

Electroless and Electrodeposition of Silver from a Choline Chloride-Based Ionic Liquid

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Abstract. The electroless and electrolytic deposition of silver from a solution containing silver nitrate in either an ethylene glycol (EG)-choline chloride based or a urea-choline chloride based ionic liquids has been carried out onto steel and copper cathodes by simple immersion, constant current and constant potential methods at room temperature. It has been found that electroless silver deposits of up to several microns have been obtained by dip coating from both urea and EG based ionic liquids without the use of catalysts. The influences of various experimental conditions on electrodeposition and morphology of the deposited layers have been investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD). It has been observed that crack free bright metallic coloured silver coatings can be obtained from both EG and urea based ionic liquids at the applied deposition potentials up to -0.40 V and applied deposition current densities up to -5.0 A m^{-2} at room temperature. The cathodic current efficiency for the deposition of Ag is about 99%.

Keywords: cyclic voltammetry, electrodeposition, electroless deposition, ethaline, reline, silver

Introduction

The electroless and electrodeposition of silver metal onto copper substrate is an important industrial process that is used primarily by the manufactures of printed circuit boards to prevent degradation of exposed copper surfaces (conduction tracks) during the time that elapses between the manufacture of the circuit board and the assembly procedure incorporating the board or component into a finished device. Typically this can be up to several months. This method of protection for copper surfaces is very effective despite the fact that silver is thermodynamically much more susceptible to aerobic oxidation. This is because silver oxide and sulphide (formed as tarnish on silver surfaces), as well as the underlying silver metal, are very soluble in the tin- and tin/lead-based molten solder that are used to bond the circuit components to the copper tracks of the circuit board.

On the contrary, copper oxides are poorly soluble in the molten solder such that, aerobic oxidation of the copper surface prior to soldering inhibits interfacial wetting at the copper/solder interface and prevents bonding of the component. In a practical device, this results in failure of the joint either through poor conductivity or because of low mechanical stress tolerance. Solder fluxes are often

used to mitigate this problem by preventing aerobic oxidation of copper surfaces, but this approach is not always successful or practical. Commercial electroless silver processes typically use an aqueous AgNO_3 solution in the presence of HNO_3 . In addition to the social and environmental concerns that surround the use of strong inorganic acids, here the use of HNO_3 , whilst necessary to the process, has an additional detrimental effect because there is competitive etching of the copper tracks during silver plating. This can be a serious problem for the electronics industry, particularly as integration densities continue to increase and consequently feature sizes become smaller. Many component failures arise because of copper etching (by the HNO_3) before the surfaces are silver plated. In addition, the aqueous process requires the use of colloidal catalyst (usually palladium metal) to sustain silver plating from beyond a few nanometers up to 1-5 μm in thickness (Djokic *et al.*, 2002; Shipley, 1961).

Sun *et al.* (2003) and Endres (2002) reported that, recently ionic liquids have received a great deal of attention in the literature as alternative solvents and electrolytes for a number of electrochemical processes. These processes range in scope from fundamental academic investigations, for example, into the structure of the solid/liquid interfaces (Ohno, 2005), or into the mechanisms of ion diffusion, to industrial processes where, the ionic liquid has the potential to replace conventional noxious aqueous media (Abbott

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et al., 2004a). A relatively new class of ionic liquid based on eutectic mixtures of choline chloride with a hydrogen bond donor species has been reported by Abbott and McKenzie (2006) and Abbott *et al.* (2004b; 2003). Abbott *et al.* (2006a; 2006b) also reported that, these liquids can be used for deposition of a range of metal coatings including Zn, Cr, Sn, Cu, and Ag at high current efficiency and also for metal dissolution processes such as electropolishing. In many cases, the use of ionic liquids as solvents overcomes the need for strong inorganic acids (e.g., chromic acid, HF, H₃PO₄, H₂SO₄) and highly toxic salts (e.g., cyanide). The aim of the present work is to develop a coating of silver on copper substrate by electroless and electrolytic deposition methods from ionic liquids based on choline chloride and hydrogen bond donors such as ethylene glycol (EG) or urea.

Materials and Methods

Chemicals. Choline chloride [HOC₂H₄N(CH₃)₃Cl] (ChCl) (Aldrich 99%) which was recrystallised from absolute ethanol, filtered and dried under vacuum. Urea (Aldrich >99%) was dried under vacuum prior to use. Ethylene glycol (EG) (Aldrich >99%), silver nitrate (AgNO₃) (Merck 99.8%), and all other chemicals were used as received.

