 mg) as a surfactant and 2,2'-dipyridyl (100 ppm) as a stabilizer.

The properties of the Cu films were analyzed by using a X-ray diffractometer (Scintag X1). The surface morphology of the Cu films was observed by the use of a scanning electron microscope (Hitachi S-4000 and Philips XL40). X-ray photoelectron spectroscopy measurements were performed with a VG Microlab 310D spectrometer system using Al K_α radiation (1486.6 eV).

III. RESULTS AND DISCUSSION

We first tried to use the Cu contact displacement method to activate the TiN substrate [4]. There were some Cu-islands on the TiN surface but the distribution was not uniform as shown in Fig. 1(a). After the above process, the substrate was immersed into the electroless Cu plating bath with glyoxylic acid as a reducing agent. The adhesion between the electroless Cu film and TiN barrier layer was poor. In order to solve the problem of the non-uniform distribution of Cu-islands on the TiN layer, we then tried to pretreat the TiN surface before the Cu contact displacement. The pretreatment method employed has been reported by Ng *et al.* [5]. The effect of 10% HF etching on the Ti 2p X-ray photoelectron spectrum (XPS) of the fully oxidized TiN is shown in Fig. 2. The binding energies of the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ core levels particular to an as-sputter deposited and oxide-free TiN surface are shown in Fig. 2. The spectrum shows a noticeable change in the overall line shape. Curve (a) of Fig. 2 shows the presence of a fully oxidized overlayer with the peak at 458.6 eV corresponding to the Ti $2p_{3/2}$ binding energy of TiO_2. A significant reduction in the peak intensity at 458.6 eV is observed in curves (b) and (c) of Fig. 2. These observed changes could be attributed to the removal of a native passivated layer of TiO_2 on top of the TiN layer by HF during etching. Therefore, a 10% HF solution was used to etch the TiN layer followed by the Cu contact displacement to activate the TiN surface. As shown in Fig. 1(b), using a 10% HF solution to pretreat the TiN surface has solved the problem of non-uniform distribution of Cu-islands on the TiN layer. In Fig. 1(c), it is apparent that the distribution of Cu-islands is very uniform. Moreover, as seen from Figs. 1(b) and 1(c), the sizes of the Cu-islands increase with the deposition time.

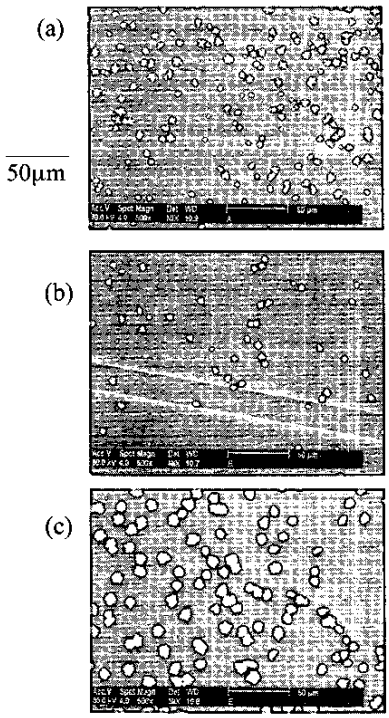


Fig. 1. SEM photographs of surface morphology. (a) non-etched, followed by the Cu contact displacement for 2 min. (b)~(c) etching with 10% HF for 30 sec. followed by the Cu contact displacement for 2 min. and 5 min. respectively.

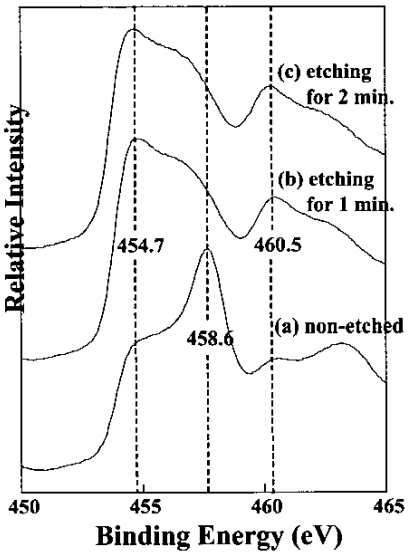


Fig. 2. (a) XPS Ti $2p_{3/2}$ and Ti $2p_{1/2}$ core-level spectra of as-deposited PVD-TiN and (b)~(c) the same TiN after 10% HF etching for different durations.

