

Effects of Additives in an Electrodeposition Bath on the Surface Morphologic Evolution of Electrodeposited Copper

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Additives in an electrodeposition bath have been frequently used to modulate the morphology of electrodeposited copper. The effects of gelatin, thiourea and chloride ions under various concentrations on electrodeposited copper were studied. The leveling and grain refining effects were identified for the use of gelatin. Thiourea acted as a grain-refining and brightening agent. Properly selected concentrations of gelatin or thiourea added in the electrodeposition bath made the adsorbed additives partly converge and optimized the leveling effects. The chloride ions increased the film roughness. In addition, the behaviors of the additives were studied based on polarization curves. Polarization contributed to the adsorption of gelatin and thiourea, which reduced the number of active sites and inhibited mass transport. The polarization curves indicate that the effects of chloride ions in combination with gelatin in the copper deposition were notably different from those of chloride ions alone. With the combination of gelatin, thiourea and chloride ions in proper concentrations, a copper deposited film with low roughness and high flatness can be obtained.

Keywords: electrodeposition; copper; gelatin; thiourea; chloride ions

1. INTRODUCTION

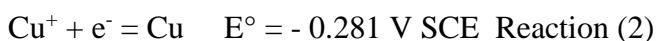
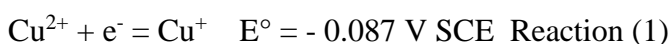
Copper electrochemical deposition is an important technology in the electronic industry to form electronic components[1,2]. The copper foil obtained through electrodeposition is also a key component in the electronic industry for printed circuits[1] and circuit interconnections due to the low cost, high deposition rates, and low toxicity. The electrochemically deposited copper has been widely used in semiconductor copper interconnect[2], wiring, chip on film, and copper-clad laminate. The control of the electrodeposition highly depends on various process parameters such as the temperature, current density, current waveform, and stirring conditions of the plating bath.

Depending on the usage purpose, organic additives can be introduced into an electroplating bath for copper electrodeposition[3–10]. The additives that affect the behavior of copper electrodeposition have attracted attention to regulate the film properties of electroplated copper in terms of surface morphology, resistivity, and crystal orientation[11–16]. The internal stress, grain size, and structure, surface shape, and roughness of the copper deposit are critical for the applications, which lead to different product performances and reliability levels. The copper electrodeposition using additives makes complicated reactions occur near and on the surface of the electrode. The desirable properties of copper deposits have been obtained and studied by using various additives such as polymers[17,18], gelatin[11–14], chloride ions[11,12,14], and thiourea[19,20].

Among them, gelatin is one of the safest additives in copper electrodeposition for the health considerations of toxicity in the industry. Gelatin is widely accepted as a grain refiner and hardener that modifies the electrochemical reactions and crystal growth of electroplating[21,22] by the preferred adsorption on surface protrusions and by interfering with the procedures and results of crystal growth. Gelatin is a protein obtained through the partial hydrolysis of collagen, which consists of a series of different amino acids connected by peptide bonds. The gelatin has a structure with several amine groups, which can cause the adsorption on the cathode surface under electrodeposition processes[21,22]. A formed film of adsorbed gelatin is believed to reside on the working electrode, and increase the overpotential. The adsorbed gelatin is expected to modulate the numbers of active sites and/or decrease the rate of mass transfer of copper ions to the electrode. It is widely accepted that the introduction of gelatin can modify the nucleation process, interfere with the instantaneous nucleation and derive smaller grains. Therefore, gelatin is frequently used as a grain refiner and leveling agent.

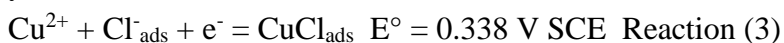
Thiourea has attracted attention to control the film properties of electroplated copper[11,19,20]. Thiourea is frequently used as a brightening or leveling agent for copper electroplating. The physical properties of copper deposits such as the hardness, strength, and toughness can be modulated by the addition of a few ppm thiourea to the copper plating bath. Thiourea strongly interacts with the surface of the cathode and inhibits the diffusion of adsorbed copper atoms on the cathode surface to produce a smooth and bright electroplated surface. Thiourea was found to react with copper or copper ions and can generate copper sulfide[23] on the copper deposit, which appears to inhibit the initial nucleation of the copper and result in the formation of small grains. The formation of sulfide ions and precipitation of copper sulfide are attributed to the degradation of thiourea at the cathode surface.