Preparation of ionic liquid. The eutectic mixtures were formed by stirring the two components together, in the stated proportions, at 75 °C until a homogeneous, colourless liquid formed. The molar ratio for the eutectic compositions was found to be 1:2 for choline chloride (ChCl) with ethylene glycol (EG) or urea. The ionic liquids, once formulated, were kept in a thermostatic oven at 30 °C prior to use.

Electrochemical and analytical study. Electrochemical investigations including potential step chronoamperometry, chronopotentiometry and cyclic voltammetry were carried out using a Hokudo Denko HAB151 Potentiostat/Galvanostat, Tokyo, Japan, equipped with a potential sweeper. Data were recorded in a computer through data acquisition system (USA) using WinDaq software. A three-electrode system consisting of a platinum (50×5×0.1 mm³) working electrode, a silver (50×10×0.2 mm³) counter electrode and a silver wire quasi-reference electrode were used in all electro-chemical studies. The working electrode was cleaned electrochemically in 1.5 mol/dm³ H₂SO₄/1.0 mol/dm³ H₃PO₄ mixtures then rinsed with deionised water, and finally dried with acetone prior to use in all measurements. All voltammograms were obtained at 30 °C with various scan rates ranging from 5 to 100 mV/s. A silver wire (immersed in ethaline/reline) quasi-reference electrode

was used in all electrochemical experiments which have been shown to have stable reference potential in chloride based eutectics. All potentials in this work are quoted with respect to Ag/1:2 ChCl-EG/urea reference electrode (which will be written as Ag/Ag(I) (note that the reference potential will be changed slightly with melts of different compositions).

Deposition of silver. The electroless plating of silver were carried out in a glass beaker containing 15 cm³ ionic liquids at room temperature (typically 25–30 °C) onto copper (50 × 10 × 0.2 mm³) or mild steel (50 × 10 × 0.2 mm³) substrates. Prior to deposition experiments, copper and steel substrates were mechanically polished to mirror finish by 600, 1000 and 2000 grit sandpaper. After polishing, the specimens were ultrasonically cleaned in deionised water, and finally dried with acetone. The substrates were then immediately immersed in ChCl:2EG (ethaline) and ChCl:2Urea (reline) ionic liquids containing AgNO₃ (0.01–0.10 mol/dm³) at different time periods (1–5 min). The electrolytic deposition of silver were carried out onto copper and steel cathodes under constant current and constant potential methods from ionic liquids (ethaline/reline) containing AgNO₃ at room temperature. Following each deposition, the resulting deposit was soaked firstly in ethanol, then in deionised water, and finally washed with acetone to remove the residual ionic liquids. The deposit was then dried with cold air.

Deposit characterisation. The surface morphologies of the samples were then examined with scanning electron microscope (XL 30 SEM, PHILIPS) and its auxiliary X-ray energy dispersive spectroscope (EDX). X-ray diffraction analysis was also performed with a Philips PW 1716 diffractometer using CuK_α radiation (40 kV, 25 mA) to explore the crystal structure of the deposits.

Results and Discussion

Cyclic voltammetry of Ag(I) in ChCl:2EG (ethaline) and ChCl:2urea (reline) ionic liquids. The cyclic voltammograms recorded on a platinum electrode in 1:2:0.05 (mole ratio) ChCl:EG:AgNO₃ (a) and Ch Cl: urea:AgNO₃ (b) ionic liquids at 30 °C with a scan rate of 10 mV/s are shown in Fig. 1. The rest potentials are + 0.44 V in ethaline and +0.22 V in reline. The scan towards negative direction consists of first reduction waves C₁ in Fig. 1a and C'₁ in Fig.1 b with the currents starting to increase at -0.03 V (C₁) and + 0.013 V (C'₁). Additional reduction waves C₂ in Fig. 1a and C'₃ in Fig. 1b are observed with the currents increase starting

again at -1.10 V and -1.00 V, respectively. The reverse scan consists of first oxidation peaks P_{a1} in Fig. 1a (+ 0.11 V) and p'_{a1} in Fig. 1b (+ 0.146 V). Additional oxidation waves are also observed with the currents starting to increase at +1.02 V for ethaline and + 0.90 V for reline. From XRD and EDX analyses, pure silver has been detected in the deposit obtained at a deposition potential of -0.12 V (from the first reduction waves C_1 and C'_1) by constant potential method. Therefore, the increases of the negative currents in the first reduction waves C_1 and C'_1 are obviously associated with the reductions of silver ions to metallic state according to the following reaction.