Fig. 3 shows the XRD patterns of (a) a copper plate, (b) a TiN substrate and (c) ~ (f) 10% HF etching followed by the Cu contact displacement. The typical cubic structure with lattice constant of $a \sim 3.62$ Å [space group: *Fm-3m*] was exhibited by the Cu plate standard sample. In curves (c) and (d), a gradual increase in the intensity of amorphous-like Cu peak at 2θ 43.3° with increasing deposition time was found. This indicates the growth of Cu-islands with an increase in the deposition time. In curves (e) and (f), no noticeable changes in the intensity of the amorphous-like Cu peak at 2θ 43.3° were found, as compared with curve (c). This indicates that the growth of Cu-islands has no relationship with pretreatment time but is in direct proportion with the deposition time. (This is due to the native oxides having been removed from the TiN surface for 30 sec.)

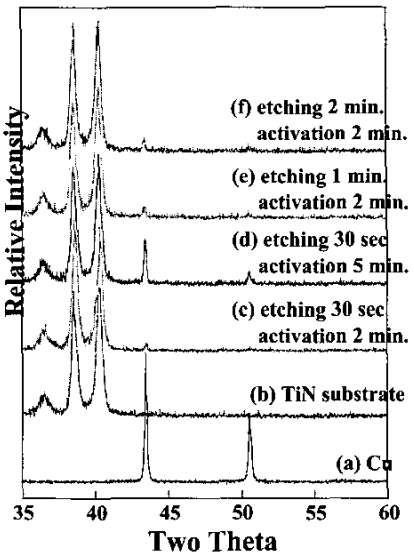


Fig. 3. XRD patterns of (a) a copper plate, (b) a TiN substrate and (c)~(f) 10% HF etching followed by the Cu contact displacement.

After the activation step, copper was deposited by the technique of electroless plating. In Fig. 4, we show the scanning electron micrograph (SEM) cross-sectional view of a Cu film deposited by contact displacement followed by electroless plating to grow the copper seed layer. There were some Cu-islands on the TiN surface, whose height was up to ~1μm which is undesirable in the course of the conductive seed layer for the subsequent electroplating step. In order to overcome this disadvantage of a Cu-island structure, we employed a thin film of the amorphous silicon (a-Si; about 1000 Å) as a displacement layer on the TiN surface.

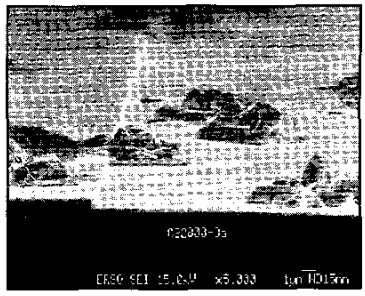


Fig. 4. SEM cross-sectional view of of Cu film deposited by contact displacement followed by electroless plating on TiN.

The amorphous silicon film can be displaced by cupric ions in hydrofluoric acid solution at room temperature. The corresponding contact displacement reactions are as follows:

$$Si + 6F^- \rightarrow SiF_6^{2-} + 4e^-$$
$$2Cu^{2+} + 4e^- \rightarrow 2Cu$$

In Fig. 5, we show the growth of Cu grains as a function of deposition time by the Cu contact displacement on the a-Si layer. As seen from this figure, an increase in the size of the Cu grains with increasing contact displacement time was found. However, the increase saturated at about 50 nm after 6 seconds.

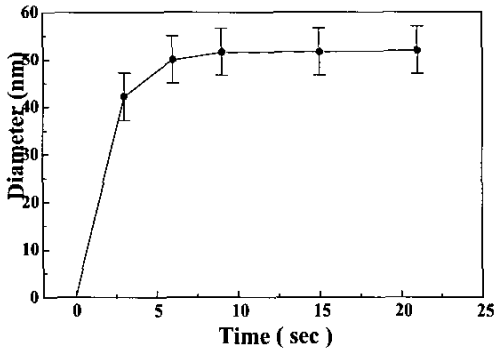


Fig. 5. Growth of Cu grains as a function of deposition time by Cu contact displacement on the a-Si layer. .