Cathodic deposition of copper in acidic sulfate solutions is commonly accepted to occur through two consecutive reactions[24]:

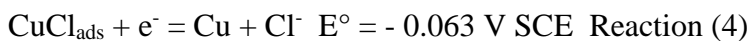


The first step is accepted as the rate-determining step.

With the presence of Cl^- , the reduction of copper accelerates through the formation of a CuCl monolayer at the electrode surface, which is attributed to the following reaction[24]:



which is subsequently reduced through the following reaction



The above chloride-mediated mechanism proceeds in parallel with the two-stage reaction of Cu^{2+} . Reactions (3) and (4) accelerate the overall reduction kinetics.

When chloride ions are added with organic additives, the adsorbed chloride ions form a complex with various additives to facilitate the adsorption of the additives and result in distinct results[1,5,11].

In practice, the currently used additives are a combination of chloride ions and two or three types of organic compounds. These additives are believed to react in a complex manner. Although the roles and reaction mechanisms are not completely clarified, to satisfy various requirements for copper plating, it is critical to investigate the effects of additives on the copper deposition in detail.

Since the morphology and film properties of copper deposit highly depend on the types and concentrations of additives, this paper reports the evolution of morphology of the copper deposit as a function of compositions of additives. In this work, the mechanism of the organic addition agent modifies the crystal growth of copper electrodeposit was studied using the cathode polarization measurement and microscopy examination of the deposit.

In the literature report, the synergetic effects of gelatin, thiourea, chloride ions on the morphology and properties of deposited copper were studied. Prior studies have reported that in solutions containing gelatin, thiourea and chlorine ions, the surface roughness of deposited copper decreased with increasing thiourea and gelatin concentrations and decreasing chloride ions concentrations[11,12]. However, the study includes the effects of a single additive on the surface morphology, and the effects when all gelatin, thiourea and chloride ions were added. The AFM was introduced to resolve the 3-dimensional surface structure in the sub-micron scale and to analyze the surface roughness. In prior related studies, only few reports include the AFM data for the surface morphology characterization[25]. We corresponded the SEM, AFM characterization and polarization curve measurements to analyze and discuss the effects of additives as a result of the surface adsorption.

2. EXPERIMENTAL

The electrochemical measurements were performed at room temperature. The copper plating electrolytes contained 1.1 mol/L CuSO_4 and 1.0 mol/L H_2SO_4 and DI water. The conditions for constant current for copper electroplating were applied by a 273 potentiostat (EG&G Princeton Applied Research Corporation) with respect to an electronic-grade copper wire reference electrode. We used an electronic-grade copper wire as an anode for copper deposition. The deposited copper layer was plated on a copper plate with 0.2 A/dm^2 to be $10 \mu\text{m}$ thick. The copper plate cathode was masked with tape to, leave an exposed area of 0.5 cm^2 . The additives were mixed with the base electrolyte at room temperature by direct addition or dilution from a stock solution. All obtained samples were rinsed with DI water and dried in a stream of N_2 after the electroplating. The surface of the copper deposit that faced the substrate is labelled as the shining side, and the surface exposed to the electroplating bath is labelled as the matte side. The surface morphologies of the matte side were investigated.

Thiourea, HCl, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and H_2SO_4 were obtained from Wako Pure Chemical Industries. The gelatin was obtained from Industrial Technology Research Institute, Material and Chemical Research Laboratories (ITRI, MCL).

Scanning electron microscopy (SEM), and atomic force microscopy (AFM) were used to investigate the surface morphology and roughness. The AFM operating mode was the tapping mode.

For electrochemical measurement, the 273 potentiostat (EG&G Princeton Applied Research Corporation) and rotating disk electrode (PINE Instrument) were used for the polarization curve measurements. The working electrode was a platinum rotating disk electrode with 5 mm diameter. An electronic-grade copper wire was used as the reference electrode, and an electronic-grade copper wire was the anode. All voltammetry experiments were performed at 5 mV/s.

