

CHEMICAL AND ELECTROCHEMICAL CHARACTERIZATION OF GOLD COMPLEX BASED ON MERCAPTOTRIAZOLE IN ACID MEDIA

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ABSTRACT

Gold complex based on mercaptotriazole can be synthesized in a wide pH range (2-12). The aim of this work was chemical and electrochemical characterization of gold complex in acid media. Raman spectroscopy, infrared spectrometry, inductively coupled plasma atomic emission spectroscopy and ultraviolet-visible spectroscopy were used for the chemical characterization of the prepared solutions. Electrochemical characterization is performed by open circuit potential measurement, cyclic voltammetry and polarization measurements.

Key words: gold complex, Raman spectroscopy, ICP, UV

1. INTRODUCTION

The electro deposition of gold is not a new process, but has been widely used in the automotive industry, biomedical processes and electronics industry, such as in computers, telecommunications, aerospace applications, etc. Electroplated gold can be classified as either soft gold or hard gold. Traditionally, gold has been plated from cyanide electrolytes, where (Au⁺) is ligated with cyanide (CN⁻). However, due to fears about safety and the disposal of process waste, there is a growing concern regarding the use of cyanide-based processes. The main problem with the use of cyanide electrolytes is their poor compatibility with many standard positive photo resists. The other principal disadvantage of cyanide is its high toxicity. The interest in developing non-toxic gold electrolytes, such as those based on a gold sulphite complex, has grown rapidly in recent years [1-5].

The possibility of electroplating soft gold specifically for the formation of micro bumps on silicon wafers from a non-cyanide bath containing both thiosulphate and sulphite as complexing agents was proposed by Osaka and co-workers [6]. Liew, Roy, Scot and Green at Newcastle have developed an electrolyte for soft gold electrodeposition which has attempted to eliminate Na₂HPO₄ and TI⁺ [7].

The thiourea bath was developed and subsequently improved by a group of investigators at Hitachi Ltd. [8]. Richter and co-workers [9] developed a thiosulfate-sulphite mixed ligand bath with ascorbic acid as the reducing agent. Krulik and Mandich [10] reported that the Au(I) thiosulfate-sulphite mixed ligand system functions as an autocatalytic bath in the absence of any conventional reducing agent. They believed that the thiosulfate-sulphite mixture itself is a reducing agent system, and that sulphite functions as the main reducing agent in this bath.

At the Institute of Mining and Metallurgy Bor a completely new electrolytic bath based on a gold complex with mercaptotriazole was developed and tested. Studies have shown that the new electrolyte can be successfully used in electrolytic baths for hard and decorative plating. Contrary to the previous complexes it showed a sufficient stability in a shorter time interval [11, 12].

2. EXPERIMENTAL

The aim of this work was chemical and electrochemical characterization of gold complex based on mercaptotriazole in acid media.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES, Produced by: Spectre, Model: Ciris Visio, Detection limit: $<0.0001\text{g/dm}^3$) and Atomic Absorption Spectrophotometer (AAS, Produced by: Perkins & Elmer, Model: 403, Detection limit: $<0.0001\text{ g/dm}^3$) were used in order to obtain content of gold in solution.

Gold complex in solution was identified using a ultraviolet-visible spectroscopy (UV-vis) using a Perkin-Elmer Lambda 15 UV-vis spectrophotometer. In these experiments, the spectra were recorded using a standard quartz cuvette with a particular electrolyte, and performing a fast scan over the wavelength of 190-900nm. The pH of electrolyte was monitored using a pH meter HANNA-Aldrich Sigma-Model C3724 1EA.

Electrochemical studies were carried out using cyclic voltammetry, open circuit potential measurement and polarization curves recording.

The experiments were carried out in a system consisting of an electrochemical cell and hardware interface for computerized control and data acquisition. In a standard three-electrode electrochemical cell, the working electrode was gold plated platinum electrode (surface $4,522\text{mm}^2$), who's potential was controlled against saturated calomel reference electrode (SCE). Platinum foil ($1\times 2\text{cm}$) served as a counter electrode. The computerized control (National Instruments card, NI-6251) and data acquisition software (Lab VIEW 8.2 platform and applications specifically developed for electrochemical measurements), fully developed by Technical Faculty in Bor [13], was used to run the electrochemical experiments.

The electrolyte volume used in experiments was 100 ml. All experiments were carried out at temperature of $25 \pm 0.5\text{ }^\circ\text{C}$. The electrolytes pH was measured before and after each electrochemical measurement.

3. RESULT AND DISCUSSION

3.1. Chemical characterization of gold complex

Bayer and Kroger method [14] was used for synthesis of mercaptotriazole. IR and Raman spectra show agreement with the spectra that can be found in the literature [12].

Inductively coupled plasma atomic emission spectroscopy, used for monitoring the concentration of gold in the electrolytes confirmed the concentration of 2.50 g/dm^3 in all synthesized electrolytes.

For Au-MT electrolyte chemical characterization, the UV-vis absorption spectra were recorded for glycine (6%), mercaptotriazole (6%), chloroauric acid (2.5 gAu/dm^3) and gold complexes with mercaptotriazole (pH 2 and 7) and are presented in plots of absorbance, A , against wavelength, λ , in nm in Figure 1.

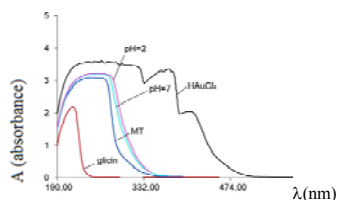


Figure 1. UV-vis absorption spectra of: glycine (6%), mercaptotriazole (6%), chloroauric acid (2.5gAu/dm^3) and gold complex with mercaptotriazole with pH 2 and 7

UV-vis absorption spectrum for mercaptotriazole shows agreement with the spectra that can be found in the literature [15]. The gold complexes at pH=2 and pH=7 have very similar lines in the spectra. Spectra at both pH values occur at lower wavelengths compared to that obtained for gold acid.

