Role of additives for copper damascene electrodeposition experimental study on inhibition and acceleration effects

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The role of copper Damascene additives is discussed based on electrodeposition results on a through-mask cathode, field emission-Auger (FE-Auger), quartz crystal microbalance (QCM), and electrochemical measurements. Adsorbed particles, several tens of nanometers in diameter, were observed on copper-electrodeposited surfaces by field emission-scanning electron microscopy (FE-SEM). These particles show a stronger oxygen intensity peak by FE-Auger than bare electrodeposited surfaces. The QCM frequency deviation did not increase with time in the CuSO$_4$ and H$_2$SO$_4$ bath without polyethylene glycol (PEG) and chloride ions (Cl$^-$) additives. The substrates were immersed in the bath with these additives, and the deviation markedly increased with time. Numerous PEG molecules were observed by FE-SEM immersed after 1000 s. The current density remained constant at a low value for the bath with PEG and Cl$^-$ additives. The current density started to increase markedly with time just after adding 1 ppm of bis(3-sulfopropyl) disulfide (SPS). Numerous PEG molecules were present on the electrodeposits before adding SPS. No PEG molecules were observed on the surface once SPS was added to the bath. The current density increased with narrower opening widths of the through-mask cathode. Despite this increase, the deposit cross sections on narrower opening widths of 2 and 10 µm were flat and no curvatures were found. Hence, deposit curvature is not the origin of the acceleration effect.

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Deligianni et al.$^{13}$ suggested that the acceleration effect is caused by the catalytic effect of the copper ion and SPS complex, and this complex accumulates inside the vias of smaller features. Farndon$^{14}$ independently proposed the existence of cuprous and thiolate complex. Recently, Kondo et al.$^{15}$ monitored the via bottom acceleration effect by using a through-mask cathode and suggested that the cuprous and thiolate complex accelerates the deposition effect at the via bottom. It was found that current densities increased with increasing the via depth. The deeper the via is, the larger the current density. With a conventional flat-plate cathode, the current-density/potential curves of Cl$^-+PEG+SPS$, Cl$^-+PEG+JGB$, and Cl$^-+PEG+JGB+SPS$ are almost identical. With a through-mask cathode, the current densities increase markedly with SPS. Moreover, Vereecken et al.$^{15}$ detected the free acceleration complex on the ring of rotating glassy carbon—platinum disk electrode.

The objective of this paper is to report detailed experimental results on Damascene electrodeposition additives of Cl$^-$, PEG, and SPS. The inhibitory effect was observed by FE-SEM, field emission Auger (FE-Auger), and QCM. The acceleration effect was analyzed by deposition on a through-mask cathode, examination of deposit cross sections, and deposition on a glassy carbon ring-disk electrode.

**Experimental**

Table I shows the bath composition. The basic bath consists of CuSO$_4$ and H$_2$SO$_4$ of 0.6 × 10$^{-3}$ and 1.85 × 10$^{-3}$ mol/L, respectively. Additives are Cl$^-$, PEG of 7500 molecular weight, and JGB, whose concentrations are shown in Table I. The bath was used for...
each experiment 1 h after bath preparation. The potential was kept constant of $-200 \text{ mV}$ from the rest potential vs. 3.33 mol/L KCl-AgCl, unless otherwise specified.

The morphology of electrodeposits was observed by FE-SEM (Hitachi S-4300). FE-Auger (Smart-200, Physical Electronics) was used to measure the Auger spectrum of oxygen, carbon, and copper at the local points of the electrodeposits. The space resolution of this FE-Auger was about 10 nm.

A QCM (HQ-series, Hokuto-denko) was connected to the potentiostat of a HZ-3000 (Hokuto-denko). A 6 MHz quartz gold electrode substrates were initially electrodeposited with pure copper from a basic bath consisting only of only CuSO$_4$ and H$_2$SO$_4$. The substrates were immersed in the additive-containing electrolyte and frequency deviation-time curves were measured. The current density-time curves were measured with a rotating disk electrode (RDE) 12 mm in diameter.

The through-mask cathodes were prepared as follows. Photore sist patterns were formed on copper foil. The patterns consisted of 30 $\mu$m wide lines of exposed copper foil surface with widths of 2, 10, and 30 $\mu$m. The pattern had ten lines of 16 mm length and 1.0 mm pitch. THB-430N (JSR Co.) photoresist was used. The photo-
frequency deviation-time curves without PEG and Cl\textsuperscript{2} additives (curve a) with PEG and Cl\textsuperscript{2} additives (curve b), and SPS additives was performed in an RDE to detect the existence of an free-accelerant complex. The rotating ring-disk electrode consisted of a glassy-carbon ring and glassy-carbon disk. The bath was the same as that used in current-density curve measurements for the through-mask cathode except that the SPS concentration was 80 ppm to improve detection.