3. RESULTS AND DISCUSSION

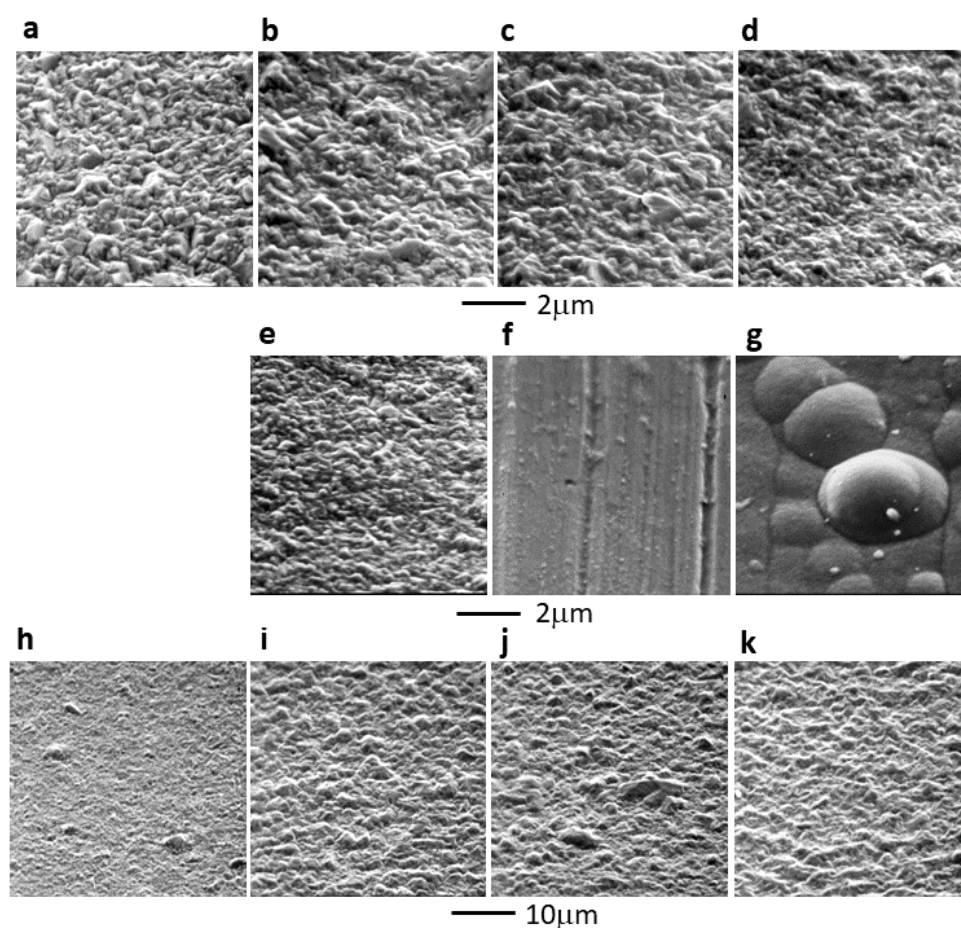


Figure 1. SEM micrographs of the copper electrochemical deposition under various concentrations of additives. (a) without additive; (b) gelatin 1 ppm; (c) gelatin 3 ppm; (d) gelatin 9 ppm; (e) thiourea 1 ppm; (f) thiourea 3 ppm; (g) thiourea 9 ppm; (h) without additive; (i) chloride ion 1ppm; (j) chloride ion 3.3 ppm; (k) chloride ion 10 ppm; (m) chloride ion 33 ppm.

To produce copper deposit with proper roughness in electronic applications, it is essential to control the film microstructure. The surface morphology of the matte side of the electrodeposited copper was studied by SEM and AFM. The results are presented in Figure 1 and Figure 2. When no additives were present, the film had a rough surface morphology, and the grain structure appeared to be more

irregular. When gelatin was added to the plating bath, a decreased grain size and a more uniform distribution of grains were obtained (Figure 1). The electrodeposited films were visibly less rough than the film derived without gelatin due to an increased coverage of gelatin adsorption on the cathode surface when the gelatin concentration increased from 0.33ppm to 9 ppm. The obtained grains with gelatin as the additive were more homogeneously distributed throughout the entire cathode surface. The observations indicate that the presence of gelatin in the electrolyte affects the nucleation and growth of the copper deposit.

