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Short Communication

Electrochemical deposition of Copper on patterned Cu/Ta(N)/SiO_2 surfaces for super filling of sub-micron features

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1. Introduction

Copper electroplating has become the mainstream method for current deep sub-micron copper interconnect for integrated circuit manufacturing because of the advantages of low electrical resistivity and high electromigration resistance over the conventional Al/Cu [1]. A typical copper metallisation process consists of: (a) a physical vapour deposition (PVD) barrier layer deposited on a patterned dielectric stack having sub-micron features; (b) a PVD copper seed layer deposited on the barrier layer; (c) electroplated copper filling on the seed layer by electroplating method; (d) chemical–mechanical polishing to remove the overfilling copper and top barrier layer. Electrochemical deposition (ECD) in the copper metallisation process has been implemented in deep sub-micron Cu interconnect of CMOS devices. This is because electrochemical plating of Cu has the several advantages of lower cost, lower processing temperature and better ability to fill vias and trenches compared to PVD and chemical vapour deposition. The technique faces new challenges for filling deep sub-quarter-micron features and requires further optimisation of the electroplating conditions, such as electroplating solution with suitable additives, electrodeposition rate, current density, electrical waveforms and temperature etc. [2–6].

Recently, a few copper electroplating additives have been studied to fill sub-micron trenches and vias [2–4]. Kelly and West [2] have reported copper filling in 300 nm trenches (aspect ratio of 2.5:1) in an acid copper electrolyte with polyethylene glycol (PEG), chloride, bis(3-sulphopropyl) disulfide and Janus Green B. Gau et al. [4] demonstrated that a novel chemical additive of hydroxyl amine sulphate could be used as a gap filling promoter in helping copper electroplating without void formation. There are also some theoretical works on the electroplated copper filling of sub-micron trenches and vias [5–6]. Takahashi and Gross [5] discussed the effects of changes of plating current density, feature geometry, additive concentration, diffusion and convection in the plating bath on filling profiles. West [6] estimated the importance of parameters such as levelling additive mobility and concentration on the process capability of filling trenches or vias of a given size.

In this paper, we report optimised copper electrodeposition onto patterned Cu/Ta(N)/SiO_2 wafers. The goal of this work is to develop electrochemical copper deposition technique with minimum additives to fill sub-micron features. It is demonstrated that, with the present formulation, copper can be electroplated into 300 nm vias with an aspect ratio of 3.4:1 under optimised experimental conditions.

2. Experimental

The samples used were cut from patterned Cu/Ta/SiO_2 or Cu/TaN/SiO_2 wafers provided by Applied Materials (Santa Clara, California). The patterned surfaces consisted of dielectric stacks (SiO_2) with sub-micron features (e.g., vias and trenches). A PVD barrier layer of titanium (Ta) or titanium nitride (TaN) was deposited on the patterned surface followed by a PVD Cu seed layer. Since the top layer of the patterned Cu/Ta/SiO_2 or Cu/TaN/SiO_2 wafers is the same material, namely PVD copper film, no differences were observed for the ECD of Cu. Therefore, in the rest of the text, we generally use 'Cu/Ta(N)/SiO_2' to refer to either 'Cu/Ta/SiO_2' or 'Cu/TaN/SiO_2'.

The electrochemical cell consisted of a piece of Cu/Ta(N)/SiO_2 used as a working electrode, a SCE reference electrode and a Pt wire counter electrode. An EG&G Model 273A potentiostat was employed. Electrodeposition was carried out in constant current mode. The electrolyte consisted of copper sulphate, sulphuric

acid, and very small amounts of chloride and PEG with an average molecular weight less than 5000.

SEM measurements were performed with a Philips XL 30 field emission scanning electron microscopy (FE-SEM). X-ray photoelectron spectroscope (XPS) measurements were performed using a VG ESCA MKII XPS instrument with a Mg K radiation beam (1286.6 eV) and an ultrahigh vacuum chamber of 10^{-10} Torr. The banding energy was calibrated against a neutral C1s peak at 284.6 eV.

The solutions were prepared with commercially available $CuSO_4 \cdot 5H_2O$, H_2SO_4 (98%), HCl (30%), PEG and Milli-Q water (>18.2 Ω cm).

