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Thiourea-Based Extraction and Deposition of Gold for Electroless Nickel Immersion Gold Process

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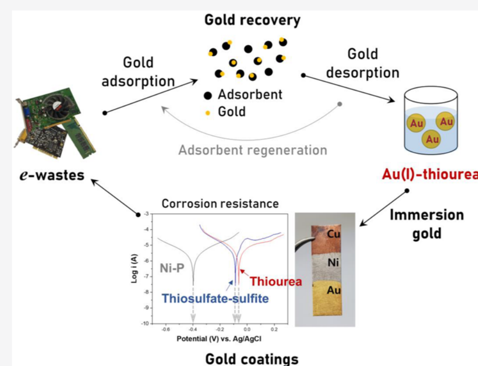
ABSTRACT: Gold electroless plating for surface finishing of electronic circuits, named electroless nickel immersion gold (ENIG), is widely practiced in the electronics packaging industry. Noncyanide substitutions of the current cyanide bath for immersion gold are being sought for environmental and safety reasons. Herein, as a promising option, a bath using a noncyanide gold complex, Au(I)−thiourea, was developed. The kinetics of gold deposition were estimated with respect to gold concentration, thiourea concentration, pH, and temperature; the transfer coefficient of gold concentration and activation energy were found to be 0.697 and 36.69 kJ·mol^{-1}, respectively. In addition, the quality of gold coating in terms of corrosion resistance was verified by electrochemical analysis. The relationship between particle size and corrosion resistance of the coating was confirmed by morphology observation through scanning electron microscopy and Tafel plots. The corrosion potential of the gold layer with thiourea was found to be −62 mV, close to that of the layer using a thiosulfate−sulfite bath, with an advantage of faster deposition rate. The results suggest Au(I)−thiourea can serve as an eco-friendly and field-implementable option for the ENIG process, helping to realize a closed-loop process of gold: recovering the precious metal from electronic wastes and reusing it in new products.



1. INTRODUCTION

Applying a thin layer of gold is a commonly employed way of protecting electric circuits such as printed circuit boards (PCBs) in the electronics packaging industry. A coating method termed electroless nickel immersion gold (ENIG) has gained particular popularity because it provides a substrate with excellent electrical conductivity, corrosion resistance, and good solderability.[1−4] In the process, nickel−phosphorus (Ni−P) is first deposited on a copper substrate via electroless plating, and afterward, gold is coated on the Ni−P through galvanic displacement reaction, known as immersion gold (IG).[5,6] Traditionally, a reaction solution for IG, or simply IG bath, contains cyanide in the form of potassium dicyanoaurate ($KAu(CN)_2$) because it enables outstanding bath stability and results in superb coating performance.[7,8] Because of its highly toxic nature, however, its use has been substantially curbed in recent years.[9,10] Alternatives, involving a noncyanide bath, are being actively sought and developed.

Two highly successful substitutes are thiosulfate and sulfite. A mixed bath of thiosulfate and sulfite has been shown to be better in terms of bath stability than when each are used separately;[11] it also possesses reducing power on account of the existence of sulfite, improving bath stability and film quality.[12,13] The coating quality has been further improved by means of including certain organic additives, even at a trace level.[3] The complexity of the bath composition, however, is problematic. Thiosulfate impacts on resultant film quality and deposition rate.[8,12] Moreover, the bath is not very compatible with the acidic photoresist process, a necessary step in the PCB manufacturing procedure, because thiosulfate is stable only at alkaline conditions.[7]

Thiourea is another promising noncyanide ligand for gold, as it forms stable gold complexes.[9,14] In fact, it has already been tested for its potential in gold recovery from several different adsorbents.[15−21] For example, it has been found to be the best ligand with respect to gold desorption from a novel porphyrin-based porous polymer, called COP-180, and also in terms of the adsorbent regeneration.[22] The application of generated gold-containing thiourea from the desorption, however, has only been proven only on levels of concept or at best proof-of-concept[23−25] and has never been tried for practical purposes.