The nucleation energy for grain formation is expected to decrease, which results in a more uniform surface morphology. The gelatin likely forms a partly covered adsorption layer, which changes the copper reduction and surface roughness of the copper deposit. Gelatin can be adsorbed onto high-surface-energy areas of the cathode such as the edges, nodules and needles.

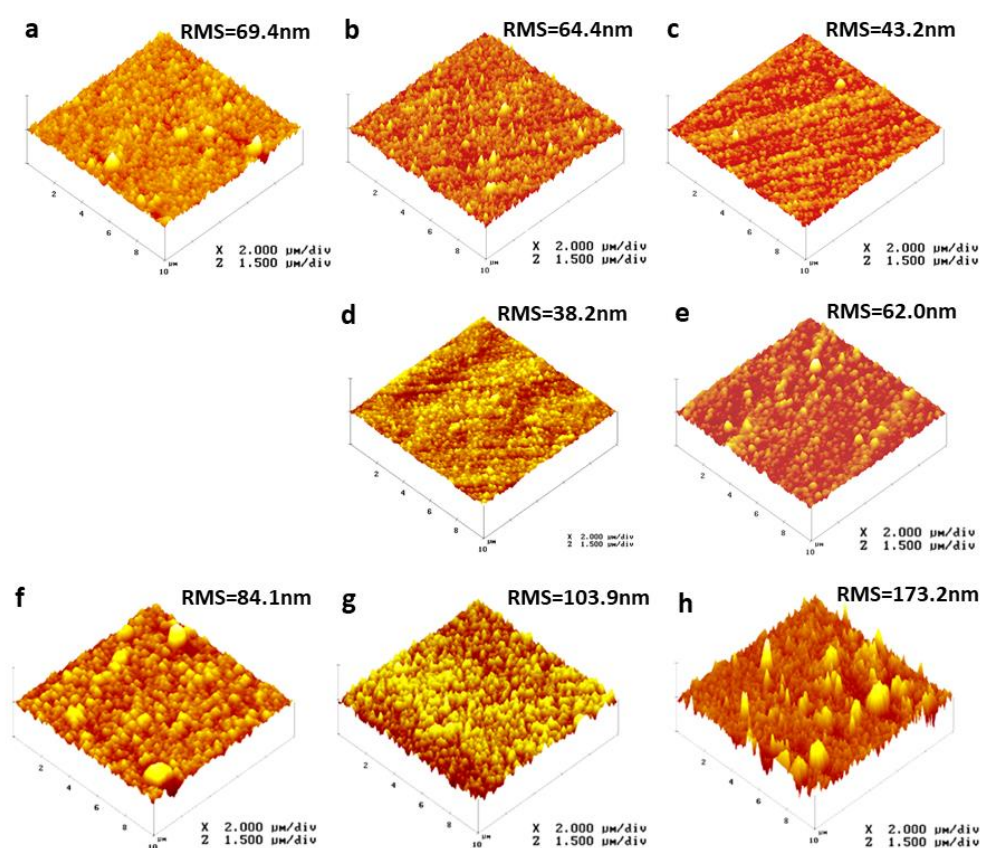


Figure 2. AFM morphological images of copper deposition in regard to roughness for various concentrations of additives. (a) without additive; (b) gelatin 1 ppm; (c) gelatin 9 ppm; (d) thiourea 1 ppm; (e) thiourea 9 ppm; (f) chloride ion 1 ppm; (g) chloride ion 10 ppm; (h) chloride ion 100 ppm.

Compared to the additive-free condition, the deposits with different concentrations of thiourea exhibited a much higher number density of the grains due to the inhibition of the grain growth and formation of larger grains, so the electroplated copper had a smooth surface in Figure 1. The mean grain size of the copper deposit decreased with increasing thiourea concentrations when the concentration was

increased from 1 to 3 ppm, and a flat surface was derived. The surface feature of the substrate of a bare copper plate can be resolved, which suggests a uniform increase in film thickness. When the thiourea concentration was increased to 9 ppm, the surface flatness and leveling effects degraded, possibly due to a nearly full coverage of thiourea on the cathode, which decreased the selectivity of adsorption on the surface protrusions compared to the case with partial thiourea coverage.

