Effect of Organic Additives On the Mechanical Properties of Copper Electrodeposits

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Owing to the surface activity of acid copper electrolytes was slightly enhanced by the presence of organic additives, the nucleation and subsequent initial growth of the deposition obtained on stainless steel substrates were changed. Accordingly, the mechanical properties of the copper deposits were influenced predominantly by the effect of organic additives. The morphology and grain size of the shiny-side of the copper deposits can be observed to explain the results of the nucleation-and-growth of the copper deposition and, subsequently, the mechanical properties of the copper deposits.

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Introduction

Organic additives are necessary in most sulfuric acid electrolytes to enhance the mechanical properties of the copper deposits to make them the material of choice in the fabrication of components of electronics. Though the influence of these additives on the adsorption, cathodic polarization, and complex ion formation was investigated,[1,2] some important aspects like why additives have different influence on the nucleation-and-growth of the deposition and the mechanical properties of the copper deposits have not been completely investigated. However, this information plays a fundamental role to facilitate the selection of optimum additives in copper electrolytes.

Two organic additives, poly(ethylene glycol) (PEG) and thiourea derivatives (TUD), were selected as additives in the copper electrolytes. Although PEG and TUD are not surfactants,[3] they do posses some limited surface-active properties. A greater surface activity means a greater surface excess of these additives.[4] Therefore, these additives have greater concentration in the electric double-layer region during electrolysis, changing the double-layer structure and then the nucleation-and-growth behavior of the deposition. This supposition is in good agreement with the result of our published literature data that shows the relative rate parameters of cyclic voltammetric stripping analysis decreased with increasing the surface activity of copper electrolytes.[5] Accordingly, different mechanical properties of the copper deposits may be expected by the effect of these additives.[6]

The synergistic effect of chloride ions and organic additives is versatile.[7] Ye el al. indicated that the presence of chloride ions decisively affected the nucleation-and-growth mechanism.[8] Therefore, the substantial influence of chloride ions on the mechanical properties of copper deposits was also examined in this study.

Experimental Procedure

Copper deposits were prepared from acid copper electrolytes containing 20 g/L of copper (as $CuSO_4 \cdot 5H_2O$) and 80 g/L of sulfuric acid. The homologous series of TUD were thiourea (TU76), ethylthiourea (TU104), and p-tolylthiourea (TU166). The number in the parenthesis is the approximate molecular weight of the TUD. In order to avoid the nodulation of the deposit,[9] the studied concentration of these TUD was 2 ppm (0.0002 percent). The average molecular weight of the PEG studied were about 400, 1000, 4000, and 6000, designated as PEG400, PEG1000, PEG4000, and PEG6000, respectively. Owing to the complex ions formation of PEG and copper ions in the electrolytes, the studied concentration of these PEG was 400 ppm.[1,10] Chloride had been added in the form of HCl to bring the free chloride concentration to a 60-ppm level in the chloride-containing electrolyte. The terms "TUD-Cl" and "PEG-Cl" were referred to the electrolytes containing 60 ppm chloride in addition to TUD and PEG, respectively. Surface activities of copper electrolytes were determined by measuring contact angles at 25 ^{o}C.

Electroplating was conducted in a laboratory parallel cell at 30 ^{o}C with a current density of 2.5 and 5 A/dm^2. The cathode was flat, bright, stainless-steel specimens (3 x 3 cm), which were polished with 1200-grit emery papers prior to plating. The anode was a flat, platinum sheet. The plating solution was agitated with a magnetic stirrer during deposition. When the deposit reached a thickness of around 30 μm, the deposited layer was separated, and the shiny side of the layer was examined for its morphology and grain size with a scanning electron microscope (SEM). In order to observe the original shape of these grains, all the SEM were performed without coating. Microhardness measurements were performed on polished cross sections using a Vickers microhardness tester with a 25 g load. The crystallographic structure of the deposits was examined by an X-ray diffractometer (XRD).

Results & Discussion

Surface Activity of the Copper Electrolytes

Contact angle of electrolyte drop on stainless steel surface is a direct measure of the surface activity of electrolyte on the cathode. A lower contact angle means a greater surface activity. Fig. 1 reveals that the contact angle of the copper electrolytes is noticeably lowered by the presence of TUD additives. This means the surface activity of the copper baths is enhanced by TUD molecules concentrating at the double layer, which may result in a different nucleation-and-growth mechanism. The results of Fig. 1 also indicate that the surface activity of the copper electrolytes tends to increase with increasing the molecular weight of TUD. Consequently, molecular weight of TUD also plays a fundamental role in determining the mechanical properties of the copper deposits.

An analogous investigation of the surface activity of PEG-containing electrolytes as shown in Fig. 2 indicates results similar to the TUD-containing electrolytes. The influence on surface activity also tends to increase with increasing the molecular weight of PEG, the same as in the case of TUD. The above results suggest that the presence of TUD or PEG may change the resultant mechanical properties.

