Abstract

In the present study, the electrochemical investigation of gold-silver alloy electrodeposition from cyanide-free bath including organic compounds were carried out. The deposition potentials and the additive effect on cathodic polarization were studied by cyclic voltammetry analysis. Nucleation and growth mechanisms of the alloy electrodeposition were determined with chronoamperometric study in the absence and presence of organic additive.

1. Introduction

The electrodeposition of gold and its alloys is a notable topic due to its broad application area in microelectronic, spacecraft and jewelry industries. Due to the cost of the production, low hardness of deposit and expected different colors the lower karat gold-silver deposition has been investigated extensively. The alloys containing %13-75 Au can be electrodeposited from free cyanide baths [1]. Unfortunately, the non-cyanide electrolytes are not stable in most cases [2] and not preferred in industry by reason of poor coating properties. The point is that the deposition mechanism of Au-Ag alloy electrodeposition from pyrophosphate buffered baths containing no free cyanide has not been investigated yet in literature. Only in patent literature the bath formulations were described. PEI (Mw=600-60000), selenium, boric acid [3], PEI-600, diethylenetriamin [4] were used as additives.

The aim of this study is the research of the use of polyethyleneimine Mw=600 (PEI600), tetraethylenepentaamine (TEPA) as brightener couple for Au-Ag alloy electrodeposition and determination of the brightener effect on nucleation and growth mechanism.

2. Experimental Procedure

Hull cell studies were conducted to determine the operating current density range for bright gold deposits. This test was carried out using a 267 ml standard cell at a constant current of 0.2A at 60 °C. Electrodeposition time was 5 minutes. 4 g/L KAu(CN)2, 3 g/L KAg(CN)2, 80 g/L potassium pyrophosphate were used as basic electrolyte and 2.5 g/L polyethyleneimine Mw=600 (PEI600), 1 g/L tetraethylenepentaamine (TEPA) were used as organic brighteners. All chemicals were of analytical grade. Distilled water was used for the preparation of solutions. The copper plates of standard Hull cell size were used as the cathode. The surfaces of copper plates were mechanically polished, degreased by ethyl alcohol and then immersed 1 minute in 5% H2SO4 for activation. The copper plate was then washed in distilled water and dried with compressed air. The platinized titanium mesh electrode was used as the anode. Electrolyte was mixed by a magnetic stirrer with 350 rpm.

The electrochemical analysis was conducted by Gamry PCI4/750™ potentiostat. The compositions of electrolytes are presented in table 1. The sweep rate was 50 mV s⁻¹ for cyclic voltammetry experiments. All experiments were carried out in a standard three electrode cell in a volume of 50 cm³. The working electrode (0.25 cm²) and counter electrode were made of platinum. The reference electrode was standard calomel electrode (SCE) and all potential values were reported vs SCE.

<table>
<thead>
<tr>
<th>Electrolyte (g/L)</th>
<th>KAu(CN)2</th>
<th>KAg(CN)2</th>
<th>K2O7</th>
<th>PEI600</th>
<th>TEPA</th>
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<tbody>
<tr>
<td>S1</td>
<td>10</td>
<td>-</td>
<td>80</td>
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<td>S2</td>
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<td>S3</td>
<td>10</td>
<td>2</td>
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<td>1</td>
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<tr>
<td>S4</td>
<td>10</td>
<td>2</td>
<td>80</td>
<td>1</td>
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</tr>
</tbody>
</table>

3. Results and Discussion

3.1 Hull cell test results

The positive effects of additives on brightness in a wide current density range was presented with Hull cell experiments. Fig. 1 shows the mirror-effect images of Hull cell cathodes electrodeposited from phosphate buffered Au-Ag electrolyte in the absence and presence of PEI600 and TEPA. It can be distinguished easily, the brightener couple have improvements on brightness whereas without brighteners dull deposit is obtained.
3.2 Cyclic Voltammetry

The electrochemical behavior of Au-Ag electrodeposition system from pyrophosphate buffered electrolyte was investigated by CV. Only cathodic potential region was discussed here. Fig. 2 shows the curve referring to Au (S1) electrodeposition has two irreversible reduction peaks. The first one at lower cathodic potential at 750 mV is seen too small here. At higher cathodic potential region at 1250 mV second reduction peak can be recognized. S2 shows the silver reduction system from solution S2. Two cathodic reduction peak is observed at 600 and 900 mV.

