Electrodeposition of Silver in Cyanide-Free Solution Containing Pyrimidine Derivative as a Complexing Agent

Atiqah Binti Jasni[1,2,z] and Sachio Yoshihara[1]

[1]*Department of Innovation Systems Engineering, Graduate School of Engineering, Utsunomiya University, 7-1-2 Yoto, Utsunomiya, Tochigi 321-8585, Japan*
[2]*R&D Department, Meltex Inc., 2-3-1 Yoshino-cho, Kita-ku, Saitama, Saitama 331-0811, Japan*

Pyrimidine derivatives, for example, 2,4-pyrimidinedione (uracil), 1-methyluracil and 5-methyluracil (thymine) can bind with metal ions in alkaline solution. 5-methyluracil (thymine) as complexing agent in electroplating solution has not been investigated due to low solubility in water. The aims of this study were to determine the potential of 5-methyluracil (thymine) as complexing agent for cyanide-free silver electroplating solution. The influence of complexing agent and polyethyleneimine on the silver electrodeposition reaction were studied. Several methods which are electrochemical quartz crystal microbalance (EQCM) and electrochemical impedance spectroscopy (EIS) have been used to study the electrochemical behavior of cyanide-free silver electroplating solution. The surface morphology and brightness of silver deposits obtained from each cyanide-free silver electroplating solution were evaluated. A semi-bright deposit was obtained from thymine and uracil-complexing silver solution while matte deposit from 5,5-dimethylhydantoin-complexing silver solution. A bright silver deposit could be obtained in the presence of polyethyleneimine. The reduction current value decreases as the amount of polyethyleneimine added increases due to inhibition effect on the silver electrodeposition reaction. The results of electrochemical quartz crystal microbalance measurement showed that the addition of polyethyleneimine in thymine-complexing silver solution does not significantly affect the resonance frequency change.

Silver electroplated films has been widely used in the engineering field for electronic industrial parts such as reflectors for LED lighting and semiconductor industrial parts such as lead frames because of its excellent in electrical and thermal conductivity and excellent in reflectivity. The silver electroplating solution which is conventionally used is an alkaline cyanide solution which mainly consist of silver cyanide and potassium cyanide.[1] This silver electroplating solution composition has been widely used since its low cost and high-quality of deposit can be produced. However, due to cyanide compounds toxicity, it is important to ensure a safe working environment, strict chemical management, and disposal.

In recent years, many organizations, including companies, research organizations and universities, have been developing cyanide-free silver electroplating solutions in accordance with increasing environmental awareness and reducing environmental impact due to Sustainable Development Goals (SDGs). Prior research has been done to develop cyanide-free silver electroplating solution to replace alkaline cyanide solution. As a result, the most effective formulations were obtained with thiosulfate,[2–4] succinimide,[5–7] hydantoin derivatives[8–12] and uracil[13,14] as complexing agents. Asakawa et al.[8] reported that a stable cyanide-free bath solution when hydantoin compound was present in the solution at a molar ratio three times that of silver. In addition, Liu et al.[10] reported that a smooth and compact silver deposit with mirror brightness and smaller grains was obtained when nicotinic acid and 5,5-dimethylhydantoin (DMH) were used as complexing agent for cyanide-free silver electroplating solution. Pizzetti et al.[12] achieved bright silver deposit when concentration of polyethyleneimine of at least 400 ppm was present in 5,5-dimethylhydantoin based silver electroplating solution however there were no report regarding microstructure of the deposit. Furthermore, Xie et al.[13] and J. Christophe et al.[14] reported that uracil as complexing agent in cyanide-free silver plating could produce a good silver deposit on copper substrate without a separate silver strike process. Moreover, J. Christophe et al.[14] achieved good adherent and ductile silver deposits on nickel coated copper substrate by using choline chloride (ChCl) based deep eutectic solvents (DES) silver strike solution.

In this research, the influence of complexing agent and addition of polyethyleneimine as additive on silver deposition reaction in the cyanide-free silver electroplating solution was studied. Here,

pyrimidine derivatives which is 5-methyluracil (thymine) with the formula $C(O)NHC(O)NHCHCCH_3$ was studied as complexing agent for cyanide-free silver electroplating solution since thymine like other pyrimidine derivatives, for example, 2,4-pyrimidinedione (uracil) and 1-methyluracil can bind with metal ions in alkaline solution.[15] However, the potential of thymine as a complexing agent in cyanide-free silver electroplating solution has not been investigated due to low solubility in water. As a comparison, 5,5-dimethylhydantoin (DMH) which is a heterocyclic organic compound with the formula $NHC(O)NHC(O)CCH_3CH_3$ and uracil the formula $C(O)NHC(O)NHCHCH$ were chosen as comparison to study the influence of complexing agent in the cyanide-free silver electroplating solution. In addition, polyethyleneimine was used as additive since it can improve the brightness of the electroplated metal in gold or silver alloy plating solutions.[16–18]

In this study, two electrochemical measurement approaches which are electrochemical quartz crystal microbalance (EQCM), and electrochemical impedance spectroscopy (EIS) were used to investigate the influence of complexing agent and polyethyleneimine on electrochemical behavior of silver in silver electroplating solution. EQCM measurement technique is utilized in various scientific fields and applications, since it is a universal in situ measurement method for monitoring deposited mass changes, metal evaporations and dissolution or corrosion and as sensors for chemical and biosensing for both in the vapor and liquid phase.[19,20] By using an EQCM electrode as a working electrodes, simultaneously measuring frequency changes with electrochemical measurement methods such as cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry (CA) and chronopotentiometry (CP), permits simultaneous tracking of two parameters such as current and weight change or electrode potential change and weight change which occurs at the electrode surface. In addition, over the years EIS has been used as one of electrochemical measurement to study interfacial reaction mechanism with applications in corrosion, biosensors, battery development, fuel cell development, sensor development and physical electrochemistry.[21–23] Differs from other electrochemical measurement techniques, EIS is a technique where the input signal is an alternating current (AC) voltage or current signal applied on electrode, and the output signal is current or voltage. This permits spectra analysis by varying the frequency of AC signal. Unlike direct current (DC) measurement, the relationship between voltage and current is expressed as impedance in EIS. While it is challenging to