In this work, therefore, a noncyanide IG bath on the basis of Au(I)−thiourea was proposed and tested as an environmentally friendly and yet practically workable option for the ENIG process. In addition to a distinctive advantage of the simplicity of bath composition, the acidic nature of the

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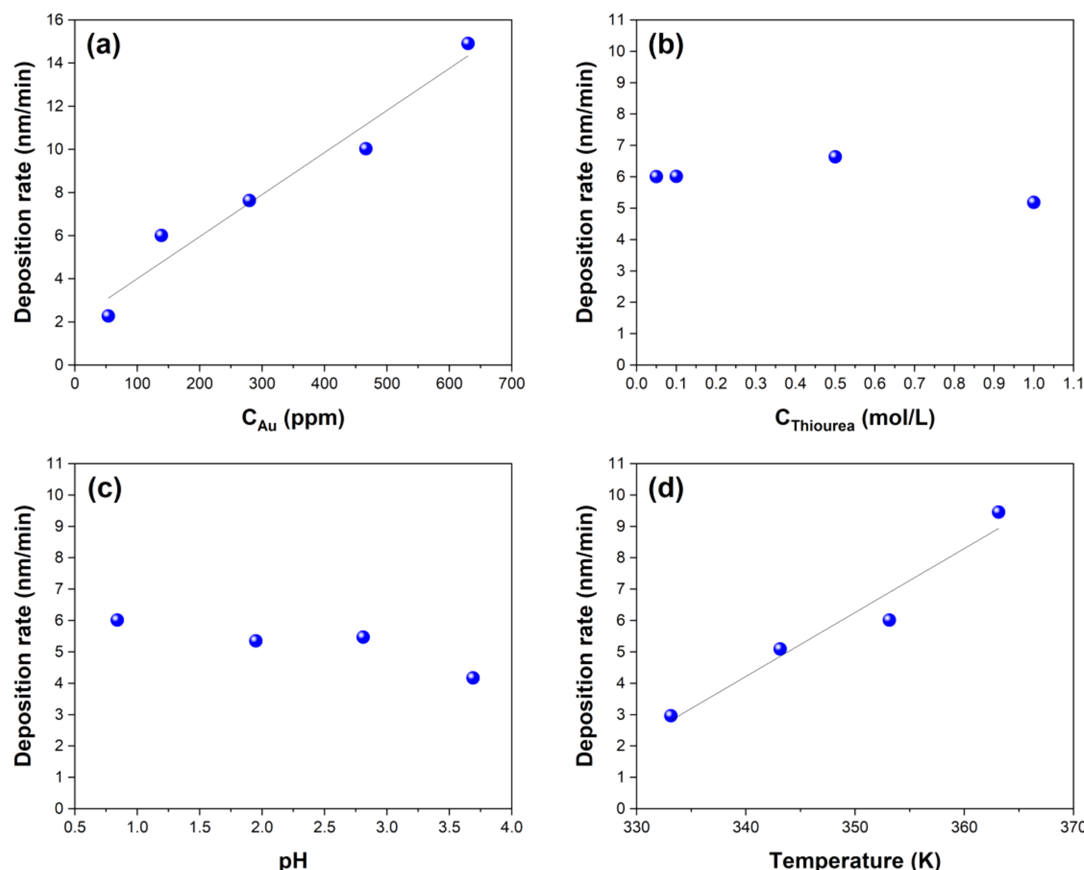

Figure 1. Effects of the plating parameters on deposition rate: (a) concentration of gold, (b) concentration of thiourea, (c) pH, and (d) depositing temperature.

thiourea-based bath has an added merit of being compatible with the pre- and postprocesses. The ability of the proposed bath to directly use gold leachates from different sources such as electronic wastes is also beneficial from both economic and environmental standpoints. In this study, gold deposition kinetics were examined with respect to bath composition and operation conditions, and the resulting gold coatings were characterized. The quality of the formed film was evaluated in terms of corrosion resistance via an electrochemical method and compared with that of coating using thiosulfate−sulfite.

2. MATERIALS AND METHODS

2.1. Materials. Nickel(II) sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$), sodium hypophosphite monohydrate ($Na_2H_2PO_2 \cdot H_2O$), sodium sulfite (Na_2SO_3), sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$), and copper foil (thickness: 0.25 mm, ≥ 99.98%) were all obtained from Sigma-Aldrich. Sodium acetate (CH_3COONa) and sodium citrate anhydrous ($Na_3C_6H_5O_7$) were purchased from Kanto Chemical Co. and Daejung Chemicals & Metals Co., respectively. Thiourea ($CS(NH_2)_2$) from Junsei Chemical Co. was used. Sulfuric acid (H_2SO_4, ≥ 95%), sodium phosphate dibasic (Na_2HPO_4), sodium hydroxide (NaOH), and sodium chloride (NaCl) were supplied from Samchun Chemicals. Gold trisodium disulphite ($Na_3[Au(SO_3)_2]$) was received from BOC Sciences. All chemicals were of analytical grade.