Morphology and Grain Size of the Deposit

Usually, it is difficult to observe the nucleation-and-growth behavior of copper deposition from the produced deposit itself, however, the morphology and grain size of the shiny side of the produced deposits in this work substantially provide the results of the nucleation-and-growth. This finding is significant in that the nucleation-and-growth behavior as well as the mechanical properties of the copper deposits can be correlated with the molecular weight of the additives.

Figure 3 shows the SEM photographs of the shiny-side, i.e. the initial copper deposits produced from chloride-free and chloride-containing electrolytes, containing no additive. The figure shows that the initial deposits produced at 5 A/dm^2 have much smaller grains than those produced at 2.5 A/dm^2, <1 µm vs. $\geq$2 µm. This is true both in the chloride-free and in the chloride-containing electrolytes. These results are consistent with the work of Getrouw and Dutra[11] who predict the initial copper deposit obtained at higher current density have a smaller critical radius, meaning finer grain and a greater number of grains.

Although there are many factors affecting the microhardness, finer grains usually imply a higher microhardness.[12,13] This correlation was born out in our microhardness results as shown in Table 1, which indicates that higher microhardness values are shown for copper deposits obtained at higher current densities, with finer grains, than those obtained at lower current densities, with larger grains.

Influence of Additives on Grain Size

Figures 4-7 show the effects of additives on grain sizes of copper deposits obtained from chloride-free and chloride-containing acid copper electrolytes. The results show that the grain size tends to decrease with increasing molecular weight of TUD and PEG. The trend holds true for deposits from both the chloride-free (Figs. 4 & 5) and the chloride-containing (Figs. 6 & 7) electrolytes. The effects of TUD and PEG on grain sizes can be attributed to the modification of the nucleation-and-growth mechanisms and the changes of surface activities afforded by the concentration of the additive molecules in the double layer, as evident from their strong effect on contact angles. The molecular weight effect can be partially attributed to the increase of the surface activities with increasing molecular weight. An increase of the effect on the nucleation-and-growth mechanism with increasing molecular weight is also a possible explanation.

The synergistic effects of combining chloride with TUD and with PEG are shown in Fig. 6 and 7, respectively. The results indicate that the effects of TUD and PEG are enhanced by chloride.

Getrouw and Dutra have attributed the synergistic effect in the case of PEG-Cl to the lowering of nucleation overpotential, which results in higher nucleation activity.[11]

Influence of Additives on Microhardness

Microhardness results, shown in Table I, indicate that microhardness tends to increase with an increase of molecular weights of TUD and PEG, and that microhardness values are higher for deposits made at a higher current density but lower for deposits from chloride containing electrolytes. The effects of molecular weight and current density on microhardness are consistent with their effects on grain size, and the increases of microhardness can be expected from the observed decreases of grain sizes.

Table 1 also indicates that deposits from PEG-containing electrolytes have higher microhardness than that from TUD-containing electrolytes. PEG as an additive appears to be more effective than TUD for the reduction of grain size.

XRD Results

X-ray diffraction patterns of copper deposits obtained from TUD-containing electrolytes and TUD-Cl-containing electrolyte are shown in Fig. 8. It indicates that the texture of deposits from the TUD-containing electrolytes and that from the TUD-Cl-containing electrolyte are significantly different, the former are predominately (111) whereas there is no preferred orientation for the latter. Since (111) orientation is the close-packed structure, it is expected that the deposits with a (111) texture will have a higher microhardness than the deposits showing no preferred orientation.[14] Thus the XRD results would predict the deposits from the TUD-containing electrolytes to have a higher microhardness than the deposits from the TUD-Cl-containing electrolytes, which is consistent with our microhardness results.

Figure 9 shows the X-ray diffraction patterns of copper deposits obtained from the PEG and PEG-Cl-containing electrolytes. It is noted that the average (111) / (200) peak intensity ratio for the deposits from the PEG and PEG-Cl-containing electrolytes are considerably higher than that for the deposits from the TUD and TUD-Cl-containing electrolytes, 3.5 vs. 2.4. This means that the former would have more (111) texture than the latter. The results are consistent with the microhardness results, which indicates that the former (*i.e.* deposits from the PEG and PEG-Cl–containing electrolytes) have higher microhardness than the latter.

The average value of the full-width-at-half-maximum (FWHM) of the diffraction peaks for the deposits from the PEG and PEG-Cl-containing electrolytes is estimated, from Fig. 9, to be 0.37, and that estimated for the deposits from the TUD and TUD-Cl-containing electrolytes is about 0.3. The more broadening of diffraction peaks for the deposits from the PEG and PEG-Cl-containing electrolytes implies that these deposits would have accumulated more internal stress in the deposits, which was actually observed during this study.

Conclusion

TU166, PEG4000, and PEG6000 are effective additives for lowering copper grain size and for increasing microhardness.

The effect on grain size and microhardness increases with an increase in current density and the molecular weight of TUD and PEG. The deposits obtained from chloride-containing electrolytes were slightly softer than that from chloride-free electrolytes.

Increases of microhardness with decreases of grain size are expected and were actually observed.

