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Effect of organic additives on structure, resistivity, and room-temperature recrystallization of electrodeposited copper

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Abstract

The effect of 3-*N,N*-dimethylaminodithiocarbamoyl-1-propanesulphonic acid (DPS) and polyethylene glycol (PEG, MW = 8000) on structure, surface roughness, and resistivity of copper electrodeposited from a sulfate–sulfuric acid bath (0.3 M CuSO₄ + 1.8 M H₂SO₄ + 70 ppm Cl⁻) has been studied by X-ray diffraction (XRD), atomic force microscopy (AFM), and four-point probe measurements. The XRD patterns of 2 μm-thick copper films reveal the presence of (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) peaks, intensity of which is dependent on the concentration of the organic additives in the plating bath. We show that addition of the above-mentioned organic additives affects the roughness of the film surface. Room-temperature recrystallization occurs in the films over the time period of several weeks if they are electrodeposited with both DPS and PEG additives present in the plating bath. It is accompanied by a change in stress, from compressive to slightly tensile, and a decrease in resistivity. The role of stress-relieving recrystallization is linked to the increase in grain size and enhancement in (1 1 1) and especially (2 0 0) texture.

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1. Introduction

The electrodeposition of Cu has been a subject of recent extensive investigations because of the attractiveness of this material for applications that require high electrical conductive layers and interconnect lines. Developing a reliable manufacturable electrodeposition process for Cu inter-

connects in the semiconductor industry and other device-specific applications, e.g. coils of the readers of the recording heads, has been a priority. Cu offers a higher electric conductivity and improved reliability with respect to Al alloys [1]. The electrodeposited Cu can be deposited with small grain size, thus providing smooth films that can be used in void-free filling of high aspect ratio trenches [1–6]. In addition, electrodeposition offers a substantially cheaper process than physical vacuum deposition (PVD) or chemical vapor deposition (CVD).

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The texture, grain size, surface morphology, and stress of electrodeposited Cu are important for device applications, as these properties can affect both performance and reliability. The texture of electrodeposited films are sensitive to a large number of deposition parameters, such as cathode potential, current density, pH, and plating bath composition. Organic molecules added in small quantities into plating copper bath solutions affect the texture [7] and facilitate the formation of uniform layers of high brightness and also improve metallurgical properties of the copper deposits [8,9]. It is known that stress can play an important role in this material and recrystallization can occur over a time period from several hours to several years after the electrodeposition at room temperature or much faster as a result of annealing. This results in potential problems for the above-mentioned applications due to associated changes in stress, resistivity, and mechanical properties that in turn can correlate with seed and buffer layer materials [6,10–17]. It is also well known that electromigration depends on texture and grain size in Cu films [18]. The recrystallization can occur at temperatures as low as room temperature and the in-depth mechanisms are poorly understood. This recrystallization, if taking place, cannot easily be avoided and special measures are taken to deal with it, e.g. a regular annealing or rapid thermal annealing at temperature in the range 300–400 °C.

We have previously reported that adding organic additives of 3-*N,N*-dimethylaminodithiocarbamoyl-1-propanesulphonic acid (DPS) and polyethylene glycol (PEG, MW=8000) organic additives to a sulfate–sulfuric acid bath can influence structure, resistivity, and morphology of the surface of copper films [19]. We also reported that Cu films electrodeposited in the presence of a combination of DPS and PEG organic additives can exhibit a complex stress-relaxing room-temperature recrystallization accompanied by a decrease in resistivity [20].

In this paper, we present an investigation of the effect of DPS in the wide range of concentration of 2–34 μM and PEG (MW=8000) on crystal structure, surface roughness, resistivity, stress, and

room-temperature recrystallization of Cu electrodeposited from a sulfate–sulfuric acid bath, which is commonly employed for Cu electrodeposition.

2. Experiment

The 2 μm -thick Cu films were electrodeposited onto 1000 Å-thick magnetron-sputtered Cu seed layer on 6-in. Si/SiO₂ substrates from a sulfate–sulfuric acid bath (0.3 M CuSO₄ + 1.8 M H₂SO₄ + 70 ppm Cl⁻) at room temperature. A set of films was prepared, with and without organic additives added to the bath, i.e. no additives, 46 μM PEG, and 46 μM PEG + 2–34 μM DPS. To ensure the quality of the electrolyte near the wafer, the electrolyte was continuously circulated and a motor driven paddle agitated the solution at a frequency of 1 Hz. A low current density of 10 mA/cm² was used in order to attain a low growth rate of 33 Å/s.

