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Electrodeposition Mechanism and Process of a Novel Cyanide-Free Gold Sulfite Bath

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Abstract: A novel cyanide-free gold sulfite process is introduced in this paper. In the bath, chloauric acid was directly employed as the main salt, and hydroxyethylidene diphosphonic acid (HEDP) was used as the stabilizer and coating grain refiner. The bath stability, the gold coating morphology and the mechanism of gold electrodeposition were studied in detail. The results showed that HEDP could significantly improve the bath stability. Moreover, the grains of the gold coating obtained from the gold sulfite bath without HEDP was rod-like, which grew gradually with the increasing of the deposition time, resulting in that the appearance of the coating turned from a golden yellow to a hazy reddish brown by the increase of the coating thickness. As HEDP was introduced into the gold sulfite bath, the gold grains were transformed to pyramidal, and the grain growth rate accompanying the increase of the coating thickness was much slower than that in the gold sulfite bath without HEDP, observing the golden bright appearance within 1 μm thickness. Electrochemical curves indicated that gold electrodeposition did not undergo a nucleation stage.

Key words: cyanide-free gold plating; gold sulfite; hydroxyethylidene diphosphonic acid; electrodeposition; gold coating

1 Introduction

Pure gold (soft gold) exhibits excellent electrical and thermal conductivity, ductility, weldability and corrosion resistance. Gold alloy (hard gold), doped with iron, cobalt, nickel or other metals, is known for the excellent wear resistance. For these physical and chemical features, soft and hard functional gold coatings deposited by electrochemical and electroless methods are extensively used in the electronic industry such as connectors, microelectronics packaging and printed circuit boards (PCBs)[1-4]. Cyanide-free gold electrodeposition has been studied and developed for over one century. Sulfite bath[5-7], sulfite-thiosulfate bath[8, 9] and cysteine bath[10] are the main Au(I) cyanide-free gold plating processes. Especially, the sulfite bath has been applied in industrial manufacturing. Furthermore, Au(III) cyanide-free gold plating processes such as 5,5-dimethylhydantoin bath[11,12], hypoxanthine bath[13, 14] and theophylline bath[15] have been reported in the last twenty years.

Gold sulfite bath possesses preferable throwing power and covering power, and the deposited gold coating can satisfy the requirements of microelectronic industry[4]. However, some disadvantages limit the development of the gold sulfite bath. For example, sulfite is easily oxidized by oxygen, leading to a poor bath stability[16]. Hence, the concentration of sulfite is usually high in the bath to stabilize Au(I) ions. High sulfite concentration may cause an increase in the viscosity of bath and sulfur inclusions in gold coating[17].

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To address these issues, Osaka et al.[8, 9, 18] introduced thiosulfate into gold sulfite baths to form gold-sulfite-thiosulfate mixed-ligand complex to improve the bath stability; He et al.[6] added citrate amine to the gold sulfite bath to increase the bath stability and refine the grain of gold coating.

In our previous work, chloauric acid was directly employed as the main salt in the gold sulfite bath[19]. Our results showed that by the introduction of the chloride ions from chloauric acid, the stability of the gold sulfite bath was improved, meanwhile, the electroreduction of gold ions was promoted and the coating grain was fine. In our another previous work, we illuminated that the dimerization of sulfite to metabisulfite was suppressed by hydroxyethylidene diphos phonic acid (HEDP) at the solid/water solution interface [20]. Researches on the mechanism of the developed gold plating process are of great importance in theory and practice. In this paper, we further introduce a novel cyanide-free gold sulfite process. In the process, chloauric acid was directly employed as the main salt, and hydroxyethylidene diphosphonic acid (HEDP) acted as the stabilizer and coating grain refiner. Based on the process, the bath stability, the morphology of gold coating and the mechanism of gold electrodeposition were studied in detail.

2 Experimental Section

2.1 Regents and Solutions

$HAuCl_4 \cdot 4H_2O$, Na_2SO_3 and NaOH were provided by Sinopharm Chemical Reagent Co. Ltd. (China). Hydroxyethylidene diphosphonicacid (HEDP, 60wt%) was purchased from Qingdao Usolf Chemical Technology Co. Ltd. (China). Except for HEDP, all the chemicals were of analytical grade.