The encapsulated specimens, prepared by imbedding them in epoxy resin, which was cut perpendicular to the copper surface and polishing. They were examined under a scanning electron microscope (SEM).

Results

Inhibition effect.—Figure 1 shows a FE-SEM micrograph of electrodeposits with PEG and Cl\textsuperscript{2} additives. Figure 1a shows electrodeposits after 15 min and (b) after 60 min of deposition. In Fig. 1a the electrodeposits had crystal diameters of 500 μm with flat surfaces. Note several 10 nm particles are present. However in Fig. 1b, the crystal surface is not flat, and several 10 nm particles are observed (see arrow in Fig. 1b). The crystal diameter is 500 μm. Adsorption of these several 10 nm particles on the electrodeposited copper surface depends on the electrodeposition time.

Identification of the particles by FE-Auger spectroscopy.—Figure 2 is a FE-SEM micrograph of an electrodeposited film in the presence of PEG and Cl\textsuperscript{2} additives after 120 min electrodeposition time. The frequency deviation-time curves measured by QCM. Figure 4a is the QCM curve when the substrate was immersed in the bath of CuSO\textsubscript{4} and H\textsubscript{2}SO\textsubscript{4} only. These substrates were immersed in the bath of CuSO\textsubscript{4} and H\textsubscript{2}SO\textsubscript{4} with PEG and Cl\textsuperscript{2} additives. The frequency deviation is almost constant and does not increase with time. Figure 3 shows the frequency deviation-time curves for the through-mask cathode except that the SPS concentration was 80 ppm to improve detection.

The white arrow labeled 1 indicates the densely adsorbed particles, and the white arrow labeled 2 indicates an area without particles.

Figure 3 is a FE-Auger spectrum corresponding to the points indicated by arrows 1 and 2 in Fig. 2. In Fig. 3a, a carbon peak exists at 295 eV, an oxygen peak at 517 eV and copper peaks at 795 and 860 eV. Carbon and copper have almost the same peak intensity. Oxygen at point 1, however, has a stronger peak intensity than point 2. Figure 3b is an enlarged spectrum from 490 to 540 eV. At 517 and 503 eV, the oxygen peak intensity is stronger for point 1 where several 10 nm particles are densely adsorbed.

PEG is (C\textsubscript{2}H\textsubscript{5}O\textsubscript{2})\textsubscript{n} and the atomic number of oxygen is same as carbon. The densely adsorbed several 10 nm particles observed by the FE-SEM are PEG molecules. Hence, we conclude that the several 10 nm particles observed by the FE-SEM are PEG molecules.

PEG molecules and QCM.—Initially pure copper was electrodeposited on the QCM substrates from a basic bath consisting of CuSO\textsubscript{4} and H\textsubscript{2}SO\textsubscript{4} only. These substrates were immersed in the bath of CuSO\textsubscript{4} and H\textsubscript{2}SO\textsubscript{4} only. These substrates were immersed in the bath of CuSO\textsubscript{4} and H\textsubscript{2}SO\textsubscript{4} with PEG and Cl\textsuperscript{2} additives. The frequency deviation is almost constant and does not increase with time. Figure 4d is a FE-SEM micrograph of copper electrodeposited film immersed for 200 s into the bath of CuSO\textsubscript{4} and H\textsubscript{2}SO\textsubscript{4} with PEG and Cl\textsuperscript{2} additives. The crystal surfaces are flat but several 10 nm PEG molecules exist. Figure 4d is that immersed for 1000 s.
surfaces are also flat, but numerous several 10 nm PEG molecules exist. These FE-SEM micrographs of c and d correspond to the increase in QCM frequency deviation in b.

PEG molecules and SPS additives.—Figure 5 is the current density-time curve with the bath of CuSO$_4$ and H$_2$SO$_4$ with PEG and Cl$^-$. Initially, the current density shows a constant value at a lower current density of 4.3 mA/cm$^2$. After 1800 s, 1 ppm of SPS was added to the bath (indicated with an black arrow in Fig. 5, and the current density markedly increased with time. After 4000 s, the current density became constant with time and remained at 18.5 mA/cm$^2$. SPS additive has an acceleration effect, and increases the current density drastically.