As an additive for lowering copper grain size, PEG is more effective than TUD. The effect is promoted by the addition of chloride to the PEG-containing electrolytes.

References

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TABLE 1

Microhardness of Copper Deposits

	Microhardness (HV)			
	Chloride-free electrolyte		**Chloride-containing electrolyte**	
Additive	**2.5 (A/dm^2)**	**5.0 (A/dm^2)**	**2.5 (A/dm^2)**	**5.0 (A/dm^2)**
-	80	91	65	78
TU76	78	97	70	85
TU104	86	122	76	93
TU166	108	130	96	115
PEG400	98	121	85	110
PEG1000	121	132	103	116
PEG4000	132	159	111	122
PEG6000	155	167	121	136

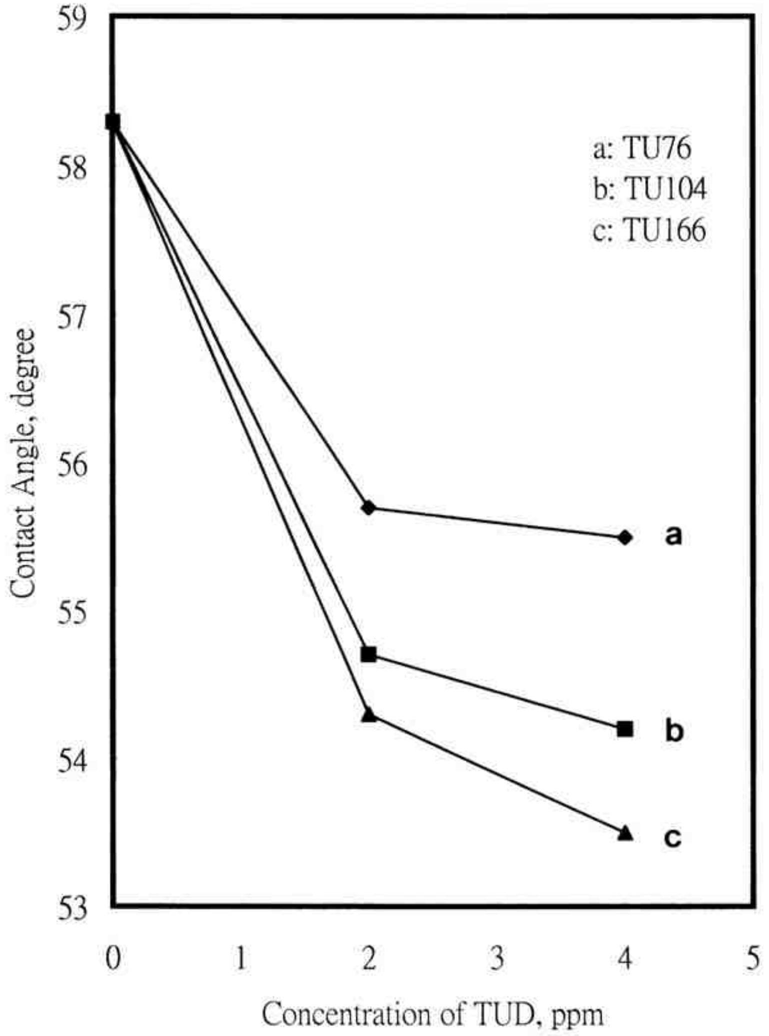

Figure 1. Contact angle of acid copper electrolytes on stainless steel as a function of TUD concentration.