The gold sulfite bath contained 0.01 $mol \cdot L^{-1}$ $HAuCl_4 \cdot 4H_2O$, 0.24 $mol \cdot L^{-1}$ Na_2SO_3, 0.05 $mol \cdot L^{-1}$ HEDP and 0.1 $mL \cdot L^{-1}$ addictive. The solution was prepared by the following procedure. Firstly, HEDP concentrate was diluted and the pH value was adjusted to above 10.0. Next, sodium sulfite was added and dissolved in the HEDP solution. Subsequently, chloroauric acid was introduced slowly and the yellow chloroauric acid was reduced to colorless gold sulfite immediately. Finally, the addictive was added and the pH was adjusted to 9.0.

2.2 Galvanostatic Electrodeposition

Gold electrodeposition was performed in the gold sulfite bath on a watt nickel pre-plated copper sheet at 45 ℃, pH 9.0 and current densities of 0.1 ~ 1.1 $A \cdot dm^{-2}$. A platinum plated titanium mesh was served as the anode and the solution was stirred slightly during the electrodeposition.

2.3 Coating Characterizations

The coating thickness was measured via a XAN-DPP X-ray fluorescence spectrometer (Fischer, Germany). The surface morphology of the gold coating was recorded by a scanning electron microscope (HITACHI S-4800, Japan).

2.4 Electrochemical Measurements

Cyclic voltammetric and chronoamperometric measurements were carried out on an Autolab PGSTAT30 potentiostat in a three-electrode cell. A gold electrode with 3 mm diameter, a platinum foil and a Hg/HgO (1 $mol \cdot L^{-1}$ KOH) electrode were employed as the working electrode, counter electrode and reference electrode, respectively. Before each electrochemical measurement, the gold electrode was polished by alumina suspension with the diameters of 0.3 mm and 0.05 mm separately, and then ultrasonically rinsed in ethanol and ultrapure water.

3 Results and Discussion

3.1 Bath Stability

Poor bath stability is one of the main problems to be solved for the gold sulfite process. To investigate the effect of HEDP on the bath stability, we varied the concentration of HEDP in the basic gold sulfite solution ($HAuCl_4 \cdot 4H_2O$ 0.01 $mol \cdot L^{-1}$, Na_2SO_3 0.24 $mol \cdot L^{-1}$, addictive 0.01 $mL \cdot L^{-1}$). Figure 1 shows the appearance of the gold sulfite solutions with various HEDP contents of 0, 0.025 $mol \cdot L^{-1}$ and 0.05 $mol \cdot L^{-1}$ which have been stored in a refrigerator for 4 months at 2 ~ 8 ℃. It can be clearly seen that the brown precipitate appeared in the solution without HEDP (Figure 1a), which means that the gold salt has been decomposed and the gold particle precipitated. However, the gold sulfite solutions with 0.025 $mol \cdot L^{-1}$ and

0.050 mol·L^{-1} HEDP remained colorless and transparent (Figure 1b and Figure 1c). Obviously, the stability of gold sulfite solution is significantly improved by HEDP, which may be attributed to the following three reasons: (I) Gold sulfite could be wrapped with HEDP by hydrogen bonds and thus its spontaneous decomposition to SO_3^{2-} and Au^+ was hindered[21]. (II) It has been reported that the molecules with N, P or O atoms could coordinate with gold ions[22]. Therefore, a weak coordination interaction may exist between HEDP and Au^+. (III) During the oxidation of SO_3^{2-} to SO_4^{2-} and disproportionation of Au^+, a decrease of the pH in solution happened ($3Au^+ \rightarrow 2Au + Au^{3+}$, $Au^{3+} + 3SO_3^{2-} + H_2O \rightarrow Au(SO_3)_2^{3-} + SO_4^{2-} + 2H^+$). By keeping the gold sulfite baths at air and room temperature for 4 months, the pH value of the bath without HEDP decreased gradually from an initial 9.0 to around 3.0 (Figure 1a); and the pH values of the baths with HEDP were still near 7 ~ 8 (Figure 1b and Figure1c). Since HEDP can buffer the pH, the oxidation rates of SO_3^{2-} and the disproportionation of Au^+ are decelerated, thus, the gold sulfite bath is stable.