When chloride ions were added, a relatively coarse film surface developed compared to the additive-free condition in Figure 1. Due to the accelerated copper reduction by chloride ion, there were higher electric field, current density and mass transfer of copper ions on the protruded areas. As a result, the surface consisted of micro-metered grains that were generated and distributed on the surface.

AFM was used to resolve the surface roughness of the copper deposit (Figure 2). The grain size and surface roughness gradually decreased when the gelatin concentration increased from 1 to 9 ppm. The grain size significantly decreased when the thiourea concentration increased from 1 to 3 ppm, and a relatively flat surface morphology formed. The leveling and grain refining effect degraded when 9 ppm thiourea was added, which is attributed to the full coverage and loss of selectivity of adsorption on the protrusions. The surface roughness and grain size increased with the addition of chloride ions, which indicates the enhanced growth of copper deposit on the larger grains due to the adsorption and the acceleration due to chloride ions.

Polarization curves are used to identify the effects of gelatin concentrations on the behaviors of the copper deposition. When the concentration of gelatin increases, the difference in current density is more significant, which suggests an increased coverage when the concentration is increased from 0.33 ppm to 9 ppm due to the enhanced gelatin adsorption (Figure 3(a)). The blocking due to gelatin reduces the number of active sites and mass transfer and causes the decrease in current density. The polarization curves show the extent of adsorption of gelatin at the surface, which affects the transport of copper ions to the surface of the cathode, and interferes with the copper deposition.

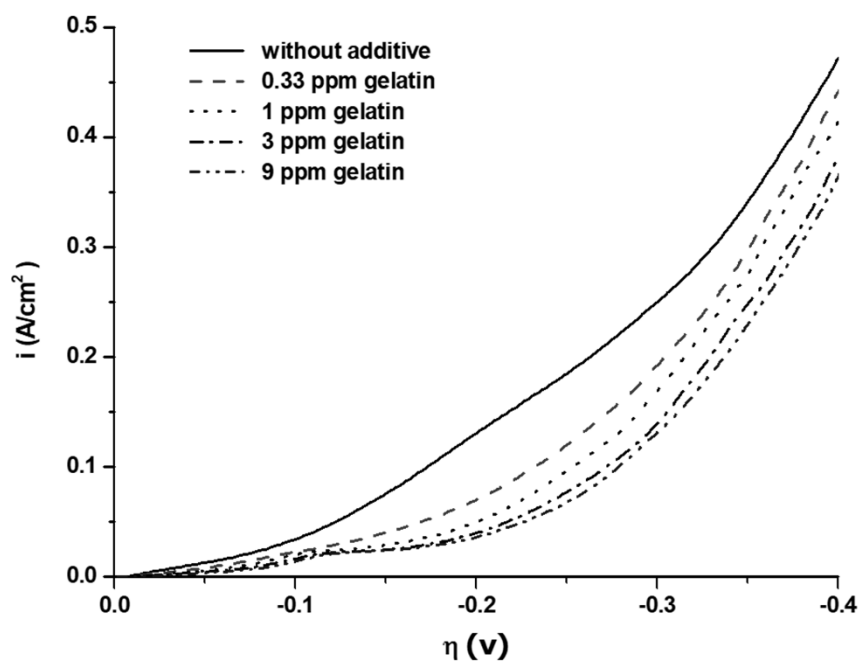
The suppression in current density is evident after the addition of thiourea (Figure 3(b)). The results indicate that thiourea causes a significant polarization due to the obvious adsorption and coverage. This result is attributed to the generation of copper sulfide on the copper deposit, which appears to inhibit the copper reduction reaction on the adsorbed area. With 9 ppm thiourea in the bath, the largest inhibition of copper deposition was found and suggests a fully coverage. However, this inhibition causes the loss of selectivity on the protrusions and degraded leveling effects as shown in the morphological analysis.