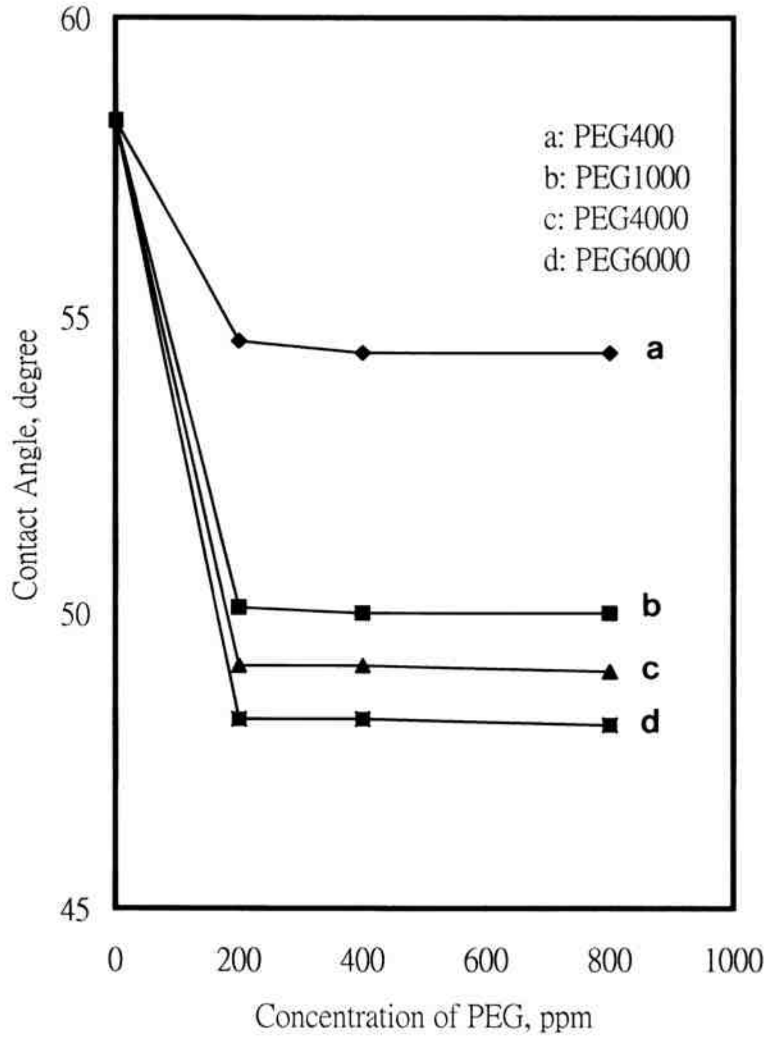

Figure 2. Contact angle of acid copper electrolyte on stainless steel as a function of PEG concentration.

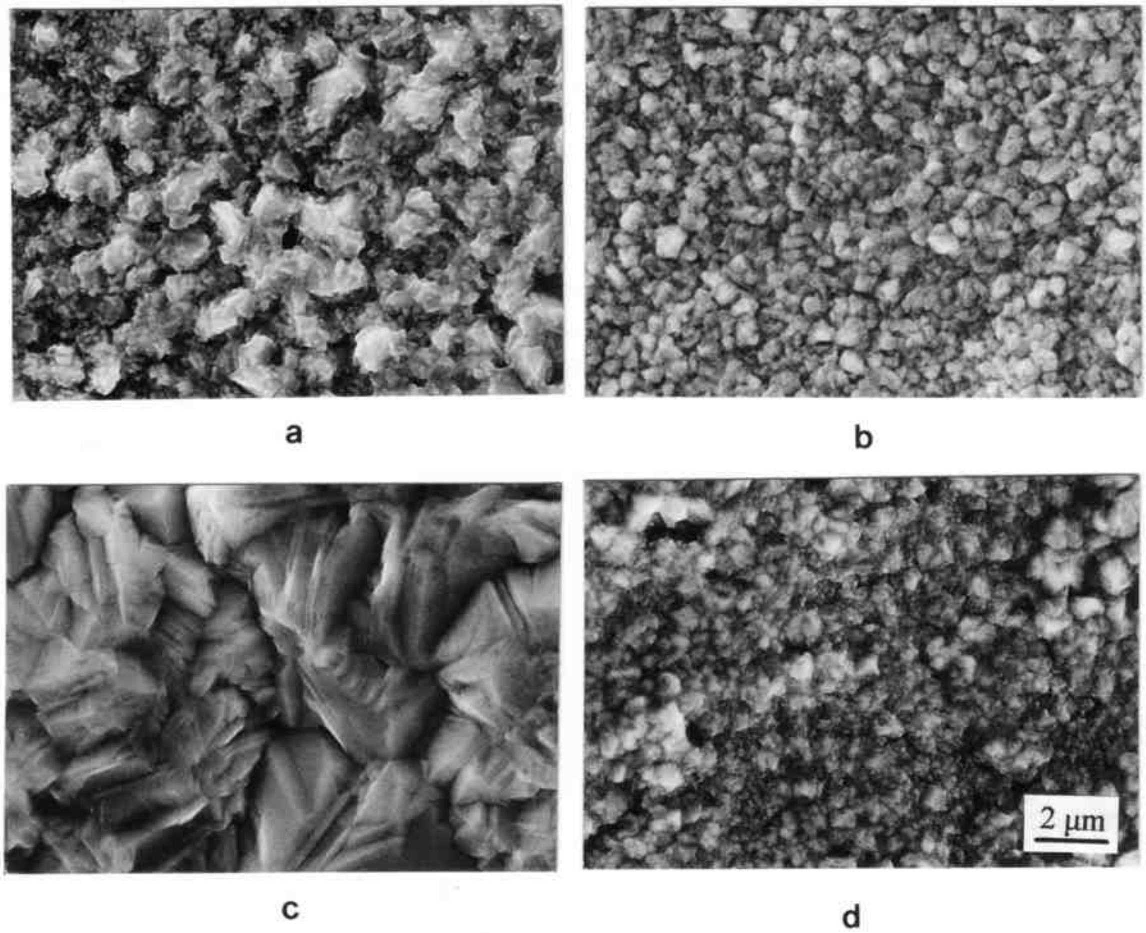

Figure 3. SEM photographs of the shiny side of copper deposits obtained from additive-free acid copper electrolytes: (a) and (b) containing no chloride with current densities of 2.5 and 5.0 A/dm^2, respectively, (c) and (d) containing chloride with current densities of 2.5 and 5.0 A/dm^2, respectively.