2.2. Preparation of Gold−Thiourea Solution. A gold-dissolved thiourea solution was obtained through a gold desorption process using a novel porous porphyrin polymer, called COP-180, as described in Son et al.[22] The gold-adsorbed polymer with a ratio of adsorbed gold to the polymer of 0.2 was applied to a thiourea solution containing 0.1 mol·L^{-1} H_2SO_4 at 50 °C for 2 h with vigorous stirring. Thiourea solutions were prepared so that concentrations varied (i.e., 0.05, 0.1, 0.5, and 1.0 mol·L^{-1}). A varied concentration of gold in the thiourea solution was obtained by changing the solid/liquid ratio in the gold desorption process. The gold concentration was confirmed by using inductively coupled plasma optical emission spectrometry (ICP-OES, 5110, Agilent Technologies).

2.3. Gold Coating Preparation. A copper foil (20 mm × 20 mm × 0.25 mm) was used as a substrate for the ENIG process. Prior to electroless plating, pretreatment comprising multiple steps was undertaken, as discussed in previous studies.[7,8] In brief, the copper substrate was treated consecutively in a basic solution for 5 min at 60 °C, in an acidic solution for 1 min at 30 °C, and in a palladium-based activating solution for 1 min at 30 °C. Electroless nickel (EN) coating on the pretreated copper foil was performed in an EN bath, which contained 25 g·L^{-1} $NiSO_4 \cdot 6H_2O$, 30 g·L^{-1} $Na_3C_6H_5O_7$, 20 g·L^{-1} CH_3COONa, and 30 g·L^{-1} $Na_2H_2PO_2 \cdot H_2O$, as described in Wang et al.,[7] at 80 °C for 15 min to obtain nickel−phosphorus (Ni−P) coating. Finally, the nickel-plated copper sheet was immersed either in gold-containing thiosulfate−sulfite or in thiourea baths, both of which were prepared from the COP-180-based gold adsorption process. The thiosulfate−sulfite bath was composed of 150 or 1500 ppm of $Na_3[Au(SO_3)_2]$, 40 g·L^{-1} Na_2SO_3, 20 g·L^{-1} $Na_2S_2O_3 \cdot 5H_2O$, and 45 g·L^{-1} Na_2HPO_4, adjusted pH to 7.[3,8] The deposited gold thickness was calculated by a difference

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between initial and final concentrations of dissolved gold in the solution measured by ICP-OES over a reaction area. The working reaction area of gold deposition, which was immersed in the gold-containing solution throughout the reaction, was 8 cm^2.

2.4. Characterization of the Coatings. The crystalline structures of the coatings were verified by X-ray diffraction (XRD) on a D/MAX-2500 from RIGAKU using Cu Kα radiation (λ = 1.5418 Å) with scattering angles (2θ) of 30−80°. Surface morphology was characterized using a field emission scanning electron microscope (SEM, Magellan400, FEI Co.).

The corrosion resistance of the coatings was measured by Tafel plot analysis using a potentiostat (CH Instruments 604C) with a three-electrode system. The copper sheets covered with nickel and gold were used as a working electrode with an area of 1 cm^2. Platinum wire and Ag/AgCl electrode (BAS Inc., RE-1B) were used as a counter electrode and a reference electrode, respectively. Tafel curves were obtained in 3.5 wt % NaCl solution with a scan rate of 5 $mV \cdot s^{-1}$.

3. RESULTS AND DISCUSSION

3.1. Effects of Deposition Conditions on IG Coatings and Kinetics Analysis. A simple thiourea-based IG solution was developed for the sake of the deposition of gold on EN coating. Plating conditions, such as gold concentration, thiourea concentration, pH, and temperature, were varied to observe their effects on plating rate, as shown in Figure 1. The deposition rate with respect to each parameter was obtained after 10 min of plating time.