3. Results and discussion

It is well known that additives play an important role in electrodeposition processes [1]. Usually, two types of additives are present in the solution, i.e., accelerator and suppressor (or levelling agent). The accelerator, usually chloride, enhances deposition of Cu on the bottom Cu seed within vias. On the other hand, the suppressor, typically a larger organic molecule, inhibits Cu deposition on the open area outside vias. Figure 1 shows the effect of additives on current–potential curves. The curve a was obtained in 0.5 M $CuSO_4$ + 1.5 M H_2SO_4 without additives. The curve with addition of only Cl^- ions (Curve b) does not change much compared with the curve without additives (Curve a). However, as PEG and Cl^- are added (Curve c), the current–potential curve shifts about 200 mV in the cathodic direction, indicating that PEG prohibits ECD of Cu on Cu seed layer by an overvoltage of ~200 mV.

Figure 2 shows copper electrodeposition into the high aspect-ratio vias. The samples used consisted of many types of vias. Figure 2a is a typical cross-sectional SEM image of a blank sample. The aspect ratio of the vias in this sample is 3.3:1 (1.25 m deep and 0.37 m wide at its bottom). It shows that there is a very thin copper seed layer along the side wall of the vias compared to thick Cu seed on the bottom and top surfaces due to step coverage from the PVD Cu process.

Copper electrodeposition into such high aspect-ratio vias was carried out. Figure 2b and c were selected from a series of cross-sectional SEM images and show the intermediate and final stages of copper deposition in the vias, respectively. These images indicate that the vias have aspect ratios higher than 3:1 (1.13 m deep and 0.33–0.38 m wide at the bottom). Figure 2b shows that the rate of copper electrodeposition at the bottom of the vias is faster than that along the sidewalls. This clearly

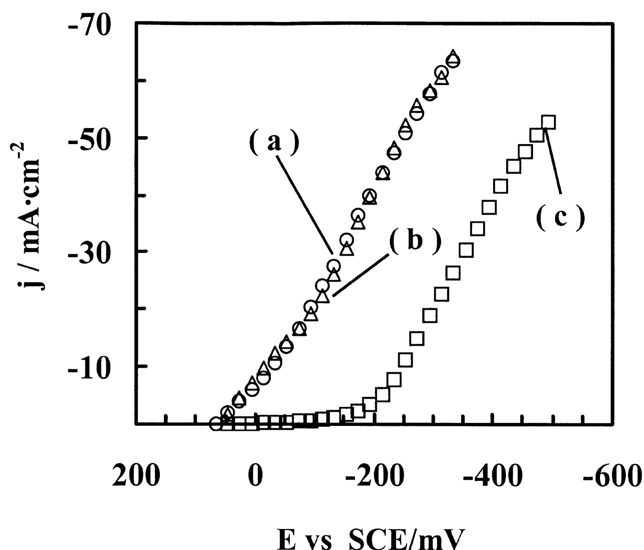

Fig. 1. Current–potential curves of copper electrodeposition on patterned Cu/Ta(N)/SiO_2 surfaces in an electrolyte containing (a): 0.5 M $CuSO_4$ + 1.5 M H_2SO_4 (○), (b): (a) + 2 mM HCl (△), and (c): (a) + 2 mM HCl + 0.625 g/l PEG (□).