[z]E-mail: j.atiqah@meltex.com
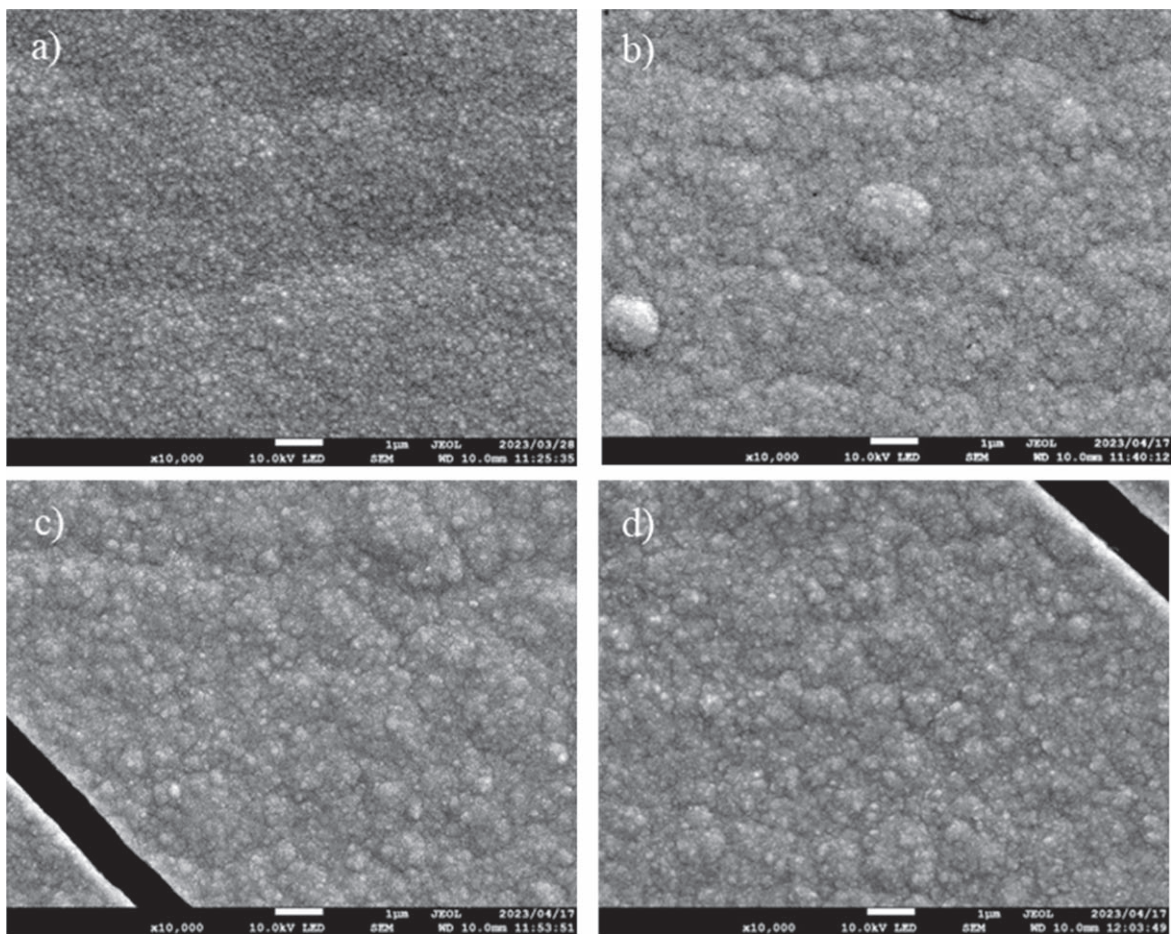
Figure 1. SEM images of the top views of silver deposits obtained from (a) bath thymine, (b) bath thymine + 100 ppm PEI-1800, (c) bath thymine + 500 ppm PEI-1800 and (d) bath thymine + 1000 ppm PEI-1800, respectively.

divide charge transfer and diffusion reaction in DC measurement, EIS permits spectra analysis by separating fast process in high frequency range, which is charge transfer and slow process in low frequency range, which is diffusion.[23] These two methods are an effective approach to study electrochemical behavior of plating solution during electrodeposition process. Furthermore, unexplored research related to the complex formation of thymine and silver ion and influence of polyethyleneimine on surface morphology of silver deposit were studied.

Table I. Bath composition for cyanide-free silver electroplating solution.

Bath type	Composition	Concentration
Thymine	Silver nitrate	$0.15 \ mol \ dm^{-3}$
	Thymine	$0.80 \ mol \ dm^{-3}$
	Potassium hydroxide	$1.00 \ mol \ dm^{-3}$
	Polyethyleneimine (M.W. 1,800)	0–1000 ppm
DMH	Silver nitrate	$0.15 \ mol \ dm^{-3}$
	5,5-Dimethylhydantoin	$0.80 \ mol \ dm^{-3}$
	Potassium hydroxide	$1.00 \ mol \ dm^{-3}$
	Polyethyleneimine (M.W. 1,800)	0–1000 ppm
Uracil	Silver nitrate	$0.15 \ mol \ dm^{-3}$
	Uracil	$0.80 \ mol \ dm^{-3}$
	Potassium hydroxide	$1.00 \ mol \ dm^{-3}$
	Polyethyleneimine (M.W. 1,800)	0–1000 ppm

Experimental

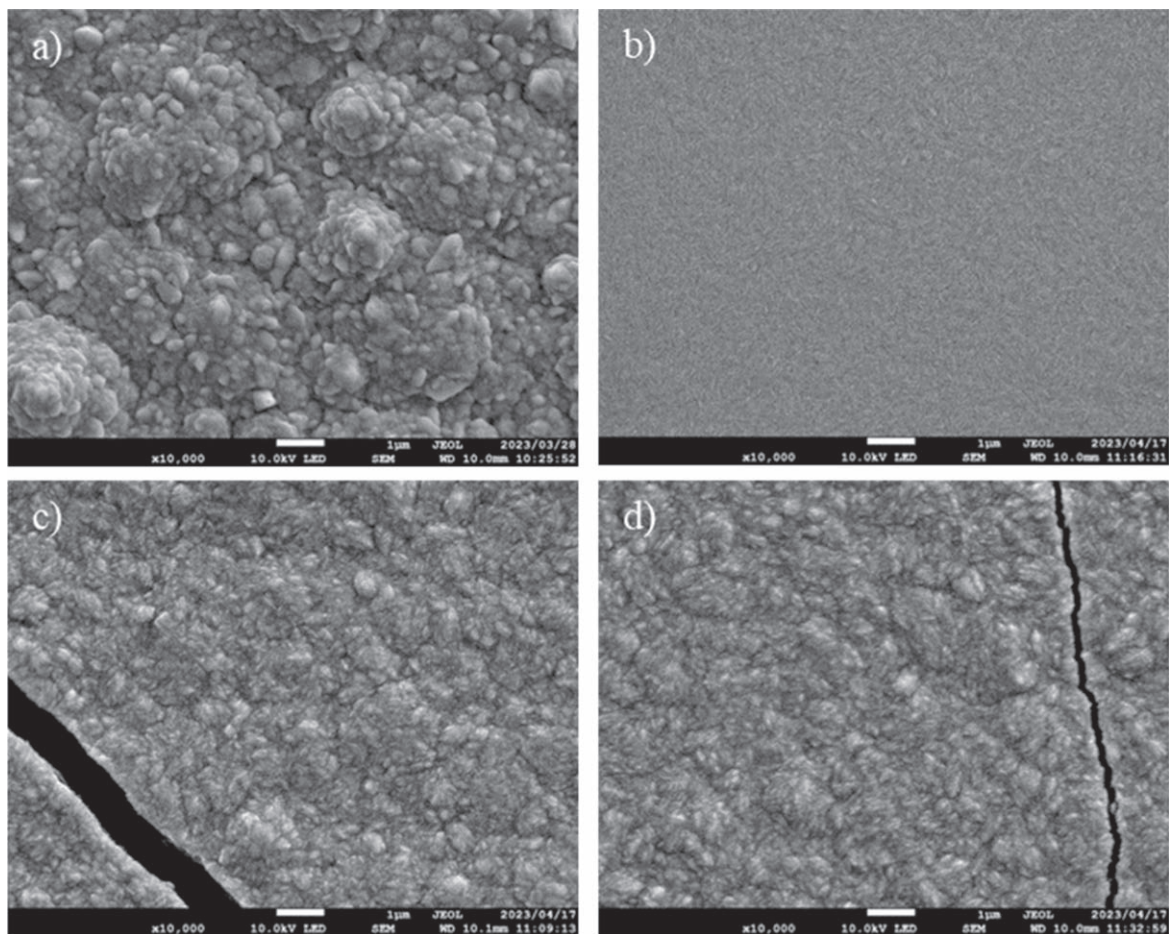***Chemicals.***—Silver nitrate, $AgNO_3$ (99.8%) and potassium cyanide, KCN (95.0%) were purchased from FUJIFILM Wako Pure Chemical Corporation. 5,5-dimethylhydantoin (>98.0%) were acquired from X.T.Y ENVIRON-TECH Co., Ltd., uracil (>97.0%) and sulphuric acid (>95.0%) were from Kanto Chemical Co., Inc., thymine (>98.0%) were from Tokyo Chemical Industry Co., Ltd., potassium hydroxide, KOH (95.5%) were from Nippon Soda Co., Ltd., nitric acid, HNO_3 (67.5%) from Saitama Yakuhin Co., Ltd., silver cyanide (>99.0%) from Tanaka Precious Metal Corporation and Melcleaner 1106 from Meltex Inc. The average molecular weight of the polyethyleneimine (PEI) (branched polymer, FUJIFILM Wako Pure Chemical Corporation) used in the experiments was 1,800 and was denoted as PEI-1800. All chemicals were used as received.