As shown in Figure 1a, the deposition rate quickened with an increase in gold concentration in the thiourea bath, which corresponded well to the general trend in electroless plating. This behavior was attributable to the fact that gold redox potential rises together with its concentration, leading to the increased deposition rate.[7,26,27] Thiourea concentration and pH were not significant contributors to the rate, as illustrated in Figures 1b,c. Although protons in the solution do not participate in the deposition reaction, the acid condition is known to still be able to stabilize the thiourea solution, specifically less than pH 4. With an increase in pH, the solution becomes less stable. The gold deposition rate also improved at high temperature, as is typical of a general chemical reaction (Figure 1d). At the elevated temperature, the migration of gold ions was likely to be quickened during deposition, as was the growth rate of clusters.[26]

Based on the results in Figure 1, the reaction rate (R) can be expressed as follows[7,27]

$$R = k_1 \times [\mathrm{Au}]^{\alpha} \times [\mathrm{CS(NH_2)_2}]^{\beta} \times [\mathrm{H^+}]^{\gamma} \times \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

where k_1 is the specific rate constant; α, β, and γ are the transfer coefficients; E_α is the activation energy; and R and T are the gas constant and temperature, respectively. Since it is apparent that pH and thiourea concentration had negligible impacts on the deposition rate, the equation can conveniently be simplified as follows:

$$R = k_2 \times [\mathrm{Au}]^{\alpha} \times \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

The transfer coefficient, α, was then obtained from a linear regression of the logarithm of deposition rate and gold concentration. The activation energy, E_α, was determined from a linear regression of the logarithm of deposition rate and $1/T$ (Figure S1). As a result, α and E_α values were found to be 0.697 and 36.69 $kJ \cdot mol^{-1}$, respectively.

3.2. Characterization of IG Coatings. The surface morphologies of IG coatings with various parameters were compared in Figure 2. As shown in Figure 2a−c, an increase in

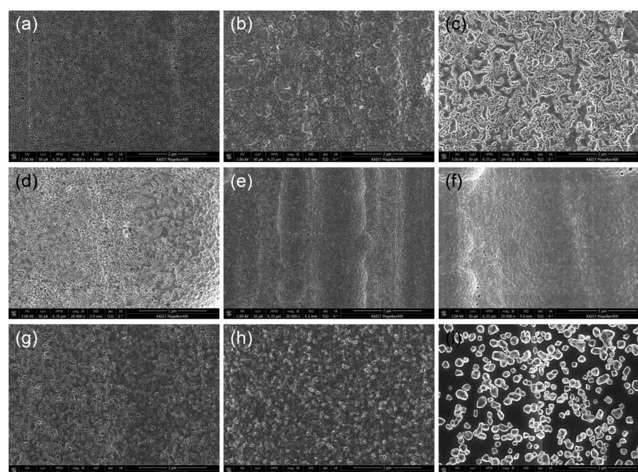

Figure 2. SEM images of Au coatings with various plating conditions: (a) 50 ppm, (b) 300 ppm, (c) 500 ppm of gold, (d) 60 °C, (e) 80 °C, (f) 90 °C of deposition temperature, (g) 0.05 $mol \cdot L^{-1}$, (h) 0.5 $mol \cdot L^{-1}$, and (i) 1.0 $mol \cdot L^{-1}$ thiourea.

gold concentration appeared to lead to enlarged particle sizes of the coatings; the increased concentration of metal ions likely contributed to the growth rate of nuclei.[26,28] Temperature, as above, exerted on the deposition, as illustrated in Figure 2d−f, revealed that the elevated temperature improved the nucleation rate of metal deposition due to accelerated diffusion.[29−32] Thiourea concentration marginally affected surface morphologies and particle sizes until it reached 0.5 $mol \cdot L^{-1}$ (Figure 2g,h). An excess amount of thiourea in the solution, on the other hand, caused aggregation and an uneven distribution of gold particles on the nickel surface (Figure 2i). This phenomenon might have arisen because thiourea molecules in the solution hinder particle nucleation of gold deposits by way of their occupying active sites on the nickel surface.[33,34]

The primary role of gold coatings in the ENIG process is to protect the electroless nickel layer, which is a soldered component, from corrosion. Thus, gold coatings are supposed to heighten corrosion resistance, and to achieve that, formed films must be uniform, pore-free, and adherent.[3] One key parameter that affects all of these requirements is the particle size of gold. Coarse particles tend to have pores on the coating surface, and fine particles, if too small, would reduce the adherent strength of the coatings. It was found that deposition rate, temperature, gold concentration, and thiourea amount were all influential factors.

