CHAPTER-III

Experimental
3. Electrodeposition of gold

3.1. Materials, chemicals and instruments used

The substrates used in this study are 4 to 5 μm electrodeposited nickel films, plated on copper panels measuring 1cm x 5cm. The Copper specimens were mechanically polished to mirror finish; they were then treated as follows,

✓ Degreasing with trichloroethylene

✓ Electrocleaned cathodically for 1 minute in the following solution:

- Sodium carbonate 20 gpl
- Trisodium orthophosphate 9 gpl
- Sodium hydroxide 7 gpl
- Temperature 80°C
- Anode Stainless steel
- Current density 4 A/dm²

✓ Swilled in running water

✓ Dipped in 5% (v/v) sulphuric acid for 15 seconds

✓ Rinsed with distilled water

✓ Nickel plated from a bright nickel bath of the following composition to a thickness of 4-6μm, using nickel as the anode.

The bath composition of nickel plating solution is,
Table 3.1. Bath composition and operating conditions for plating electrodeposited nickel

<table>
<thead>
<tr>
<th>Constituents</th>
<th>gpl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulphate</td>
<td>240gpl</td>
</tr>
<tr>
<td>Nickel chloride</td>
<td>40gpl</td>
</tr>
<tr>
<td>Boric acid</td>
<td>30gpl</td>
</tr>
<tr>
<td>Temperature</td>
<td>50°C</td>
</tr>
<tr>
<td>Current density</td>
<td>2A/dm²</td>
</tr>
</tbody>
</table>

✓ Washed thoroughly and dipped in 5% (v/v) sulphuric acid followed by washing in running and distilled water rinse.

The standard bath composition and operating conditions followed for gold plating are listed below,

Table 3.2. Standard bath composition and operating conditions for plating electrodeposited gold

<table>
<thead>
<tr>
<th>Constituents</th>
<th>Concentration/operating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAuCl₄</td>
<td>0.15M</td>
</tr>
<tr>
<td>Sodium sulfite</td>
<td>0.5M</td>
</tr>
<tr>
<td>Sodium thiosulphate</td>
<td>0.5M</td>
</tr>
<tr>
<td>Stabilising agents</td>
<td>--</td>
</tr>
<tr>
<td>Additives</td>
<td>--</td>
</tr>
<tr>
<td>Temperature</td>
<td>30°C</td>
</tr>
<tr>
<td>Anode</td>
<td>Platinum</td>
</tr>
<tr>
<td>Current density</td>
<td>0.5-2.5 A/dm²</td>
</tr>
<tr>
<td>Duration</td>
<td>30 minutes</td>
</tr>
</tbody>
</table>

As shown in Table 3.2, HAuCl₄, a commonly available trivalent gold salt is used as the source of gold to make up the bath, but the Au(III) in this salt is reduced immediately to Au(I) upon addition of Na₂SO₃ forming the Au(I)sulfite complex. This complex is converted to a Au(I)-thiosulphate complex and/or
Au(I) thiosulphate-sulfite mixed ligand complex upon addition of NaS₂O₃ because of the greater stability of those complexes than the sulfite complex [1,2]. All the chemicals used for carrying out the experiments were of analar grade. D.C regulated power supply (Aplab) was used as the current source for all the deposition studies.

3.2. Plating procedure

3.2.1. Estimation of gold

Analysis of gold sulfite-thiosulphate complex in the bath was done as follows. 20ml of the solution was taken and treated with 25 ml of Conc. H₂SO₄ and heated to white fumes, cooled and added 10 ml of Conc HNO₃. Repeated with the additions of Conc.HNO₃ and heated until gold sponge coagulates and the solution becomes clear. It was then cooled and treated with 100ml of water at 60°C. It was then filtered through a previously weighed sintered crucible. Then gold sponge in the crucible was washed with hot water and then dried in an oven at 110°C. It was then cooled in desiccator and weighted [3].

\[
\text{Gold present in gpl} = \text{Weight of gold precipitate} \times 50
\]

3.2.2. Current Efficiency

Copper specimens of size 1cm x 5 cm were mechanically polished and degreased with trichloroethylene. One side of the specimen was masked with lacquer. The specimens were alkaline cleaned cathodically in the alkaline cleaning solution for 3-5 minutes. They were then inserted in to a 100 ml beaker containing the electrolyte. Pure platinum anode of the area (1cm x
2cm) was used. Deposition was carried out at constant current densities in the range of 0.5-2.5 A/dm² for 30 minutes. A copper coulometer was used to follow the charge flown in the circuit. The temperature was maintained at 30°C. After deposition the cathode was removed, washed well with distilled water, dried and weighed.

Experiments were carried out in 100 ml beaker containing gold plating bath of the above composition. With optimum concentration of the addition agents and each experiment was repeated minimum twice with a fresh electrode to get reproducible results.

From the difference in weight of the cathode current efficiency was calculated using the formula,

\[
\text{Current Efficiency (\%)} = \frac{\text{Experimental Weight}}{\text{Theoretical Weight}} \times 100
\]

Thus, the influence of additives on the cathode current efficiency was studied.