Silver electroplating solution.—All solutions were prepared with deionized water. Silver electroplating solution was obtained by dissolving complexing agent in potassium hydroxide solution before adding silver nitrate. After complete dissolution, the bath pH was adjusted to pH 13 by addition of potassium hydroxide solution. The bath composition and operating conditions for silver electroplating solution was shown in Table I.

Electrodeposition of silver and characterization of silver deposit.—Silver plating was performed using magnetic stirrer at agitation rate 500 rpm at 5 mA cm^{-2} for 20 min at 25 °C. Copper substrates were used for samples and silver plates (99.99%) were used as anode. Prior to silver plating experiment, pretreatment using
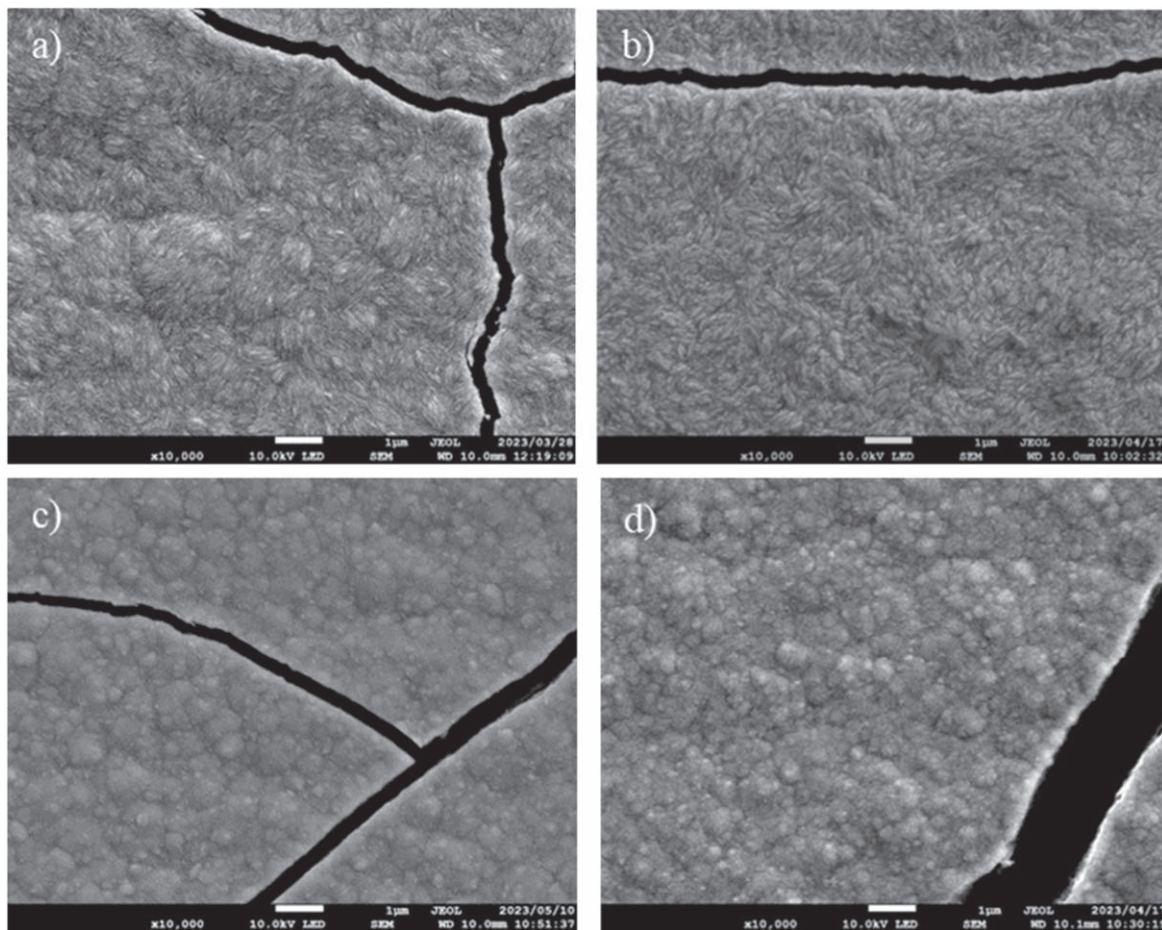
Figure 2. SEM images of the top views of silver deposits obtained from (a) bath DMH, (b) bath DMH + 100 ppm PEI-1800, (c) bath DMH + 500 ppm PEI-1800 and (d) bath DMH + 1000 ppm PEI-1800, respectively.

Table II. Bath composition and operating conditions for pretreatment process and silver strike.

Process	Chemical and bath composition		Treatment condition	
Electrolytic alkaline cleaner	Melcleaner 1106	45 g dm^{-3}	Current density	10 mA cm^{-2}
			Immersion time	120 s
			Temperature	60 °C
Acid pickling	Sulphuric acid	100 g dm^{-3}	Immersion time	60 s
			Temperature	25 °C
Silver strike	Silver cyanide	2.65 g dm^{-3}	Current density	10 mA cm^{-2}
	Potassium cyanide	95 g dm^{-3}	Plating time	10 s
			Temperature	25 °C
			Anode	Stainless steel (SUS304)

alkaline electrolytic cleaner and acid pickling was performed before silver strike (0.1 μm) was applied on a copper substrate in advance. The bath composition and operating conditions for pretreatment process and silver strike was shown in Table II. The brightness of silver deposit was measured using densitometer ND-11 (Nippon Denshoku Industries Co., Ltd.). While morphology of silver deposit was examined by scanning electron microscopy (SEM) (JEOL Ltd. JSM-7800F) and focused ion beam system (FIB) (JEOL Ltd. JIB-4000). For the cathode current efficiency, a copper plate was cut into 25 mm × 25 mm pieces was used. Electrolysis of 117 coulombs was performed at 25 °C and the efficiency was determined from the difference in weight before and after plating.

Electrochemical measurements.—Electrochemical measurements were conducted using a three electrodes system connected to potentiostat (BioLogic Science Instruments SP-150). A silver wire (99.99%) was used as counter electrode and saturated calomel electrode (SCE) as reference electrode. A platinum disk electrode with a diameter 3 mm was used as working electrode. Prior to each experiment, the working electrode was polished using 1.0 μm polishing diamond on a wetted diamond polishing pad. Then the working electrode was polished using 0.5 μm polishing alumina on alumina polishing pad and rinsed with deionized water to remove any trace of alumina and finally dried by air drying. No nitrogen bubbling was applied, and bath temperature was maintained at 25 °C

Figure 3. SEM images of the top views of silver deposits obtained from (a) bath uracil, (b) bath uracil + 100 ppm PEI-1800, (c) bath uracil + 500 ppm PEI-1800 and (d) bath uracil + 1000 ppm PEI-1800, respectively.

during electrochemical measurement. The rotation of working electrode was controlled at 500 rpm by using RRDE-3A rotating ring disk electrode rotator (ALS Co., Ltd.). Linear sweep voltammogram was recorded between 0 and −2.0 V at a sweep rate of 10 mV s^{-1}. In addition, electrochemical impedance spectroscopy (EIS) was recorded at frequency range 100 kHz to 20 mHz with amplitude of 5 mV at −0.75 to −1.03 V vs SCE.

Electrochemical quartz crystal microbalance (EQCM) QCM922A (Seiko EG&G Co., Ltd.) connected to potentiostat (BioLogic Science Instruments SP-150) was used to evaluate the electrochemical behavior of silver complex in silver electroplating solution. The platinum sputtered on both sides of the crystal was a central circle of 5 mm diameter. Prior to each experiment, the platinum sputtered crystal was clean with 10 vol% nitric acid to dissolve and remove impurity metals from electrode surface. The maximum resonance frequency change was set to ±500 kHz and quartz crystal microbalance response was recorded between 0 and −2.0 V at a sweep rate of 10 mV s^{-1}. A silver wire (99.99%) was used as counter electrode and saturated calomel electrode (SCE) as reference electrode.