The effect of particle size on the performance of IG film was further examined by electrochemical analysis. Corrosion potentials (E_{corr}) and corrosion currents (I_{corr}) were calculated from Tafel curves using CHI electrochemical equipment. Gold films from 0.05 and 0.1 $mol \cdot L^{-1}$ thiourea had more positive

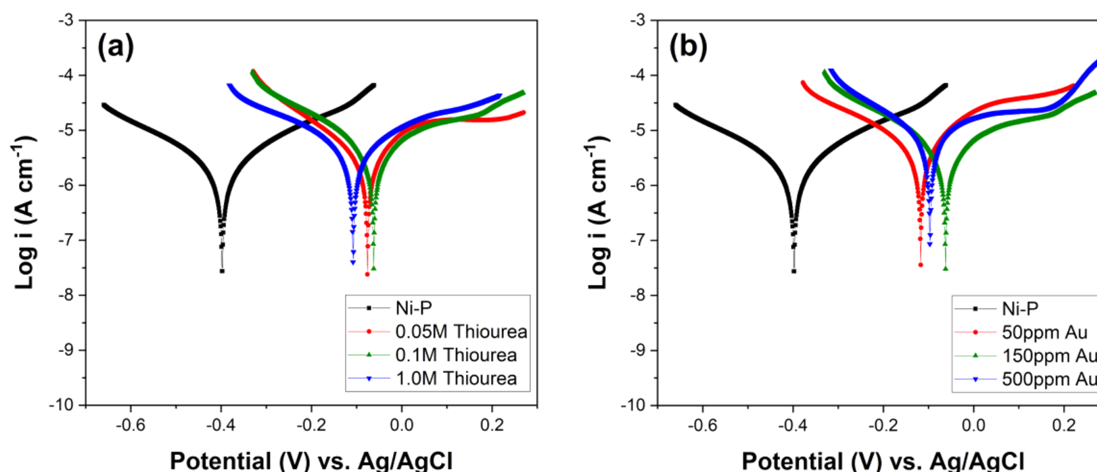

Figure 3. Tafel curves of EN and IG coatings: (a) with variations in thiourea concentration and (b) with variations in Au concentration.

corrosion potentials than from 1.0 mol·L^{-1} thiourea solution (Figure 3a), implying better performance in corrosion resistance with a lower thiourea concentration range. This was in line with the result shown in Figure 2i; nonuniform and coarse particles of gold on the nickel surface exhibited a large area of voids, which would result in less efficient protection from corrosion.

Although a high gold concentration enhanced the deposition rate, large and coarse particles might promote porosity of the film and consequently affected corrosion resistance with lower values of E_{corr} (Figure 3b). On the other hand, fine gold particles were deposited with a low concentration of gold (Figure 2a) and resulted in good corrosion resistance with positively shifted E_{corr}. The adhesion of the coating, however, was not strong enough, as the film was easily peeled off even by a mild physical abrasion, as shown in Figure S2.

Higher temperature seemed to lead to a faster and finer deposition of gold. On the basis of all factors, therefore, an optimal deposition condition for coating was determined to be 0.1 thiourea and 0.1 mol·L^{-1} sulfuric acid with 150 ppm gold at 80 °C (Figure 2e).

3.3. Performance of Au Coatings and Comparison between Coatings Using Thiourea and Thiosulfate–Sulfite Bath. The performance of gold films from gold–thiourea complex ($Au[CS(NH_2)_2]_2^+$) was compared with the coating from gold–thiosulfate–sulfite complex ($Au(S_2O_3)(SO_3)_2^{5-}$). The thickness of IG coatings of each bath was adjusted to 0.08 μm.

The appearances and surface morphologies from SEM analyses of the coatings are shown in Figure 4. Both gold coatings presented similar characteristics at least in appearance with the fine gold particles. In addition, in both cases, black dots were observed on the film surfaces, which are generally known as black pad, black spot, or pinhole pad defects. The hyperactive corrosion of Ni–P appeared to cause such defects, which have a negative impact on the soldering process.[35,36] These defects, however, can be minimized by controlling the thickness of the IG film and phosphor content in the EN layer, whose optimal condition has to be obtained through a separate, in-depth study. Figure 5 shows XRD patterns of EN and both IG coatings covering copper. The crystallinity of copper and gold was confirmed, while that of Ni–P was not, indicating an amorphous state of Ni–P deposition.[37] The plane of Au (111) was dominant in both IG coatings.

