

Investigation of the Effect of Acidity and Polyethylene Glycol on Electrochemical Deposition of Trivalent Chromium Ions

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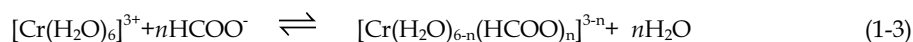
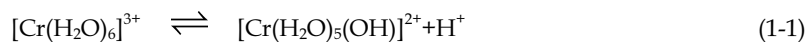
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Abstract:

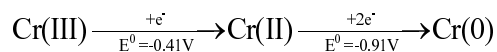
The effect of solution acidity and organic additives, polyethylene glycol (PEG), on the trivalent chromium electroplating was systematically investigated in the view point of solution stability, electroreduction of trivalent chromium ions and characterization of deposition layer. It was found that, the concentration of fraction chromium complexes in the trivalent chromium bath containing formic acid is strongly depended on pH value. PEG molecules were stable in trivalent chromium bath containing formic acid *via* studies on electrospray ionization mass spectrometry (ESI-MS) and UV-Vis. However, the presence of PEG molecules decreased the reductive current of hydrogen evolution, increasing of current efficiency higher about 10 % compared with solutions without PEG. Moreover, PEG additives developed the nodular morphology during electroreduction of trivalent chromium ions with the increase of solution acidity and enhanced its current efficiency by maintaining the consumption of complexant, formic acid, at a low speed. In this study, the effect of solution acidity was emphasized important, there, it controlled the formation of complexes in the solution, cathodic film (CF) during deposition, and properties of deposited layer. By electrochemical quartz crystal microbalance (EQCM), studies show that chromium electrodeposition occurs via the formation of intermediate complexes and adsorption on the cathode surface, which hinder the penetration of ions from bulk solution to the cathode surface.

1. Introduction

The aqueous trivalent chromium baths contain a trivalent chromium salt as $\text{Cr}_2(\text{SO}_4)_3$ characterized by ions such as $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. In the solution containing complexing agent, some HCOO^- ions replaced of H_2O molecules, together with the hydrolysis of aquation:



The solution acidity has strong effected on the formation of complexes in the solution, and it plays the role of deposition. The electroreduction of chromium involves two consecutive steps:



However, the deposition process itself is rather complicated. The change of solution pH and additive can control the quality of deposition. Hence, in this study, electrodeposition of chromium from a Cr(III) bath containing PEG and formic acid was investigated. The purpose of this investigation was to examine of stability and effect of PEG in the plating solution, the effect of pH to the formation of complexes and suggest mechanistic schemes related to the formation of intermediate complexes of chromium during deposition.

2. Experimental, Result and Discussion

The experiment was carried out using the stock solution of trivalent chromium as following table 1. The stability of solution was examined by UV-Vis, ESI-MS and theory calculation, effect of PEG was examined during electroreduction which including measurement of current efficiency, concentration of HCOOH, and chromium ions.

The mechanism of chromium deposition was studied on electrochemical quartz crystal microbalance (EQCM). The samples were characterized by SEM, XRD, XPS and SEM morphology.

Table 1 Bath composition and operating conditions

Composition	Experimental range	Unit
Chromium (III) sulfate	250	g/l
Formic acid	50	g/l
Boric acid	40	g/l
Potassium chloride	75.5	g/l
Anode	MMO	
Temperature	Room temperature	
pH	Variable	
Current type	DC	
Current density	10	ASD

3. Conclusions

The acidity was emphasized great important for the formation of complexes in the trivalent chromium plating solution. Increasing pH value caused increase concentration of hydrolyzed chromium. However, when pH value changed from 1.5 to 3.5 it makes increased concentration of complexes $[\text{Cr}(\text{H}_2\text{O})_n(\text{HCOO})_m]^{3-m}$, which is making metal chromium deposition easier. At pH 2.5, it is existed $[\text{Cr}(\text{H}_2\text{O})_n(\text{HCOO})_m]^{3-m}$ with $m = 1, 2, \text{ and } 3$. In fresh solution, mainly complexes $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ at pH 1.5 and completely convert to hydroxide at pH 6.0. At pH 6.0, in the solution containing formic acid, not only existed on $[\text{Cr}(\text{H}_2\text{O})_n]^{3-n}$ but also on $[\text{Cr}(\text{H}_2\text{O})_n(\text{OH})(\text{HCOO})_m]^{2-m}$.

PEG molecule additives were stable, absorption on the electrode surface, reduced hydrogen evolution during electrodeposition. The effect of PEG by the adsorbed, blocked some part of an electrode surface. It also adsorbed on the cathodic film layer during deposition. The highest CE was achieved at pH 2.5. The presence of PEG make the amorphous deposited layer was nodular structures, smoother and micro-cracks occurred on the surface.

References

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