Study of Direct Cu Electrodeposition on Ultra-Thin Mo for Copper Interconnect

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Abstract

Direct electrodeposition (ECD) process of copper film on ultra-thin molybdenum film is investigated in both copper sulfate - sulfuric acid (CuSO_4 - H_2SO_4) acidic bath and copper sulfate - ethylenediamine (CuSO_4 - En) neutral bath (pH = 7.5). The neutral electrolyte containing 0.03 M CuSO_4 and 0.06 M En was chosen to avoid excessive corrosion of Mo and introduction of other ions. The complexing effect of En affects the electrodeposition process of Cu on Mo. Potentiodynamic polarization curves and scanning electron microscopic characterization show that Cu can be electroplated in CuSO_4 - En bath with lower corrosion rate, greater nucleation density and shorter fully-covering time than that in CuSO_4 - H_2SO_4 bath. The fitting results of current-time transients using Scharifker and Hill's model support the instantaneous nucleation and growth of Cu on Mo in both CuSO_4 - H_2SO_4 bath and CuSO_4 - En bath (with background electrolyte) at the initial stage of electrodeposition. By using an optimized two-step plating process (at the current density of 8 mA/cm^2 in the first step for a short time and 4 mA/cm^2 in the second step), the resistivity of direct ECD Cu on Mo was almost the same to that of ECD Cu on Cu/Mo in the same plating bath.

1. Introduction

As ULSI (Ultra Large Scale Integrated Circuits) device keeps scaling down, signal delay caused by Cu/low k interconnect due to increased resistivity and capacitance has become one of the major concerns. The present sputtered Cu seed/Ta/TaN trilayer technology becomes increasingly difficult to fulfill the requirement of electroplating step. It is getting increasingly hard to sputter conformal Cu seed layer inside deep trenches, which would cause void formation after electroplating and chemical mechanical polishing (CMP) process and result in significant resistance increase and reliability issue. Direct Cu plating onto ultra-thin diffusion barrier layers is desirable for further seamless electrochemical filling of the trench [1]. However, direct Cu electroplating process on diffusion barriers is very complex compared to that on Cu seed layer due to much higher resistivity of those barriers in comparison to Cu seed layer. Also Cu nucleation and growth on different barrier materials will be significantly different due to the different surface lattice structure of the barriers and different adhesion and interface properties between Cu and each kind of diffusion barriers [2]. Recently, Ru, Ir, and Co have been considered as adhesion materials for direct Cu plating [1, 3-5]. Ru (5 nm)/Ta₂N₅ (5 nm) was only stable up to 450 °C though the failure was due the formation of TaSi₂ [6], and Co (10 nm)/Ta₂N₅ (10 nm) can also stand 600 °C annealing for 30 min [7]. Ir (5 nm)/Ta₂N₅ (5 nm) bilayer was an effective barrier for blocking copper diffusion of up to 600 °C for 1 h according to Ref. [8].

Molybdenum has relatively low electrical resistivity ($\sim 6 \mu\Omega\cdot\text{cm}$), high melting point and good thermal stability. Mo has been used in the fields of nuclear power [9], photovoltaic [10] and TFT display as electrodes [11]. There are also reports showing potential application of Mo as liner to Cu. It is reported that Cu metallization with Mo (5 nm)/MoN (5 nm) as barrier stack can be stable at up to 600 °C for 10 min [12]. Sputtered Mo (5 nm)/WN (5 nm) bi-layer remained thermally stable up to at least 775 °C [13]. Our previous study on Mo based barrier also showed that CoMo alloy [14], MoTa alloy and Mo/TaN stack [15] could be good

diffusion barrier to Cu. Mo (5 nm)/TaN (5 nm) can be thermally stable up to 600 °C annealing [11], and the adding of Co or Ta to form alloys results in better barrier performance against Cu diffusion [10, 11]. In comparison to currently hot-researched Ru and Co, Mo has better chemical mechanical polishing properties than Ru and Mo is not as easily corroded as Co.

Direct plating of Cu onto very thick (600 nm) sputtered Mo film on glass substrate in a commercial acidic electrolyte has been reported recently, which aims to study electrodeposition of Cu-containing alloys to form the thin film absorber in the photovoltaic application [16]. P. Ren et al. chose an electroplating system containing CuSO₄ and C₆H₅Na₃O₇ to deposit Cu films on pure Mo substrate [17]. However, direct electrodeposition of Cu on ultra-thin Mo film still needs to be investigated, because corrosion of Mo could be an important issue during electroplating process in Cu interconnect structure.

