Formulation and characterization of electrolyte for decorative gold plating based on mercaptotriazole[☆]

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ABSTRACT

A procedure for the formulation and characterization of a gilding electrolyte based on mercaptotriazole is described. It was found that the electrolyte can be synthesized in a wide pH range, so solutions with different pH values (2, 4, 7, 9 and 12) have been prepared and analyzed. 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.

1. Introduction

The electrodeposition 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, and aerospace applications. [1–5]. The combination of excellent electrical conductivity and high corrosion resistance has led to its widespread use as the standard material for interconnections, bond pads, contacts, as well as conductors, electrodes, and other passive components [6].

Electroplated gold can be classified as either soft gold or hard gold [7].

Soft gold electrodeposition has traditionally been performed using gold cyanide or gold sulphite electrolytes. However both of these electrolytes have inherent problems regarding long term sustainability as well as process incompatibility [1–3,8]. This has led to the search for alternative electrolytes [9–11].

Traditionally, gold has been plated from cyanide electrolytes, where (Au^+) is ligated with cyanide (CN^-). The cyanide electrolyte is exceptionally stable with the stability constant of AuCN being 10^{38} [6]. However, due to fears about safety and the disposal of process waste, there is a growing concern regarding the use of cyanide-based processes [6,9,10]. 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 [3,8,11,12]. The interest in developing non-toxic gold electrolytes, such as those based on a gold sulphite complex, has grown rapidly in recent years [7,13–17].

Over the past few years there has been some interest in gold deposition from an electrolyte containing two different complexants, sulphite as well as thiosulphate. This electrolyte was originally proposed by Osaka and co-workers who used it to deposit soft gold, which was comparable to gold deposited from a sulphite electrolyte [18–20].

Osaka and co-workers [19,20] investigated the possibility of electroplating soft gold from a thiosulphate–sulphite mixed ligand bath, specifically for application to the formation of micro bumps on silicon wafers. This bath is operated at a slightly acidic pH of 6.0, and at a mildly elevated temperature of 60 °C. It is highly stable, and there is no need to add any stabilizer to suppress spontaneous decomposition. They also added phosphoric acid as a buffering agent and thallium ions to soften the deposits. The desirable attributes of this thiosulphate–sulphite electrolyte was that it was stable at near neutral pH, which provided compatibility with photo resists, and that it was more stable than either gold sulphite or gold thiosulphate electrolytes [21].

The possibility of electroplating soft gold specifically for the formation of microbumps on silicon wafers from a non-cyanide bath containing both thiosulphate and sulphite as complexing agents was proposed by Osaka and co-workers [19]. Liew, Roy, Scot and Green at Newcastle have developed an electrolyte for soft gold electrodeposition which has attempted to eliminate Na_2HPO_4 and Tl^+ [22].

The thiourea bath was developed and subsequently improved by a group of investigators at Hitachi Ltd. [23].

Richter and co-workers [24] developed a thiosulphate–sulphite mixed ligand bath with ascorbic acid as the reducing agent. The possibility of developing these baths was initially investigated based on the well-known mixed potential theory combined with partial polarization curves measured at a gold electrode.

Krulik and Mandich [25] reported that the Au(I) thiosulphate–sulphite mixed ligand system functions as an autocatalytic bath in the absence of any conventional reducing agent. They believed that the thiosulphate–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 [26], it retained a sufficient stability in a period of at least three months [27,28].

Detailed investigations were carried out in order to determine the optimum conditions for obtaining quality decorative gold plating from this electrolyte and to compare it with the quality of gold plating obtained from the classic electrolyte [29,30]. Based on experimental investigations, it could be concluded that the quality of decorative gold plating, obtained from a gold complex based on mercaptotriazole, satisfies all requirements of decorative gold plating. The most important advantage of this electrolyte is ecological, as the gold could be regenerated by simply settling with hydrogen peroxide in which the sulphur is precipitated [30].

