

Influence of trisodium citrate on the Cu electrodeposition by sequential underpotential deposition of Pb and surface-limited redox replacement of Cu

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The combination of an all-wet barrier/seed process and Cu electrodeposition can be used to fabricate conformal Cu interconnects. This process usually uses a Co-based barrier deposited by electroless plating. However, as Co is more electrochemically active than Cu, the Co dissolves readily in the acidic Cu²⁺ electrolyte during the subsequent Cu electrodeposition. This paper describes the trisodium citrate enhanced deposition of Cu on a Co/SiO₂/Si substrate via alternating the underpotential deposition of Pb and surface-limited redox replacement of Cu. The nucleation mechanisms and properties of the Cu films were evaluated using scanning electron microscopy, X-ray diffraction, and an electrochemical analyzer. The results show that the complexation of Pb²⁺-Cit³⁻ induced a low coverage of the Pb adlayer during the underpotential deposition. The grain growth led to progressive nucleation for 1 mM trisodium citrate, and shifted gradually toward instantaneous nucleation as the trisodium citrate concentration was increased to 5 mM. The Cu (111) texture was obtained with the 1 mM trisodium citrate addition. However, a high trisodium citrate concentration tended to cause Cu oxidation. The enhancement of the formation of a Cu film by the addition of trisodium citrate via the proposed processes was demonstrated..

Keywords: trisodium citrate, nucleation of Cu film, electrochemical deposition, underpotential deposition of Pb, surface-limited redox replacement of Cu

1. INTRODUCTION

A conformal deposition method is crucial in the fabrication of Cu interconnects as the feature sizes of devices shrink. The conventional Cu interconnect fabrication process consists of an electrodeposited Cu film on a sputtered Cu seed and a Ta/TaN stacked barrier layer. The use of a

vacuum process to sputter the Cu seed and the Ta/TaN barrier followed by a wet chemical process to electrodeposit the Cu film complicates the fabrication of Cu interconnects. Moreover, scaling down the dimensions of the devices makes the conformal deposition of the Ta/TaN barrier and the sputtered Cu seed layer increasingly challenging. Hence, developing an entire wet chemical deposition process is essential for the implementation of Cu interconnect processes.

Wet electroless plating of a Cu film on an electroless deposited Co-based sublayer has been widely studied in Cu interconnect processing [1,2]. In addition, electrochemical growth via underpotential deposition (UPD) and surface-limited redox replacement (SLRR) have also been used in the fabrication of Cu nanofilms [3-5]. The use of Cu-SLRR and Pb-UPD on the Co/SiO₂/Si substrate is critical because Co dissolves easily in the conventional acidic Cu electrolyte due to galvanic corrosion [6]. Thus, the presence of an additive in the Cu electrolyte is essential to avoid Co dissolution. There have been many studies on the effects of additives in electrolytes on the growth of Cu films [7-10]. The complexation of the ethylenediamine (En) and the Cu²⁺ ions in an alkaline Cu electrolyte has been observed to form a CuEn₂⁺ species [11]. En in a Cu nitrate electrolyte can also decrease the OH⁻ absorption, and thus prevents the oxidation of the Cu seed [12]. The complexation of the Cu²⁺ and the En also reduces the exchange rate and prevents the corrosion of the Co substrate [13]. This complexation can promote a more homogeneous Cu deposition due to the decrease in the rate of the Cu replacement [14-16].

Although many studies have been published concerning the effects of additives on the electrodeposition of Cu films, minimal information is available on the effects of trisodium citrate (TSC) in an acidic electrolyte on the Cu electrodeposition on the Co/SiO₂/Si substrate by the UPD and the SLRR processes. The results from this work demonstrate the function of TSC in complexation with Pb²⁺ and Cu²⁺ with improved Cu film-formation. Thus, this study may help to explain the role of TSC on the nucleation mechanism of a Cu film on the Co/SiO₂/Si substrate.

2. EXPERIMENTAL PROCEDURES

The Cu film was prepared on a SiO₂/Si substrate coated with 20 nm of Co that was deposited by a radio frequency sputtering at a power of 50 W under 0.53 Pa Ar working pressure. Before the electrochemical deposition process, in situ cleaning of the Co/SiO₂/Si substrate was performed to remove the surface oxide layer by a cyclic voltammetry (CV) scan in a 1.0 mM TSC solution (Hayashi Pure Chemical), scanning from +100 mV to -1500 mV for 1 cycle at a scan rate of 10 mV/s. CV scans were also used to examine the reductive potentials of the Pb electrolytes at a scan rate of 10 mV/s from +100 mV to -1500 mV. To form the Cu adlayer, a sacrificial Pb monolayer (ML) was first deposited via UPD at a potential range between -490 mV and -620 mV, determined from the CV scans, for 60 s, since Pb has a more negative formal potential [4,5]. In the process, a Pb²⁺ electrolyte was flowed into the deposition cell and, which was maintained for 60 s at the chosen potential to form the sacrificial UPD-Pb monolayer. Then, the blank solution, 1.0 mM TSC solution (Hayasi Pure Chemical), was flushed into the deposition cell for 10 s to remove the Pb²⁺ electrolyte. After that, a Cu²⁺ electrolyte was introduced into the deposition cell at the open circuit potential (OCP) to allow the Cu-SLRR to