Ethylenediamine (En) can chelate and effectively stabilize both cupric and cuprous ions in aqueous solutions, so it can be used as an additive for non-cyanide alkaline electroplating of Cu [18]. CuSO₄ - En bath has been used for direct plating of Cu onto Co in the alkaline investigated by S. Armini and our group [3, 4].

In this paper, direct electrodeposition processes of Cu on thin Mo layer in CuSO₄ - H₂SO₄ acidic bath and CuSO₄ - En neutral bath were compared. The mechanism of Cu nucleation on Mo electrodeposited in both solutions was investigated. Plating conditions for direct Cu electroplating on Mo were further optimized in order to achieve lower resistivity.

2. Experimental

N-type Si (100) wafers were loaded into vacuum after RCA cleaning and HF dipping. The base pressure was under 5×10^{-5} Pa and the working pressure was 2.2×10^{-1} Pa with 10 sccm Ar flow. Mo films were deposited by DC sputtering. Mo layers with the thickness of 20 nm were deposited on blank wafers for electrochemical analyses and nucleation mechanism study. Mo-covered wafers were then cut into coupons and clamped in a Teflon holder leaving

$1 \times 1 \text{ cm}^2$ area exposed outside used for electroplating measurements ($1.5 \times 1.5 \text{ cm}^2$ for Cu electroplating processes under galvanostatic control). The electroplating process of Cu was carried out in both $\text{CuSO}_4 - \text{H}_2\text{SO}_4$ acidic bath and $\text{CuSO}_4 - \text{En}$ neutral bath, respectively. The acidic bath, 0.5 in pH value, consisted of 0.03 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 0.3 M H_2SO_4 , and the neutral bath consisted of 0.03 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 0.06 M En with the pH value of 7.5, considering chelating effect between En and Cu^{2+} [4]. Aqueous solutions with 3 M H_2SO_4 or 3 M KOH were used to adjust the pH values of electroplating bath when pH values other than 0.5 or 7.5 were needed. Na_2SO_4 was introduced as background electrolyte to increase the conductivity of the electrolyte. No organic additives were used.

All electrochemical measurements were carried out using PARSTAT2273 electrochemical workstation in a standard three-electrode setup. A platinum coil was used as the counter electrode and the reference electrode was a saturated calomel electrode (SCE). Linear sweep voltammetry (LSV), chronoamperometry (CA) and potentiodynamic polarization tests were carried out. The LSV measurements started from the open circuit potential (OCP) value of Mo in the solution to the potential at which severe hydrogen evolution happened with the scan rate of 5 mV/s, 10 mV/s, 20 mV/s and 50 mV/s. The CA tests were performed at various potential values according to the electroplating solution with the duration of 10 s. Potentiodynamic polarization curves were obtained by scanning at 5 mV/s, from 250 mV below the OCP value of Mo to 250 mV above the OCP value. Electrochemical impedance spectroscopy (EIS) was used to measure the solution resistance (R_s). The measurements were conducted at potentials 10 mV more negative than the OCP value for Mo in acidic and neutral baths. The AC amplitude was 10 mV and the frequency ranged from 100 kHz to 100 mHz. Electroplating processes under galvanostatic control with magnetic stirring were carried out to optimize the condition of Cu plating on Mo, during which the platinum coil was replaced by Cu electrode as counter electrode. The distance between anode and cathode was 20 cm in our plating tank. Potential-time transients were also

recorded during electroplating processes. All potentials were reported with respect to SCE, uncorrected for ohmic potential drop (E_{IR}).

After electrodeposition, all samples were cleaned by ultrasonic oscillation in isopropyl alcohol (IPA) for 5 min and dried by nitrogen flow before other tests. Sheet resistance of the samples was measured by a 4D four point prober (FPP). The surface and cross sectional morphologies of the electrodeposited wafers were observed by scanning electron microscopy (SEM).

