Mechanisms of Triethanolamine on Copper Electrodeposition from 1-Hydroxyethylene-1,1-diphosphonic Acid Electrolyte

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The effect of triethanolamine (TEA) as a second ligand was studied on the electrodeposition of copper in 1-hydroxyethylene-1,1-diphosphonic acid (HEDPA) electrolyte. The electrochemical behavior of copper deposition was investigated by cyclic voltammetry and electrochemical impedance spectroscopy. The introduction of TEA suppresses the electrodeposition of the copper and promotes the dissolution of copper anode, resulting in fine grains and smooth bright deposits. The “Coordination–Adsorption” theory was proposed to explain the mechanism of action of TEA. The introduction of TEA in the HEDPA electrolyte induces the formation of the CuTEA(OH)2 coordination compounds. The formed CuTEA(OH)2 coordination compounds adsorb on the electrode surface and inhibit the growth of the copper crystal nucleus.

Cyanide copper plating possesses outstanding bonding force and is widely applied as an undercoat for steel die casting parts, zinc die casting parts, and bulk aluminum materials. 1 Because of the high toxicity of cyanide, alternative cyanide–free copper–plating techniques have been developed very rapidly in recent decades. The representative cyanide–free copper–plating systems include pyrophosphate2 and have been developed very rapidly in recent decades. The representatives were carried out by an AutoLab PGSTAT 30 electrochemical workstation, using a three–electrode system with glassy carbon electrode as the working electrode, saturated calomel electrode as the reference electrode, and a platinum electrode as the auxiliary electrode. The glassy carbon electrode was polished to mirror by a piece of 0.05 μm α–Al2O3 powder–covered wetting fine cloth and then rinsed with double–distilled water for several times before each experiment. The tests included cyclic voltammetry (CV) and electrochemical impedance spectroscopy. The solution was purged with N2 for 3 min prior to assay and kept static during testing. The experimental conditions were as follows: temperature, was 25°C; pH, = 9.2; the amplitude of the applied sine wave potential, was 5 mV; the frequency range, was 0.1 Hz–100 kHz; and the applied potential difference, was −1.0 V.

In the electrolyte containing three different amounts of added TEA, the potential difference was set as −1.25 V (vs. SCE). Potentiostatic electrodeposition was conducted on copper electrodes for 10 min (S = 0.25 cm2), and the morphology of the copper coating obtained from electrodeposition was then observed using a Hitachi S–4700 field emission scanning electron microscope.

Results and Discussion

Fig. 1 shows the CV curves of the HEDPA copper–plating systems at different TEA concentrations. In the anodic oxidation region, as the potential difference increases, three oxidation peaks A1, A2, and A3

Experimental

The electrolytic solution for measurement consisted of 0.16 M CuSO4, 0.48 M HEDPA and TEA of various concentrations (0.038 M, 0.076 M, 0.114 M, 0.152 M). The experiments were carried out at room temperature and all reagents were analytical grade. All of the solutions were prepared with double–distilled water and the pH value was adjusted to 9.2 with 1.0 M of NaOH. The electrochemical experiments were carried out by an AutoLab PGSTAT 30 electrochemical workstation, using a three–electrode system with glassy carbon electrode (area S = 0.071 cm²) as the working electrode, saturated calomel electrode as the reference electrode and a platinum electrode as the auxiliary electrode. The glassy carbon electrode was polished to mirror by a piece of 0.05 μm α–Al2O3 powder–covered wetting fine cloth and then rinsed with double–distilled water for several times before each experiment. The tests included cyclic voltammetry (CV) and electrochemical impedance spectroscopy. The solution was purged with N2 for 3 min prior to assay and kept static during testing. The experimental conditions were as follows: temperature, was 25°C; pH, = 9.2; the amplitude of the applied sine wave potential, was 5 mV; the frequency range, was 0.1 Hz–100 kHz; and the applied potential difference, was −1.0 V.

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appear. In the alkaline system, these three oxidation peaks A1, A2, and A3 are ascribed to the formations of Cu₂O, CuO, and CuO/Cu(OH)₂, respectively. With increasing TEA, the effect of TEA on A1 is not obvious, while the two sharp anode peaks, A2 and A3, develop into a broad anode peak, and the current intensity of the anode peak increases with the TEA. Similar to what was proposed by Ravindran Further increase of concentration of TEA caused the disappearances of second and third anodic peaks during zinc-nickel alloy electrodeposition from sulfamate bath. The results indicate the addition of TEA can avoid the formation of Cu(OH)₂ on the surface of copper anode and ensure the continuous dissolution of the anode. By measuring the weight loss of copper anode, it was found that under the same amount of quantity of electric charge (1 A·h), the copper weight loss with a solution containing 0.114 M TEA was 5.9% higher than that without TEA. This is probably because TEA directly reacts with the OH⁻ concentrated near the anode surface and then forms copper complexes such as CuTEA(OH)₂, inhibiting Equation 1.

\[
\text{Cu}_2\text{O} + \text{H}_2\text{O} + 2\text{OH}^- \rightleftharpoons 2\text{Cu(OH)}_2 + 2\text{e}^- \quad [1]
\]