Results and Discussion

Electrodeposition of silver on copper.—The SEM images in Figs. 1, 2 and 3 show the top views of silver deposits obtained from each silver electroplating solutions with and without the addition of PEI-1800. A silver deposit with a smooth and homogenous layer of microstructure was obtained from thymine-complexing silver solution (Fig. 1a). In contrast, the microstructure of the silver deposit was fine grains with small domes when 100 ppm of PEI-1800 was

added to thymine-complexing solution (Fig. 1b). However, signs of cracks were observed on the silver deposit when the concentration of PEI-1800 increases, which might be attributed by adsorption of polyethyleneimine on silver film during plating reaction (Figs. 1c and 1d). It can be suggested that inclusion of polyethyleneimine during plating reaction increases the internal stress which resulted in cracks on the silver deposit.

On the contrary, a silver deposit with microstructure of small-sized polygonal crystal structure was obtained from DMH-complexing silver solution (Fig. 2a). In contrast, a silver deposit with a smooth fine grain was obtained with the addition of PEI-1800 into bath DMH (Fig. 2b). Similarly, thymine-complexing silver solution, signs of cracks were found on the silver deposit when the concentration of PEI-1800 increases (Figs. 2c and 2d).

For uracil-complexing silver solution, a silver deposit with fine sized crystal structure was obtained even without the addition of PEI-1800 (Fig. 3a). However, cracks were observed on the silver deposit since the thickness was greater than 5 μm. In general, the film thickness is proportional to internal stress in the film. So, it can be suggested that as the plating film thickness increases, the tensile stress increases which attributed cracking in electrodeposited silver since there are no signs of cracks when then thickness was lesser than 5 μm. A silver deposit with fine sized crystal structure was obtained with the addition of PEI-1800 into bath uracil and the silver size become finest when the concentration was 100 ppm (Fig. 3b). However, the microstructure of the silver deposit was spherical shape when the concentration of PEI-1800 increases (Figs. 3c and 3d).

In addition, Figs. 4, 5 and 6 show cross-sections of silver deposits obtained from each silver electroplating solutions with and without
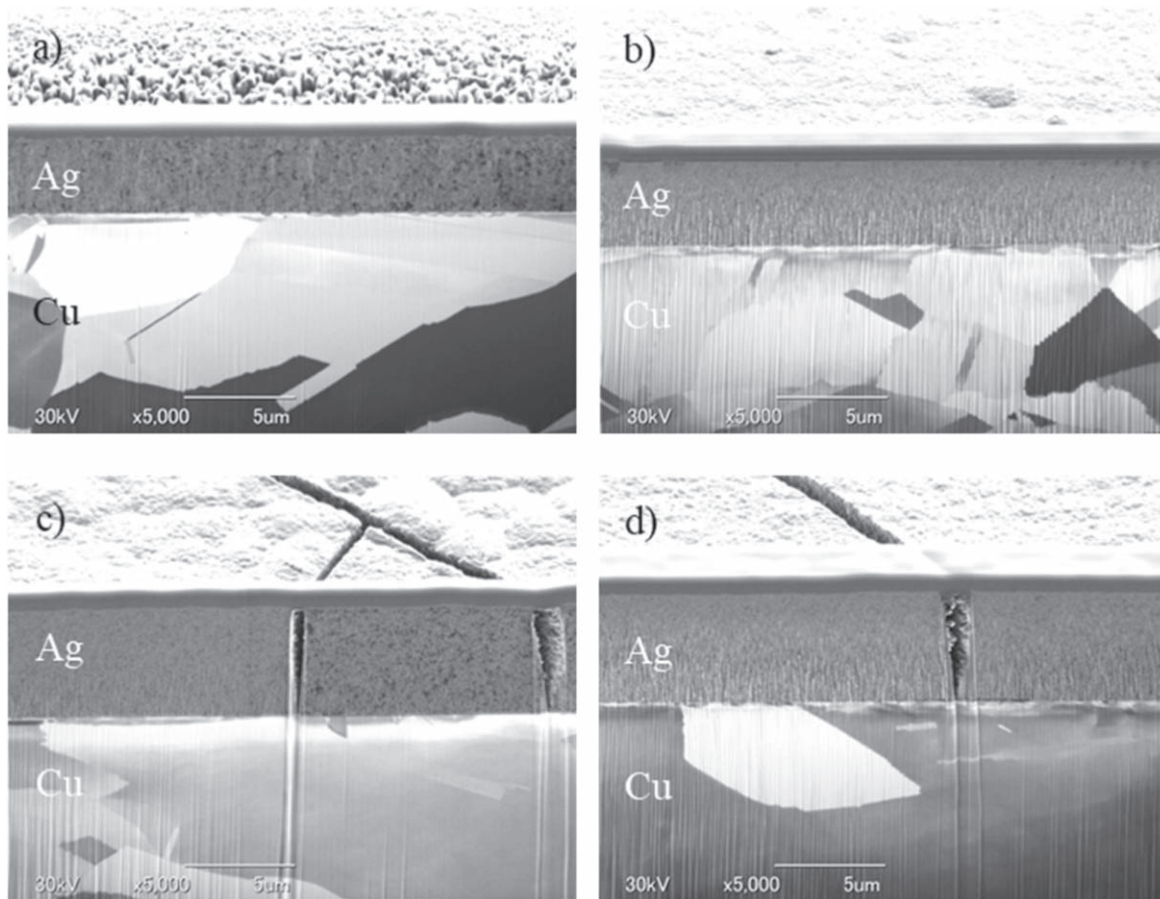
Figure 4. Cross-section images of silver deposits obtained from (a) bath thymine, (b) bath thymine + 100 ppm PEI-1800, (c) bath thymine + 500 ppm PEI-1800 and (d) bath thymine + 1000 ppm PEI-1800, respectively.

the addition of PEI-1800. The cross-sections of silver deposits obtained from thymine-complexing silver solution shows that the crystal size was slightly finer than that of silver deposits obtained from uracil-complexing silver solution. In addition, the crystal size of the silver deposit of DMH-complexing silver solution (Fig. 5a) was largest than that of the thymine and uracil-complexing silver solutions (Figs. 4a and 6a). The cross-sections of silver deposits with the addition of PEI-1800 (Figs. 4b–4d, 5b–5d and 6b–6d) show that the crystal sizes were finer than that from the base bath (Figs. 4a, 5a and 6a).

Influence of polyethyleneimine on surface brightness.—The brightness of silver-plated film is generally represented in GAM units. The measured values of GAM units for example measured by Densitometer Model 144 (Graphic Arts Manufacturing) or Micro Colorimeter VSR400 or Densitometer ND-11 (Nippon Denshoku Industries Co., Ltd.) for matte silver-plated film is between 0 to 0.5, while semi-bright silver-plated film is between 0.4 to 1.0 and bright silver-plated film is 0.8 and above. From Fig. 7, the gloss concentration of silver-plated film from thymine-complexing silver solution without PEI-1800 was approximately 1.0 which refer that bright film was deposited on the substrate. In addition, a change in gloss concentration was observed when PEI-1800 was added especially when 100 ppm of PEI-1800 was added to thymine-complexing silver solution. On the contrary, the gloss concentration of silver-plated film from cyanide-free silver electroplating solution containing DMH was 0.0 which refer that matte film was deposited on the substrate. Moreover, the gloss concentration was between 0.8 to 2.0 when PEI-1800 was added to DMH-complexing silver solution which refer that bright film was deposited on the substrate and the highest gloss concentration was obtained when 100 ppm of

PEI-1800 was added to bath DMH. Pizzetti et al.[12] also obtained similar results when polyethyleneimine with molecular weight 600 was added to DMH-complexing silver solution. On top of that, the gloss concentration of silver-plated film from cyanide-free silver electroplating solution containing uracil without PEI-1800 was approximately 1.0 which refer that bright film was deposited on the substrate. However, from Fig. 7, there is hardly any significant change was observed in gloss concentration when PEI-1800 was added to uracil-complexing silver solution.