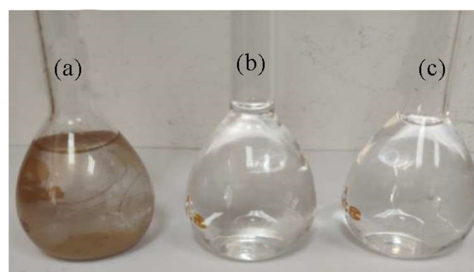

Figure 1 Appearances of the gold sulfite baths after keeping for 4 months: (a) without HEDP; (b) HEDP 0.025 mol·L^{-1}; (c) HEDP 0.050 mol·L^{-1}. (color on line)

3.2 Coating Morphology and Appearance

Effects of HEDP on the morphology and appearance of gold coating were also investigated. Gold coatings with the deposition time of 1 min, 5 min, 10 min and 20 min in the gold sulfite bath without HEDP ($HAuCl_4 \cdot 4H_2O$ 0.01 mol·L^{-1}, Na_2SO_3 0.24 mol·L^{-1}, addictive 0.1 mL·L^{-1}) were prepared in a constant current density of 5 mA·cm^{-2}. Figure 2 shows the morphology and appearance of the obtained coatings. It can be seen that deposition for 1 min, the grains were very fine and compact (Figure 2a) with a golden bright appearance (the upper left corner of Figure 2f). As the deposition time was extended to 5 min, the coating presented rod-like grains with a length of around 200 nm (Figure 2b), and the appearance was slightly foggy and reddish-brown (the upper right corner of Figure 2f). As the deposition time were further extended to 10, 15 and 20 min, the rod-like grains grew gradually, leading to the coatings in fog-

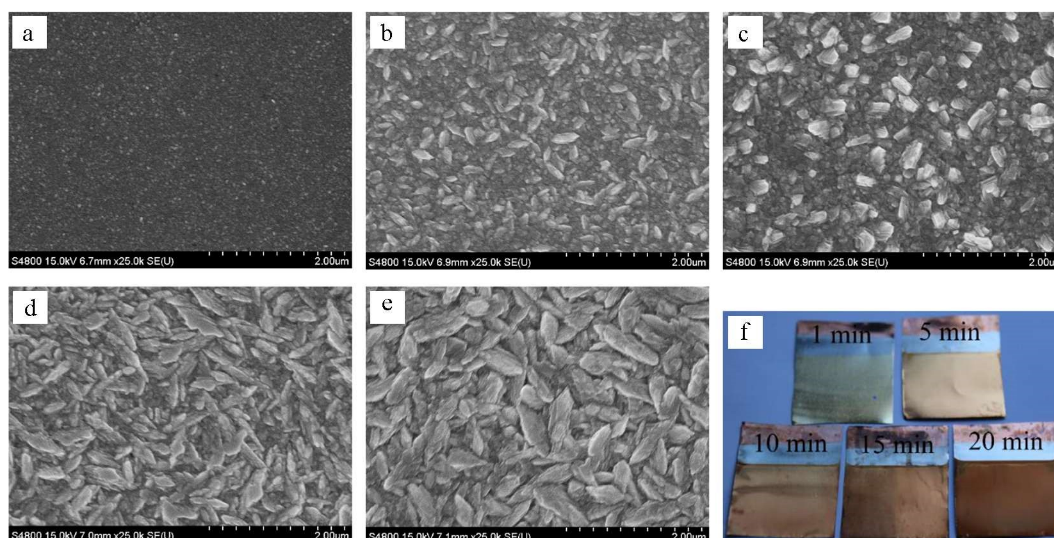

Figure 2 Morphologies of the gold coatings from the gold sulfite bath without HEDP for various deposition time: (a) 1 min; (b) 5 min; (c) 10 min; (d) 15 min; (e) 20 min; (f) photographs showing the appearance of gold coatings. (color on line)

gier and more reddish-brown. As deposition for 20 min, the thickness of gold coating was 0.7 μm, the length of the rod-like grains reached 400 nm (Figure 2e), and the coating showed a deep foggy and reddish-brown appearance (the lower right corner of Figure 2f). The results in Figure 2 reveal a key problem during gold electrodeposition with a low gold ion concentration, that is, with the increases of deposition time and coating thickness, the size of coating grains increased gradually, and thus, the gold coating turned from golden bright to foggy and reddish-brown.