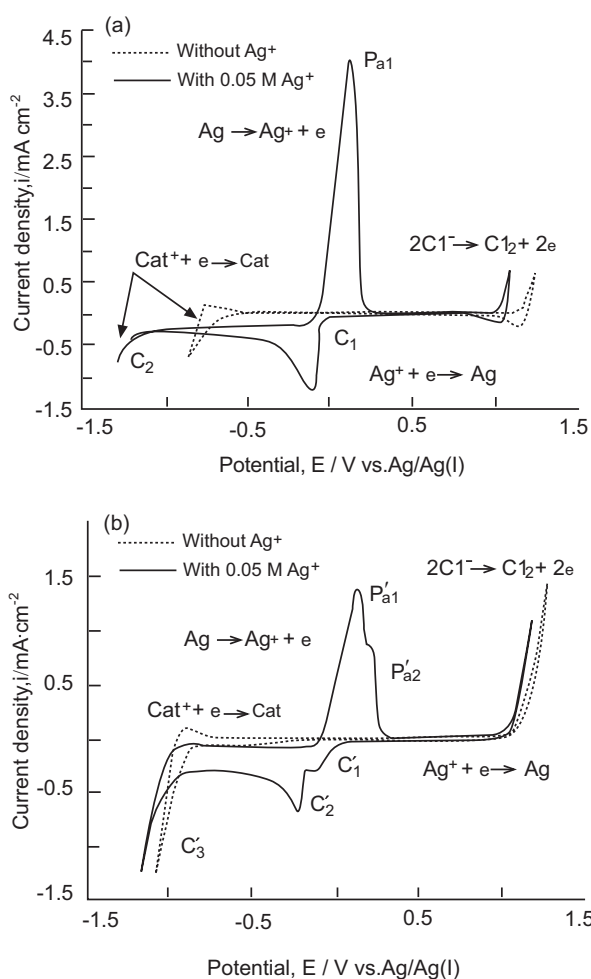
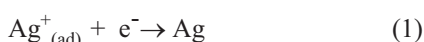


Fig. 1. Cyclic voltammograms recorded on a platinum electrode in ChCl:2EG (a) and ChCl:2urea (b) ionic liquids containing 0.05 M AgNO_3 at 30 °C with a scan rate of 10 mV/s.

Compared with the voltammograms obtained in the absence of AgNO_3 , dotted curves in Fig. 1a and Fig. 1b, the reduction waves appeared at -0.72 V in ethaline and -0.90 V in reline correspond to the reduction of cationic species (Cat^+) into these ionic liquids, while the oxidation waves appeared at +1.2 V in ethaline and +1.0 V in reline correspond to the oxidation of chloride ions (anions) to molecular/gaseous chlorine according to following reaction.

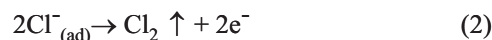


Figure 2 shows the effect of sweeping potentials on the cyclic voltammograms recorded on a platinum electrode in 1:2:0.05 (mole ratio) ChCl:urea: AgNO_3 ionic liquids at 30 °C with a scan rate of 10 mV/s. It is readily seen from the voltammograms that the first reduction wave C'_1 corresponds to the second oxidation peak P'_{a2} and the second reduction wave C'_2 corresponds to the first oxidation peak P'_{a1} . Pure silver has also been detected in the deposit obtained at a deposition potential of -0.12 V and -0.22 V (from the first C'_1 and second reduction waves C'_2) by constant potential method. Therefore, the increases of the negative currents in the first and second reduction waves (C'_1 and C'_2) are also associated with the reductions of silver ions to metallic state.