Cathode current efficiency.—When thymine was used as complexing agent in cyanide-free silver electroplating solution, the cathode current efficiency value was 76.8% while DMH was 76.5% and uracil was 79.0%. It can be assumed that hydrogen is generated as a side reaction during plating process which resulted in decreased in cathode current efficiency to less than 100%. In addition, there are only slightly changed in cathode current efficiency when PEI-1800 was added to thymine-complexing silver solution. On the contrary, an increase of 5.7% in cathode current efficiency was observed when PEI-1800 was added to DMH-complexing silver solution. On top of that, an increase of 8.5% in cathode current efficiency was observed when PEI-1800 was added to uracil-complexing silver electroplating solution. It can be suggested that polyethyleneimine promote the reduction of silver by adsorption at the silver deposit and solution interface. Thus, less hydrogen would be generated during plating with addition of polyethyleneimine in the cyanide-free silver electroplating solution.

Influence of complexing agent on electrochemical behavior of silver complex in silver electroplating solution.—Linear sweep voltammetry measurements were conducted to investigate the
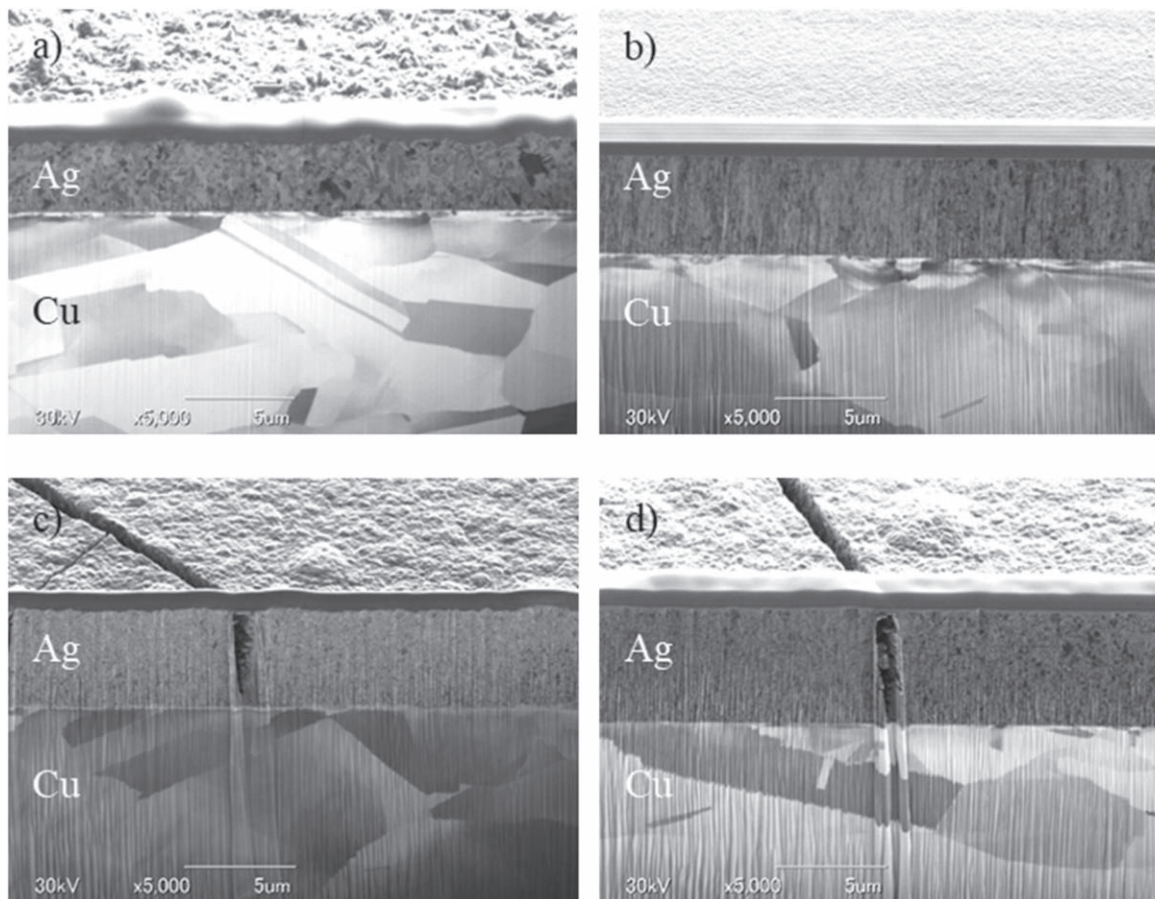
Figure 5. Cross-section images of silver deposits obtained from (a) bath DMH, (b) bath DMH + 100 ppm PEI-1800, (c) bath DMH + 500 ppm PEI-1800 and (d) bath DMH + 1000 ppm PEI-1800, respectively.

influences of complexing agent on electrochemical behavior of silver complex in the silver electroplating solution. In general, linear sweep voltammetry method is used to study the deposition potential of electroplating and current efficiency and hydrogen evolution in electroplating. While EQCM measurements allows in situ monitoring of the resonance frequency change on the surface of the working electrode during electrodeposition reaction. In this study, deposition potential was the smallest potential at which resonance frequency changed was observed when current was applied, indicating that deposition reaction is occurring. Figure 8 displays the linear sweep voltammograms obtained on a platinum electrode in each silver electroplating solution. When thymine was used as complexing agent, the silver deposition is approximately at -0.87 V, and the current increases from -0.87 V, and even more on the negative side, below -1.79 V (yellow in Fig. 8 (top)). An inflection points approximately at -1.16 V was recorded, which correspond to the potential at which metal deposition and hydrogen evolution to occur in parallel (yellow line in Fig. 8 (top)). Even though, the current increased on the negative side, below than -1.79 V, there was no resonance frequency change was observed, suggesting that the hydrogen evolution reaction was mainly occurred (yellow line in Fig. 8 (bottom)). Furthermore, from the Δf–E curve, the resonance frequency change in the potential range of silver reduction wave ($-0.87 \sim -1.79$ V) was 112.6 kHz. The Sauerbrey equation as shown below is a linear relationship between the resonance frequency of an oscillating quartz crystal and mass changes. Here, m/A is mass change per unit area, N_q is mass sensitivity constant, ρ is density of crystal, f_0 is initial resonance frequency of crystal electrode and f is final resonance frequency of crystal electrode.

$$m/A = \{-N_q \cdot \rho \cdot (f - f_0) \times 10^6\}/f_0^2$$

From this equation, the corresponding mass change of 112.6 kHz was 0.12 mg cm^{-2}.

In addition, when DMH was used as complexing agent in silver electroplating solution, the silver deposition potential is approximately at -0.39 V, and the current increases from -0.39 V, and even more on the more negative side, below -1.26 V. An inflection point was recorded at approximately -0.88 V which correspond to the potential at which metal deposition and hydrogen evolution begin to occur in parallel (blue line in Fig. 8 (top)). Even though, the current increased on the negative side, below than -1.26 V, there was no resonance frequency change was observed, suggesting that the hydrogen evolution reaction was mainly occurred (blue line in Fig. 8 (bottom)). In addition, the resonance frequency change in the potential range of the silver reduction wave ($-0.39 \sim -1.26$ V) was 82.0 kHz, corresponding to mass change of 0.088 mg cm^{-2}.