3. Results and Discussion

3.1 Cu Electrodeposition and Nucleation on Mo in CuSO_4 - H_2SO_4 bath

3.1.1 Current-potential characteristics

Figure 1 shows the linear sweep curves for Mo in acidic bath containing 0.03 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 0.3 M H_2SO_4 with different scan rates. The LSV started from the OCP value of Mo (+0.04 V) in the bath to -0.8 V. For the scan rate of 5 mV/s, the onset of Cu deposition on Mo appeared at -0.08 V, followed by a diffusion limited peak at -0.19 V with the peak current density (i_p) of 3.2 mA/cm^2 . The cathodic current increased sharply at -0.55 V due to the hydrogen evolution. The Cu reduction peak shifted to -0.22 V, -0.23 V and -0.24 V when the scan rate was increased to 10 mV/s, 20 mV/s and 50 mV/s, respectively, indicating that Cu reduction on Mo substrate in this system is irreversible. The peak current density i_p in the irreversible electrode reaction can be expressed by the following equation [19]

$$i_p = kn(\alpha_c n_\alpha)^{1/2} C_0 D^{1/2} \nu^{1/2} \quad (1)$$

where n is total number of electrons; α_c is the transfer coefficient of cathode process; n_α is the number of electrons transferred up to the rate determining step; C_0 is the bulk concentration; D is the diffusion coefficient; ν is the scan rate and k is a constant. The linear relationship between i_p and $\nu^{1/2}$ demonstrates that the reduction process was performed under diffusion

control [19].

3.1.2 Nucleation and growth

Initial nucleation and growth kinetics of the metallic nuclei on different material surfaces is critical because it determines the quality of electrodeposited metal film. The nucleation process of Cu on Mo substrate was investigated by chronoamperometry in $\text{CuSO}_4 - \text{H}_2\text{SO}_4$ acidic bath. The current-time transients at different potential (from -0.20 V to -0.45 V) are shown in Fig. 2(a) with the duration of 10 s. The current increased rapidly at first due to activation of substrate surface for Cu nucleation, and then a dramatic current drop occurred due to diminishing concentrations of reducible ionic species in the surface depletion region. The current transient until the steady-state can be fitted well by the Cottrell equation [20]

$$i = \frac{nFD^{1/2}C_0}{\pi^{1/2}t^{1/2}} \quad (2)$$

where i is current density; n is the number of electrons involved; F is Faraday constant; D is the diffusion coefficient; t is the time and C_0 is the bulk concentration. This also indicates the diffusion-controlled growth of Cu, consistent with the current-potential characteristics discussed above.

Scharifker and Hills developed a mathematical model to describe the nucleation mechanisms with current-time transients [21]. The models for instantaneous and progressive nucleation are given by equations (2) and (3), respectively [21],

$$(i/i_m)^2 = 1.9542(t_m/t)\{1 - \exp[-1.2564(t/t_m)]\}^2 \quad (3)$$

$$(i/i_m)^2 = 1.2254(t_m/t)\{1 - \exp[-2.3367(t/t_m)]\}^2 \quad (4)$$

where i_m and t_m are the maximum current and the corresponding time, respectively.

The curves plotted using Scharifker and Hill's model and our experimental results are shown in Fig. 2(b). Before the current reached the maximum (i_m) ($t < t_m$), the experimental curves at the potentials from -0.3 V to -0.45 V ranged within the interval delimited by instantaneous and progressive plots. After t_m , the experimental curves at low potentials were

away from the instantaneous curve but the curves at the potentials of -0.4 V and -0.45 V followed the instantaneous nucleation and growth after reaching the i_m ($t > t_m$).

The SEM images of Cu electrodeposited on Mo under -0.4 V for different time were shown in Fig. 3. We can't observe any Cu nuclei using SEM for the samples with the deposition time of 0.1 s and 0.2 s even though the nucleation and growth of Cu had started indicated by Fig.2. An even distribution of Cu nuclei was observed in Fig. 3(a) and (b), in consistent with the instantaneous nucleation and growth model predicted by Scharifker and Hill's model. For the sample with the deposition time of 5 s, seen from Fig.3(c), the number of Cu nuclei continued to increase with growth of Cu nuclei at the same time, which is the characteristic of progressive nucleation. However, it should be noticed that t_m was 0.14 s for the deposition potential of -0.4 V and the duration of 1s has exceeded the range of $t/t_m = 5$ shown in Fig. 2(b). It is observed that the nuclei geometry was dendritic rather than hemispherical in Fig. 3, which was also observed in the cases of Cu nucleation on glassy carbon in $\text{CuSO}_4 - \text{H}_2\text{SO}_4$ solution [20], and on modified native oxide of Si in $\text{CuSO}_4 - \text{Na}_2\text{SO}_4 - \text{H}_3\text{BO}_3 - \text{H}_2\text{SO}_4$ solution [22]. Adding of additives in $\text{CuSO}_4 - \text{H}_2\text{SO}_4$ bath also resulted in similar dendritic nuclei geometry of Cu on Mo according to previous research [16]. The dendritic nuclei geometry of Cu can be explained by growth of Cu over the existing low-density nuclei because this would require lower energy than forming new Cu nuclei [22].

