Formation of nanoscale twins in Cu films with controllable orientations by electrodeposition

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Introduction:

As the electronic chips continuously shrink, the interconnecting technology need a new materials for 3-D interconnects. Electroplated copper with high density nano-twins that have superior mechanical strength and low resistivity become a potential candidate. However , the texture of electroplated nanotwin structured Cu playing an important role in oxidation and electromigration has not been studied yet.

In the conventional copper electrodeposition procedure, Cl^- is a common additives in the electrolyte due to the increases of electrolyte conductivity and acceleration of Cu reduction.

$$Cu^{2+} + e = Cu^{+} \qquad E^{\circ} = -0.087\ V_{SCE} \qquad (1)$$

$$Cu^{+} + e = Cu \qquad E^{\circ} = 0.281\ V_{SCE} \qquad (2)$$

$$Cu^{2+} + Cl_{ads}^{-} + e = CuCl_{ads} \qquad E^{\circ} = 0.338\ V_{SCE} \qquad (3)$$

$$CuCl_{ads} + e = Cu + Cl- \qquad E^{\circ} = -0.063\ V_{SCE} \qquad (4)$$

Eq. (1) and (2) is the standard reaction of Cu reduction, and the former is the rate determination step. If the reaction in acid sulfate electrolyte with Cl^- additives, another parallel proceeds (eq. (3) and (4)), the formation of CuCl, would lead to accelerate the overall reaction.

Experimental procedure:

Electrolyte: $CuSO_4$ 1M, with/without NaCl in different concentration
pH value: adjust to 1 by H_2SO_4
Anode: pure Cu sheet; Cathode: Si/SiO_2 /Ti(30nm)/Cu(75nm)
Current density: DC case: 45 mA/cm^2
pulse current case: 2 A/cm^2, on time: 0.02 s, off time: 1 s
The electroplated Cu films analyted by SEM, XRD and nanoindentation.
The followings are the measuring condition of XRD and nanoindentation.
XRD: 40^0-80^0 , 2^0/min
Nanoindentation: max load:5 mN, duration:5 s

Experimental results and discussion:

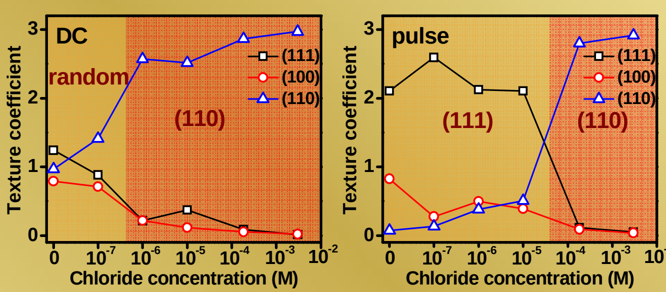

Figure 1: (a) Texture coefficient of electroplated Cu films by DC with different Cl^- concentration; (b) texture coefficient of electroplated Cu films by pulse current with different Cl^- concentration. All the texture coefficients are calculated from XRD data as the deposition time is 20 minutes.

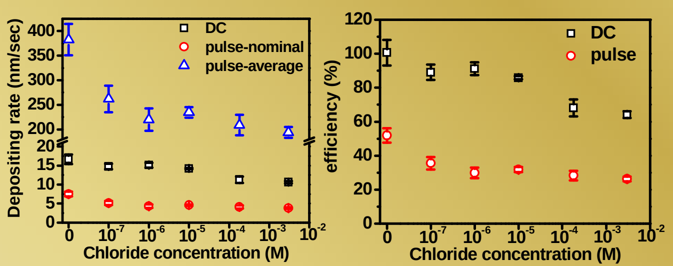

Figure 2: (a) Deposition rate of electroplated Cu films by DC and pulse current with different Cl^- concentration ; (b) the current efficiency of DC and pulse current with different Cl^- concentration.

$$Texture\ Coefficient = \frac{I(hkl)/I_0(hkl)}{\frac{1}{n}\sum I(hkl)/I_0(hkl)}$$

$I_{(hkl)}$: measured relative intensity
$I_{0(hkl)}$: relative intensity of the corresponding plane given in JCPDS data
n : number of reflections

From figure 1 and 2, there are many difference between DC and pulse current case.