occur by replacing the UPD-Pb for 60 s. The UPD of Pb and the SLRR of Cu were repeated for 50 cycles. The results shown in our previous study [13] indicated that addition of 0.7 mM En can improve the Cu-SLRR on the substrate via the UPD-Pb and SLRR-Cu. Thus, this study fixed the concentration of the En at 0.7 mM and varied the concentration of the TSC from 1 mM to 5 mM in the electrolyte to evaluate the growth and properties of the Cu film that were grown after the subsequent 50 cycles of alternating Pb-UPD and Cu-SLRR. The Cu electrolyte consisted of 1.0 mM $\text{Cu}(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ (Sigma-Aldrich) and 0.7 mM $\text{C}_2\text{H}_4(\text{NH}_2)_2$ (Shimakyu's Pure Chemical). The Pb electrolyte was composed of 1.0 mM $\text{Pb}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (Sigma-Aldrich) and 0.7 mM $\text{C}_2\text{H}_4(\text{NH}_2)_2$. The Cu film was then deposited by sequentially performing the UPD-Pb and SLRR-Cu in the respective electrolytes with different concentrations of TSC from 1 mM to 5 mM.

The potential and current measurements were performed using an electrochemical workstation (Metrohm Autolab PGSTAT101). The deposition cell was equipped with a gold wire as the auxiliary electrode and an Ag/AgCl (3 M KCl, Bioanalytical Systems Inc.) reference electrode. The crystalline structure of the film was examined via X-ray diffractometry (XRD, Bruker AXS D8A25) with $\text{Cu K}_{\alpha 1}$ radiation. The electrical resistivities of the films were determined using the standard four-point probe method. The surface morphologies of the Cu films were inspected by field emission scanning electron microscopy (FESEM, JEOL JSM-7500F). The detailed photoelectron spectra were examined using an X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD) operated at 15 kV, excited by Mg-K_{α} radiation (1253.6 eV). The binding energies of the XPS spectra were calibrated by the C 1s peak at 284.6 eV.

3. RESULTS AND DISCUSSION

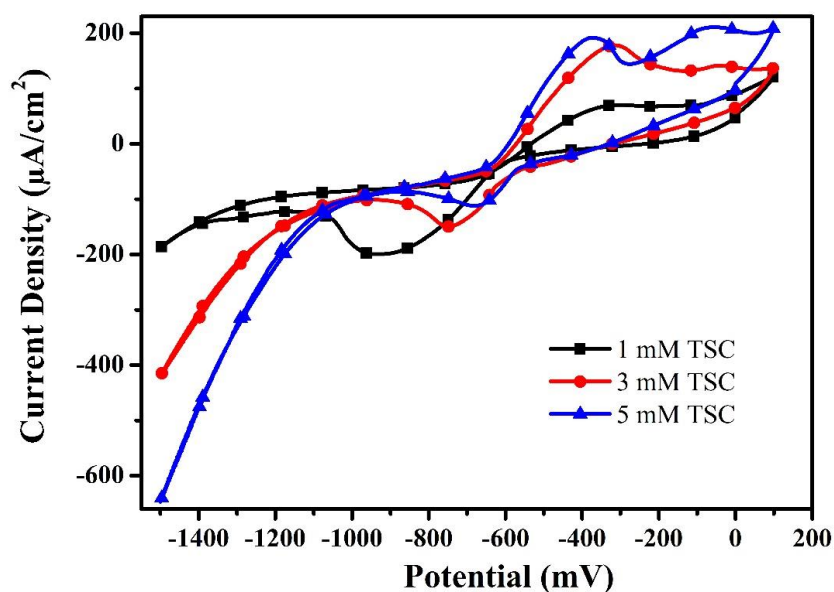


Figure 1. Cyclic voltammograms of the Pb^{2+} electrolytes with different TSC concentrations on the $\text{Co/SiO}_2/\text{Si}$ at a scan rate of 10 mV/s.