After the activation process on the a-Si layer, the copper seed layer was prepared by the technique of electroless plating. The overall oxidation/reduction reaction for the electroless Cu plating system can be expressed as follows:

(a) For formaldehyde

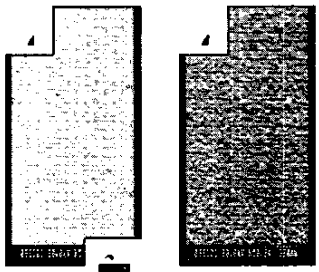
$$(CuEDTA)^{2-} + 2HCHO + 4OH^- \rightarrow Cu + 2HCOO^- + 2H_2O + H_2 + EDTA^{4-}$$

(b) For glyoxylic acid

$$(CuEDTA)^{2-} + 2CHOCOOH + 4OH^- \rightarrow Cu + 2HC_2O_4^- + 2H_2O + H_2 + EDTA^{4-}$$

In Fig. 6, we show SEM photographs of surface morphology of Cu films on the a-Si layer: (a) after contact displacement and (b) ~ (e) after Cu contact displacement and then Cu electroless plating for (b) 1 min., (c) 2 min., (d) 3 min. and (e) 4 min. with glyoxylic acid as the reducing agent. It is found that with increasing deposition time, there is an increase in the grain size of Cu. Moreover, after Cu electroless plating, a smooth Cu surface is also observed. Therefore, the development of amorphous Si as a displacement layer on the TiN surface can solve the problem of Cu-island structures and allows subsequent reaction. The film thickness increases with the deposition time. Up to 4 min., the film thickness can be approached around 40 nm.

(a)-(b)



(c) - (e)

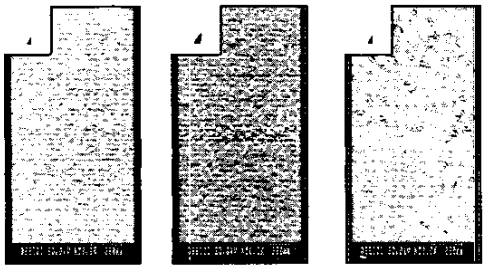


Fig. 6. SEM photographs of surface morphology of Cu films on a-Si. (a) after Cu contact displacement and (b) ~ (e) after Cu contact displacement and then Cu electroless plating for (b) 1 min., (c) 2 min., (d) 3 min. and (e) 4 min. with glyoxylic acid as the reducing agent.

In Fig. 7, we show scanning electron microscopic (SEM) photographs of surface morphology of Cu active films after contact displacement process with 5 M of HF on TaSiN. It is found that Cu active films on TaSiN also have the island-structure but the distribution is more dense and the size of Cu grains is smaller (50-100 nm) with round morphology. The result indicates that a smooth Cu layer can be deposited on the TaSiN surface. It is proved that the TaSiN layer can act as amorphous Si to obtain a smooth Cu layer which is better than that of TiN with an island Cu layer.

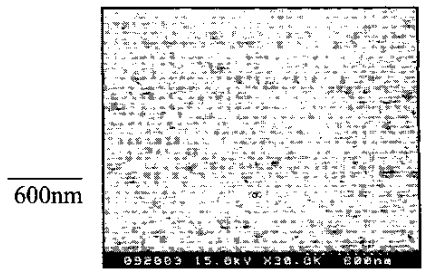


Fig. 7. Scanning electron microscopic (SEM) photographs of surface morphology of Cu active films after contact displacement process with 5 M of HF on TaSiN.

V. CONCLUSIONS

The development of the amorphous Si to be the displacement layer on the TiN surface can solve the problem of Cu-island structure and the smooth Cu surface is observed after Cu electroless plating. Furthermore, we have successfully used glyoxylic acid instead of formaldehyde as the reducing agent in the electroless Cu plating bath to grow Cu seed layer. This results can lead us to grow a nano-sized copper seed layer on the TaSiN layer.

ACKNOWLEDGEMENT

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