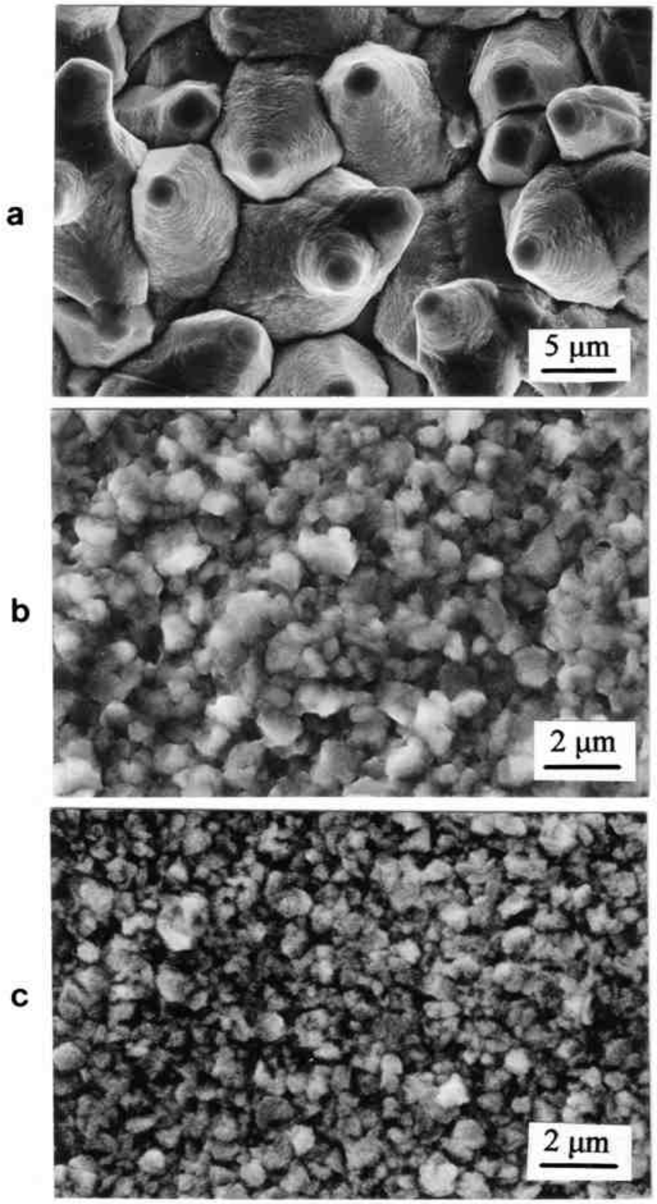

Figure 4. SEM photographs of the shiny side of copper deposits obtained at 2.5 A/dm^2 from chloride-free acid copper electrolytes, containing (a) TU76, (b) TU104, and (c) TU166.

