Effects of Cyclohexane- Monoxime and Dioxime on the Electrodeposition of Cobalt

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ABSTRACT

Electrodeposition of cobalt was studied in presence of two additives, cyclohexane oxime (CHO) and cyclohexane dioxime (CHD), which differ by one oxime group. Cyclic voltammetry (CV), potentiostatic deposition with pulsed rotation rates, and galvanostatic deposition with injections of additives were carried out to understand the formation and breakdown of intermediate species that suppress cobalt electrodeposition. While strong and fast suppression was observed for CHD on cobalt deposition, the suppression effect of CHO was much less pronounced. A negative differential resistance in CV was observed for CHD due to a breakdown of suppression, which was related to the reduction of absorbed Co-CHD chelate species. A critical rotation rate was defined for CHD as the minimum rotation required to enable a fully suppressed deposition state. An inversely proportional relation between additive concentration and the square root of critical rotation rate demonstrated an equilibrium between the diffusion of the intermediate in solution and the consumption of intermediate by incorporation into deposit. While a pair of adjacent oxime groups was necessary for a strong fast suppression effect, bulkier molecular structures and stronger chelating resulted in stronger suppression.

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1. Introduction

Copper back-end-of-line (BEOL) interconnect was invented in late 1990's [1,2] and has been used since then for its superior conductivity, reliability and scalability. However, as the dimension of interconnect structures approaches or even falls below the electron mean free path of copper, the copper resistivity in such very fine structures exponentially increases [3–8]. This is because the electron scattering at interfaces between copper and surrounding materials and at grain boundaries can occur more often than the intrinsic electron scattering and dominate the material resistivity. Therefore, materials with much shorter electron mean free path are of interest [9] because of the insensitivity to scaling even if they have a higher bulk resistivity than copper. Among a list of candidate materials, cobalt has been identified as a front runner [10,11] because of its very short mean free path and relatively low cost.

Electrodeposition of copper interconnects has been studied for more than a decade and the mechanism of a so-called super conformal electrodeposition (or superfilling) has been well understood [12–14]. A preferential deposition at the bottom of a trench results in the defect free formation of interconnect structures. Superfilling of copper are generally accepted as a result of a synergistic interaction of two organic additives during copper electrodeposition[12–19]. An accelerator promotes the deposition rate at the bottom of the trench with respect to the top, where the rate is suppressed by a suppressor. A concentration gradient of suppressor can be present across the depth of the trench, resulting in a lower concentration of suppressor to facilitate the accelerator at the bottom of the trench[19–22]. Such synergistic mechanism between two-component additive system has been exercised for a few other metals[23–26].

On the other hand, a negative differential resistance (NDR), observed as an s-shaped cyclic voltammetry[27–30], has also been found to enable preferential deposition at the bottom of structures due to a positive feedback between deposition and adsorbate consumption (less suppression). Two stable steady states at a single deposition potential can be achieved in such systems. Bottom up deposition in deep silicon via is a result of two different deposition steady states, i.e, fast deposition at the bottom and suppressed deposition at the top[30–32].

A list of different organic additives was previously studied for the superfilling of iron group metals in to sub–50 nm interconnect

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structures using NiFe as an example[33]. Nitrogen groups such as amine and imine were found to suppress the deposition rate whilst thiol groups to accelerate the deposition. A dioxime molecule, dimethylglyoxime (DMG), showed strong and fast suppressing effect on cobalt electrodeposition[34]. In addition, an agitation dependency of the suppression effect was observed, which is expected to potentially enable superconformal filling of cobalt interconnects.

This paper reports a study on the effects of steric structures of oxime molecules on the suppression effect of cobalt electrodeposition. Fig. 1 compares the molecular structures of DMG and cyclohexane dioxime (CHD), which have two methyl groups and a 6-member alkyl ring, respectively. In addition, the role of the pairing of two dioxime groups are also studied with cyclohexane oxime (CHO), which is identical with CHD except for having only one oxime group.

2. Experimental

2.1. Electrochemical cell

A three-electrode cell with a glass frit to separate the cathode and anode solutions was used for the studies. A saturated calomel electrode (SCE) was used as a reference electrode and was placed in a compartment attached to that cathode via a capillary tube. All potentials were measured in reference to this SCE. The anode was a 99.95 at%. cobalt strip placed in the anolyte compartment. The cathode was a platinum rotating disk electrode (RDE) with 5 mm in diameter. The RDE was pre-plated in a cobalt makeup solution before each experiment and was rotated at 100 rpm throughout the studies unless otherwise specified.

2.2. Materials

The cobalt makeup solution contains 0.3 M $CoSO_4$, 0.4 M H_3BO_3, and 0.1 g/L sodium dodecyl sulfate (SDS). The pH of Co solution was adjusted to 4.0 with H_2SO_4. Concentrated solutions of 0.1 wt% (1,000 ppm) CHO and of 0.7 wt% (7,000 ppm) CHD were prepared and added to the Co makeup electrolyte to a predetermined concentration. The studies were carried out using weight concentrations of additives. The molar weights of $—CH_2—$, $—NH—$ or $—O—$ groups are all similar and the total number of such groups are similar at a constant weight concentration of additive. A 0.2 M HCl solution was used to anodically strip the Co from the Pt RDE between each experiment. All salts and organic additives were at least ACS grade and deionized (DI) water with 18 MOhms were used in all experiments.

2.3. Procedures

The detailed experimental procedure of electrochemical studies was similar to a previous report for DMG[34]. A layer of about 100 nm cobalt was pre-plated using the makeup solution at $-10\,mA/cm^2$ for 40 seconds. This cobalt layer is to eliminate the

nucleation effect and keep substrate consistent among experiments. Cyclic voltammetry, chronopotentiometry with additive injections, and chronoamperometry with modulated agitations were carried out to understand the role of oxime groups. Impedance analysis was also carried out to measure the solution resistance, which was 53 ohm and did not change upon the addition of different additives. An Autolab 302N potentiostat was used for all the electrochemical studies.

3. Results and Discussion

3.1. Cyclic voltammetry

The effect of CHD on Co electrodeposition was first investigated with cyclic voltammetry (CV). The Pt RDE was pre-plated before each CV experiment with about 100 nm Co, which resulted in a change of open circuit potential from $-0.3\,V$ for Pt to $-0.48\,V$ for Co. The potential was therefore swept from $-0.48\,V$ to $-1.5\,V$ at a rate of 5 mV/sec. Fig. 2(a) shows the CV results at different concentrations of CHD. A previous study on DMG showed that the partial current density of Co deposition was much more significant than the side reactions for the electrolytes used[34]. Therefore, CVs can be directly compared to show the effect of additives. Co deposition started at around $-0.7\,V$ with no CHD present and steadily increased to $-1.5\,V$. The addition of 10 ppm of CHD caused a suppression of Co deposition up to about $-0.8\,V$, below (less

Fig. 2. Cyclic voltammetry of cobalt electrodeposition on RDE at 100 rpm in presence of (a) CHD and (b) CHO at various concentrations.

Fig. 1. Molecular structures of dimethylglyoxime (DMG), cyclohexane dioxime (CHD), and cyclohexane oxime (CHO).