Furthermore, when uracil was used as complexing agent, the silver deposition potential was approximately at -0.38 V, and the current increases from -0.38 V, and even more on the negative side, below -1.52 V. Moreover, there is an inflection point at -1.12 V, which correspond to the potential at which metal deposition and hydrogen evolution begin to occur in parallel (grey line in Fig. 8 (top)). Even though, the current increased on the negative side, below than -1.52 V, there was no resonance frequency change was observed, suggesting that the hydrogen evolution reaction was mainly occurred and outweighs the deposition reaction (grey line in Fig. 8 (bottom)). Furthermore, from the Δf–E curve, the resonance frequency change in the potential range of silver reduction wave
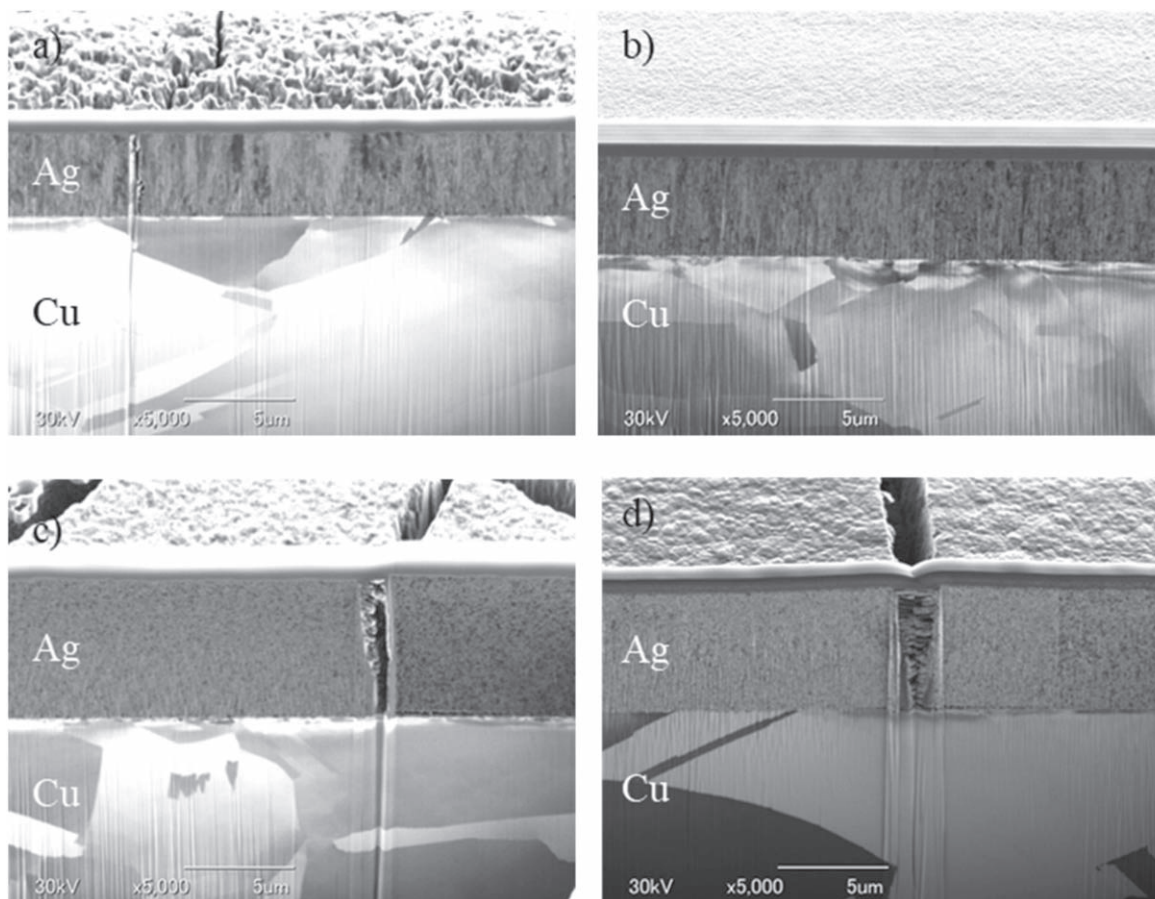
Figure 6. Cross-section images of silver deposits obtained from (a) bath uracil, (b) bath uracil + 100 ppm PEI-1800, (c) bath uracil + 500 ppm PEI-1800 and (d) bath uracil + 1000 ppm PEI-1800, respectively.
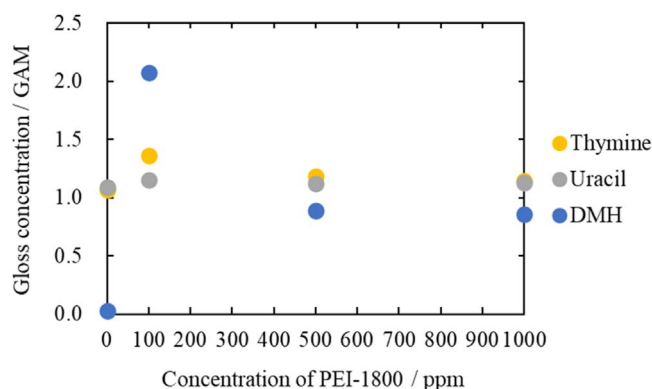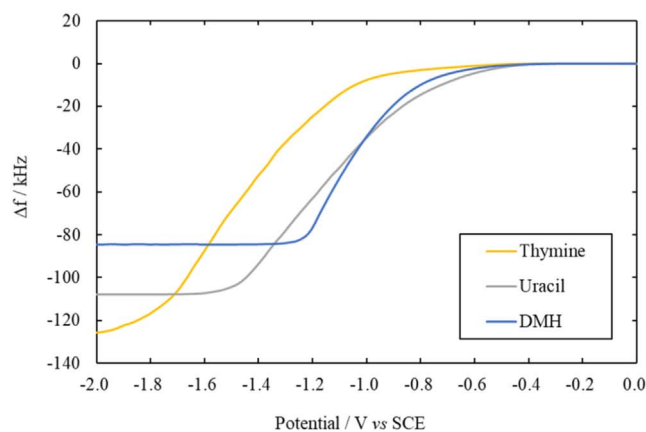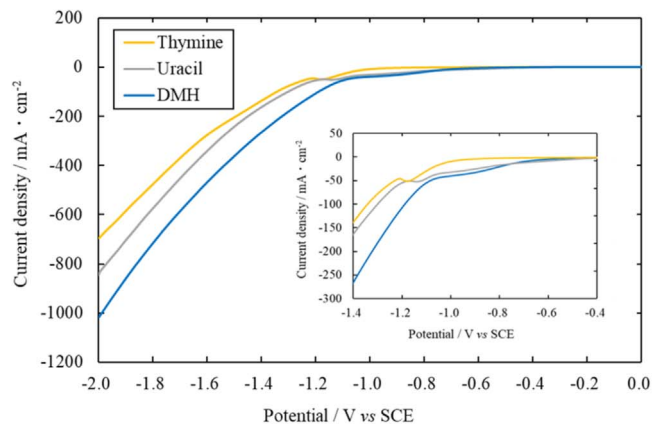

Figure 7. Influence of concentration of PEI-1800 on film brightness.

($-0.38 \sim -1.52$ V) was 105.1 kHz, corresponding to mass change of 0.11 mg cm^{-2}.

As mentioned earlier, EIS measurements were conducted to further study electrochemical behavior of silver complex in the silver electroplating solution. EIS measurements were carried out at -1.03 V (thymine), -0.75 V (DMH) and -0.85 V (uracil) at a Pt electrode with 3 mm diameter. These voltages are equivalent to 10 mA cm^{-2} from the linear sweep voltammograms as shown in Fig. 8. The Nyquist plots are shown in Fig. 9 and equivalent circuits depicted by the Nyquist plot are shown in Fig. 10. Table III shows the values of all elements in the equivalent circuit corresponding to Fig. 9. Here, R$_{sol}$ is solution resistance of silver plating solution and R$_{ct}$ is charge transfer resistance during silver deposition, which a

smaller value of charge transfer resistance R$_{ct}$ means that charge transfer reactions are more likely to occur, while a larger value means that charge transfer reactions are less likely to occur since the charge transfer reaction is proportional to current, the charge transfer resistance R$_{ct}$ is a guideline for how unlikely the reaction is to occur.[22] In addition, C$_{dl}$ is electric double-layer capacitance between electrode and silver electroplating solution. R$_2$ is second set of resistance and C$_2$ is second set of capacitances. It can be assumed that these components represent either the impedance are caused by interaction of silver ions with complexing agent layer or diffusion through the Nernst diffusion layer. From analysis of these three Nyquist plots as shown in Fig. 9, the diameter of the capacitive loop obtained from silver plating solution containing uracil was found to be significantly bigger than that from DMH and thymine especially at high frequency range. These curves displayed in Fig. 9 were approximated double capacitive loop, suggesting that the silver deposition process at 10 mA cm^{-2} were hybrid controlled by charge-transfer and ion diffusion. From these results, the curves of each silver electroplating solutions were very similar which suggest that there is hardly any significant change in electrochemical deposition mechanism occurred on the cathode due to complexing agent.