The current density significantly increased when chloride ions were added into the electrolyte bath (Figure 3(c)). This result is consistent with the proposed mechanism in the literature. With no other additives, it will promote the reduction of copper at the cathode. The Cl^- - Cu^{2+} ligand has a shorter bond length than the H_2O - Cu^{2+} ligand, so the copper deposition becomes easier[4].

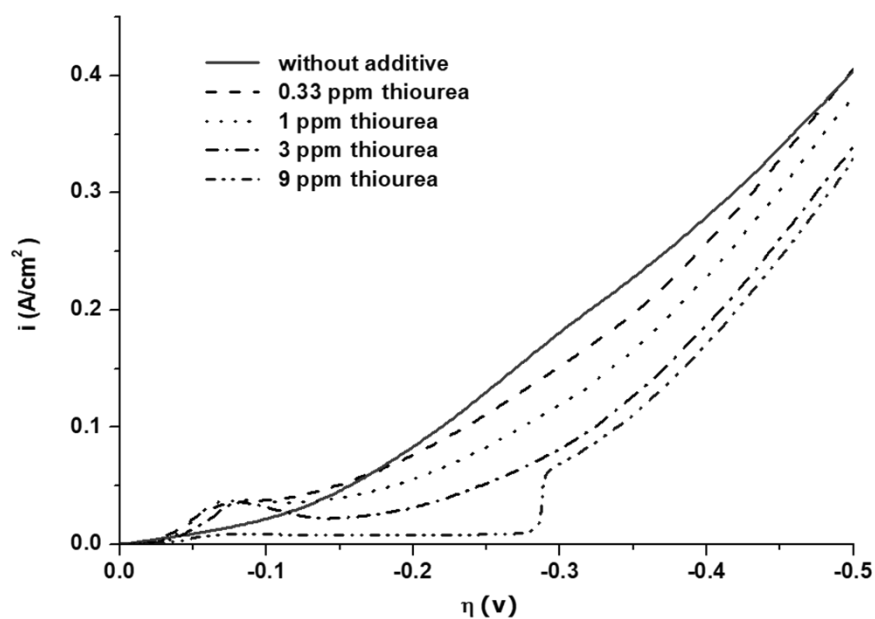
The halide adsorption can accelerate the copper deposition rate, while the co-adsorption of polymer significantly inhibits the copper deposition by limiting the access of Cu^{2+} to the cathode. The combined addition of gelatin and chloride ions substantially decreases the current density as shown in Figure 3(d) in comparison to the additive-free case. The copper deposition reaction is inhibited due to the gelatin- Cl^- layer, which restricts the access of cupric ions to the metal surface. The gelatin- Cl^- complex is more easily adsorbed on the cathode surface than the polymer alone, and its generation strongly inhibits the copper deposition. The complex formation is attributed to the interactions between

adsorbed chloride ions and amine groups of the gelatin molecule. However, when the overpotential is further increased, due to the breakage of the complex effect, the current inhibition decreases.

(a)



(b)