As is shown in Fig. 3(d), after 50 s under the deposition potential of -0.4 V, the electrodeposited Cu could not form continuous film on Mo surface. This would result in severe Mo corrosion in $\text{CuSO}_4 - \text{H}_2\text{SO}_4$ bath. Additionally, the low Cu nucleation density and the dendritic nature of electroplated Cu on Mo in $\text{CuSO}_4 - \text{H}_2\text{SO}_4$ bath make it not suitable for interconnect.

3.2 Cu Electrodeposition and Nucleation on Mo in the $\text{CuSO}_4 - \text{En}$ bath

3.2.1 Mo corrosion in electroplating bath

It is very important to study corrosion of ultrathin barrier in electroplating bath because severe corrosion of barrier will result in void formation or even failure in the following electroplating process. The corrosion of Mo in CuSO₄ - En bath with different pH values (from 3.5 to 11) was investigated first. Fig. 4(a) gives the Tafel plots for 20 nm-thick Mo in 0.03 M CuSO₄ and 0.06 M En with the pH values of 4.0, 7.5 and 10.0. The corrosion current density was obtained by fitting linear Tafel equations on anodic and cathodic Tafel regions of the polarization curves. The variation of calculated corrosion current (I_{corr}) and corrosion potential (E_{corr}) with different pH value is shown in Fig. 4(b). The corrosion potential of Mo linearly decreased with increased pH values over the pH range of 3.5 – 11. The slope was about -0.045 V/pH, similar to the reported value of -0.048 V/pH in Ref. [23].

As is shown in Fig. 4(b), I_{corr} was lowest, with an almost stable value of 16 $\mu\text{A}/\text{cm}^2$ in the solution with pH value varied from 7.5 to 8.5. Lower pH value resulted in much larger corrosion current. At pH 3.5, I_{corr} was about 304 $\mu\text{A}/\text{cm}^2$. When pH value was higher than 8.5, the I_{corr} also increased, about 200 $\mu\text{A}/\text{cm}^2$ at pH 10 and 11. According to Ref. [18], HEn^+ predominates at pH values between 6.848 (pK_{a1}) and 9.928 (pK_{a2}) in the En-water system at 25 °C. The relatively low I_{corr} shown in Fig. 4(b) between pH 7.0 and 8.5 corresponds to predominating CuEn_2^{2+} in the bath. According to our previous results, 0.06 M En can fully chelates 0.03 M Cu^{2+} in aqueous solution ($\text{En}:\text{Cu} = 2:1$) [4]. Under about pH 4 (varied with different concentrations of Cu^{2+} and En), Cu^{2+} predominates in the bath [18] resulting in the rapidly increasing I_{corr} . According to the potential - pH equilibrium of Mo, Mo oxides tend to dissolve in the solution with pH value higher than 7 due to formation of soluble HMoO_4^- and MoO_4^{2-} [23, 24]. So the pH value of 7.5 was chosen for our electroplating bath since the I_{corr} was kept at a low level and no Na^+ or K^+ was involved. Also Mo wouldn't be covered by insoluble oxides under this pH value.

We also made a comparison between corrosion of Mo in acidic and neutral solutions. Fig. 5 shows the Tafel plots for the Mo film in electroplating baths consisted of 0.03 M

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.03 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 0.3 M H_2SO_4 , and 0.03 M CuSO_4 and 0.06 M En, respectively. The corrosion current density in the bath with 0.03 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was $203 \mu\text{A}/\text{cm}^2$. The adding of 0.3 M H_2SO_4 increased the corrosion current to $3100 \mu\text{A}/\text{cm}^2$, which was much larger than that in the neutral bath ($15 \mu\text{A}/\text{cm}^2$). The complexing of Cu^{2+} with En effectively suppressed the corrosion of Mo during electroplating.