Figure 3 shows the morphology and appearance of the gold coatings with the deposition time of 1 min, 5 min, 10 min and 20 min in the gold sulfite bath with HEDP ($HAuCl_4 \cdot 4H_2O$ 0.01 mol·L^{-1}, Na_2SO_3 0.24 mol·L^{-1}, HEDP 0.05 mol·L^{-1}, addictive 0.1 mL·L^{-1}) in a constant current density of 5 mA·cm^{-2}. As the depositions were processed for 1 min and 5 min, the coating grains became fine and dense (Figure 3a, Figure 3b) with a bright appearance (the upper part of Figure 3f). As deposition for 10 min, the grains presented a pyramidal morphology (Figure 3c). As the deposition time were extended to 15 and 20 min, no significant changes occurred to the coating morphologies (Figure 3d, Figure 3e) and the coating appearance still remained dull bright (the lower part of Figure 3f). As deposition for 20 min, a dull bright gold coating with a thickness of 1 μm was obtained. Therefore, it may conclude that HEDP can significantly improve the quality of gold coating. As HEDP was introduced to the bath, the gold grains were transformed from rod-like to pyramidal, whose growing rate was much decreased, resulting in a golden bright coating appearance.

The morphology and the appearance of the gold coatings for the deposition of 10 min with various current densities in the sulfite-HEDP bath are shown in Figure 4. It is clear that the morphology of the coating is influenced by the current density. When the current density was as low as 0.1 A·dm^{-2}, the grains were very fine and dense (Figure 4a). With the increasing of current density, the grain size increased gradually and resulted in a pyramidal morphology. As the current density was increased to 0.9 ~ 1.1 A·dm^{-2}, the size of pyramidal grains was about 1 μm (Figure 4e and Figure 4f) and the coating appearance was slightly foggy (Figure 4g). Compared with the results from the gold sulfite bath without HEDP in Figure 2, the average coating grain size was much smaller and the appearance was brighter even through at a high deposition current density. This indicates that HEDP can also refine coating grain size at high current densities.

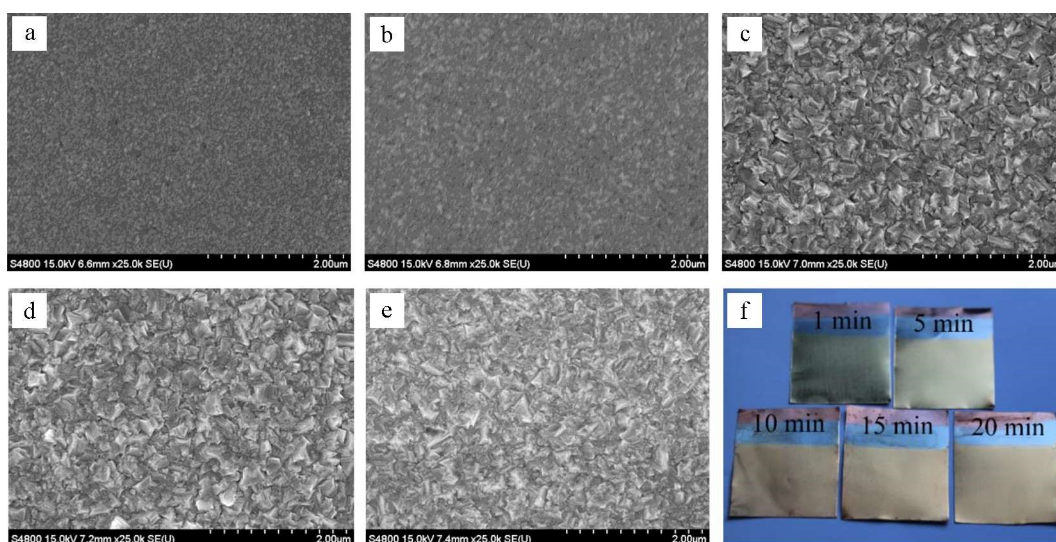

Figure 3 Morphologies of the gold coatings from the sulfite-HEDP bath for various deposition time: (a) 1 min; (b) 5 min; (c) 10 min; (d) 15 min; (e) 20 min; (f) photograph showing the appearance of gold coatings. (color on line)