3.2 Electrochemical characteristics

Change of open circuit potential of gold in solutions with pH values of 2, 4, and 7 was monitored during 60s. Steady state values of open circuit potential and pH of electrolytes before and after

electrochemical polarization measurements are shown in Table 1. Measurements were performed on freshly prepared electrolytes.

Table 1. Steady state values of open circuit potential and pH values of electrolyte before and after polarization measurements

Predicted pH	2	4	7
Open circuit potential (V vs. SCE)	+0.206	-0.028	-0.029
Measured pH (before p.m.)	1.85	4.20	7.10
Measured pH (after p.m.)	1.95	4.40	7.05

It can be seen that with the increase of pH of electrolyte, open circuit potential shifts to more negative values. The most negative OCP of -0.029 V vs. SCE was measured at pH=7, while at pH 4 and pH 7 the measured steady state values of open circuit potential are almost equal: -0.028 or -0.029 V vs. SCE.

After electrochemical polarization measurements, pH value of acidic electrolytes increased, as shown in Table 1. Increasing of pH after polarization measurements in acid solutions proves that hydrogen is evolved in parallel with deposition of gold.

Cyclic voltammograms presented in Figure 2 were recorded with a scan rate of 100 mV/s, in the following potential ranges: for pH 2: (+1.6 ÷ -0.6) V vs. SCE; for pH 4: (+1.6 ÷ -1.5) V vs. SCE and for pH 7: (+1.5 ÷ -1.3) V vs. SCE. Potential ranges were ordered by the start of gaseous hydrogen (bottom) and gaseous oxygen (upper limit) evolution.

Polarization curves were recorded with a scan rate of 5 mV/s in the following potential ranges: for pH 2: (+0.2 ÷ -0.6) V vs. SCE; for pH 4: (+0.2 ÷ -1.1) V vs. SCE and for pH 7: (+0.2 ÷ -1.2) V vs. SCE. The curves for the electrolyte with a gold concentration of 2.5 g/dm³ recorded at different pH values are presented in Figure 3. From these curves the limiting current densities can be determined.

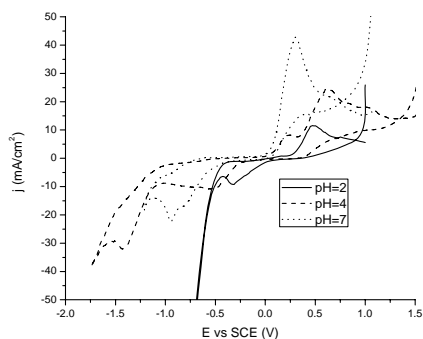


Figure 2. Cyclic voltammograms of the electrolytes with the gold concentration of 2.5 g/dm³ at different pH values: a) pH = 2, 4 and 7

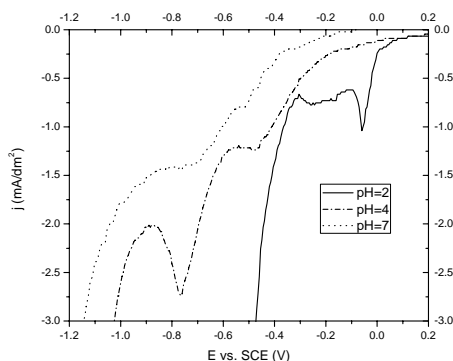


Figure 3. Polarization curves for the electrolyte with gold concentration of 2.5 g/dm³ at pH = 2, 4 and 7

From the cyclic voltammograms for electrolytes with different pH values recorded with a potential scan rate of 100 mV/s presented in Figure 2 it can be noted that with an increase in pH the cathodic current waves shift to more negative potentials. In the anodic part, all the voltammograms are of a similar shape. Current density for pH 7 is the smallest over the whole course of the curve. The voltammogram recorded for the electrolyte of pH 2 is significantly different to the others, because in

its cathodic part a sharp current peak appears at a potential of about -0.15 V vs. SCE, and from -0.5 V vs. SCE the cathodic current begins to rise sharply, indicating the beginning of gaseous hydrogen evolution. The voltammogram obtained at pH 4 has two cathodic peaks. The first peak is on potential of -0.58 V vs. SCE and the second on potential of -1.48 V vs. SCE. From -1.55 V vs. SCE the cathodic current begins to rise, which also indicates gaseous hydrogen evolution. The cathodic polarization curves in Figure 3 exhibit two separated diffusion plateaus. The first plateau shows that limiting current densities for electrolytes with pH 2 and pH 4 are almost equal (around 0.06 mA/cm²). This value is higher than the limiting current density for cyanide (0.05 A/dm²), and similar to the values recorded for the other non-cyanide electrolytes [15].

4. CONCLUSION

This study shows the method for chemical and electrochemical characterization of electrolyte based on gold complex with mercaptotriazole in acid media which could be used for decorative plating baths and its chemical and electrochemical properties. UV-vis spectroscopy showed that the spectra of the gold complex at pH 2 and pH 7 have very similar lines in the spectra. Spectra at both pH values occur at lower wavelengths compared to that obtained for gold acid. Open circuit potential is the most positive at pH 2. With increasing of pH value it becomes negative, indicating the binding of gold in the form of stable complexes. The highest value of the limiting current density was observed for the electrolyte with pH 7.

5. ACKNOWLEDGMENT

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