Film thickness was measured using a Dektak profilometer. Microstructure was determined by performing the symmetric 2θ – θ and pole figure scans using a four-circle Philips X'Pert X-ray diffractometer (XRD) with Cu tube. Surface roughness of the films was characterized using atomic force microscopy (AFM). Film stress was measured by a Tencor Stress Measurement System. Resistivity was determined by a four-point probe measurement.

The properties mentioned above were measured repeatedly every one-to-five days over the course of four weeks after the electrodeposition to appropriately characterize the room-temperature recrystallization occurring in the Cu film electrodeposited with 46 μM PEG + 34 μM DPS additives in the plating bath. This study of the room-temperature recrystallization was possible because the room-temperature recrystallization in our films was fast enough to be complete in a reasonable amount of time and slow enough to let several measurements be taken before it ends. Our process, with 46 μM PEG and 2–34 μM DPS added to the electrodeposition bath, resulted in films in which room-temperature recrystallization was taking place over the time period of several weeks, thus providing an ideal case for the experiment.

3. Results and discussion

Resistivity and r.m.s. surface roughness properties of the Cu films deposited with and without the organic additives of PEG and DPS are summarized in Table 1. Roughness was measured using $10 \times 10 \mu\text{m}^2$ AFM scans of the surface of the films. Resistivity of the film deposited without organic additives is the same as the bulk value for pure Cu at room temperature, $1.65 \mu\Omega \text{ cm}$ [21]. Film resistivity increases by about 20% if PEG is added to the bath. If both PEG and DPS are added to the bath, resistivity decreases with time, with the change complete by the end of about four-week time period. R.m.s. roughness also increases when PEG is added to the bath. Addition of both PEG and DPS results in the films that are much smoother than those deposited without the additives. The more DPS is added to the bath, the lower is the roughness of the films. When concentration of DPS is increased to $34 \mu\text{M}$, r.m.s. roughness is as low as 10 nm. This result is important because low roughness would be preferred when Cu is electrodeposited into narrow trenches. Unlike the case of the resistivity, we did not detect any significant change in roughness of the films over the time period of four weeks.

Seven 2θ - θ XRD scans of Cu films electrodeposited with different concentrations of the PEG and DPS organic additives to the plating bath are

Table 1
The effect of the PEG and DPS organic additives on surface roughness and resistivity of electrodeposited Cu films

Additives	R.m.s. roughness (sheet films) (nm)	Resistivity (sheet films)
None	70	$1.65 \mu\Omega \text{ cm}$
$46 \mu\text{M}$ PEG	250	$2.0 \mu\Omega \text{ cm}$
$46 \mu\text{M}$ PEG + $2.2 \mu\text{M}$ DPS	30	Decreasing w/time
$46 \mu\text{M}$ PEG + $4.6 \mu\text{M}$ DPS	25	Decreasing w/time
$46 \mu\text{M}$ PEG + $8.6 \mu\text{M}$ DPS	20	Decreasing w/time
$46 \mu\text{M}$ PEG + $16 \mu\text{M}$ DPS	15	Decreasing w/time
$46 \mu\text{M}$ PEG + $34 \mu\text{M}$ DPS	10	Decreasing w/time

shown in Fig. 1. The scans were taken 1.5 months after the deposition to ensure that all time-dependent changes in the structure had occurred at room temperature. All of them are characteristic of face-centered cubic crystal lattice. The crystallographic structure of Cu films is preferentially (111) textured in all the films, except the one electrodeposited with the highest DPS concentration. However, as it will be shown below, even that film was (111) textured in as-deposited state. This is probably due to the lower surface energy of the (111) planes aligned parallel to the surface [22]. It can be seen (Fig. 2), that the area of the (111) peak is the highest in two cases: the film plated without any additives and the film plated with PEG + the highest concentration of DPS, $34 \mu\text{M}$. This means that these two films have the strongest (111) texture. The remaining films with poorly defined texture actually have the mixed texture – like (311) + (111) or (200) + (111). This becomes even more obvious if we take into account the fact that the natural intensity of the (200) peak is 40%