The static corrosion rates of the 100 nm-thick Mo films in the CuSO_4 - H_2SO_4 and CuSO_4 - En solutions were obtained by measuring the sheet resistance variation using FPP. The static corrosion rate of Mo in the CuSO_4 - En bath was about 0.7 nm/min, much smaller than that in the acidic bath (2.6 nm/min), in accordance with the results of corrosion current.

3.2.2 Current-potential characteristics

Figure 6(a) and 6(b) compare the linear sweep curves for Mo in neutral bath containing 0.03 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 0.06 M En at different scan rates (5 mV/s, 10 mV/s, 20 mV/s and 50 mV/s) without and with 1 M Na_2SO_4 respectively. The LSV started from the OCP value of Mo. In Fig.6(a), for the scan rate of 5 mV/s, the cathodic current increased slowly until -0.5 V representing the onset of Cu deposition on Mo in CuSO_4 - En, which was more negative than that in CuSO_4 - H_2SO_4 bath (-0.08 V). The cathodic current then increased to a platform at the current density of $4.2 \text{ mA}/\text{cm}^2$. No diffusion limited peak was observed. The cathodic current increased rapidly again below -1.5 V due to severe hydrogen evolution.

However, after adding 1 M Na_2SO_4 as background electrolyte in the CuSO_4 - En bath, for the scan rate of 5 mV/s, the onset of Cu deposition was about -0.5 V , and the diffusion limited peak appeared at -0.75 V with the peak current density (i_p) of $2.0 \text{ mA}/\text{cm}^2$. The larger onset deposition potential and the missing diffusion limited peak in Fig. 6(a) were caused by the uncompensated solution resistance (R_s) during electrochemical measurement. The R_s values were 79Ω and 7Ω for 0.03 M CuSO_4 - 0.06 M En bath and 0.03 M CuSO_4 - 0.3 M H_2SO_4 bath, respectively. Adding 1 M Na_2SO_4 as background electrolyte in the CuSO_4 - En

bath reduced the R_s to 8 Ω . Hydrogen evolution became severe below -1.2 V. A linear relation between i_p and $v^{1/2}$ was also found indicating the diffusion-controlled process of Cu electrodeposition.

Compared with the CuSO_4 - H_2SO_4 solution, the presence of En as complexing agent had an effect on the ECD process. The onset reduction potential of CuEn_2^{2+} (-0.5 V) in CuSO_4 - En bath was more negative than that of Cu^{2+} (-0.08 V) in CuSO_4 - H_2SO_4 due to the complexing effect of En, and the neutral pH of CuSO_4 - En bath lowered the potential for massive hydrogen evolution.

3.2.3 Nucleation and growth

Fig. 7 shows the current-time transients under the potential from -0.8 V to -1.8 V for 0.03 M CuSO_4 - 0.06 M En bath. Though the plots were still characterized by initial increase in current density and decay as described before, it should be noticed that the current decay was much slower than that in CuSO_4 - H_2SO_4 bath and failed to obey the Cottrell equation, so the nucleation in this situation didn't fit the Scharifker-Hills nucleation model. The possible reason could be the impact of solution resistance [20].

In order to investigate the nucleation model further, we performed chronoamperometry measurements and fitting for Cu deposition from solution containing 0.03 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.06 M En and 1 M Na_2SO_4 . The addition of background electrolyte improved the conductivity of the solution and eliminated the uncompensated resistance. The results are shown in Fig. 8(a) and (b). It can be seen that in Fig. 8(a) the current-time profiles consisted of an initial current peak due to charging of the double layer [1], followed by a rise and decay of current as is described above. After adding Na_2SO_4 in the solution, the current decay was linearly dependent with $t^{1/2}$ according to Eq. (2), the Cottrell equation, indicating the diffusion-controlled growth of Cu. The fitting of the current-time transients in the Scharifker and Hill's model is shown in Fig. 8(b). It can be seen that the curve fit for the instantaneous

nucleation in the range of -1.0 V and -1.1 V. However, the experimental curves shifted towards the progressive nucleation at less negative potentials (-0.7 V to -0.9 V). The deviation of the experimental curves when $t/t_m < 1$ was caused by the charging of the double layer. However, the addition of Na_2SO_4 may have other effects on the nucleation process of Cu on Mo which is not discussed further here.