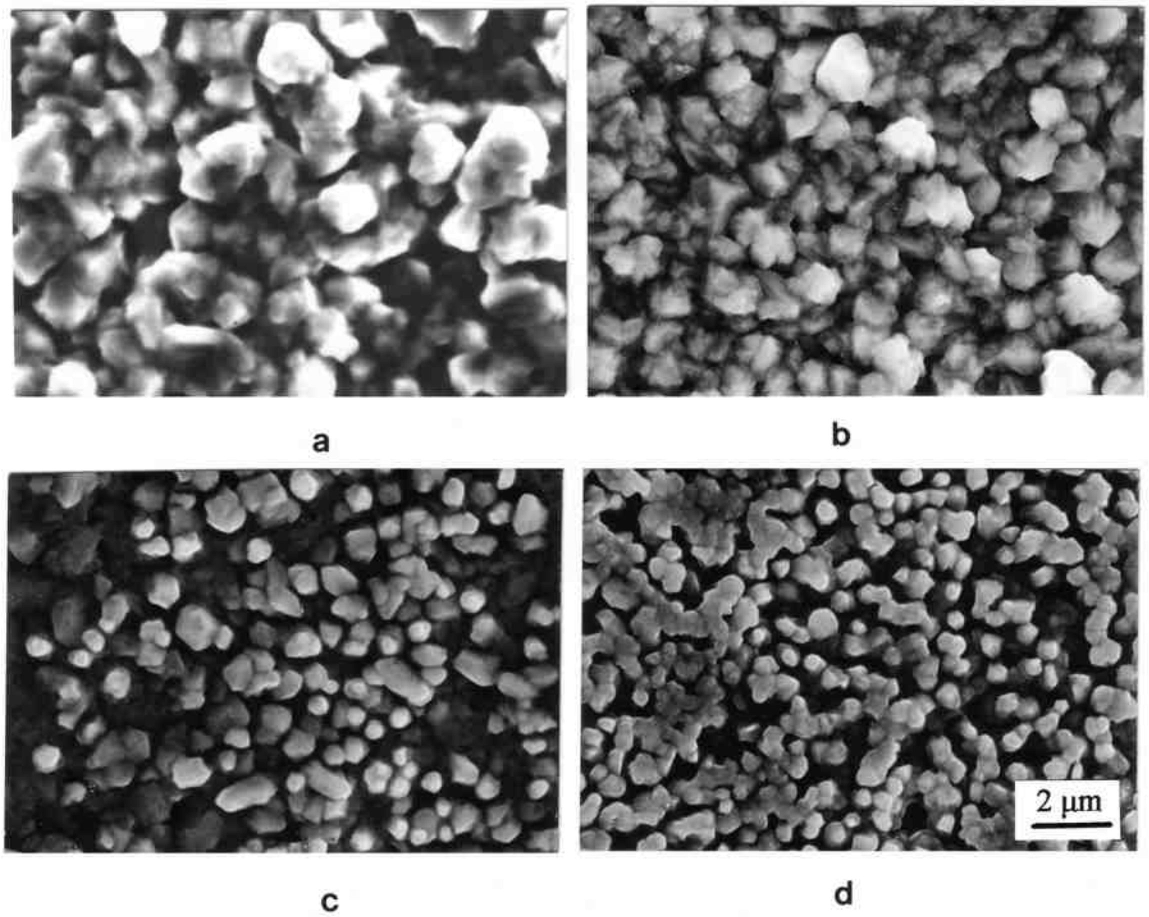

Figure 5. SEM photographs of the shiny side of copper deposits obtained at 2.5 A/dm^2 from chloride-free acid copper electrolytes, containing (a) PEG400, (b) PEG1000, (c)PEG4000, and (d) PEG6000.

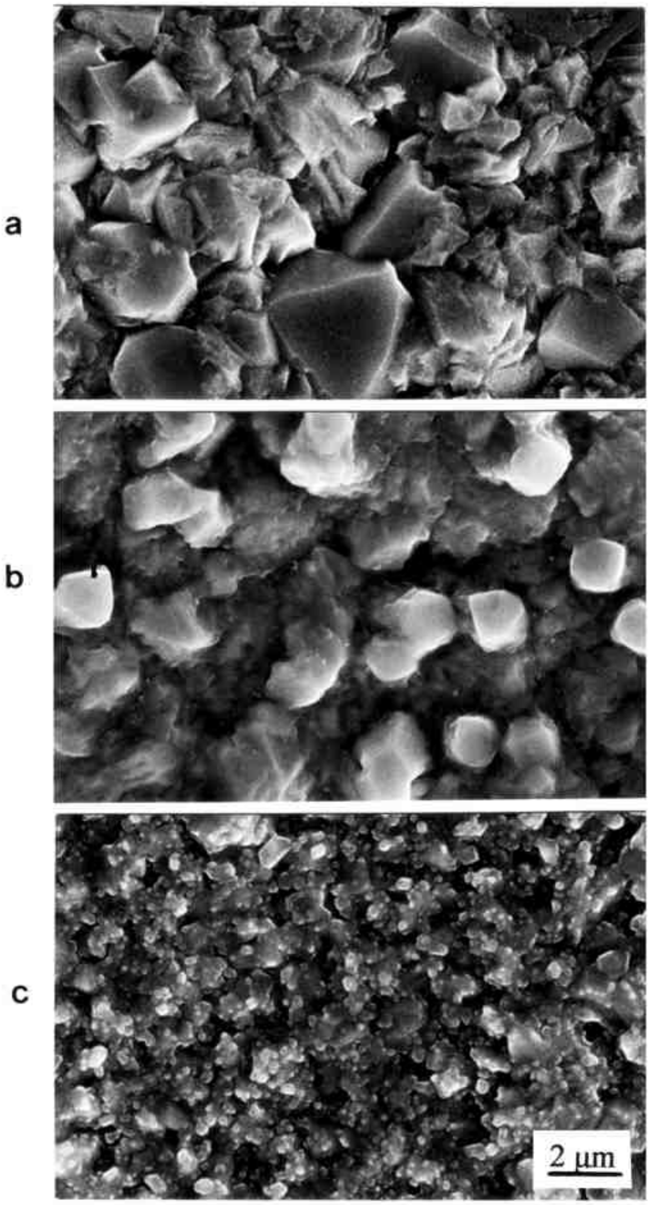

Figure 6. SEM photographs of the shiny side of copper deposits obtained at 2.5 A/dm^2 from chloride-containing acid copper electrolytes, containing (a) TU76, (b) TU104, and (c) TU166.