It can be seen from the voltammograms that more cathodic limits lead to increasing charge for more anodic dissolution process. The two reduction waves and two oxidation peaks could be due to the deposition of silver with different

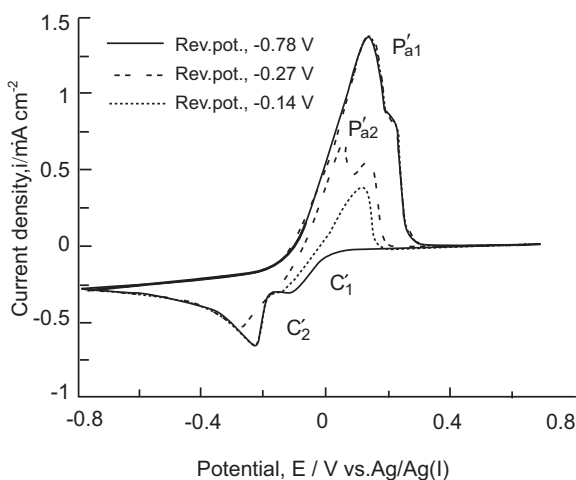


Fig. 2. Effect of sweeping potentials on the cyclic voltammograms recorded on a platinum electrode in ChCl:2urea ionic liquids containing 0.05 M AgNO_3 at 30 °C with a scan rate of 10 mV/s.

morphologies (Fig. 2). The two different morphologies must result from different growth mechanisms. One possibility could be the initial growth of a large number of nuclei on the surface where some of which stop growing giving a material with a different morphology. Alternatively, some aspect of the interfacial layer structure could neutralise the surface energy of the growing particle. Similar morphology had been reported by Abbott *et al.* (2010) for the deposition of aluminium from chloroaluminate based ionic liquids.

Figure 3 shows the effect of AgNO_3 concentrations on the cyclic voltammograms recorded on a platinum electrode in $\text{ChCl}:\text{2EG}$ (a) and $\text{ChCl}:\text{2urea}$ (b) ionic liquids at 30°C with a scan rate of 10 mV/s . It is readily seen from the voltammograms that, the magnitudes of the current densities of first reduction waves C_1 and C'_1 ,

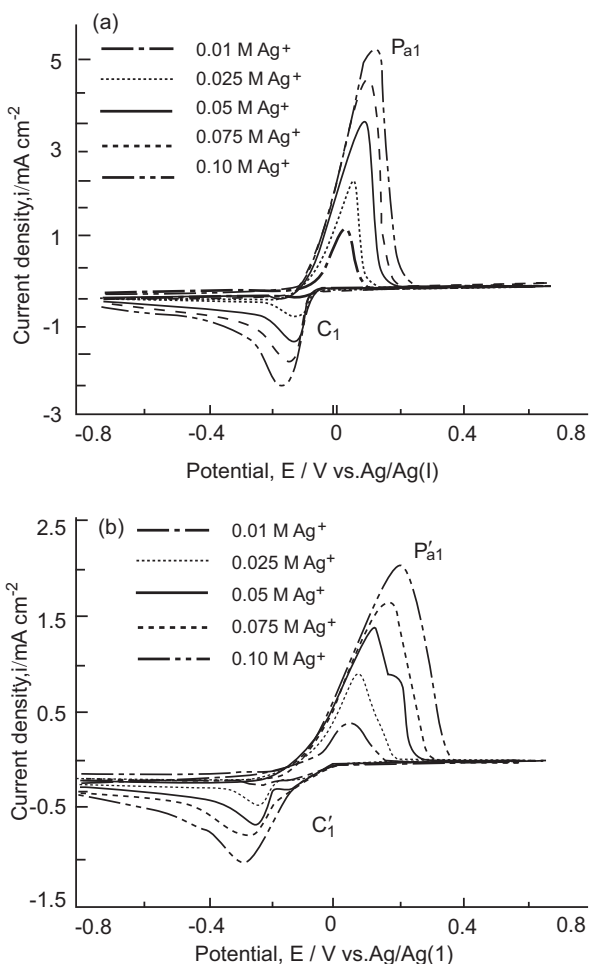


Fig. 3. Effect of AgNO_3 concentrations on the cyclic voltammograms recorded on a platinum electrode in $\text{ChCl}:\text{2EG}$ (a) and $\text{ChCl}:\text{2urea}$ (b) ionic liquids at 30°C with a scan rate of 10 mV/s .

which are attributed to the reductions of silver ions to metallic silver, increase with the increase of the AgNO_3 concentration added into the ionic liquids. The same phenomena are observed with the first oxidation peaks P'_{a1} (Fig. 3a) and P'_{a1} (Fig. 3b), which also shows the increase in current densities with the increase of AgNO_3 concentrations. As the magnitudes of the reduction current densities of silver (C_1 and C'_1) increase; the magnitudes of the oxidation peak current densities (P_{a1} and P'_{a1}) also increase, therefore, it is concluded that the first oxidation peaks P_{a1} and P'_{a1} are attributed to the dissolution of the deposited silver into this ionic liquid.