The TSC electrolyte contains $\text{C}_6\text{H}_5\text{O}_7^{3-}$ (Cit^{3-}) and Na^+ ions. Thus, the pH value of the studied Pb^{2+} electrolyte increased from 5.58 to 7.22 with the addition of 1 mM to 5 mM TSC. The pH value is comparable with that of the 0.1 M TSC in H_2O [17]. A CV scan was first performed to determine the reductive potential of the Pb^{2+} electrolyte with different TSC concentrations, as shown in Fig. 1. The reductive current for the electrolyte with the 1 mM TSC addition begins to increase significantly at -600 mV, followed by a distinct peak of reductive potential appearing at -920 mV. Finally, an increase in the reductive current occurs at -1380 mV due to hydrogen generation. The results obtained from the CV scans also show that the reductive potential of the Pb^{2+} electrolyte is -720 mV for 3 mM TSC and -650 mV for 5 mM TSC. The TSC complexation has a weak dependence on the alkaline Cu electrolyte [18]. However, in this study, it was observed that the reductive potential decreases with increasing TSC concentration in the acidic Pb^{2+} electrolyte. This tendency also differs from that of the En addition in the Pb^{2+} electrolyte because of the absorption of the En on the $\text{Co/SiO}_2/\text{Si}$ substrate [13]. The complexation of sodium citrate and potassium sodium tartrate has also been found to shift the reductive potential to a more negative potential [19]. In this study, the TSC causes the reductive potential to shift to a less negative potential. This result may be due to the TSC compensating for the En, which caused the delay of the cathodic reduction of the Pb^{2+} ions [20]. When the CV scans back to a positive potential, the corresponding oxidation peak occurs at -320 mV for 1 mM TSC, -320 mV for 3 mM TSC, and -330 mV for 5 mM TSC. The oxidation potential of the Pb^{2+} electrolyte does not appear to be affected by the small amount of TSC added.

The average peak potential of the reduction and oxidation during the CV scan is usually applied for the UPD of Pb because the average peak potential is independent of the sweep rate [21,22]. Thus, this work used the potentials of -620 mV, -520 mV, and -490 mV for the Pb-UPD for the electrolytes with 1 mM, 3 mM, and 5 mM TSC additions, respectively. Figure 2 shows current-time curves that were recorded during the respective UPD of Pb for the Pb^{2+} electrolyte with different TSC concentrations. Initially, the current increases dramatically with time, and then, the current transient reaches a maximum value due to the electrical double layer near the Co surface that has rapidly adsorbed the oncoming Pb^{2+} ions and become charged [23]. In this stage, the applied potential overcomes the activation energy for the Pb nucleation and causes the reduction of the Pb^{2+} ions on the $\text{Co/SiO}_2/\text{Si}$ substrate. Subsequently, the current decreases steadily with time until reaching a stable value. This observation indicates that the UPD-Pb has been terminated, since the UPD occurs at the potential prior to the potential for the bulk deposition [24]. The current transient observed in the current-time curve requires a progressively shorter time to reach the peak as the concentration of the TSC in the electrolyte increases. The fast transient of current may be due to the Cit^{3-} in the TSC that further compensates the complexation of En with the Pb^{2+} [25].

Figure 2 shows current-time curves that were recorded during the respective UPD of Pb for the Pb^{2+} electrolyte with different TSC concentrations. As can be seen the current initially increases dramatically with time. Then, the current transient reaches a maximum value due to the electrical double layer near the Co surface is rapidly adsorbed and charged with the oncoming Pb^{2+} ions [23]. In this stage, the applied potential overcomes the activation energy for Pb nucleation and causes the reduction of the Pb^{2+} ion on the $\text{Co/SiO}_2/\text{Si}$ substrate. After that, the current decreases steadily with time until reaching a stable value. This indicates that the UPD-Pb has been terminated due to the UPD

occurs at the potential prior to the potential for bulk deposition [24]. The current transient observed in the current-time curve requires progressively shorter time to reach the peak when the electrolyte was added with more TSC. The fast transient of current might due to the Cit^{3-} in the TSC further compensates the complexation of En with the Pb^{2+} [25].