Figure 5a is the FE-SEM micrograph of copper electrodeposited at 1800 s from the bath of CuSO$_4$ and H$_2$SO$_4$ with PEG and Cl$^-$. Numerous PEG molecules (indicated with white arrow) exist, and the crystal diameter is about 500 nm. After SPS is added at 3000 s (Fig. 5b), the PEG molecules are no longer present. The crystal diameters become 100 nm and refinement occurs. The SPS additive has the effect of removing PEG molecules from copper electrodeposited surfaces and of refining copper electrodeposited crystals.

Acceleration effect, electrochemical detection by through-mask cathode.—The through-mask cathode is known to detect the via bottom acceleration effect by SPS. Through-mask cathodes consist of pattern widths of 2, 10, and 30 $\mu$m and are illustrated in the inset in Fig. 6. The current-density/potential curves without SPS were measured for different opening widths of through-mask cathodes. The additives were PEG, Cl$^-$, and JGB (Fig. 6). Without SPS, it is clear that the current density does not depend on the opening widths of through-mask cathodes.

Next, the current-density/potential curves with SPS were measured for different opening widths of through-mask cathodes. Figure 7 shows the current-density/potential curves with additives of (a) Cl$^-$ + PEG + SPS and (b) Cl$^-$ + PEG + SPS + JGB. The opening widths are 2, 10, and 30 $\mu$m. It is clear that the current density depends on the opening widths. The narrower the opening widths, the greater the current densities. The through-mask cathodes detected the via bottom acceleration effect. Moreover, it is clear that the via bottom current densities increase with decreasing width of the through-mask cathode and this occurs with (Fig. 7a) JGB and without (Fig. 7b) JGB. These current density increases are due to the via bottom acceleration effect of SPS.

From the view point of the detection of free cuprous and thiolate complex, we made a similar experiment to that done of Vereecken et al.. Figure 8 shows the results of our ring-disk electrode experiment in the case of 0.5 and 0.9 V of disk electrode. SPS oxidation occurs at potential of 0.9 V and no SPS oxidation occurs at 0.5 V. Next, the ring electrode potential ($E_{RING}$) was fixed at 0.5 and 0.9 V. Since a larger $I_{RING}$ was detected at SPS oxidation potential of 0.9 V, the hatched area in Fig. 8 must correspond to the oxidation of free SPS complex.
Deposit cross sections on the through-mask cathodes.—Josell et al. proposed an acceleration mathematical model based on the curvature formation at via bottom. Since narrower opening widths of through-mask cathodes show an acceleration effect, the deposited cross sections on the through-mask cathodes were observed in order to identify the existence of the curvatures. The additives are PEG, Cl⁻, JGB, and SPS. It was found that the deposits are always flat, and no curvature was observed. The deposit curvature is thus not the origin of the acceleration effect.

Figure 10 shows the schematic illustration of the inhibition and acceleration effects of the Damascene electrodeposition. PEG molecules inhibit the electrodeposition reaction by adsorption on the copper electrodeposit. The free acceleration complex of cuprous and thiolate forms. With narrower via opening width, the acceleration complex accumulates within the via. This increases the via bottom current density and accelerates the via bottom growth. This model is based on the free acceleration complex of cuprous and thiolate. The acceleration complex that accumulates within the vias may also remove the via bottom PEG molecules adsorption, as has been observed in Fig. 5b.

Conclusions

The role of additives for copper Damascene has been discussed experimentally based on electrodeposition morphology, FE-Auger, QCM, and electrochemical measurements with a through-mask cathode. Particles several tens of nanometers in size were observed by FE-SEM on copper surfaces after an electrodeposition time of 60 min. These particles show stronger FE-Auger spectrum oxygen-peak intensity than bare copper electrodeposit surfaces. PEG is an oxygen-containing polymer, and these particles observed by the secondary electron image of FE-SEM are PEG molecules.

The QCM substrates were immersed into CuSO₄ and H₂SO₄ solution without PEG and Cl⁻ additives. The QCM frequency deviation does not increase with time. When the substrates were immersed into CuSO₄ and H₂SO₄ solution with PEG and Cl⁻ additives, the QCM frequency deviation markedly increase within 100 s. Numerous PEG molecules were observed by FE-SEM on the substrate.

The current density shows a constant, low value of 4.3 mA/cm² with the bath of CuSO₄ and H₂SO₄ with PEG and Cl⁻ additives. Once 1 ppm of SPS was added to the bath, the current density started to increase markedly with time. The SPS additive is an accelerator which increases the current density drastically. Numerous PEG molecules were present on the substrate before the addition of SPS. No PEG molecules were present after SPS was added to the bath. Refinement of the copper electrodeposit occurs, and the crystal diameter shrinks to 100 nm. The SPS additive has the effect of removing PEG molecules and refines the deposit grain structure.

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