For the cathode reduction region in the figure, the cathode current intensity around –1.41 V decreases with increasing TEA content, indicating the inhibitory effect of TEA on the copper deposition on glassy carbon electrode. Similar results were observed by Calderón et al. during copper electrodeposition from an alkaline Cu-TEA solution. In the copper-plating solution containing HEDPA in the pH range 9–10, [Cu(OH)_2L_2]⁶⁻ (L = HEDP) coordination compound mainly exists. When TEA is added into this solution, however, Equation 2 probably follows, and the balanced reaction as shown in Equation 3 may also occur as the added TEA competes with HEDPA to coordinate Cu²⁺. The formed CuTEA(OH)₂ will be adsorbed on the electrode surface, inhibiting the reduction of copper coordination compound to copper.

\[
\text{Cu}^{2+} + \text{TEA} + \text{OH}^- \rightleftharpoons \text{CuTEA(OH)}_2 \quad [2]
\]

\[
[\text{Cu(OH)}_2L_2]^{6-} + \text{TEA} \rightleftharpoons \text{CuTEA(OH)}_2 + 2\text{L}^{4-} \quad [3]
\]

The CV curves within the potential difference range between –1.05 to –1.35 V in Fig. 1 are magnified, compared, and shown in Fig. 2. “Inductive electric current loop” is formed in the potential surface. The Nyquist figures show that after the addition of TEA, the arc diameter of the semicircle in the first quadrant, representing the resistance of electrochemical reactions, increases with increasing amount of added TEA. This also suggests the inhibitory effect of TEA on the discharging of the HEDPA coordination compound. Inductive resistance arc exists in the mid–frequency in the fourth quadrant and is the inductance component caused by the absorption/desorption of the intermediate products on the electrode’s surface during the reduction reactions. The inductive resistance arc increases obviously with increasing TEA addition amount. The Bode figure shows the presence of a weak peak in the frequency range 0–10 Hz, probably ascribed to the intermediate adsorption products on the electrode’s surface. The peak and valley become obvious as the concentration of TEA increases, further indicating that the addition of TEA promotes the adsorption of intermediate products on the electrode’s surface.

The morphologies of copper plating deposited from the solutions at different TEA concentrations are shown in Fig. 4, indicating that without the addition of TEA in the HEDPA system, the grain of copper plating becomes coarse and the surface is not smooth, with humps. As the TEA concentration increases, the grain of copper plating becomes fine and the surface gets smooth. It is considered that this can be explained by the "coordination–adsorption" mechanism: when the TEA concentration in the solution is high, (1) the competitive coordination...
between TEA and HEDPA forms the copper’s coordination compound Cu(HEDPA)(TEA)(OH), which is more stable than that formed in the system without TEA. The discharging of this copper coordination compound requires a higher overpotential. (2) TEA in the free state or the freshly formed CuTEA(OH) or Cu(HEDPA)(TEA)(OH) may be adsorbed on the surfaces of electrode, and the newly formed crystal nucleus inhibits further growth of crystal nucleus. The specific model is shown in Fig. 5.

In Fig. 5, the crystal nucleus of the primary copper plating formed by the discharging of the more stable complex Cu(HEDPA)
(TEA)(OH) is smaller than those formed in the solution without TEA or only with a small amount of TEA. If there is no adsorption, the film on the surface of the copper crystal nucleus by primary copper plating will continuously grow into the copper grains with irregular shape and large size. However, when TEA or Cu(TEA)(OH) or Cu(HEDPA)(TEA)(OH) is adsorbed on the surface of the primary copper crystal nucleus, further growth of the primary copper crystal nucleus is inhibited, and the copper crystallization overpotential will increase because of the adsorption effect. These effects provide the kinetic conditions for the formation of new crystal nucleus, and thus a new layer of copper crystal nucleus with finer and larger amount of grains are formed by the electrocrystallization process, based on the adsorption film. As this process was repeated, a smooth and fine copper deposition layer was obtained finally.

Conclusions

The addition of appropriate amount of TEA in the Cu²⁺–HEDPA–OH⁻ system was found to improve the quality of the copper deposition layer formed in the Cu²⁺–HEDPA–OH⁻ system. The CV curves and electrochemical impedance testing results indicate that with increasing TEA concentration of the solution, the reduction peak currents decrease, varying the range of “Inductive electric current loop” and increasing the capacitance arc diameter. These variations indicate the inhibitory effect of TEA on the copper electrodeposition on glassy carbon electrodes in Cu²⁺–HEDPA–OH⁻ system, resulting in the fineness and smoothness of the obtained copper deposition layers.

As the second ligand, the effect of TEA’s electrochemical reaction mechanism on the Cu²⁺–HEDPA–OH⁻ system was mainly realized by the complexation and adsorption actions: TEA complex with Cu²⁺ in the competition with HEDPA to form the more stable Cu(HEDPA)(TEA)(OH) type coordination compounds. The excess TEA in the free state in the solution or the newly formed coordination compounds Cu(TEA)(OH)₂ or Cu(HEDPA)(TEA)(OH) can be adsorbed on the surface of the electrode. Such adsorptions can increase the copper reduction overpotential, thus inhibits the growth of the copper crystal nuclei of primary copper and promotes the formation of new crystal nucleus, and finally makes the surface of the copper deposition layer smooth and dense.

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