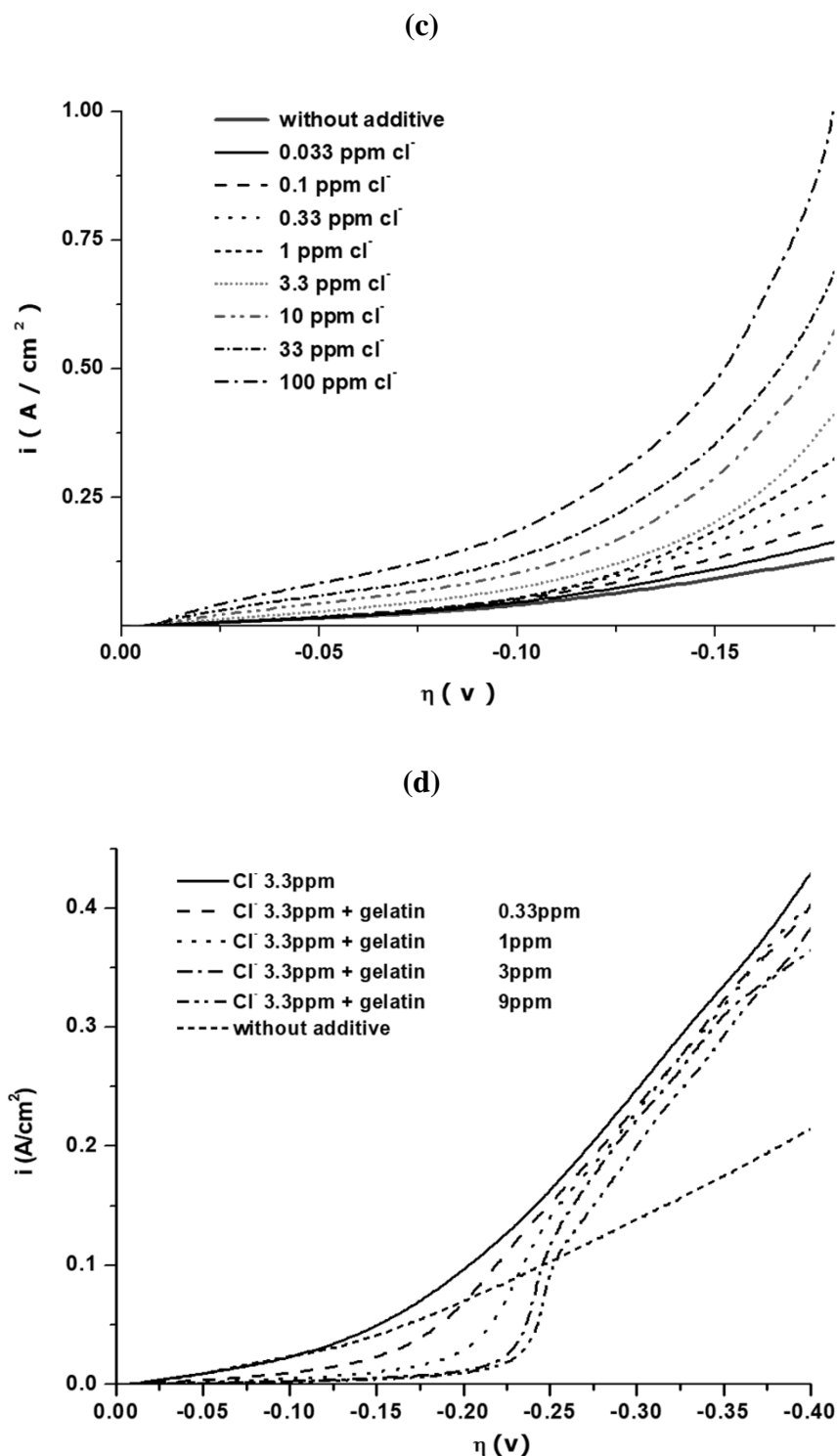


Figure 3. Polarization curves of the copper electrochemical deposition for various concentrations of additives: (a) gelatin; (b) thiourea; (c) chloride ion; (d) chloride ion 3.3 ppm and gelatin.

While the gelatin and thiourea were simultaneously added, the effects of leveling and grain refining coexisted, and the uniformity appeared to significantly improve as shown in Figure 4. The additional incorporation of low-concentration chloride ions in the bath with gelatin and thiourea is found

to further enhance the leveling and grain refiner effects, and eventually result in a copper deposit film with high flatness and smaller grains (Figure 4).