### 3.2.3. Throwing power

Throwing power is a measure of the ability of an electrolyte to deposit coatings of uniform thickness over a component of irregular shape. The most commonly used technique for measuring throwing power utilize the Haring Blum cell with cathodes, disposed at different distances from a central anode and all the electrodes completely filling the cell cross-section. Perforated stainless steel anode (4.3 x 5.5 cm) and the nickel coated copper cathode (4.3 x 5.5 cm) were positioned in the cell. Throwing power is expressed by the empirical formula,
Where M is ratio of the weights of metal deposited on the two cathodes, and L is the primary current distribution ratio, usually taken as the ratio of the distances of the two cathodes from the common anode.

3.2.4. Effect of plating variables on the thickness of the deposit

3.2.4.1. Effect of Current Density

Various current densities such as 0.5, 1.0, 1.5, 2.0 and 2.5 A/dm$^2$ were tried in the present studies. The nickel coated copper plates were placed in the electrolytic solutions mentioned above with different current densities impressed for one hour. Then the panels were removed, washed with water, dried and weighed. From the weight of the deposits, the thickness of the deposit was calculated assuming uniform deposition.

\[
\text{Rate of deposition (\mu m/hr)} = \frac{W \times 10^4}{\rho \times a \times t}
\]

\[W=W_2 - W_1\]

Where,

- $W_1$ - Initial weight of the sample
- $W_2$ - Final weight of the sample
- a - Area of the base metal (in cm$^2$)
- $\rho$ - Density of the deposit (g/cc)
- $t$ - time for deposition in hours
3.2.4.2. Effect of Temperature

Nickel coated copper plates were placed in the electroplating bath and the electrolysis carried out for 30 minutes with the solutions maintained at 30, 40, 50, 60, 70 and 80°C. Then the panels were removed washed with water, dried and then weighed. From the weight of the deposit, the thickness of the deposit was calculated.

3.2.4.3. Effect of pH

Nickel coated copper plates were placed in the electroplating bath at different pHs say 2, 4, 6 and 8. The electrolysis was carried out at a constant current density 2.0 A/dm² and at temperature 60°C. Then panels were removed washed with water, dried and then weighed. From the weight gain, the thickness of the deposit was calculated.

3.2.4.4. Effect of stabilizing agents

Different baths were prepared by varying the concentrations of EDTA and citric acid respectively at a current density of 2.0 A/dm², while keeping the concentrations of other constituents in the plating bath unchanged. The panels were placed in electroplating solution for 30 minutes and electrolysis was carried out. Then the panels were removed washed with water, dried and weighed. From the weight of the deposit, the thickness of the deposit was calculated.
3.3. UV studies for bath characterization

The gold complexes in solution were identified using ultraviolet-visible spectroscopy using a Shimadzu-UV-visible-2401 spectrophotometer. In these experiments, the spectra were recorded after filling a standard quartz cuvette (cell path length of 1.0 cm) with the particular electrolyte, and absorbance was recorded at a fast scan over the wavelength range of 200-500 nm. The quartz cuvette was rinsed and dried after each scan before filling it with the next solution. In these experiments, the spectra for 0.5 M Na$_2$SO$_3$ and 0.5M Na$_2$S$_2$O$_3$ were gathered first and used as baseline corrections for subsequent traces. UV spectroscopy analysis was repeated for all the other constituents of the combined electrolyte, i.e., diluted HAuCl$_4$, gold sulfite prepared in the laboratory (0.15 M HAuCl$_4$, 0.5 M Na$_2$SO$_3$) and gold thiosulphate (0.15 M HAuCl$_4$, 0.5M Na$_2$S$_2$O$_3$). Finally, the UV spectra of the gold thiosulphate-sulfite bath in presence and absence of stabilizing agents were measured. The photograph of the system is shown in Fig. 3.1.

3.4. Physical properties of the deposit
3.4.1. Microhardness measurements

Hardness of the electrodeposited gold surfaces obtained from baths with various additives were measured using a LECO microhardness Tester Model M400 by the static indentation method. A diamond pyramid was pressed into the deposit under a load of 50 gms for 15 seconds and the load was removed. Each electrodeposit used for this measurement was of 2µm thickness. The microhardness in kgmm$^{-2}$ was determined in each case by using the formula,
HV = 1854 x l/d²

Where, I being the load applied in grams and d is the diagonal of the indentation in micrometers.

3.4.2. Adhesion

From the functional viewpoint the most fundamental requirement of gold plating is adequate adhesion of the coating to the substrate to which it is applied. The degree of adhesion obtained in any particular case is critically dependent on the correct choice of pretreatment.

To evaluate the adhesion of the gold plated copper specimens bend tests were employed. In this test the specimens were bent forward and backward through an angle of 90° until fracture of the basis metal occurs. If no peeling, flaking and/or blister formation is seen after the test, the adhesion is satisfactory.

3.4.3. Porosity

3.4.3.1. Electrographic Tests

Porosity is of greater importance for coating that is more cathodic than the base metal and is determined by means of tests in which the chemical reactivity of the substrate compared to the coating is chosen as the best parameter.