The effect of scan rates on the cyclic voltammograms recorded on a platinum electrode in $\text{ChCl}:\text{2EG}:\text{0.05 AgNO}_3$ (a) and $\text{ChCl}:\text{2urea}:\text{0.05 AgNO}_3$ (b) ionic liquids at 30°C are presented in Fig. 4. For a reversible system, peak potential

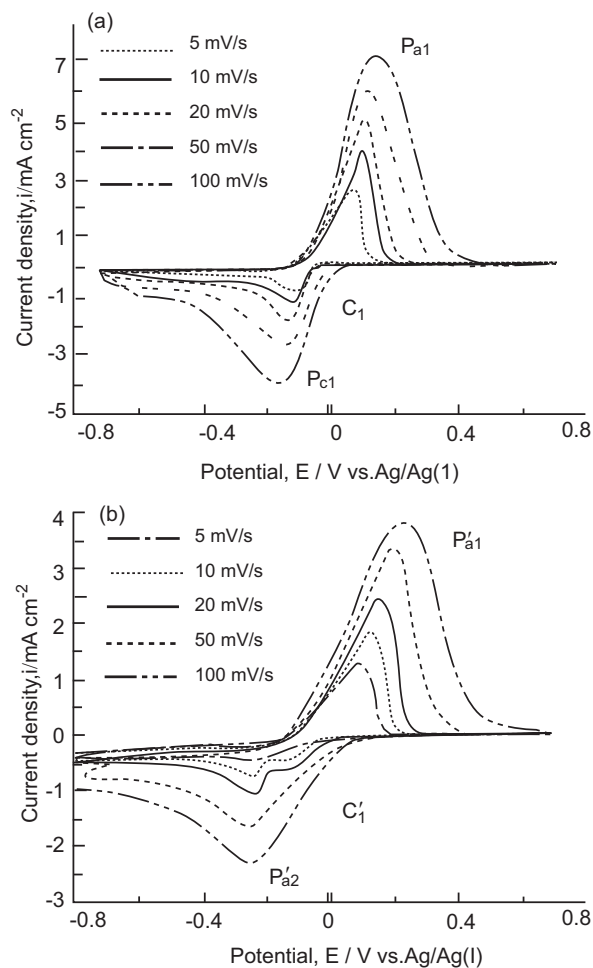


Fig. 4. Effect of scan rates on the cyclic voltammograms recorded on a platinum electrode in $\text{ChCl}:\text{2EG}$ (a) and $\text{ChCl}:\text{2urea}$ (b) ionic liquids containing 0.05 M AgNO_3 at 30°C .

E_p is independent of the scan rate (v), and the peak current density (i_p) is proportional to the square root of scan rate ($v^{1/2}$). In the present study (Fig. 4a), the cathodic peak potentials ($E_{p/c}$) are -0.135, -0.14, -0.141, -0.142 and -0.145 V for 5, 10, 20, 50 and 100 mV/s scan rates and the anodic peak potentials ($E_{p/a}$) are 0.095, 0.098, 0.10, 0.105 and 0.115 V for 5, 10, 20, 50 and 100 mV/s scan rates, respectively. In Fig. 4b, the cathodic peak potentials ($E_{p/c}$) are -0.223, -0.224, -0.225, -0.23 and -0.24 V for 5, 10, 20, 50 and 100 mV/s scan rates and the anodic peak potentials ($E_{p/a}$) are 0.13, 0.14, 0.15, 0.20 and 0.22 V for 5, 10, 20, 50 and 100 mV/s scan rates, respectively. It is evident from these results that the peak potentials for the reduction and oxidation waves of silver are almost independent of the scan rates indicating the systems are reversible in nature. Variations in peak current densities of C_1 and C'_1 with the square root of scan rate (i_p vs. $v^{1/2}$) are shown in Fig. 5. For a reversible system, the relationship between the cathodic peak current density i_p and the square root of the scan rate $V^{1/2}$ is given by Baird and Faulkner (1980):

$$i_p = (2.69 \times 10^5) n^3 D_{Ag(l)}^{1/2} C_{Ag(l)*} V^{1/2} \quad (3)$$

where:

$C_{Ag(l)*}$ = the concentration of silver ions in the bulk solution, D = the diffusion coefficient of silver ions, A = the surface area of the electrode, n = the number of electron transferred during reduction reaction and V the scan rate. The linear increases in the peak current densities of C_1 and C'_1 with the square root of scan rate,