1. For the DC case, the texture change from random to (110) dominated; however, the texture change from (111) to (110) dominated in the pulse current case.
2. The transition Cl^- concentration for pulse case is higher than DC case.
3. The deposition rate and current efficiency decrease with increasing of Cl^- concentration in the electrolyte for both case.
4. The deposition rate and current efficiency for DC case are higher than pulse current case.

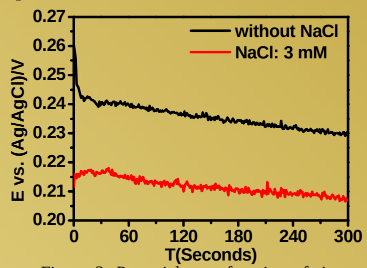

Figure 3: Potential as a function of time during direct current deposition with current density of 45 mA/cm^2.

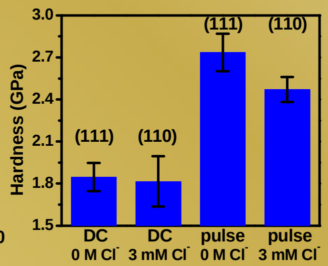

Figure 4: The hardness of electroplated Cu films with different texture for DC and pulse current case by nanoindentation.

The potential as function of time during direct current electrodeposition with current density of 45 mA/cm^2 show the overpotential of electrolyte with 3 mM Cl^- is lower than that without Cl^-. ,as shown in fig. 3. From electrochemistry theory, the overpotential would decrease when electrodeposition is under the same current density in the electrolyte with higher Cl^- concentration.

Figure 4 shows the hardness of electroplated Cu films with different texture for DC and pulse current case. There is no significant difference betwen (111) and (110) texture. However, the pulse current case has an ultrahigh strength. From literature and calculation, the pulse current case with high current density would lead to the formation of nanotwin in the Cu films and the nanotwins spacing is about 20 nm from Hall-Patch equation.

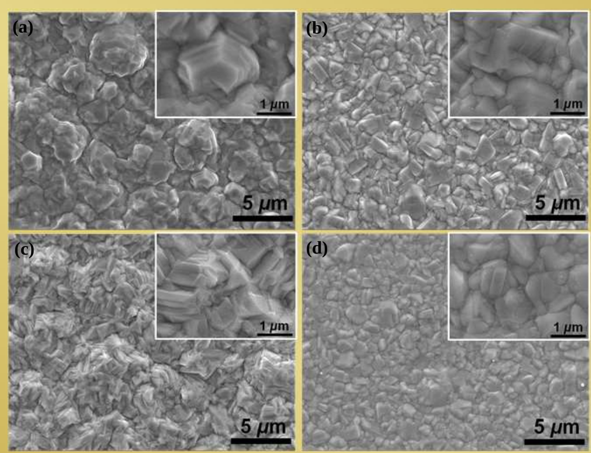

Figure 5: SEM images of different Cl^- concentration for DC and pulse current case. (a) DC without Cl^- (b) pulse current without Cl^- (c) DC with 3mM Cl^- (d) pulse current with 3mM Cl^-

The SEM images show surface morphology of electroplated Cu films with/without Cl^- for DC and pulse current case. The morphology indicate the (111) texture with granular grains and (110) texture with plate-like grains, as shown in fig. 4 .

Conclusions:

1.The texture of electroplated Cu films could be easily adjusted by different concentration of chloride in the electrolytes.
2.The change of overpotential in the electrolytes with different chloride concentration with the same current density would believed to cause the chloride effect and the difference between DC and pulse current case.
3.The Cu films deposited by pulse current have high hardness than those by direct current due to the formation of nanotwins.