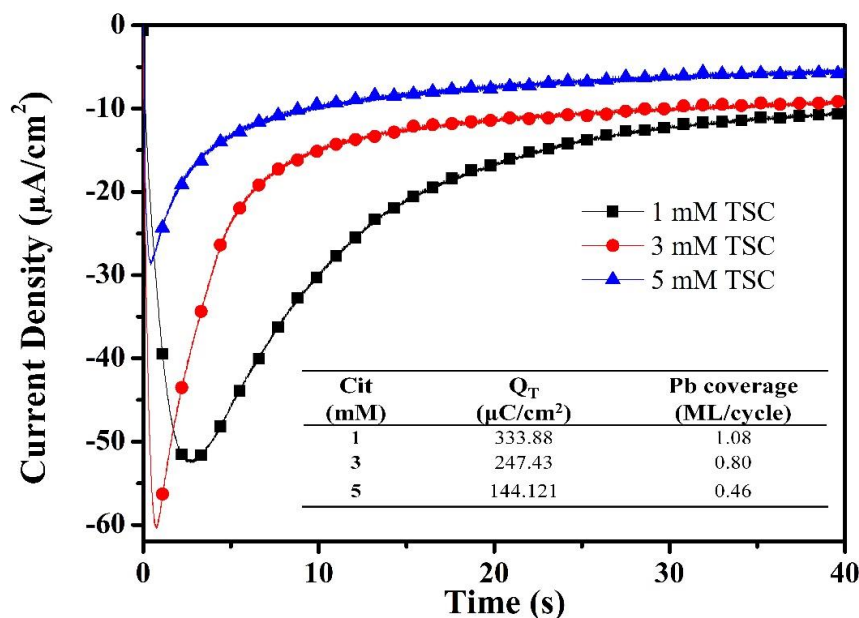


Figure 2. Current-time curves for the underpotential deposition of Pb recorded for various TSC concentrations in the Pb^{2+} electrolyte. The inset Table shows electrical charge and Pb coverage for the adlayer prepared using various TSC concentrations.

Integration of current-time curve shown in Fig. 2 can obtain the deposition charge of the respective UPD-Pb. Moreover, the formation of one Pb monolayer requires a charge of $570 \mu\text{C}/\text{cm}^2$ [22,26]. So, the respective charge obtained from the current-time curve yields the coverage of the UPD-Pb for one deposition cycle, as shown in the table inset in Fig. 2. Table inset shows the UPD-Pb coverage decreases with increasing the concentration of TSC. This finding suggests the citrate ions absorbed on the electrode surface and hindered the charge transfer [27]. Note that both Cit^{3-} and En can complex with Pb^{2+} , but the stability constant of $\text{Pb}^{2+}\text{-Cit}^{3-}$ complex is lower than that of $\text{Pb}^{2+}\text{-En}$ complex [28,29]. Thus the competition reaction between Cit^{3-} and En favors the formation of $\text{Pb}^{2+}\text{-En}$ complex. In this study, available Pb^{2+} ions after the formation of $\text{Pb}^{2+}\text{-En}$ may form $\text{Pb}^{2+}\text{-Cit}^{3-}$ complex. So, the complexation of $\text{Pb}^{2+}\text{-Cit}^{3-}$ becomes inevitable when more TSC was added in the electrolyte. Thus, high TSC concentration reduces the coverage of Pb adatoms during the Pb-UPD.

Figure 3 shows the potential-time curves for the replacement of UPD-Pb by Cu^{2+} recorded during the OCP. In this replacement process, the redox potential difference between Cu and Pb initiates the Cu^{2+} exchanges the UPD-Pb, and forms a Cu adlayer. In this state, the potential increases progressively and become positive until reaching a stable value when the replacement of the UPD-Pb by the Cu^{2+} has completed. The time required for the potential to reach stability is 36 s for 1 mM TSC,

21 s for 3 mM TSC, and 4 s for 5 mM TSC. The TSC addition in the electrolyte significantly decreases the time to reach the stable potential.

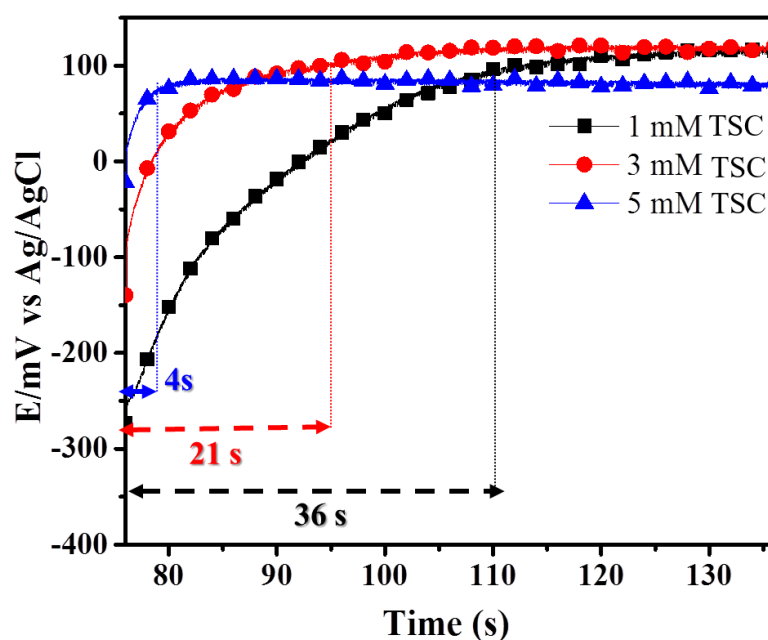


Figure 3. Potential-time curves for the Cu-SLRR deposited in the electrolytes with different TSC concentrations.