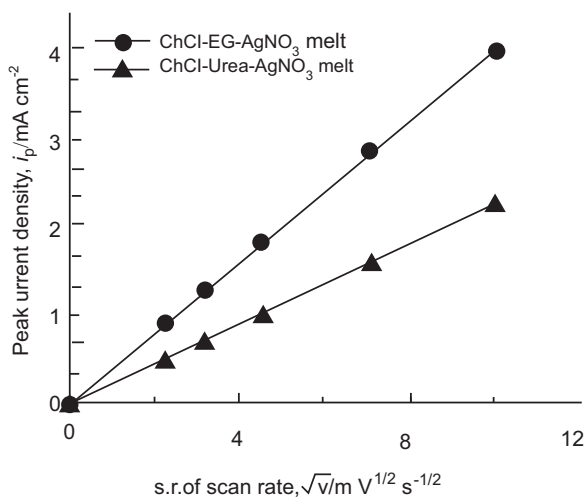


Fig. 5. Variations in cathodic peak current densities with the square root of scan rate for the reduction of silver ions in ethaline (a) and reline (b) containing 0.05 M $AgNO_3$.

as shown in Fig. 5, indicate that the reduction processes of silver ions in both $ChCl:2EG$ and $ChCl:2urea$ based ionic liquids are controlled by diffusion.

Electroless deposition of silver from ethaline and reline.

The camera images of electroless deposited silver layer obtained from both ethaline and reline based ionic liquids at different immersion time and different $AgNO_3$ concentrations are shown in Fig. 6. The deposits are smooth, shiny, and good adherence. The deposits are not peeling off by hand scratching. The scanning electron micrographs of silver electroless deposits obtained from 1:2:0.05 (mole ratio) $ChCl:EG:AgNO_3$ and $ChCl:urea:AgNO_3$ at 30 °C are shown in Fig. 7. The SEM images show that the surfaces are free from crack. Fig. 8a and 8b show the EDX profile for the SEM images of Figs 7a and 7b, respectively. Pure silver has been detected in the deposited layer by EDX analysis. There is no spectrum for residual chloride ions in the EDX profile indicate no incorporation of the ionic liquid in the deposits. Therefore, it is concluded that eutectic based ionic liquids of $ChCl:2EG$ (ethaline) and $ChCl:2urea$ (reline) can be used for the electroless deposition of bright metallic colour silver on a metallic substrate.

Electrodeposition of silver from ethaline and reline.

Silver electrodeposition experiments have been carried out on steel and copper cathodes under constant potential and constant current methods from both EG and urea based ionic liquids at room temperature. All of the electrodeposits obtained on Pt and Cu substrates at the applied deposition potentials ranging from -0.20 to -0.40 V and the applied deposition current densities ranging from -1.0 to -5.0 A/m² appear to be smooth and silver metallic colour. There is no apparent rupture on the deposit surface and the deposits do not peeling off by hand scratching. However, the

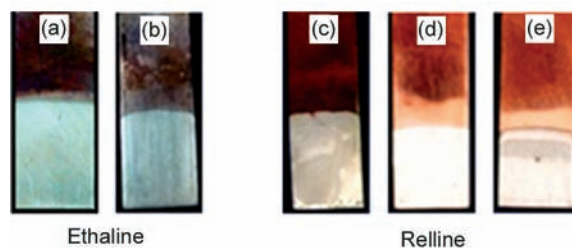


Fig. 6. Camera images of silver electroless deposits on copper substrates obtained from ethaline (a, b) and reline (c, d, e) containing 0.10 M $AgNO_3$ at 30 °C. Immersion time: a, b, c, 4 min; d, 2 min and e, 1 min.