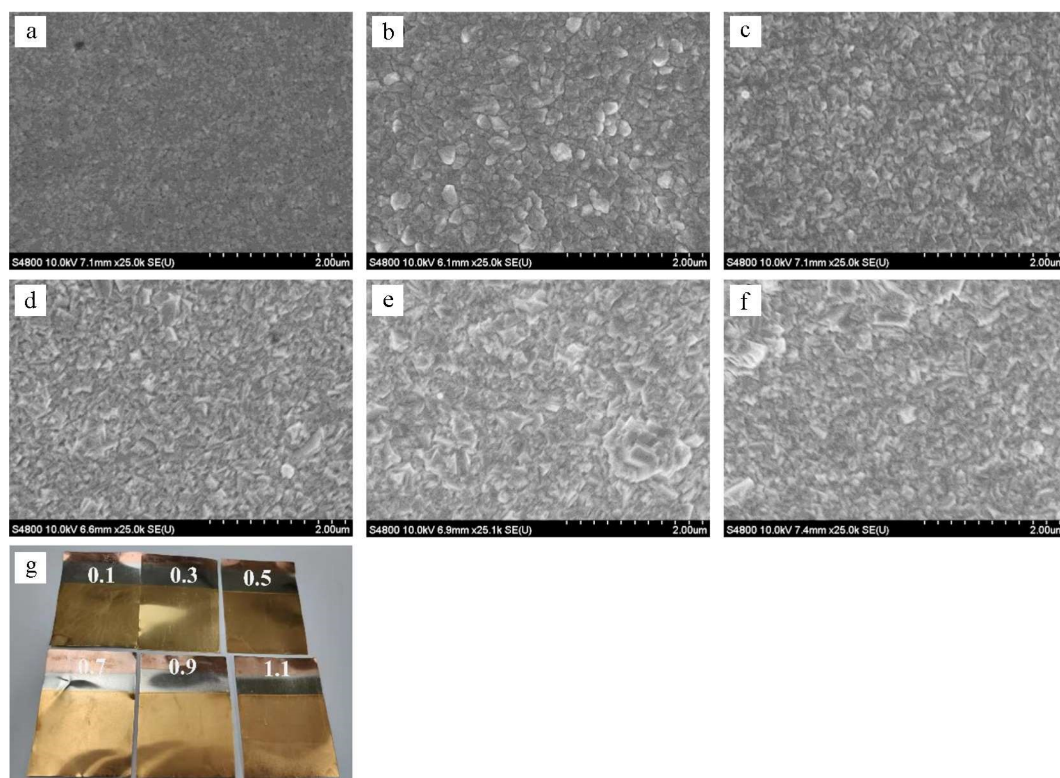

Figure 4 Morphologies of the gold coatings from the sulfite-HEDP bath under various current densities: (a) 0.1 A·dm^{-2}; (b) 0.3 A·dm^{-2}; (c) 0.5 A·dm^{-2}; (d) 0.7 A·dm^{-2}; (e) 0.9 A·dm^{-2}; (f) 1.1 A·dm^{-2}; (g) photograph showing the appearance of gold coatings. (color on line)

3.3 Electrochemical Analysis

The electrochemical behaviors of Au(I) in the sulfite-HEDP bath on a gold electrode and a nickel electrode were studied in detail. Figure 5 shows the polarization curves of the Au(I) electroreduction with and without HEDP on a gold electrode. The curves were scanned negatively from -0.1 V to -1.1 V at a scan rate of 10 mV·s^{-1}. For the bath without HEDP (Figure 5 Curve 1), a gold electroreduction peak appeared at -0.87 V with a peak current density of -0.68 mA·dm^{-2}. For the bath with 0.05 mol·L^{-1} HEDP (Figure 5 Curve 2), the peak potential shifted slight positively to around -0.85 V and the peak current density increased to -0.74 mA·dm^{-2}. The results in Figure 5 illustrate that the electroreduction of Au(I) was accelerated by HEDP. This may be due to that HEDP was wrapped around gold sulfite ions by hydrogen bond to form $Au(SO_3)_2^{3-}\cdot x$HEDP complex ions[21], and then accelerated the mass transfer of gold sulfite.