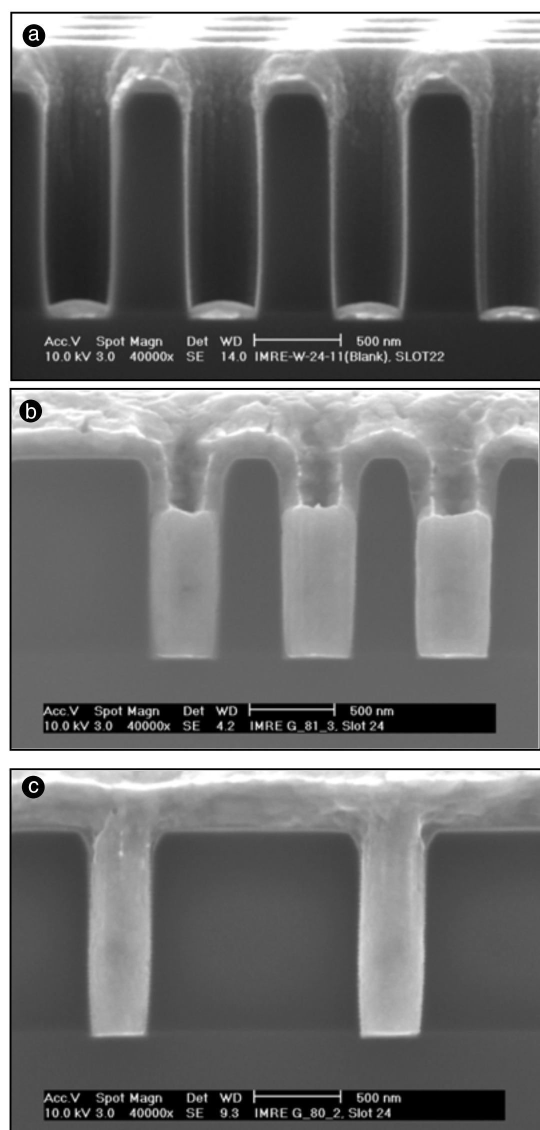

Fig. 2. Cross-sectional SEM images of (a) blank and (b–c) copper electrodeposited Cu/Ta(N)/SiO_2 vias. The current density and time for the electrodeposition are (b) 1 mA/cm^2, 600 s, and (c) 5 mA/cm^2, 400 s, respectively. The electrolyte is 0.5 M $CuSO_4$ + 1.5 M H_2SO_4 + 2 mM HCl + 0.625 g/l PEG.

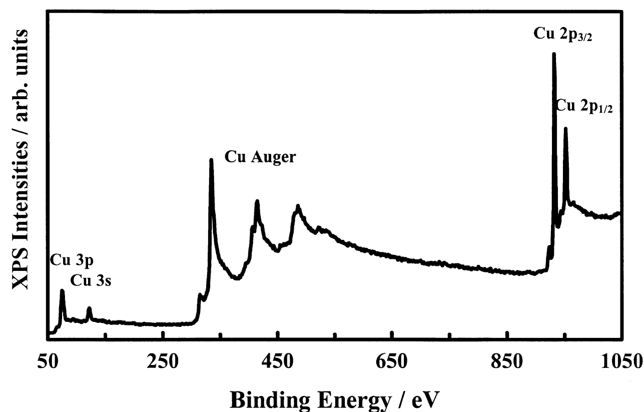

Fig. 3. XPS spectrum of the electrodeposited copper.

demonstrates that the growth of electrodeposited copper is by the so called 'super-filling' mechanism [1]. As shown in Figure 2b, it is clear that PEG greatly suppresses the deposition rate on the top surface next to the via opening by strong adsorption of the suppressor on the Cu seed layer. In contrast, Cu deposition at the bottom of the vias is much faster because PEG has a lower diffusion coefficient than Cu ions and chloride. The concentration gradient of PEG does not form or the concentration of PEG on the Cu seed of vias bottom is very low until two-thirds of Cu filling. This result is consistent with the cyclic voltammogram in Figure 1. The intermediate SEM image (Figure 2b) clearly shows that the suppressor (PEG) plays a very important role in super filling of Cu as also discussed theoretically [5–6]. Besides the additives, Cu ion concentration and current density are also important factors for Cu filling [5]. This type of copper filling could be obtained only with optimised experimental conditions, including an electroplating solution with suitable additives, electrodeposition rate and time and applied current density. The present process provides a good filling profile in the vias. Figure 2c shows that the vias are fully filled with copper: there are no voids or seams observed.

Figure 3 shows an XPS spectrum indicating the elements present in the electrodeposited copper. All peaks originate from copper and there are no obvious peaks for other elements, such as C, Cl, O and S, although they are components of the electroplating solution. This indicates that the concentrations of these elements are very low and beyond the detection limit of the XPS instrument (about 1% atomic concentration). The resistivity of the electrodeposited Cu was 2 Ω cm when measured with four-probe measurement before self-annealing and other thermal processes thus indicating that the deposited copper is of good quality.

4. Conclusions

Copper electrodeposition on patterned $Cu/Ta(N)/SiO_2$ surfaces for filling sub-micron vias with a width of 300 nm and an aspect ratio of 3.4:1 was demonstrated. SEM and XPS measurements were used to characterise the deposition profile of the electrodeposited copper film and the impurities in the film, respectively. It is possible to fill the vias without voids or seams under optimised electrodeposition conditions with electrodeposited Cu of 2 Ω cm resistivity. A further study of the mechanism of copper deposition is needed.

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