The behavior is also different from that of the En addition because En can strongly complex with Cu^{2+} and decrease the exchange rate between the Cu^{2+} and UPD-Pb [13]. This study shows that the replacement can be accelerated with a high TSC concentration in the electrolyte, implying that the Cit^{3-} may enhance the Cu-SLRR. Furthermore, the surface concentration of Cu-Cit-H is higher than that of Cu^{2+} when the electrolyte is added with the TSC present [30]. The high concentration of Cu-Cit-H thus leads to the reduction of Cu through decomplexation. Additionally, the replacement time between the Cu^{2+} and UPD-Pb is coverage dependent [31]. A high UPD-Pb coverage generally requires a long replacement time. The 5 mM TSC has the lowest UPD-Pb coverage and, therefore, results in the shortest replacement time for the UPD-Pb and Cu^{2+} . The stable potential for the 5 mM TSC addition is +80 mV, which is lower than that of the 1 mM (+115 mV) and 3 mM (+118 mV) TSC additions. The stable potential indicates the standard electrode potential value of Cu^{2+} and Co for the initial stage and the value of Cu^{2+} and Cu when the $\text{Co/SiO}_2/\text{Si}$ has been covered by Cu adatoms. Thus, the low stable potential for the 5 mM TSC addition reflects the low coverage of the resultant Cu adlayer.

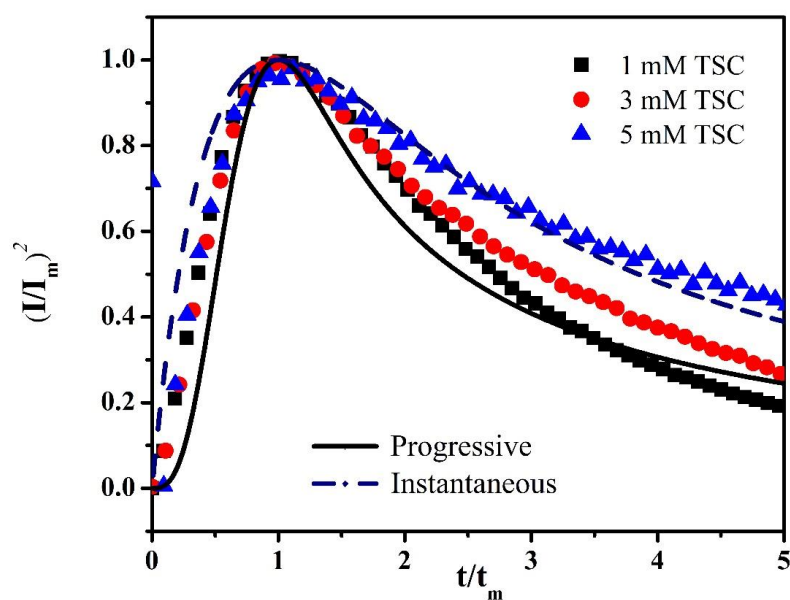


Figure 4. $(I/I_m)^2$ vs. t/t_m curves for the UPD-Pb in the electrolytes with various TSC concentrations.