The acceleration effect of HEDP on Au(I) electroreduction is also observed on a nickel electrode. Figure 6 shows the cycle voltammetric curves of Au(I) electroreduction with and without HEDP on the nickel electrode. The curves were scanned negatively from -0.1 V to -1.1 V, then positively to -0.1 V at a scan rate of 10 mV·s^{-1}. As shown in Figure 6 Curve 1 for the bath without HEDP, gold sulfite ions started being reduced at -0.65 V, and then the cathode current increased rapidly by the negative shift of potential. As 0.05 mol·L^{-1} HEDP was introduced to the gold sulfite bath (Figure 6 Curve 2), the onset potential remained at -0.65 V, but the average cathode current was increased by 40%. No electroreduction peaks can be found in both Figure 6 Curves 1 and 2 on the nickel electrode, which can be attributed to the simultaneous hydrogen evolution reaction during the electroreduction of gold sulfite ion and the hydrogen evolution potential on a nickel electrode is more positive than that on a gold electrode.

The results of the electrochemical experiments in-

dicate that HEDP accelerates the electroreduction of gold sulfite ion, but cannot explain the brightening and refining effects of HEDP on the gold coating. In our previous work[20], we confirmed that HEDP suppresses the dimerization of sulfite to metabisulfite by studying the interfacial reaction of sulfite. Therefore, the dissociated and reduced Au(I) species were transformed from multiple complexes ($Au(SO_3)_2^{3-}$, $Au(SO_3)(S_2O_5)^{3-}$, $Au(S_2O_3)(S_2O_5)^{3-}$) to a single complex ($Au(SO_3)_2^{3-}$). It can be deduced that the reduction of a single gold complex and a weaker hydrogen evolution reaction lead to fine grains and a bright appearance.

Notably, no current loop appeared in Figure 6, indicating that the electroreduction of gold sulfite ion on a nickel electrode did not undergo a nucleation stage[23]. The chronoamperometric curves for the electroreduction of gold sulfite ion in the bath with and without HEDP on a gold electrode and a nickel electrode are shown in Figure 7. The step potentials on the gold electrode and the nickel electrode were -0.85 V and -0.90 V, respectively. All the currents in Figure 7 decayed from a large charge current for electrochemical double layer to a steady gold sulfite electroreduction current, rather than the typical nucleation and growth curves that the current increases first and then decreases following the double layer charging current. Obviously, the current-time transients proved that the eletrodeposition of gold on a gold electrode or a nickel electrode did not undergo a nucleation stage[24, 25], and the gold crystals grew di-

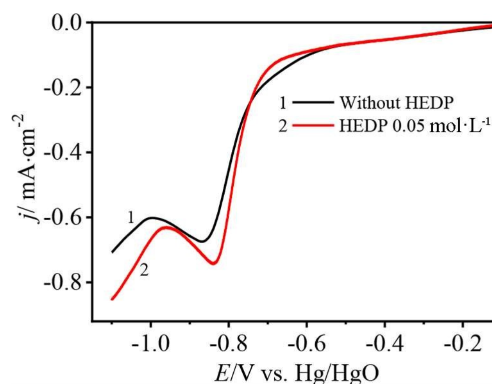

Figure 5 Polarization curves for electroreduction of gold sulfite ions on a gold electrode at a scan rate of 10 mV·s-1 without HEDP (Curve 1) and with 0.05 mol·L-1 HEDP (Curve 2). (color on line)

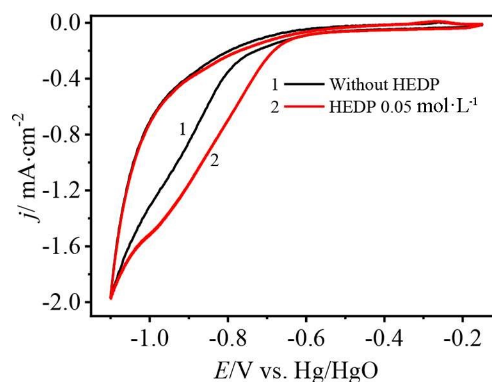

Figure 6 Cycle voltammetric curves for electroreduction of gold sulfite ion on a nickel electrode at a scan rate of 10 mV·s-1 without HEDP (Curve 1) and with 0.05 mol·L-1 HEDP (Curve 2). (color on line)