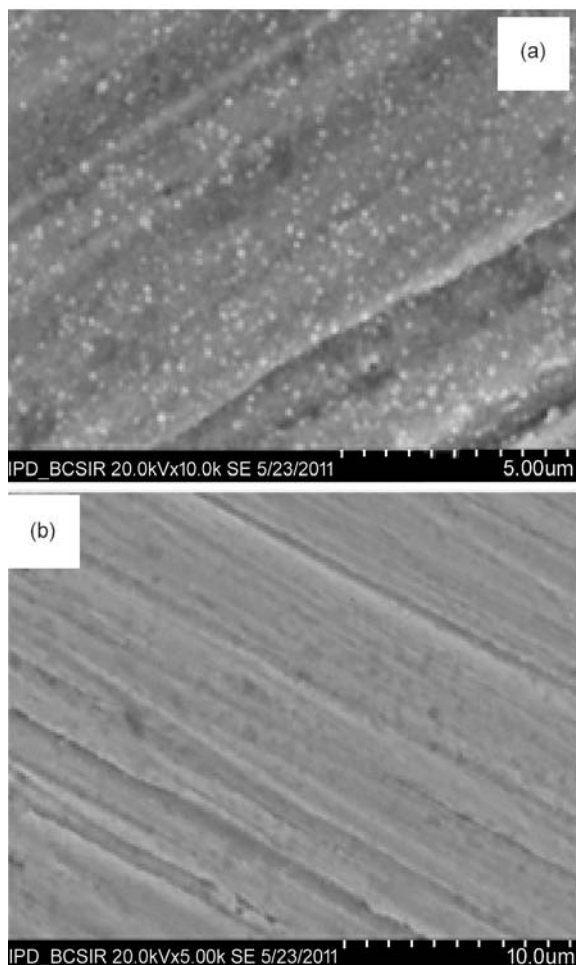


Fig. 7. SEM images of silver electroless deposits on Cu substrates obtained from mole ratios of 1:2:0.05 in ChCl:EG:AgNO₃ (a) and ChCl:urea:AgNO₃ (b) ionic liquids at 30 °C. Immersion time: (a) 3 min and (b) 5 min.

deposits obtained at the applied deposition potential of -0.60 V are not smooth due to high deposition over potential. The SEM images of the electrodeposited silver layer on copper cathodes under constant potential method from both EG and urea based ionic liquids are shown in Fig. 9. The electrodeposited crystals are angular and also nodular in shape and in the order of 1~3 μm in size. From SEM images it is clear that the crystal sizes in the electrodeposited thin films are bigger than the electroless deposited thin films. However, it is difficult to get thick coating in electroless method. The thickness of the deposited layers is approximately 4~6 μm, which has been controlled by adjusting the total charge applied.

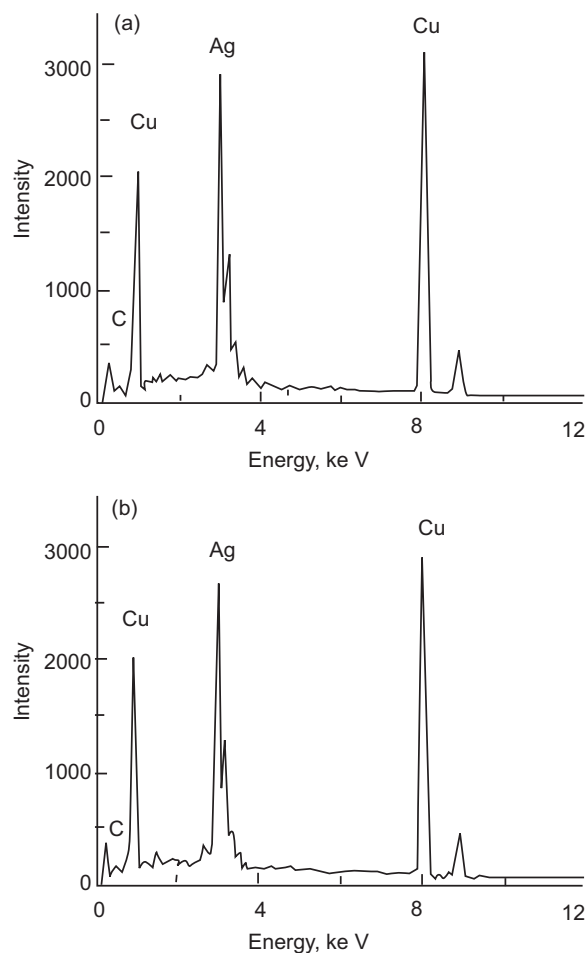


Fig. 8. EDX profile for the SEM images of Figs 7(a) and 7(b).

The acquired diffraction patterns for the deposits obtained from mole ratios of 1:2:0.05 in ChCl:urea:AgNO₃ ionic liquids at applied deposition potential of -0.25 V is shown in Fig. 10. The diffraction peaks at $2\theta = 38.1^\circ$, 44.3° , 64.4° , and 77.4° are for Ag (111), Ag (200), Ag (220) and Ag (311), respectively. The diffraction peaks are very sharp, indicating the deposit has the crystalline structure. The current efficiency for the deposition of pure silver is about 99%. However, additional diffraction peaks at $2\theta = 43.3^\circ$, 50.45° , and 74.1° corresponding to copper (substrate) are also observed in Fig. 10.