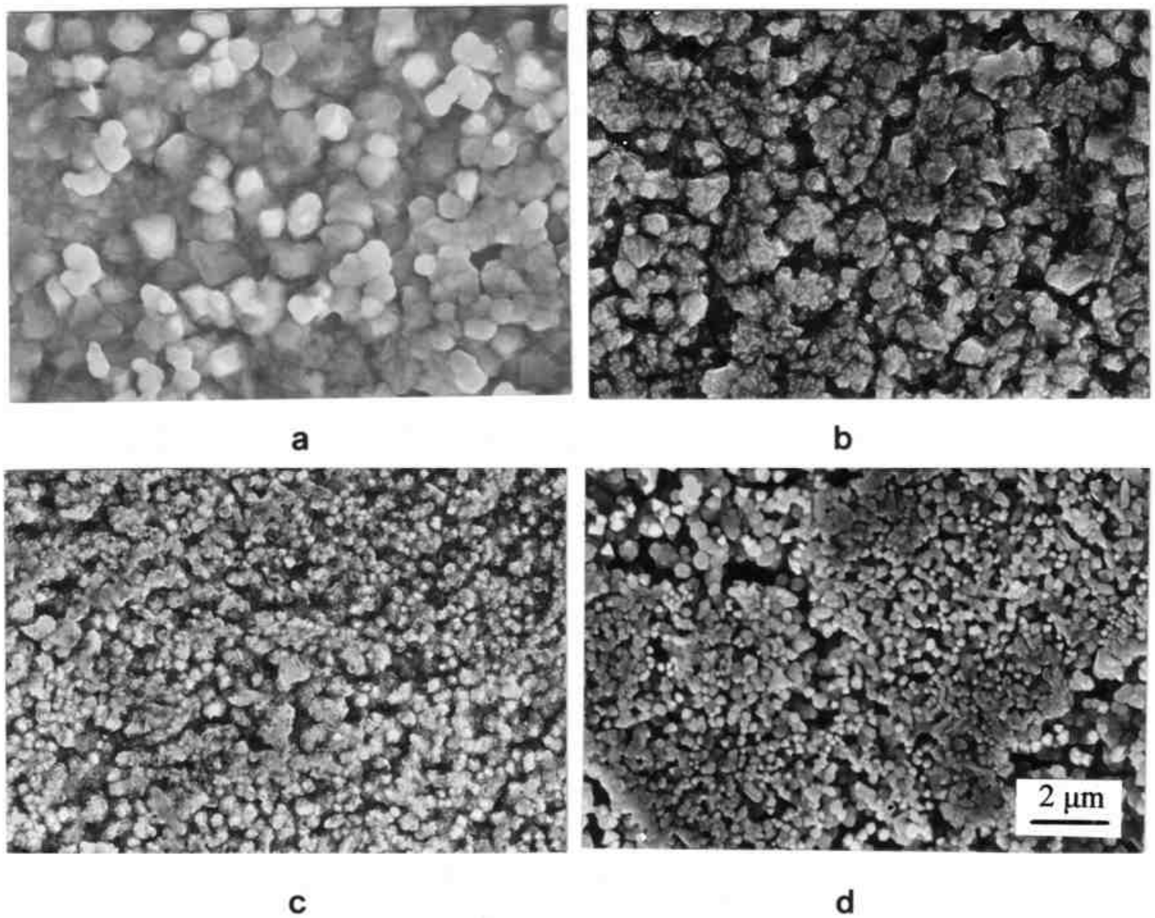
a b c d

Figure 7. SEM photographs of the shiny side of copper deposits obtained at 2.5 A/dm^2 from chloride-containing acid copper electrolytes, containing (a) PEG400, (b) PEG1000, (c)PEG4000, and (d) PEG6000.