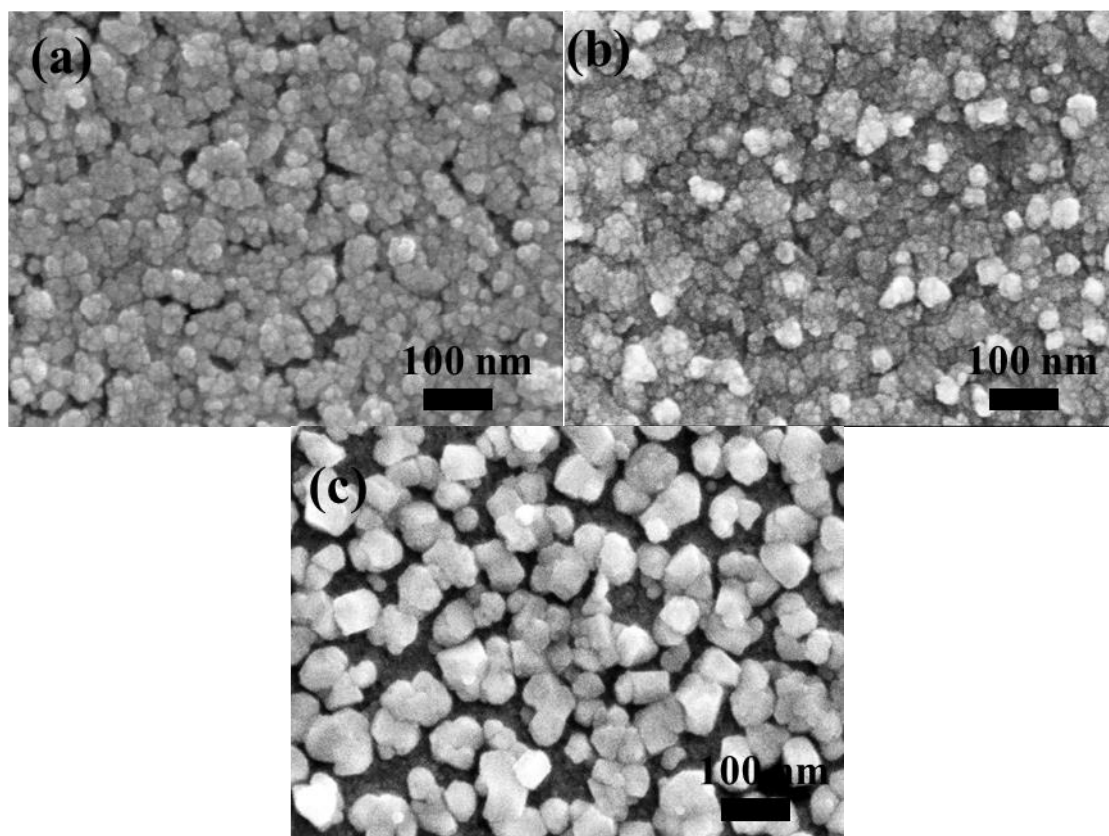


Figure 5. Surface morphologies of the SLRR-Cu films deposited in the Cu electrolytes with various TSC concentrations of (a) 1 mM, (b) 3 mM, and (c) 5 mM.

The current-time curves can be used to describe the nucleation mechanism in the form of $(I/I_m)^2$ vs. t/t_m [32-34]. The nucleation curves for the Pb-UPD with the various TSC concentrations are shown in Fig. 4. The nucleation follows the progressive nucleation process for the 1 mM TSC, and changes to an instantaneous nucleation process as the TSC concentration increases to 5 mM. The nucleation type is between progressive and instantaneous for the 1 mM TSC electrolyte [35]. This study further shows that the addition of 0.7 mM En and 1 mM TSC in the electrolyte causes more progressive nucleation. However, the addition of more TSC in the electrolyte gradually converts the nucleation of the UPD-Pb. The tendency of the nucleation behavior is opposite to that of the En addition, in which increasing the En concentration tends to cause the progressive nucleation [13]. Additional TSC induces the formation of more Pb^{2+} complexes with Cit^{3-} and forms $(PbCit_2)^{4-}$ in the electrolyte [29]. Thus, the nucleation transition alters the distribution of the nuclei, which is reflected in the surface morphologies that will be discussed in the following section.

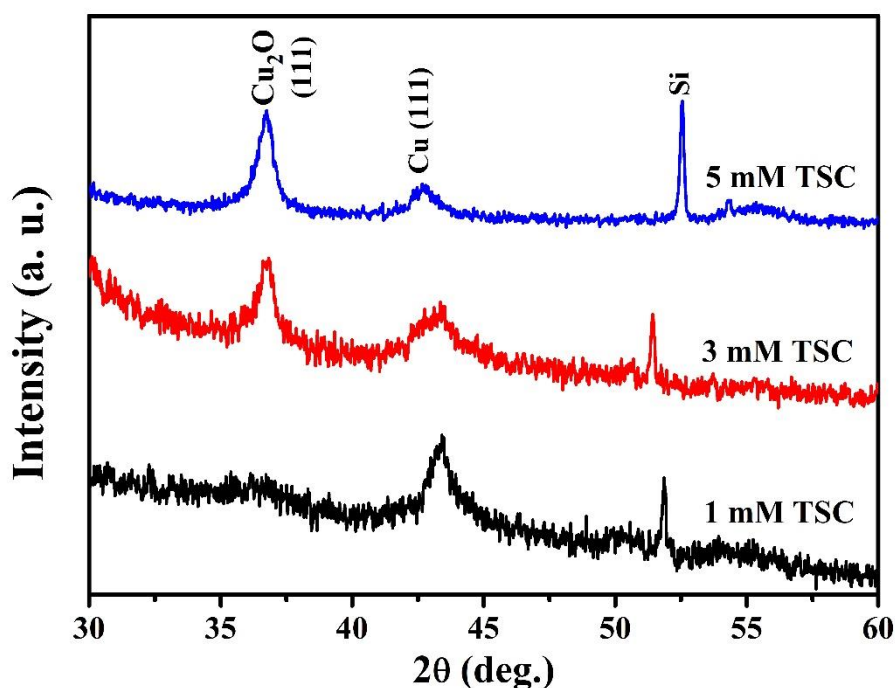


Figure 6. Structural results examined by XRD for the SLRR-Cu films deposited with various TSC concentrations.

Cu^{2+} ions in the electrolyte may lead to an exchange of the Co on the substrate before replacing the UPD-Pb adatoms ($E^0 Pb/Pb^{2+} = -0.125$ V/SHE) according to the standard potential values of Cu and Co ($E^0 Cu/Cu^{2+} = +0.34$ V/SHE, $E^0 Co/Co^{2+} = -0.28$ V/SHE). The high TSC concentrations in the studied electrolyte produce a lower UPD-Pb coverage. Thus, the Cu^{2+} electrolyte may cause a galvanic corrosion on the Co substrate if the UPD-Pb adatoms are incapable of covering the entire Co surface. The variation in the surface morphology of the resultant 50-cycle SLRR-Cu thin film is shown in Fig.