In this paper we report on: (1) the method of formulation of the electrolytes for decorative gold plating based on a gold complex with mercaptotriazole at different pH levels; and (2) chemical and electrochemical characterization. The gold complexes existing in solution have been examined by UV–vis spectrophotometry and compared with the spectra of other non-cyanide gold complexes. Electrochemical methods are used to determine the characteristics of the electrolyte at different pH.

2. Experimental

2.1. Chemicals

For the synthesis of the gold complex with mercaptotriazole the following chemicals were used: gold powder (99.99% Mining and Metallurgy Institute Bor); hydrochloric acid p.a. (Zorka, Sabac); nitric acid p.a. (Zorka, Sabac), glycine (min. 99%, Alkaloid Skopje), potassium hydroxide (Merck, Germany), distilled water (5 μS/cm) and mercaptotriazole. Mercaptotriazole was synthesized in our laboratory. Thiosemicarbazide, CH_5N_3S (min 98%, Merck, Germany) and formamide p.a. (Alkaloid, Skopje) were used in this synthesis.

2.2. Methods

2.2.1. Raman spectroscopy

Raman spectra of synthesized mercaptotriazole were recorded in the "backscattering geometry", using a μ-Raman system with a Jobin Yvon T64000 three monochromator, and a CCD (charge-coupled-device) detector. As a source for the excitation an Ar laser 514 nm was used. All measurements were done at a laser power of 80 mW. Raman spectra were recorded in the frequency range 100–3500 cm^{-1} with a resolution of 4 cm^{-1}.

2.2.2. IR

Analysis of the mercaptotriazole was done by infrared spectrometry using a Perkin-Elmer 983G Infrared spectrophotometer using the KBr technique (finely pulverized sample), in the range 100–4000 cm^{-1}.

2.2.3. Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

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

2.2.4. Ultraviolet–visible spectroscopy

The gold complex in solution was identified using ultraviolet–visible spectroscopy 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 by performing a fast scan over the wavelength of 190–900 nm.

2.3. Electrochemical techniques and procedures

Electrochemical studies were carried out using cyclic voltammetry, open circuit potential measurement and polarization measurements 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 a gold plated platinum electrode (surface 4.522 mm^2), whose potential was controlled against the saturated calomel reference electrode (SCE). Platinum foil (1 cm × 2 cm) served as a counter electrode.

The computerized control (National Instruments card, NI-6251) and data acquisition software (LabVIEW 8.2 platform and applications specifically developed for electrochemical measurements), fully developed by the Technical Faculty in Bor [31], were used to run the electrochemical experiments. The hardware consisted of a PC, AD/DA converter (PCI-E 20 428 produced by Burr-Brown) and an analog interface developed at the University of Belgrade, Technical Faculty in Bor.

The electrolyte volume used in the experiments was 100 ml. All experiments were carried out at a temperature of $25 \pm 0.5\,°C$.

The pH and conductivity of the electrolytes were measured before and after each electrochemical measurement.

Before the start of each experiment, the electrochemical cell was rinsed twice with distilled water, and then with working solution.

The open circuit potential was monitored for a period of 60 s.

Cyclic voltammograms were recorded with a scan rate of 100 mV/s, in the following potential ranges:

(a) for pH 2: (+1.6 to −0.6) V vs. SCE
(b) for pH 4: (+1.6 to −1.5) V vs. SCE
(c) for pH 7: (+1.5 to −1.3) V vs. SCE
(d) for pH 9: (+1.2 to −1) V vs. SCE
(e) for pH 12: (+1.5 to −1.3) V vs. SCE

Polarization curves were recorded with a scan rate of 5 mV/s in the following potential ranges: for pH 2: (+0.2 to −0.6) V vs. SCE; for pH 4: (+0.2 to −1.1) V vs. SCE, for pH 7: (+0.2 to −1.2) V vs. SCE; for pH 9 and 12 (0.0 to −1.3) V vs. SCE.