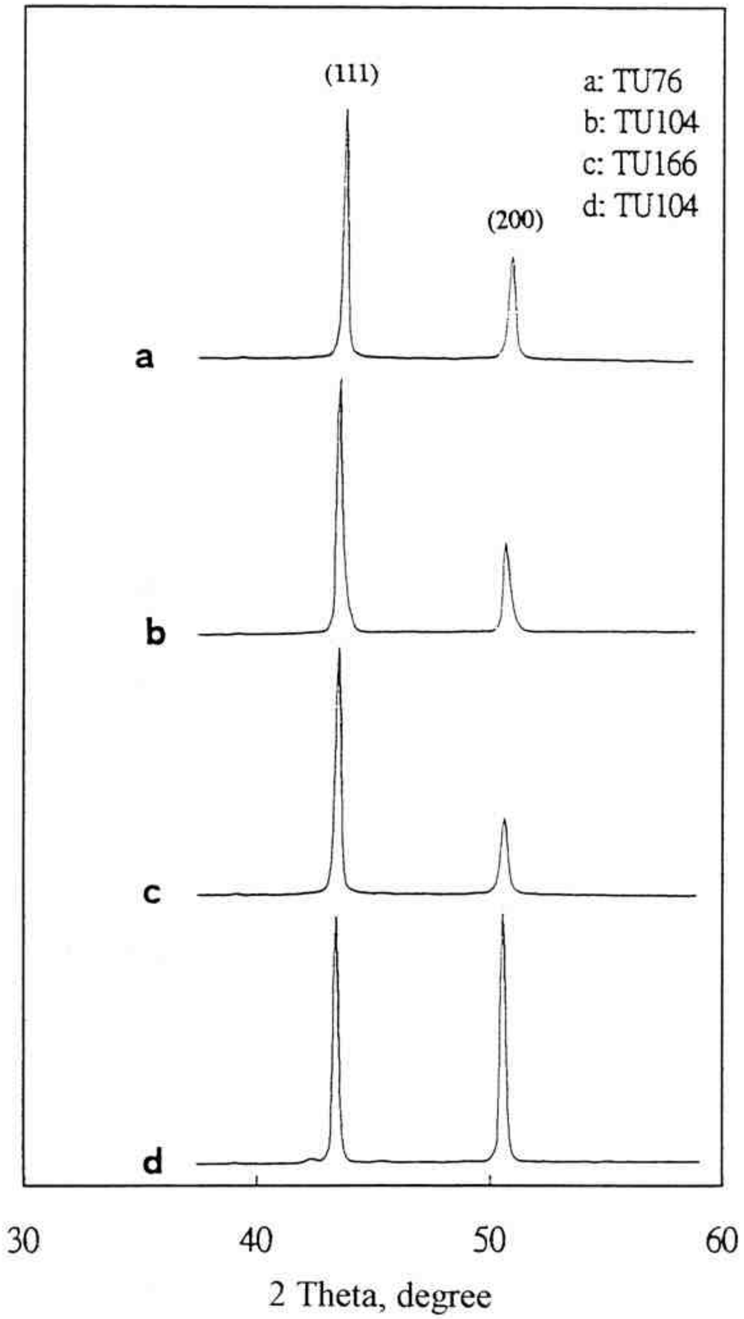

Figure 8. X-ray diffraction patterns of copper deposits obtained at 5 A/dm^2 from TUD-containing acid copper electrolytes (a to c) and from TUD-CI-containing acid copper electrolyte (d).

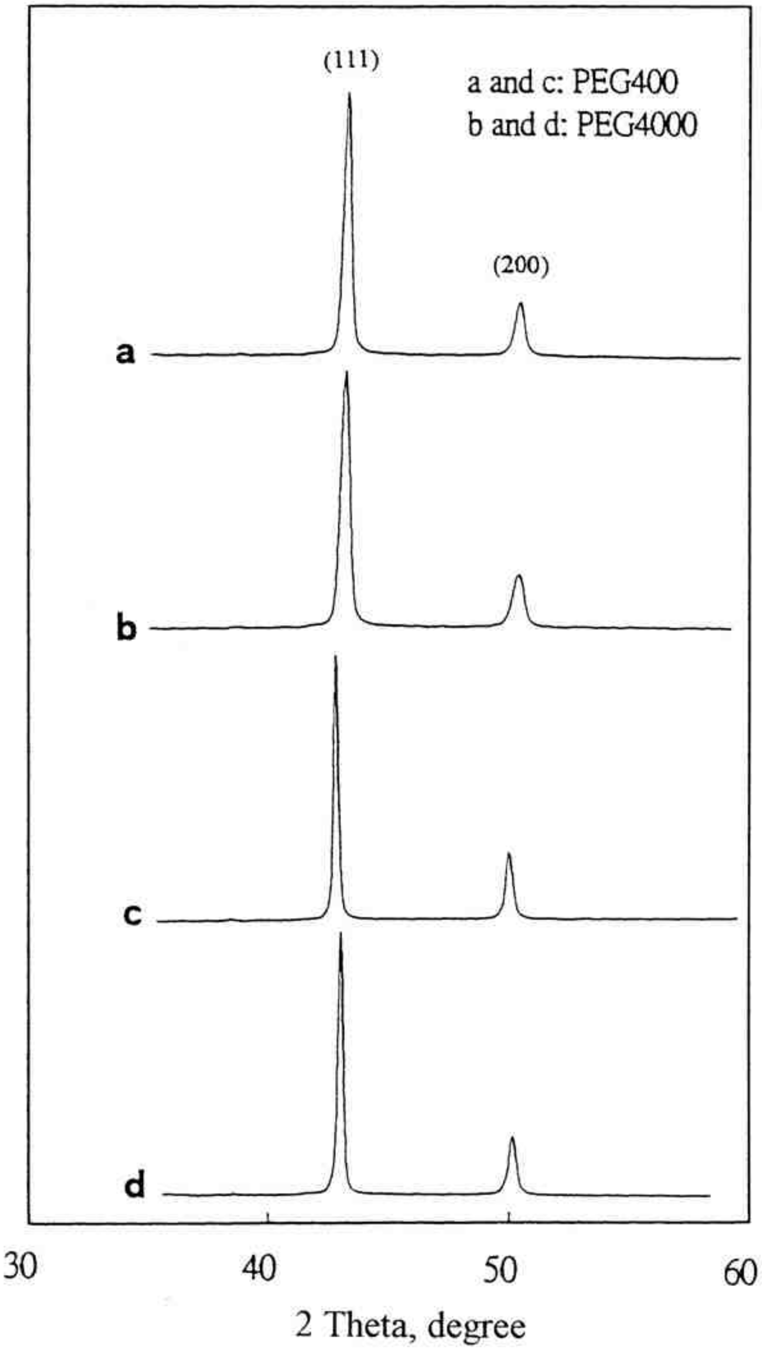

Figure 9. X-ray diffraction patterns of copper deposits obtained at 5 A/dm^2 from PEG-containing acid copper electrolytes (a and b) and from PEG-Cl-containing acid copper electrolyte (c and d).