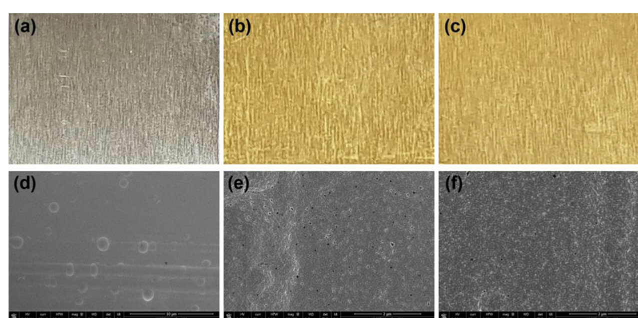

Figure 4. Photographic images of (a) EN coating, (b) IG coating from $Au(S_2O_3)(SO_3)_2^{5-}$, and (c) IG coating from $Au[CS(NH_2)_2]_2^+$. SEM morphologies of (d) EN coating, (e) IG coating from $Au(S_2O_3)(SO_3)_2^{5-}$, and (f) IG coating from $Au[CS(NH_2)_2]_2^+$.

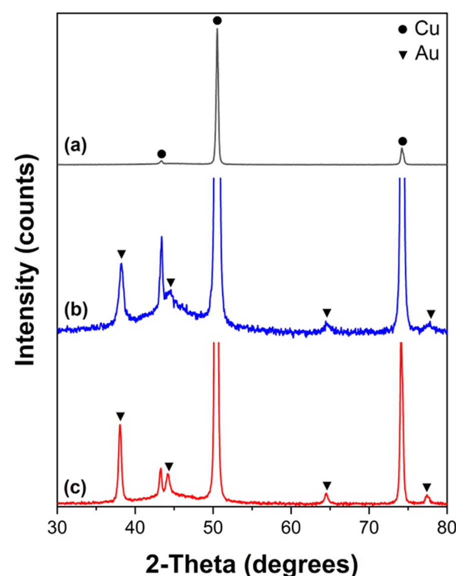

Figure 5. XRD patterns of (a) EN coating, (b) IG coating from $Au(S_2O_3)(SO_3)_2^{5-}$, and (c) IG coating from $Au[CS(NH_2)_2]_2^+$.

Figure 6a depicts potentiodynamic polarization curves of EN and IG coatings to evaluate corrosion resistance, a quality indicator of a gold layer. Corrosion potentials (E_{corr}) and corrosion currents (I_{corr}) of each coating were obtained from Tafel curves performed in 3.5 wt % NaCl solution at room

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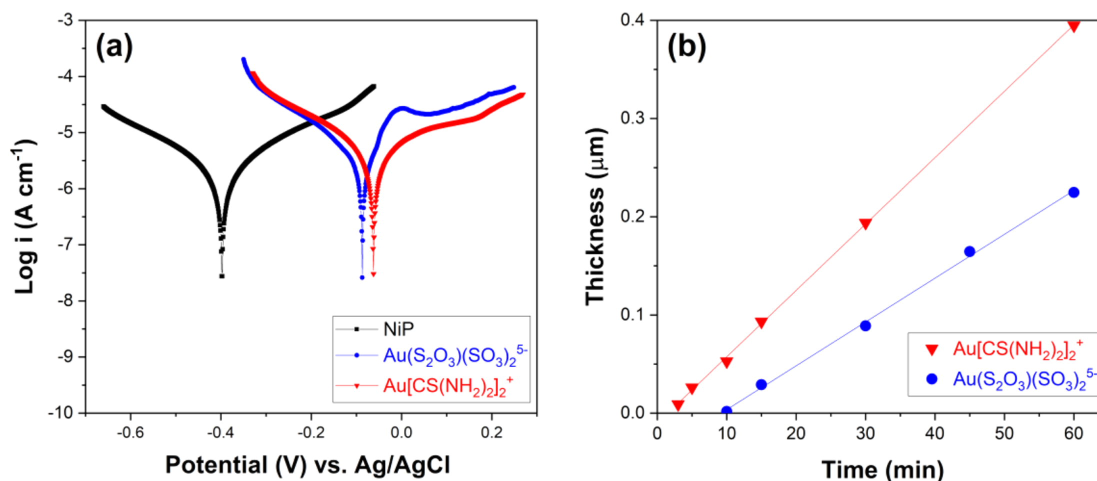


Figure 6. (a) Tafel curves of EN coating, IG coating from $Au(S_2O_3)(SO_3)_2^{5-}$, and IG coating from $Au[CS(NH_2)_2]_2^{+}$. (b) Deposition rate of gold deposition using $Au(S_2O_3)(SO_3)_2^{5-}$ and $Au[CS(NH_2)_2]_2^{+}$.