The porosity was evaluated by using an electrographic method [4]. In this method, the specimen was made an anode against a Pt cathode in an electrolytic cell containing a viscous solution prepared by adding 10ml of 5% NH₄OH and 6ml of a saturated solution of DMG in methanol into a solution made by dissolving 27gms of gelatin in 273ml of boiling water. A constant
current of 4 mA/cm² was passed for 15 sec. This procedure results in pink
discoloration where the substrate Ni is exposed through pores because of the
anodic formation of Ni-DMG complex. The discolored spots were counted in
equally divided spaces and the porosity was evaluated statistically (the
number of pores per unit area).

3.5. Electrochemical experiments

3.5.1. Conductivity

The cell was calibrated with 0.01 M KCl over the range of 15-
30°C for which detailed conductivity data were available [5], and the cell
constant of 1 cm⁻¹ did not vary outside the accuracy of the bridge. The
following solutions were used for UV and Conductivity studies and the
solutions were prepared with triple distilled water and reagent grade
chemicals, and are listed below;

1. 0.15 M HAuCl₄
2. 0.15 M HAuCl₄ + 0.5 M Na₂SO₃
3. 0.15 M HAuCl₄ + 0.5 M Na₂S₂O₃
4. 0.15 M HAuCl₄ + 0.5 M Na₂SO₃ + 0.5 M Na₂S₂O₃
5. 0.15 M HAuCl₄ + 0.5 M Na₂SO₃ + 0.5 M Na₂S₂O₃ + EDTA
6. 0.15 M HAuCl₄ + 0.5 M Na₂SO₃ + 0.5 M Na₂S₂O₃ + citric acid

3.5.2. Cyclic voltammetric studies

The cathodic electrodeposition of gold was carried out using EG&G
Electrochemical Impedance Analyzer, Model 6310, with M398 Software. A
three electrode cell assembly was used. Platinum foil and gold were used as
the working electrode and large area of Pt foil used as the counter electrode and SCE was used as the reference electrode. The photograph of the system is shown in Fig. 3.2. The basis of electrodeposition of gold was evaluated by cyclic voltammetry. The potential range was -1000 to -100 mV for the studies of gold on platinum while the range was -1 V to 1.4 V for gold on gold electrodes. The experiment was carried out for different concentrations of HAuCl₄, sodium thiosulphate, sodium sulfite, EDTA, citric acid and additives with various scan rates, pHs and temperatures. The electrochemical cell setup is shown in Figure 3.3.

3.5.3. Electrochemical impedance spectroscopy

The EIS experiments were carried out at the D.C deposition potential with superimposed AC voltage of amplitude 10 mV in the frequency range of 100 mHz to 100 KHz using EG&G impedance analyzer, Model 6310 Software Model M270. The coated gold and platinum foils were used as the working and counter electrodes respectively. The SCE was used as the reference electrode. The gold plating solutions were used as the electrolyte medium. The photograph of the system is shown in Fig. 3.2

The real part (Z') and the imaginary part (Z") of the cell impedance were measured for various frequencies. Impedance measurements were carried out in gold baths in the presence and absence of stabilizing agents with optimum concentration of the additives that give bright deposits. From the impedance diagrams the charge transfer values are calculated.
3.6. Structural investigations

3.6.1. Scanning Electron Microscopy (SEM)

The morphology of the electrodeposited gold was examined through Scanning Electron Microscopy. The gold deposit obtained in sulfite-thiosulphate bath with and without stabilizing and addition agents at optimized plating conditions have been examined for their morphology through SEM, JEOL Instrument, Gold coating was sputtered, if needed.

3.6.2. Atomic force microscopy (AFM)

Atomic force microscopy (Digital Instruments Nanoscope E (AFM) was used to check the surface morphology of the gold coating on nickel coated copper substrate.

3.6.3. X-ray diffractions studies

The crystal structure of the gold deposit grains was examined through X-ray diffraction. The crystallinity of the gold deposits was evaluated through the X-ray diffraction studies. The XRD spectra were taken by using X-ray diffractometers, JDX 8030 instrument. The particle size of the deposit is computed from,

\[ D_{hkl} = \frac{k\lambda}{\beta\cos\theta} \]

Where \( k \) is Scherrer constant with the value of 1, \( \lambda \) X-ray wavelength (0.1544 nm for Cu target), \( \theta \) Bragg angle, and \( \beta \) peak half-width in radiation unit.
3.6.4. Elemental analysis

Elemental analysis of the gold coating samples was carried out using Energy Dispersive Spectrometer.

3.7. Effect of additives on the gold Plating process

Different organic additives such as sodium lauryl sulfate, pyridine thiourea and aniline were tried in thiosulphate-sulfite stabilized bath and studies were carried out as in the earlier cases for the influence of plating parameters, rate of deposition and quality of deposits.

The gold deposits were examined through Scanning electron microscope, and XRD studies.
Figure 3.1 Shimadzu-UV-visible-2401 spectrophotometer
Figure 3.2 Electrochemical impedance analyzer EG & G Princeton Applied Research, Model 6310.
Figure 3.3 Electrochemical Cell Setup
Reference