Surface morphologies of Cu deposited on Mo in 0.03 M CuSO_4 - 0.06 M En bath under the potential of -1.4 V from 0.1 s to 50 s were observed through SEM to define the nucleation process of Cu, shown in Fig. 9. At initial stage from 0.1 s to 0.5 s, Cu nucleation density increased from 6×10^8 / cm^2 (0.1 s) to 6×10^9 / cm^2 (0.5 s), then the Cu island density remained almost unchanged till the islands started to merge with each other. The even distribution of Cu nuclei after 5 s indicated the instantaneous nature of the nucleation and growth of Cu on Mo.

The deposited Cu nuclei geometry on Mo in CuSO_4 - En solution was in the shape of hemisphere rather than the dendritic nuclei deposited in CuSO_4 - H_2SO_4 bath. One possible reason is the 30-times-greater nucleation density of Cu on Mo in CuSO_4 - En solution than that in CuSO_4 - H_2SO_4 solution. Cu followed the instantaneous nucleation and growth on Mo in the initial stage of electrodeposition in both CuSO_4 - H_2SO_4 bath and CuSO_4 - En bath.

3.3 Optimization of electroplating conditions

Cu electroplating on Mo was also carried out under galvanostatic control in the neutral bath containing 0.03 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 0.06 M En with solution agitation and a Cu electrode acted as anode. Different current densities were applied while controlling the total charge density of 1.36 C/ cm^2 (equivalent Cu thickness of 500 nm under the assumption of a current efficiency of 100%) by varying deposition time. Potential-time transients were recorded in Fig. 10. The inset of Fig. 10 shows potential as a function of time for the current density of 4 mA/ cm^2 only with different features of interest indicated. The potential dropped

from OCP to the start of P_0 right after applying current. P_0 represented formation and growth of Cu islands under the cathodic current. The start of P_1 corresponded to fully coalescence of Cu films and the potential remained. Duration of P_0 presented in Table 1 decreased with increasing applied current density. For the current density of 8 mA/cm^2 , duration of P_0 was about 50 s, however, the potential-time curve was less smooth because the current density might have exceeded the current density limited by the diffusion coefficient and concentration of CuEn_2^{2+} ions [3].

Calculated from sheet resistance and thickness (measured from cross-sectional SEM images) of plated Cu, resistivity values of Cu under different plating conditions are summarized in Fig. 11. For Cu plated at the current densities from 3 to 8 mA/cm^2 , resistivity decreases with increasing current density, because shorter coalescence time at higher current density results in Cu films with better quality. In order to decrease the resistivity further, a two-step plating process was carried out, that is to apply a high current density to achieve short coalescence time in the first step and a low current density to continue to plate Cu. The resistivity values were also shown in Fig. 11. Results show that resistivity of Cu plated at the current density of 8 mA/cm^2 for 50 s and 4 mA/cm^2 for 240 s was the lowest ($2.4 \mu\Omega\cdot\text{cm}$), which is close to that of Cu plated on Cu (5 nm)/Mo (20 nm) at the current density of 4 mA/cm^2 for 340 s ($2.3 \mu\Omega\cdot\text{cm}$).

Though Cu have been successfully electrodeposited directly on Mo in the neutral CuSO_4 - En bath, bottom-up superfilling of Cu in trenches and vias still can't be achieved due to lack of effective additives. Further research needs to be carried out for the application of direct electrodeposition of Cu on Mo and the neutral CuSO_4 - En bath.

Conclusion

This work investigates the direct electrodeposition process of Cu on thin Mo film in both CuSO_4 - H_2SO_4 acidic bath and CuSO_4 - En neutral bath ($\text{pH} = 7.5$) without additives. A