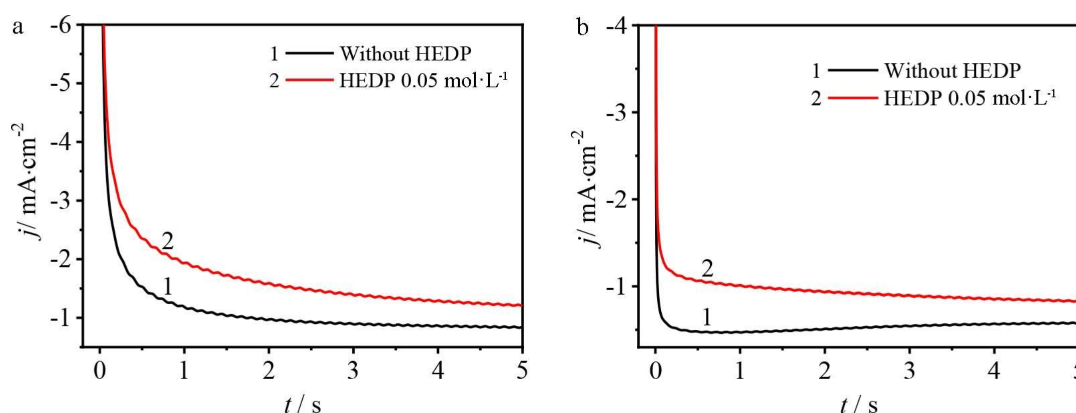

Figure 7 Chronoamperometric curves of the gold sulfite electroreduction: (a) -0.85 V at a gold electrode; (b) -0.90 V at a nickel electrode. (color on line)

rectly along the crystal plane of the substrate. Revisiting the SEM images of the grain growing processes in Figure 2 and Figure 3, we can deduce that since the gold crystals grew directly alone the crystal plane of the substrate rather than undergoing a nucleation stage, the grain size increased gradually with the increase of deposition time, and it was difficult to deposit a thick gold coating with fine and dense grains (Figure 2). For the sulfite-HEDP bath (Figure 3), the growing rate of grians was slowed. However, it is inevitable that the grian size will be increased by the extension of deposition time eventhough with HEDP. Therefore, optimizing the bath components and deposition conditions to promote the gold nucleation is the key factors for obtaining bright gold coatings with fine and dense grians.

5 Conclusions

A cyanide-free gold plating process using chloroauric acid as the main salt directly was introduced in this paper. The bath composition consisted of 0.01 $mol \cdot L^{-1}$ $HAuCl_4$, 0.24 $mol \cdot L^{-1}$ Na_2SO_3, 0.05 $mol \cdot L^{-1}$ HEDP and 0.01 $mol \cdot L^{-1}$ addictive. With the introduction of HEDP, the bath stability was improved significantly and the coating grains became refined. The grains of the gold coating obtained from the bath without HEDP was rod-like, which grew gradually with the increase of the deposition time, resulting in that the appearance of the coating turned from a golden yellow to a hazy reddish brown. As HEDP was introduced to the bath, the gold grains were transformed to a pyramid shape. The growing rate of the pyramidic grains was much slower than that of the rod-like grains, therefore, the coating in the thickness of 1 μm still presented a golden bright appearance. By suppressing the dimerization of sulfite at the solid/liquid interface, HEDP induced the dissociated and reduced Au(I) species to be transformed from multiple complexes to a single complex, resulting in fine coating grains.

Regardless of the introduction of HEDP in the bath, the electroreduction of gold sulfite ion did not undergo a nucleation stage, which is related to the poor appearance of the thick gold coating. By optimizing the bath components and deposition conditions to promote gold nucleation, it is expected to obtain bright gold coatings with fine and dense grains. This work is helpful to provide practical guidance for both understanding the mechanism of gold electrodeposition and devoloping gold electrodeposition process.

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亚硫酸盐无氰电沉积金新工艺及机制

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摘要: 直接以氯金酸作为主盐、羟基乙叉二膦酸(HEDP)作为镀液稳定剂和镀层细化剂、结合添加剂, 组成亚硫酸盐无氰镀金新工艺; 研究镀液稳定性、镀层形态及金电沉积机制。结果表明, HEDP 可明显提升镀液稳定性; 不含 HEDP 的亚硫酸盐镀金液中, 镀层呈棒状晶粒并随沉积时间延长而逐渐生长, 导致镀层外观随镀层厚度增加由金黄色转变为红棕色。镀液含有 HEDP 时, 金晶粒形态由棒状转变为棱锥状, 且棱锥状晶粒随沉积时间延长生长速率较小, 镀层厚度为 1 μm 时仍呈现金外观。电化学实验表明金电沉积不经历成核过程。

关键词: 无氰镀金; 亚硫酸金; 羟基乙叉二膦酸; 电沉积; 金镀层