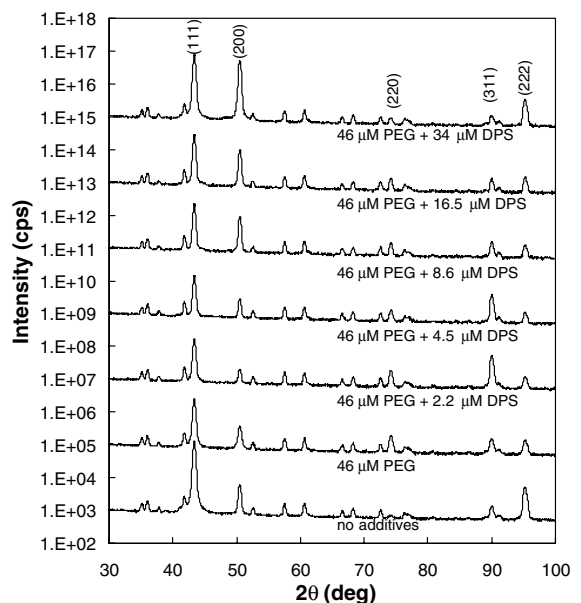


Fig. 1. XRD scans of the Cu films electrodeposited with and without the PEG and DPS organic additives. All the scans except one at the bottom were shifted along the Intensity axis. However, they originally had the same background intensity as one at the bottom.

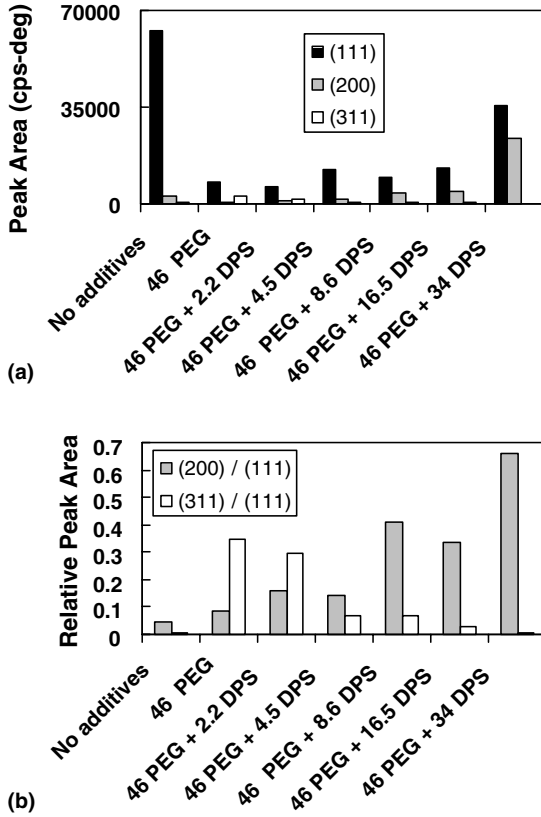


Fig. 2. Absolute (a) and relative (b) areas of the most significant XRD peaks of the Cu films electrodeposited with and without the PEG and DPS organic additives.

of the intensity of the (111) peak and the natural intensity of the (311) peak is 20% of the intensity of the (111) peak. This competition of two or more orientations results in poorly textured films. Overall, the additives seem to control the resulting structure of the electrodeposited Cu films.

The dependence of the grain size values on the presence and concentration of the PEG and DPS organic additives is shown in Fig. 3. The grain size was calculated from the 2θ - θ XRD scans using Scherrer's formula after adjusting XRD peak broadening for lattice distortions using Philips X'Pert Organizer software. We believe that this is the way to determine the average grain size in these films because plated films tend to be composed of equiaxed grains, when plated beyond the thickness of few thousand angstroms [23]. The roughness of the films (the values are shown in Table 1) seems to

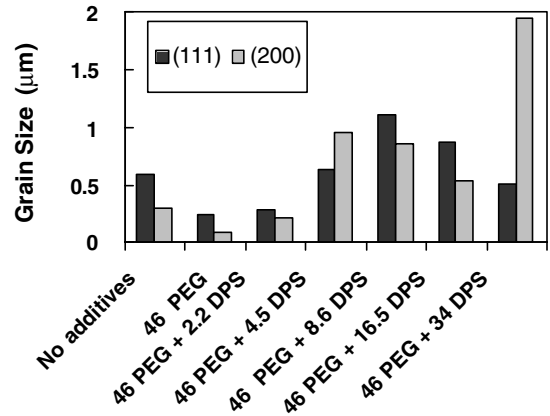


Fig. 3. Grain size dependence on the presence of the PEG and DPS additives in the Cu plating bath.

correlate with the grain size. Counter-intuitively, the smooth films have large grains, while the rough films consist of small grains.