Conclusion

This work shows that the ionic liquids based on eutectic mixtures of choline chloride and hydrogen bond donors such as ethylene glycol or urea can be used as electrochemical solvents. Crack free smooth and bright metallic coloured silver can be electroless and electrolytic deposited onto steel and copper cathodes from ethaline and reline

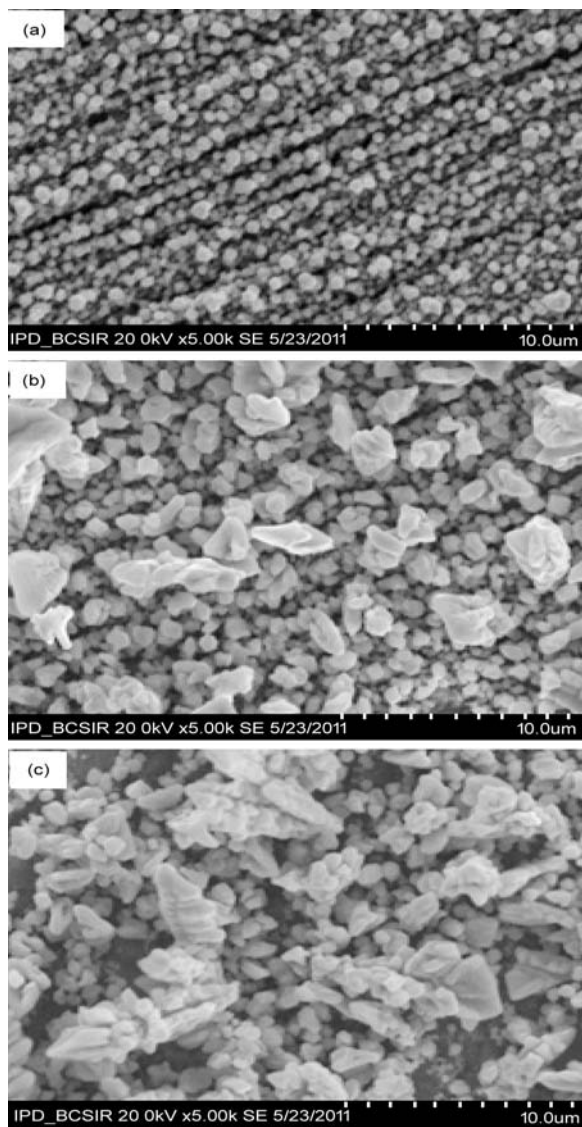


Fig. 9. SEM images of silver electroless deposits on Cu cathodes obtained from ethaline (a, c) and reline (b) ionic liquids containing 0.05 M AgNO_3 at 30 °C. Applied deposition potential: (a) -0.20 V, (b) -0.25 V and (c) -0.30 V.

based ionic liquids containing AgNO_3 at room temperature. The silver electrodeposits obtained at the applied deposition potentials up to -0.40 V and applied deposition current densities up to -5.0 A/m^2 are smooth and bright metallic colour.

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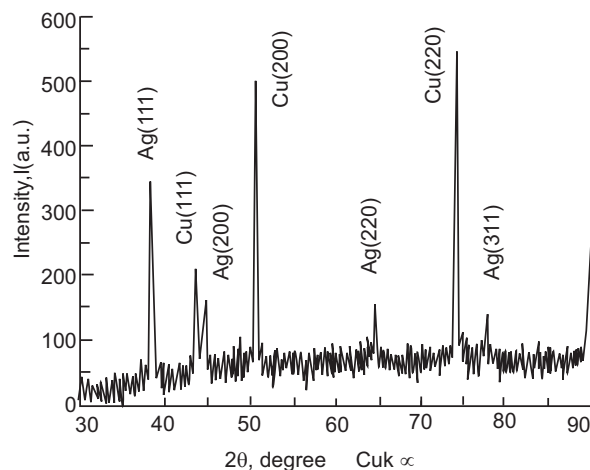


Fig. 10. X-ray diffraction pattern of silver electrodeposit obtained on copper from mole ratios of 1:2: 0.05 in $\text{ChCl}:\text{urea}:\text{AgNO}_3$ ionic liquid at 30 °C and -0.25 V.

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