5. Figure 5(a) shows that the Cu film has small but less uniform nuclei with moderate area density for the electrolyte with the 1 mM TSC addition.

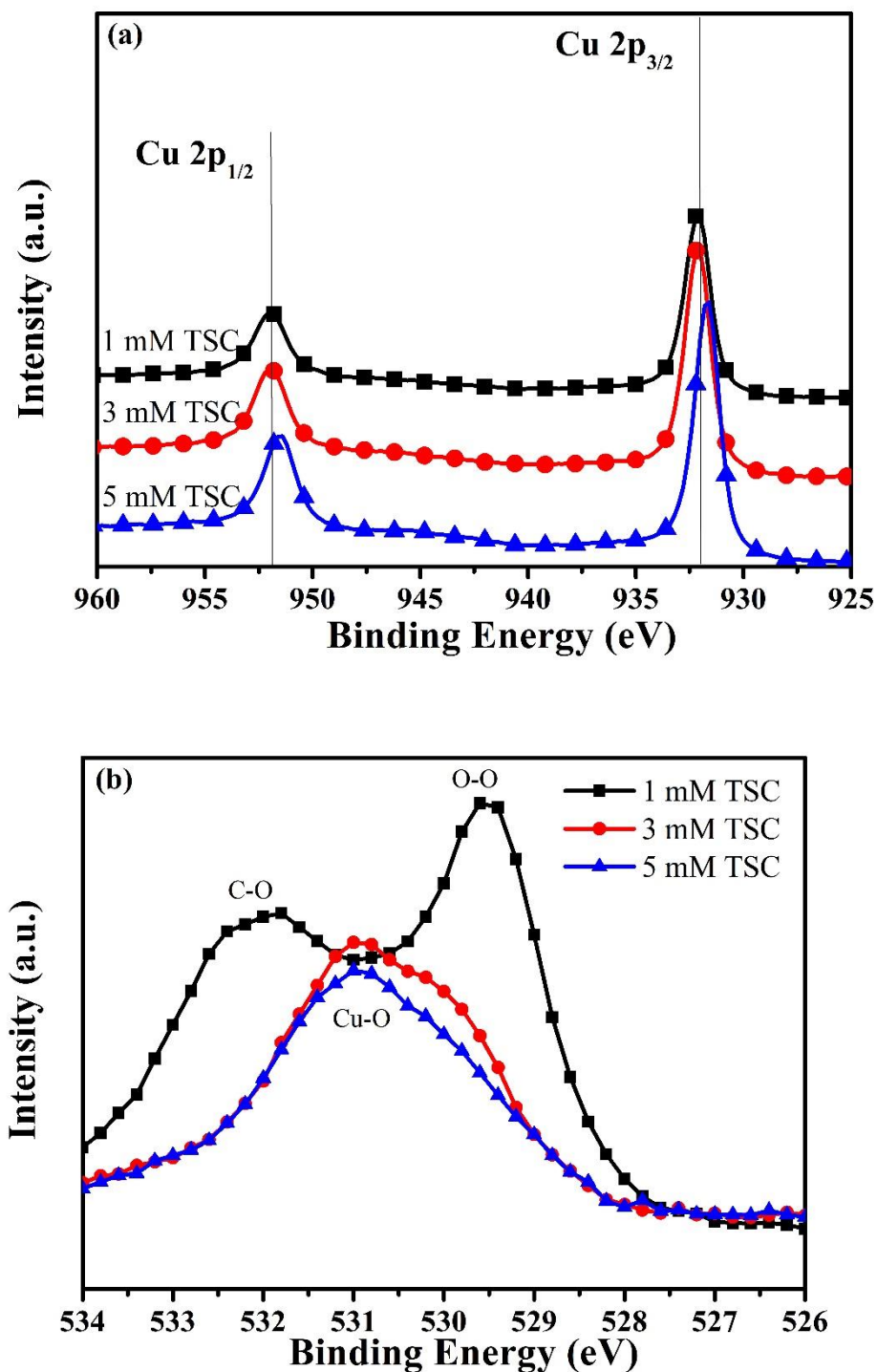


Figure 7. (a) Cu 2p bonding photoelectron spectra and (b) Cu-O bonding photoelectron spectra for the SLRR-Cu films deposited with various TSC concentrations.

This observation implies that the film growth is dominated by progressive nucleation, where nuclei grow at prior positions and on newly developed nuclei [36]. The SLRR-Cu film has an uneven grain size when the electrolyte is added with 3 mM of TSC, as shown in Fig. 5(b). This result means that the nucleation is in between progressive and instantaneous nucleation. For the TSC concentration of 5 mM shown in Fig. 5(c), the SLRR-Cu film has large nuclei accompanied with an exposure of the Co/SiO₂/Si substrate. This finding indicates that the high TSC concentration induces instantaneous nucleation because the nuclei form and grow at the same nucleation sites available during each deposition cycle. Thus, nuclei grow without the formation of newly activated nuclei.