We also performed the (111) pole figure Ψ -scans. They are shown in Fig. 4. Only half of the scans are shown. However, they were confirmed to be symmetric with respect to the $\Psi = 0$ axis. The

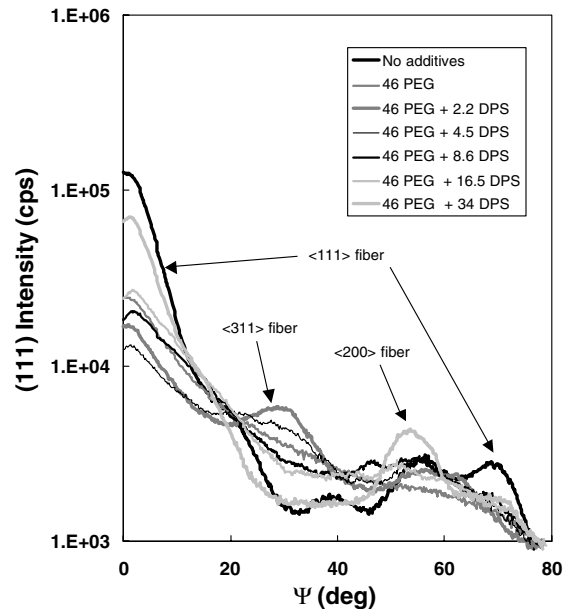


Fig. 4. The cut through the (111) pole figure of the Cu films electrodeposited with and without the PEG and DPS organic additives.

presence of the zero-angle dip in the scans on the films electroplated using the mixture of the PEG and DPS additives correlates with the presence of the resistivity aging effect at room temperature (Table 1).

We used the film electrodeposited in the presence of 46 μM PEG and 34 μM DPS to carefully investigate the time-dependent changes of structure, surface roughness, stress, and resistivity. As a result of the room-temperature recrystallization, the area of the (111) peak increases (Fig. 5). What is more important, the area of the (200) peak greatly increases by more than one order of magnitude. The dependence of the ratio of the areas of the (200) and (111) peaks on time after the deposition is also shown in Fig. 5. As it was already mentioned above, the natural intensity of the (200) peak is 40% of that of the (111) peak, so that as a result of recrystallization, our Cu films

from (111) textured in as-deposited state, become more (200) than (111) textured about 10 days after the deposition. The associated changes in grain size of the (111) and (200)-oriented grains are shown in Fig. 6. Four weeks after the deposition the grain size of the (111)-oriented grains increased by almost four times while the grain size of the (200)-oriented grains increased by about 50 times.

It is known that electrodeposited Cu films can have a substantial amount of randomly oriented grains [24]. We think that these randomly oriented grains serve as a source of the material for the growth of both (111) and (200) textures when recrystallization occurs. However, it is interesting that the room-temperature recrystallization did not result in a significant change in the surface roughness.

The dependence of the Cu film resistivity on time after the deposition is shown in Fig. 7. Resistivity decreases from 2.0 to 1.75 $\mu\Omega\text{ cm}$ over the same time range as the recrystallization takes place. The decrease in resistivity is known to be associated with recrystallization because the recrystallization leads to the increase in grain size, thus decreasing the relative part of the grain boundaries, which are responsible for higher resistivity [12]. The decrease in resistivity can also be explained by decrease in concentration of other defects, e.g. vacancies, dislocations, etc. Finally, the improvement in texture can also lead to a decrease in resistivity because the misalignment of adjacent grains decreases.

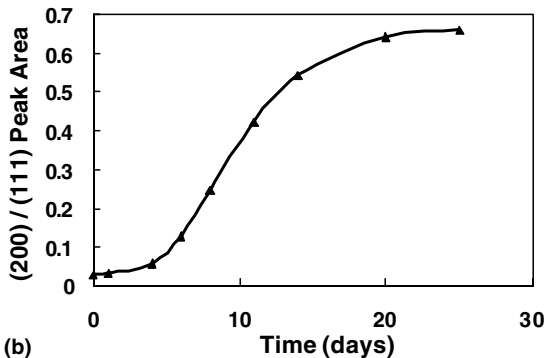
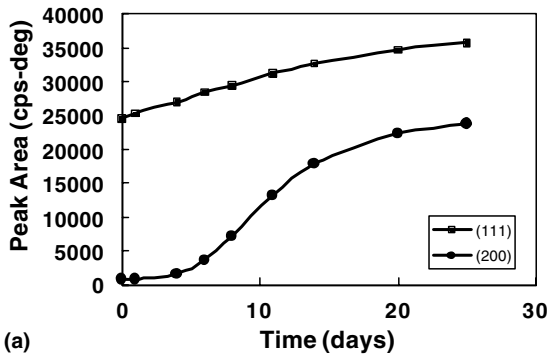


Fig. 5. Dependence of the absolute (a) and relative (b) areas of the (200) and (111) XRD peaks of the Cu film on time after the electrodeposition.