Fig. 3 shows the Au-Ag electrodeposition system from pyrophosphate buffered electrolyte. Au and Ag is deposited simultaneously in a wide range of electrochemical conditions [5]. S3, the solution not containing additives, has two different reduction peaks. At lower negative potentials at 850 mv a broad peak occurs. The second reduction potential is about 1250 mV. With the addition of brightener couple, the reduction scenario is changed. The depolarization occurs at lower negative potentials and the first reduction peak is shifted to 600 mV. It can be followed from curve S4. The second reduction peaks occurs at 1250 mv which has sharper current density growth according to S3 with the effect of brightener addition.

3.3 Chronoamperometry

The chronoamperometry method has been utilized to study the nucleation and growth mechanism of Au-Ag alloy electrodeposition with and without brighteners (PEI600 and TEPA) addition. The potential was held 10 s at 0.0 V then stepped to working potential to initiate nucleation growth on electrode. Fig. 4 shows chronoamperometric curves for Au-Ag alloy electrodeposition without brighteners. At low cathodic potentials (Fig. 4a), a double layer formation occurs in first few seconds which is observed as a sharp increase of current density. At high cathodic potentials double layer charging is not observed. Except this, each j-t response crosses through a maximum followed by a subsequent decline in current. After that deposition growth proceeds with a constant current. Fig. 5 shows j-t transients for Au-Ag alloy electrodeposition with brighteners. Generally typical j-t responses are observed.

In following j-t transients were fitted to the three-dimensional (3D) nucleation and diffusion controlled growth model of Sharifker and Hills [6]. The model also describes for two different nucleation precesses. Instantaneous nucleation means that nucleation occurs in all active sites at the beginning and then growth occurs. Progressive nucleation means that sites become active for nucleation during electrodeposition. For theoretical curves two equations were derived for progressive and instantaneous nucleation (Eqs. (1) and (2)) [6].

\[
\frac{I^2}{I_m^2} = \frac{1.2254}{t/t_m} \left(1 - \exp \left(-2.3367 \left(\frac{t}{t_m}\right)^2\right)\right)^2 \quad (1)
\]

\[
\frac{I^2}{I_m^2} = \frac{1.9542}{t/t_m} \left(1 - \exp \left(-1.2564 \left(\frac{t}{t_m}\right)\right)\right)^2 \quad (2)
\]
As shown in fig. 6, the experimental data of the low cathodic potential for solution without brighteners fits well to the model for 3D instantaneous nucleation with diffusion controlled growth after double layer charging region (first few seconds). On the other hand, for high cathodic potential 3D progressive nucleation and growth mechanism occurs. Figure 7 contains the comparison of the theoretical non-dimensional plots with the experimental data for solution with brighteners. The curve for low cathodic potential (-0.650 V) exhibits a somewhat progressive nucleation fit, but with a sharper sloped peak. This could be conceived as an additional process occurring as well as diffusion controlled nucleation. For high cathodic potential 3D instantaneous nucleation and growth mechanism well fits with the experimental data.

**Figure 4.** Potentiostatic j-t transients for Au-Ag reduction in solution S3 (without brightener) (a) at low cathodic reduction potential (-0.850 V), (b) at high cathodic potential region from -1.000 V to -1.250 V.

**Figure 5.** Potentiostatic j-t transients for Au-Ag reduction in solution S4 (with brightener couple) (a) at low cathodic reduction potential (-0.600 and -0.650 V), (b) at high cathodic potential region from -1.100 V to -1.250 V.

**Figure 6.** Comparison of the theoretical non-dimensional plots with the experimental data in Fig. 4 (j-t transients for solution without brighteners) (a) for low cathodic potential (-0.850 V), (b) for high cathodic potential (-1.100 V).
4. Conclusion

In the present study of Au-Ag electrodeposition from pyrophosphate buffered solutions, the effect of brightener couple, PEI600 and TEPA, were investigated. The Hull cell experiments show that the combined additives improved bright coatings in a wide current density range. Cyclic voltammetry experiments represent that at high cathodic potential region reduction occurred in the form of more sharply current density growth with the addition of brighteners. At low cathodic potential region reduction peak was shifted to more positive potentials due to the depolarizing effect of the brighteners.

The analysis of j-t transients indicate that, with the addition of PEI600 and TEPA, the nucleation and growth mechanisms for Au–Ag alloy deposition is changed totally. In the presence of brighteners, the nucleation mechanism is 3D-progressive at relatively low negative potentials, while it is 3D-instantaneous at high overpotentials with diffusion controlled growth mechanism. It is obviously asserted that with the addition of PEI600 and TEPA, brightener couple, an enhancement of Au-Ag alloy electrodeposition at high cathodic potentials occurs.

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References