Figure 6 shows the XRD results of the resultant Cu film. The Cu film deposited with the addition of 1 mM TSC has a diffraction peak of Cu(111) at $2\theta = 43.2^\circ$. However, the diffraction peak of Cu₂O(111) ($2\theta = 36.7^\circ$) was observed upon the addition of 3 mM and 5 mM TSC, associated with a lower peak intensity of Cu(111). A high TSC concentration increases the tendency of Cu oxidation in this process.

The Cu and O bonding states of the SLRR-Cu films were analyzed by XPS to investigate the effect of the TSC in the electrolyte on the deposition of the SLRR-Cu film. Figure 7(a) shows the XPS Cu 2p spectra for the SLRR-Cu film prepared in the electrolyte with different TSC concentrations. The Cu core level spectra can be curve-fitted with peak components for Cu 2p_{1/2} (952.0 eV) and Cu 2p_{2/3} (932.1 eV) [37]. As shown, the Cu core level spectrum shifts toward a lower binding energy with increasing TSC concentration, indicating that the Cu may bind with other elements. The O 1s spectra of the SLRR-Cu films are shown in Fig. 7(b). Cu-O binding can occur for the 3 mM and the 5 mM TSC additions. However, only C-O and O-O bindings appear when 1 mM TSC is added. Thus, the high TSC concentration caused the Cu oxidation in this study.

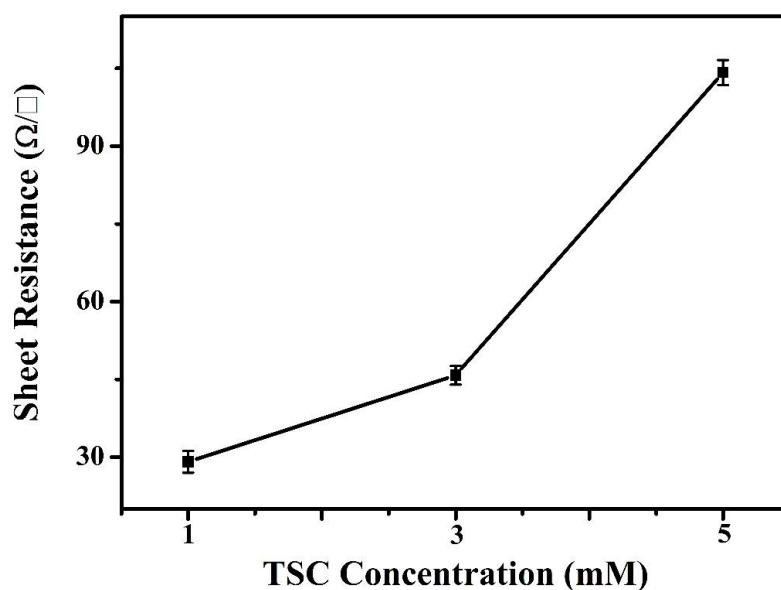


Figure 8. Sheet resistances for the SLRR-Cu films deposited with different TSC concentrations.

Figure 8 shows sheet resistances of the SLRR-Cu films prepared in the electrolyte with different TSC concentrations ranging from 1 mM to 5 mM. The Cu film deposited with 1 mM TSC has a sheet resistance of $29.1 \Omega/\square$. As the concentration of the TSC increases, the sheet resistance of the Cu film increases from $45.8 \Omega/\square$ for 3 mM TSC to $104.2 \Omega/\square$ for 5 mM TSC. This finding indicates that the subsequent Cu-SLRR occurs imperfectly because of the low coverage of the UPD-Pb on the substrate and/or the oxidation of the SLRR-Cu in the electrolyte with a higher TSC concentration. The Cu film deposited from the electrolyte with 1 mM TSC has the highest UPD-Pb coverage, thus providing more Pb atoms on the surface for the subsequent replacement of Cu^{2+} . Moreover, Cu_2O formation also causes the film to have a high sheet resistance. Only Cu(111) was obtained for the 1 mM TSC addition. Those properties suggest that the 1 mM TSC addition is appropriate for the Pb-UPD and Cu-SLRR processes.

4. CONCLUSIONS

This study indicates that a proper TSC addition can enhance the Cu film deposited on the Co/SiO₂/Si substrate via alternating the UPD-Pb and SLRR-Cu processes. The addition of 1 mM TSC and 0.7 mM En significantly improves the growth of the Cu film due to the compensation of the TSC in the reaction induced by the En complex with the Cu^{2+} . However, a high concentration of TSC induces the oxidation of the SLRR-Cu film. The resultant Cu(111) texture has the lowest sheet resistance for the addition of 1.0 mM TSC. The results may be useful in the electrodeposition of Cu film using the acidic electrolyte.

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