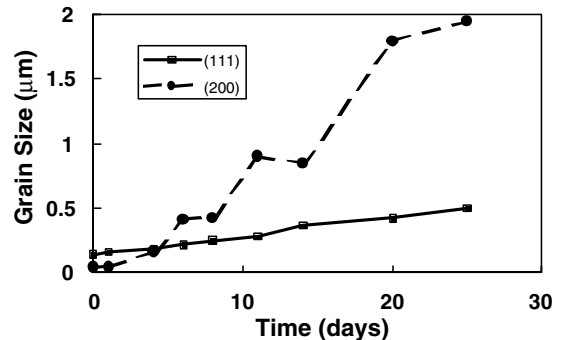


Fig. 6. Dependence of the grain size of the (200) and (111)-oriented grains of the Cu film on time after the electrodeposition.

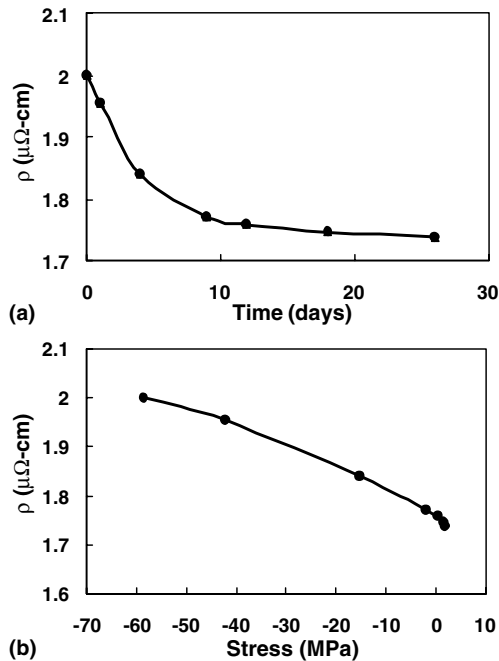


Fig. 7. Resistivity of the 2 μm-thick Cu film versus time after the electrodeposition (a). Resistivity versus stress in the same film (b).

To understand the driving force of the above-described recrystallization and the associated decrease in resistivity, we performed stress measurements over the course of the same time period. The correlation of resistivity and stress during recrystallization is also shown in Fig. 7. Stress changes from moderate compressive to slight tensile during the four-week time after the deposition. The correlation of the change in stress with the change in crystal structure and especially the change in resistivity clearly demonstrates that stress is the driving force of the recrystallization in our Cu films. It is known that biaxial stress changes to more tensile stress as a result of grain growth [25,26]. Thus, compressive stress is relaxed through recrystallization, which in turn leads to decrease in resistivity. The energy provided by stress of such a magnitude as in our samples should be enough for grain growth [11].

It is known that for Cu, the elastic strain energy density is the lowest for the (200) texture and the highest for the (111) texture [17], while we already

mentioned above that the (111) texture is the most favorable from the point of view of the surface energy minimization. These two facts are the key to understanding the complex recrystallization behavior in our Cu films and could explain both the enhancement of the (111) texture and the significant enhancement of the (200) texture.

4. Conclusions

The structure, surface roughness, and resistivity of the electrodeposited Cu films was studied as a function of the presence and concentration of the organic additives of 3-*N,N*-dimethylaminodithiocarbamoyl-1-propanesulphonic acid (DPS) and polyethylene glycol (PEG, MW=8000) organic additives from a sulfate-sulfuric acid bath (0.3 M CuSO₄+1.8 M H₂SO₄+70 ppm Cl⁻). The structure of the films (texture and surface roughness) is controlled by the presence and concentration of the additives. It was shown that resistivity and especially its time dependence at room temperature depends strongly on the presence and concentration of the PEG and DPS additives. We showed that a complex stress-relaxing room-temperature recrystallization occurs in the films, accompanied by a decrease in resistivity. The role of the recrystallization is linked to the increase in grain size and enhancement in (111) and especially (200) texture.

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