In addition, according to the fitting parameters listed in Table III, there is no significant change in values of R$_{sol}$ since each silver electroplating solution contained same concentration of complexing agent and potassium hydroxide. However, the values of R$_{ct}$ and R$_2$ showed the most change, where silver electroplating solution containing thymine showed the smallest R$_{ct}$ while silver electro-plating solution containing DMH showed the largest R$_{ct}$ value. This indicates that the cathodic discharge process of Ag$^+$ and Ag-complexes on the cathode were affected by complexing agent in the silver electroplating solution, in accordance with the results of

Figure 10. Equivalent circuits used for the analysis of electrochemical impedance spectroscopy spectra of cyanide-free silver electroplating solution.
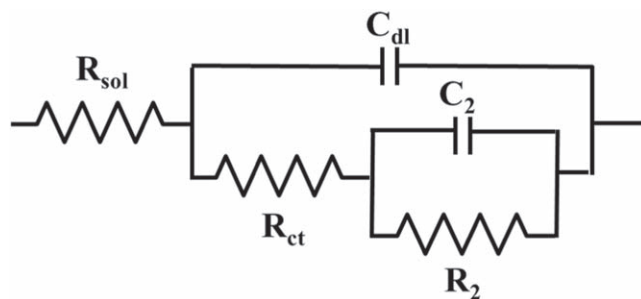

Figure 8. Linear sweep voltammograms recorded at a Pt electrode (top). Quartz crystal microbalance response recorded at a Pt electrode (bottom). Electrolyte concentration: 0.15 mol dm^{-3} silver nitrate + 0.80 mol dm^{-3} thymine (yellow line), 0.15 mol dm^{-3} silver nitrate + 0.80 mol dm^{-3} DMH (blue line) and 0.15 mol dm^{-3} silver nitrate + 0.80 mol dm^{-3} uracil (grey line). Scan rate = 10 mV s^{-1}, T = 25 °C, agitation rate = 500 rpm. Inset shows the enlarge view of voltammograms in range −0.4 ∼ −1.4 V.
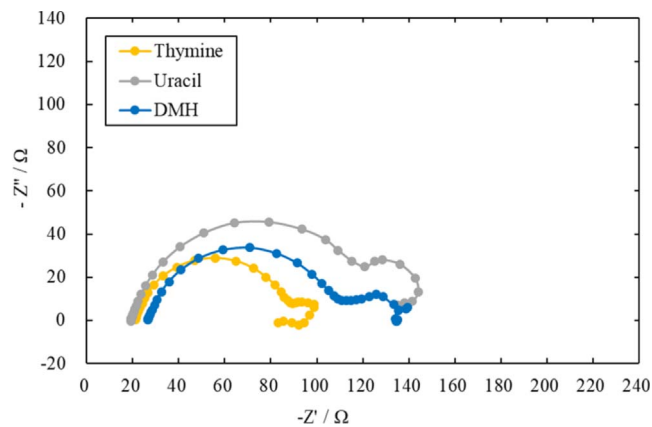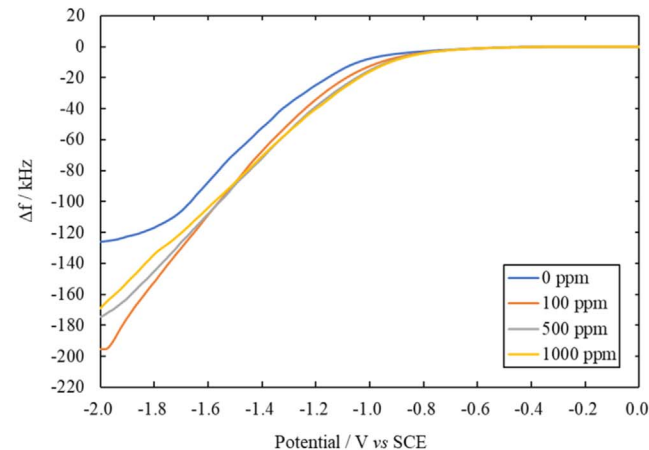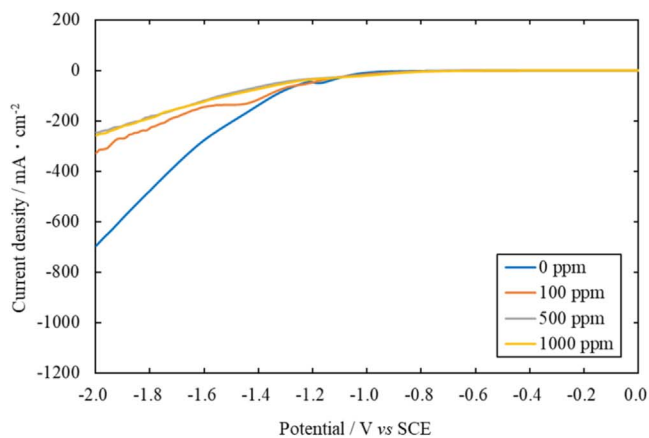

Figure 9. Nyquist plots for silver electrodeposition process with different complexing agent at −1.03 V (thymine), −0.75 V (DMH) and −0.85 V (uracil) at a Pt electrode. Electrolyte concentration: 0.15 mol dm^{-3} silver nitrate + 0.80 mol dm^{-3} thymine + 1.00 mol dm^{-3} potassium hydroxide (yellow line), 0.15 mol dm^{-3} silver nitrate + 0.80 mol dm^{-3} DMH + 1.00 mol dm^{-3} potassium hydroxide (blue line), 0.15 mol dm^{-3} silver nitrate + 0.80 mol dm^{-3} uracil + 1.00 mol dm^{-3} potassium hydroxide (grey line). T = 25 °C, agitation rate = 500 rpm.

Figure 11. Linear sweep voltammograms (top) and quartz crystal microbalance response (bottom) in thymine bath with various PEI-1800 concentrations recorded at a Pt electrode. Concentration of PEI-1800: (blue line) 0, (orange line) 100 ppm, (grey line) 500 ppm, (yellow line) 1000 ppm. Scan rate = 10 mV s^{-1}, T = 25 °C, agitation rate = 500 rpm.

Table III. The values of all elements in the equivalent circuit corresponding to Fig. 10.

Bath type	R_{sol}/Ω	R_{ct}/Ω	C_{dl}/F	R_2/Ω	C_2/F
Thymine	21.42	30.96	1.54×10^{-5}	38.19	4.59×10^{-5}
DMH	27.85	77.03	8.99×10^{-6}	29.17	3.02×10^{-3}
Uracil	19.72	73.94	2.49×10^{-4}	45.94	4.62×10^{-3}

the EQCM measurements. As mentioned earlier, the amount of deposition until hydrogen generation for thymine is 0.12 mg cm^{-2}, DMH is 0.088 mg cm^{-2} and uracil-complexing silver solution is