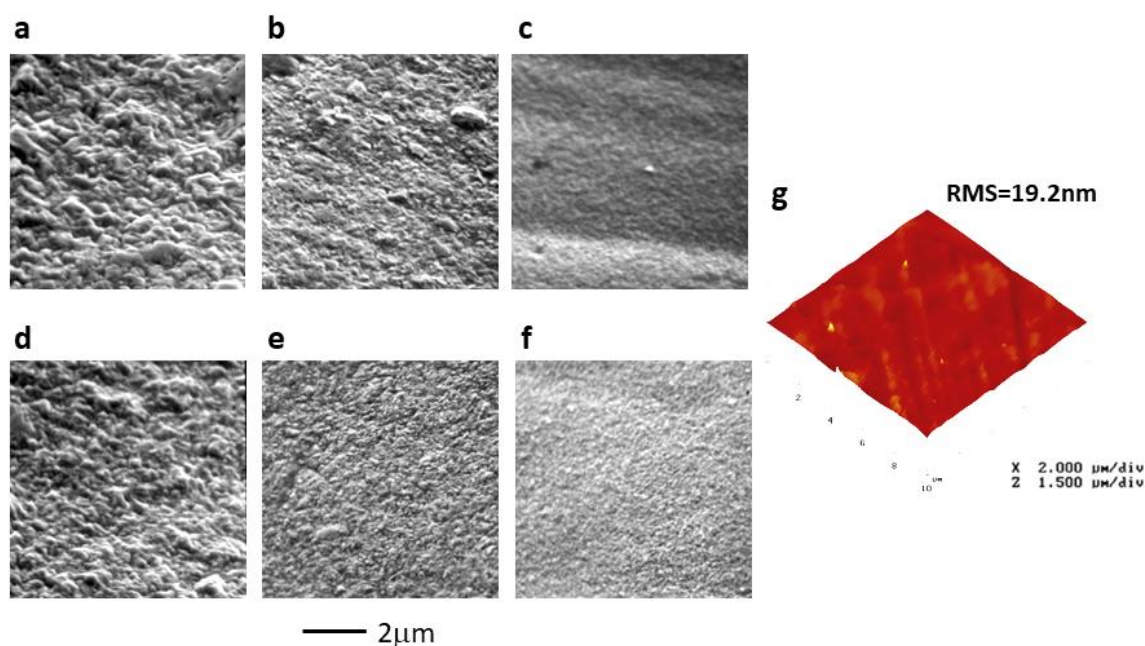


Figure 4. SEM micrographs of the copper electrochemical deposition under various concentrations of additives: (a) gelatin 1 ppm; (b) gelatin 1 ppm and thiourea 3 ppm; (c) gelatin 1 ppm, thiourea 3 ppm and chloride ion 3.3 ppm; (d) gelatin 9 ppm; (e) gelatin 9 ppm and thiourea 3 ppm; (f) gelatin 9 ppm, thiourea 3 ppm and chloride ion 3.3 ppm. (g) AFM morphological images of the copper deposition to show the roughness for gelatin 9 ppm, thiourea 3 ppm and chloride ion 3.3 ppm.

The improvement in grain refining and film uniformity can be attributed to the increased nucleation sites, uniformed nucleation rate and growth. The presence of the gelatin-Cl⁻ complex adsorbed on a high-current-density area limits the current density at the protrusions, and thiourea refines the grain size growth. This result is shown in the corresponding SEM and AFM images in Figures 4(f) and 4(g).

The effect and behavior of a single additive were studied in the literature to evaluate the additive effects on copper electroplating. The additives include polyethylene glycol (PEG)[13,26], gelatin[7,13,22], chloride ion[4,24] and thiourea[19,20,23]. Among these studies, only few studies reported the synergetic effect of different additives. The synergetic effects of gelatin, thiourea, chloride ion on the morphology and properties of deposited copper were studied using the SEM, surface roughness, EBSD (electron scattering diffraction pattern) and polarization curves in the literature[11,12,27,28]. In our study, the synergetic effects of a combination of gelatin, thiourea and chloride ion were studied, and the results were revealed by the surface morphology and polarization curves. The effects of individual additives of gelatin, chloride ion, thiourea were also studied as a function of concentrations to clarify and compare the role of individual components in the electrolyte. In this paper, the AFM was introduced to characterize the surface morphology of the deposited copper.

4. CONCLUSIONS

The study reports the effects of gelatin, thiourea and chloride ion in the copper electrodeposition bath on the electrodeposited copper. The evolution of copper deposit morphology was revealed as a function of the concentrations of gelatin, thiourea and chloride ion. The concentration is a key parameter that affects the adsorption and coverage of the additives. The proper dosage of gelatin or thiourea can make the additives partly cover the surface and enhanced the selectivity on the protrusions of the surface of the copper deposit. The polarization curves show that the adsorption and coverage of the additives increase with higher concentrations. Under a high dosage of gelatin or thiourea, a nearly fully coverage of the adsorption layer results in degraded leveling effects due to the loss of selectivity of inhibition on protrusions. Additionally, the combined usage of gelatin, thiourea and chloride ion with proper concentrations results in a copper deposit with high flatness, refined grains and low roughness.

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