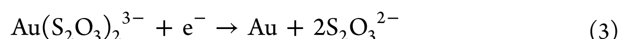
temperature, and they are summarized in Table 1. Both IG coatings from both the thiosulfate-sulfite and thiourea baths

Table 1. Corrosion Properties of EN and IG Coating

sample	E_{corr} (mV)	I_{corr} (μA)
Ni−P	−397	1.983
$Au(S_2O_3)(SO_3)_2^{5-}$	−87	3.788
$Au[CS(NH_2)_2]_2^{+}$	−62	3.832

had improved corrosion resistance, showing positively shifted corrosion potentials compared with the EN coating that had −397 mV corrosion potential. The corrosion potentials of gold films from the thiosulfate-sulfite and thiourea baths were −87 and −62 mV, respectively, and the trend was even in agreement with the results of corrosion currents, which represent the kinetic aspect of corrosion. These values strongly supported that the gold coating using the thiourea bath performed well and was comparable with that using the thiosulfate−sulfite solution in terms of corrosion resistance.

The deposition rate of IG using both baths was compared when the concentration of gold was maintained at 150 ppm for both IG processes at 80 °C (Figure 6b). Thiourea was found to be better with regard to deposition rate than thiosulfate−sulfite. This was attributable to the fact that deposition kinetics is linked with the potential difference of redox reactions, that is, nickel oxidation and gold reduction, in galvanic displacement.[38,39] The redox potential of gold−thiosulfate complex is 0.15 V vs SHE, shown in eq 3,[40,41] while that of gold−thiourea complex is in the range of 0.35 to 0.4 V vs SHE (eq 4).[42,43]



$$Au(S_2O_3)_2^{3-} + e^- \rightarrow Au + 2S_2O_3^{2-} \quad (3)$$

$$Au[CS(NH_2)_2]_2^{+} + e^- \rightarrow Au + 2CS(NH_2)_2 \quad (4)$$

Considering that the oxidation potential of nickel is −0.26 V vs SHE, the coupled reaction with the gold−thiourea complex, which had a substantially higher redox potential difference (>0.61 V versus 0.41 V), is supposed to take place in heightened deposition kinetics.

4. CONCLUSION

In this work, a novel, safe path of immersion gold onto electroless nickel substrate via a Au(I)−thiourea complex was developed for the electroless nickel immersion gold (ENIG) process. Gold deposition was accelerated by an increase in gold concentration and temperature, but this was not the case with thiourea concentration and pH: the transfer coefficient of gold concentration was 0.679, and the activation energy was 36.69 kJ·mol^{-1}. Gold particle sizes appeared to impact on coating performance in terms of corrosion resistance. Very fine or coarse particles, which inevitably had poor adherence and high porosity, ended up lowering the corrosion resistance of the resulting gold film. Too much thiourea also caused aggregated, bulky, irregular particle formation, resulting in comparatively large exposure of nickel surfaces, and with that, poor resistance to corrosion. The quality of gold films formed with the thiourea bath under optimal conditions was found to be similar or marginally better than that of another safe bath candidate, the thiosulfate−sulfite bath, in terms of morphology, corrosion resistance, and deposition rate. It appears that the gold−thiourea bath has great potential to be applied as a safe and workable bath option for the commercial ENIG process. Given that it is well compatible with new and powerful gold adsorbents such as COP-180, the thiourea-based approach can make it possible to realize a closed-loop, complete process for gold between manufacturing and waste.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.0c00493.

Linear regression of (a) logarithm of deposition rate and gold concentration (b) logarithm of deposition rate and $1/T$; photographic image of IG coating with the deposition condition of 50 ppm Au after a mild physical attack (PDF)

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Notes

The authors declare no competing financial interest.

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