0.11 mg cm^{-2}. Furthermore, silver electroplating solution containing uracil showed the largest R_2 while silver electroplating solution containing DMH showed the smallest R_2 value among three silver
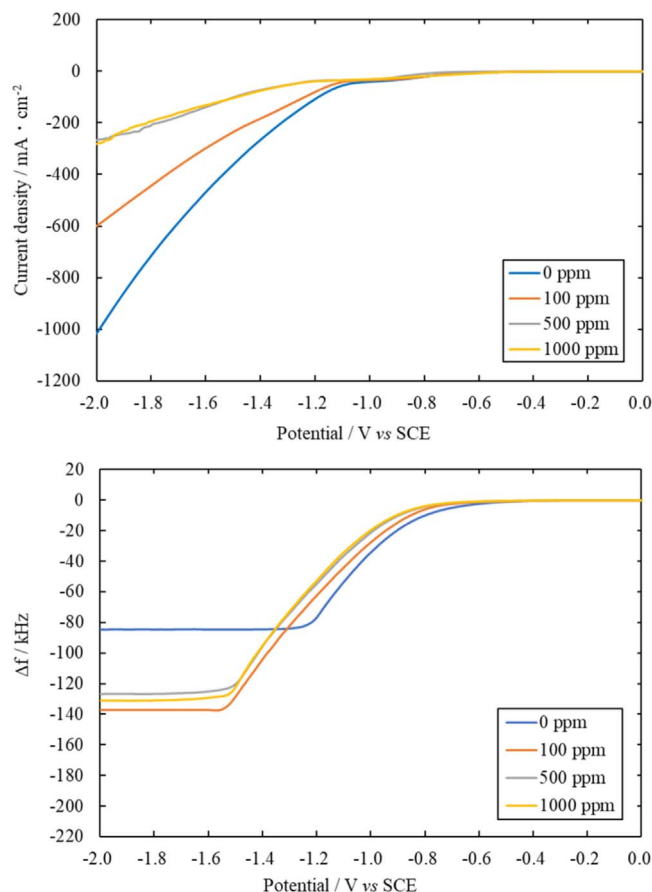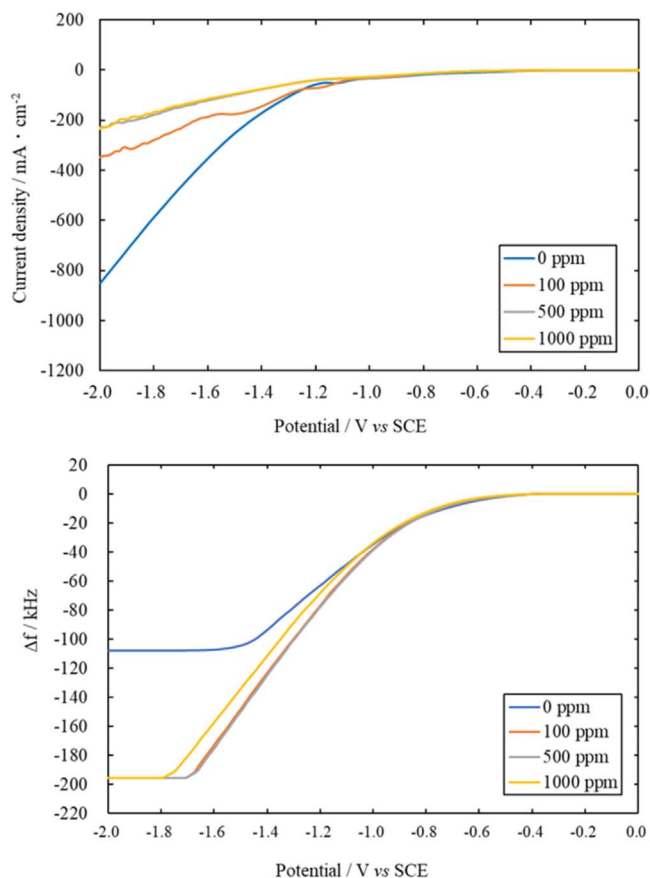
Figure 12. Linear sweep voltammograms (top) and quartz crystal microbalance response (bottom) in DMH bath with various PEI-1800 concentrations recorded at a Pt electrode. Concentration of PEI-1800: (blue line) 0, (orange line) 100 ppm, (grey line) 500 ppm, (yellow line) 1000 ppm. Scan rate = 10 mV s^{-1}, T = 25 °C, agitation rate = 500 rpm.

Figure 13. Linear sweep voltammograms (top) and quartz crystal microbalance response (bottom) in uracil bath with various PEI-1800 concentrations recorded at a Pt electrode. Concentration of PEI-1800: (blue line) 0, (orange line) 100 ppm, (grey line) 500 ppm, (yellow line) 1000 ppm. Scan rate = 10 mV s^{-1}, T = 25 °C, agitation rate = 500 rpm.

electroplating solutions. There are several possibilities that can be considered regarding the R$_2$. Firstly, it can be assumed that excess of complexing agent in the plating solution adsorbed into the plating film during plating reaction and exist as R$_2$. Secondly, it can be suggested that complexing agent or ligand which dissociates from the silver ion in the silver electroplating solution during plating reaction acted as barrier layer against the charge transfer and exists as R$_2$.

Influence of PEI-1800 on electrochemical behavior of silver complex in silver electroplating solution.—Linear sweep voltammetry measurements and electrochemical quartz crystal microbalance (EQCM) were conducted to study the influence of PEI-1800 on silver electroplating solutions. Figures 11–13, the reduction current value decreased as the amount of PEI-1800 added in cyanide-free silver electroplating solution increased which in line with the results obtained by Pizzetti et al.[12] and Xie et al.[13] In addition, the reduction current value is greatly suppressed by addition of PEI-1800 for DMH and uracil-complexing silver solution compared to thymine-complexing silver solution. In addition, Figs. 11–13 display quartz crystal microbalance response recorded on a platinum electrode in each silver electroplating solution with various PEI-1800 concentration. From Fig. 11, the addition of PEI-1800 in thymine-complexing silver electroplating solution does not significantly affect the resonance frequency change of EQCM. However, for DMH and uracil-complexing silver solution, the resonance frequency change of EQCM increased with the addition of PEI-1800 (Figs. 12 and 13). As mentioned prior, the hydrogen generation is suppressed, and the current efficiency of silver electroplating is increased with the

addition of PEI-1800. Furthermore, resonance frequency change tends to decrease as the concentration of PEI-1800 increases especially in silver electroplating solution containing DMH and uracil. So, it can be assumed that silver plating reaction was suppressed as the amount of adsorbed polyethyleneimine increases, which in line with suggestion by Xie et al.[13] that polyethyleneimine inhibits reduction reaction of silver by adsorption on the silver and solution interface.

Conclusions

In this research, electrodeposition of silver in the presence of thymine as complexing agent and polyethyleneimine with average molecular weight 1,800 as additive was studied. The authors have found that thymine could be used as potential complexing agents for silver electroplating solution based on the plating performance and electrochemical behavior. The surface deposit showed that thymine was more effective as complexing agent in silver electroplating solution to produce semi-bright silver deposit than uracil and DMH even without adding polyethyleneimine. In addition, a matte silver deposit was obtained from DMH-complexing solution while a semi-bright with signs of cracks was obtained from uracil-complexing solution. The results from electrochemical quartz crystal microbalance analysis showed that silver deposition amount up to hydrogen potential during cathodic potential sweep from thymine and uracil-complexing solution were larger than that of DMH-complexing solution. In addition, each cyanide-free silver electroplating solution showed similar capacitive loops which proposed that there were no significant changes in electrochemical deposition mechanism occurred on the cathode.

Moreover, polyethyleneimine as additive was found to be effective on producing bright silver deposit. However, cracks were found in the silver deposit from thymine and DMH-complexing solution as the concentration of polyethyleneimine increases. The results from linear sweep voltammetry measurements showed that the reduction current value decreases as the amount of polyethyleneimine added increases due to inhibition effect on the silver electrodeposition reaction. In addition, the inhibition of polyethyleneimine also affect the cathode current efficiency of cyanide-free silver electroplating solution. Furthermore, the results from electrochemical quartz crystal micro-balance analysis showed that the addition of polyethyleneimine in thymine-complexing silver solution does not significantly affect the resonance frequency change. However, the resonance frequency change increases with the addition of polyethyleneimine in DMH and uracil-complexing silver solution.

Nevertheless, further research on other aspects, for example, solderability test, contact electric resistance and hardness of deposit is required to determine cyanide-free formulation for silver electro-deposition which suitable in industrial practice.

ORCID

Atiqah Binti Jasni https://orcid.org/0009-0000-2738-4233

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