neutral electrolyte containing 0.03 M CuSO_4 and 0.06 M En was used in the research, considering both Mo corrosion control and chelating effect between En and Cu^{2+} . The Cu nucleation and growth mechanism on Mo follows instantaneous model during electrodeposition in CuSO_4 - En bath with Na_2SO_4 as background electrolyte, as well as that in CuSO_4 - H_2SO_4 bath. The corrosion rate of Mo in CuSO_4 - En bath is much lower than that in CuSO_4 - H_2SO_4 bath due to the neutral pH value and complexing effect between En and Cu^{2+} . The nucleation density of Cu deposited on Mo in CuSO_4 - En bath ($6 \times 10^9 / \text{cm}^2$ under the potential of -1.4 V vs. SCE) is about 30 times greater than that from CuSO_4 - H_2SO_4 bath (under the potential of -0.4 V vs. SCE). And the hemispherical geometry of Cu nuclei on Mo deposited in CuSO_4 - En bath is more suitable for application in interconnect structure than the dendritic geometry deposited in CuSO_4 - H_2SO_4 bath. A two-step plating process was carried out to lower the resistivity of Cu directly electroplated on Mo in CuSO_4 - En solution. The resistivity of direct ECD Cu on Mo after condition optimization (at the current density of 8 mA/cm^2 in the first step for a short time and then 4 mA/cm^2 in the second step) was almost the same to that of ECD Cu on Cu/Mo in the same plating bath.

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Figure Captions

Figure 1. Linear sweep plots for electrodeposition of Cu in the acidic bath containing 0.03 M CuSO_4 and 0.3 M H_2SO_4 at different scan rates. In the insert: Peak current density (i_p) as a function of square root of scan rate (v).

Figure 2. (a) Current-time transients of copper during electrodeposition on Mo in the acidic bath containing 0.03 M CuSO_4 and 0.3 M H_2SO_4 and (b) Corresponding Scharifker-Hills models.

Figure 3. SEM images of Cu clusters deposited on 20 nm Mo at the constant potential of -0.4 V for (a) 0.5 s, (b) 1 s, (c) 5 s and (d) 50 s, respectively, in the acidic bath of 0.03 M CuSO_4 and 0.3 M H_2SO_4 .

Figure 4. (a) Tafel plots for Mo in 0.03 M CuSO_4 - 0.06 M En bath with pH value of 4, 7.5 and 10.0 and (b) Corrosion current and corrosion potential variation of Mo with pH value in 0.03 M CuSO_4 - 0.06 M En bath.

Figure 5. Tafel plots for Mo in the acidic bath with 0.03 M CuSO_4 and 0.3 M H_2SO_4 , in the bath with 0.03 M CuSO_4 and in the neutral bath with 0.03 M CuSO_4 and 0.06 M En.

Figure 6. Linear sweep plots for electrodeposition of Cu in the neutral bath containing (a) 0.03 M CuSO_4 and 0.06 M En and (b) 0.03 M CuSO_4 , 0.06 M En and 1 M Na_2SO_4 at different scan rates. In the insert: Peak current density (i_p) as a function of square root of scan rate (v).

Figure 7. Current-time transients of copper during electrodeposition on Mo in the neutral bath containing 0.03 M CuSO_4 and 0.06 M En.

Figure 8. (a) Current-time transients of copper during electrodeposition on Mo in the bath containing 0.03 M CuSO_4 , 0.06 M En and 1 M Na_2SO_4 and (b) Corresponding Scharifker-Hills models.

Figure 9. SEM images of Cu clusters deposited on 20 nm Mo at the constant potential of -1.4 V for (a) 0.1 s, (b) 0.2 s, (c) 0.5 s, (d) 1 s, (e) 5 s, and (f) 50 s, respectively, in the neutral bath of 0.03 M CuSO_4 and 0.06 M En.

Figure 10. Potential-time transients for Mo in the neutral solution of 0.03 M CuSO₄ and 0.06 M En at current densities of 3, 4, 6 and 8 mA/cm² for different durations with the total charge density of 1.36 C/cm². In the inset: Potential-time transient at the current density of 3 mA/cm² only with the different features of interest indicated: P₀ for Cu nucleation and growth before fully convergence of Cu islands, P₁ for copper deposition after fully convergence.

Figure 11. Resistivity of directly electroplated Cu on Mo under different plating conditions (the total charge density of 1.36 C/cm²) in the neutral solutions of 0.03 M CuSO₄ and 0.06 M En.

Table Captions

Table 1. Duration of part P_0 obtained at potential-time transients in Fig. 10.

Table 1 Duration of part P_0 obtained at potential-time transients in Fig. 10.

Current Density (mA/cm ²)	3	4	6	8
Duration of P_0 (s)	220	125	120	50