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Magnetic Properties of Thin Cu/Co Multilayers Made by Electrodeposition

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We have investigated the magnetic properties of electroplated thin Cu/Co multilayers by using electrolytes made of copper sulphate and cobalt sulphate and by applying alternating plating voltage. While the multilayers plated with pure electrolyte showed superparamagnetism, those plated with organic additives showed ferromagnetic behavior. These changes are attributed to the so-called "self-annealing" effect and reduction of grain size caused by the organic additives.

Key words : Copper, Cobalt, Electroplating, Multilayer, Organic additive

1. Introduction

Electroplating has been in use to fabricate various magnetic materials and devices for decades [1-4]. Recently, copper electroplating has made great progress in the semiconductor industry for fabrication of metallic interconnects. One of the interesting features of the Cu interconnect process is that the plating chemistry utilizes organic additives. The additives play an important role in achieving the super-fill process, where plating is faster at the recess and is slower at top planes.

Depending on the roles in baths, organic additives are categorized as accelerators and suppressors. An accelerator is a catalyst and enhances plating current density and, therefore, plating speed. A suppressor is usually a polymer and prohibits plating [4]. Super-fill process is obtained by the adequate accelerators and the suppressors. Additives also alter the grain growth mechanism and change material properties such as crystalline structure, hardness, and surface smoothness [5]. In addition to enabling the super-fill process, additives are known to contribute to the so-called "self-annealing" process where the Cu grains grow slowly at room temperature after deposition. It takes place only when the electrolytes contain proper additives [6-11]. In this work, we have applied the self-annealing phenomenon of Cu to a magnetic structure in an attempt to develop a new magnetic device. Especially, we have investigated the electrochemical characteristics of a few organic materials, applied them in the deposition of thin Cu/Co multilayers, and observed the change of magnetic properties.

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2. Experiments

Electrochemical properties of organic materials were investigated with a cyclic voltammetry (CV) system consisting of a potentiostat (EG&G 273), a rotating disk electrode (RDE), a counter electrode, and a Ag/AgCl reference electrode. In this system, an alternating voltage is applied on the RDE and metallic ions are alternately deposited on and stripped off the surface of the RDE and the current during each cycle is measured. The plating current density is obtained from the integration of the voltammogram [12, 13]. Since the voltammogram area is proportional to the number of charges transferred in the reactions, changes of it allow us to determine the role of each additive. Additives causing the increase of the current density are called as accelerators. The other additives reducing the current density are known as suppressors. Amongst a few organic additives we investigated in the Cu- and Co-electrolytes, SPSA (Sulfopropyl disulfide sodium salt) and DPSA (Dimethyldithiocarbamic acid) had significant effects and we were focused on effect of these materials.

Electrodeposition was carried out using a conventional three terminal method, i.e., with a working electrode, a Ag/AgCl reference electrode, and a flat platinum plate as a counter electrode [12]. The working electrode was fabricated by physical vapor deposition of ~150 nm Cu

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on Si(100) substrates. A potentiostat (Solartron, SI 1286) was used as a power supply for the deposition. Plating voltage was –0.3 V for Cu and –0.95 V for Co, respectively. The Cu/Co electrolyte was made using 120 g/L $CoSO_4 \cdot 7H_2O$, 1.7 g/L $CuSO_4 \cdot 5H_2O$ [1,3], and 50 ppm of chloride ions. Cu/Co multilayers were plated by applying alternating voltage pulses between –0.3 and –0.95 V. By controlling the pulse widths, we could adjust the thickness of the layers.

3. Results and Discussion

We carried out CV analyses of the two accelerators, i.e., SPSA and DPSA, in the mixture of Cu- and Co-electrolytes. Figure 1 shows the increase of current density by SPSA and DPSA in the electrolyte. In proportion to the concentrations of the additives, the current densities increase with different strengths [14]. Note that DPSA is a stronger accelerator than SPSA.

First of all, we have tested effect of the additives on the grain size of Cu films. In order to investigate it, we applied ~0.5 V for rapid Cu deposition. Figure 2 shows the change of the grain size by SPSA and DPSA observed by SEM (scanning electron microscope). Fig. 2(a) is the surface of the Cu film plated with the electrolyte only. The rms (root-mean-square) grain size was ~0.75 μm. As

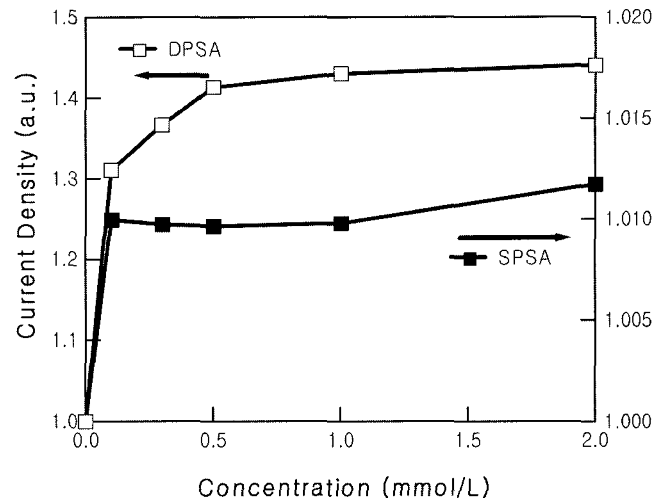

Fig. 1. Increase of plating current density by SPSA and DPSA obtained by the cyclic voltammetry.

we add ~0.5 mmol/L of SPSA, the grain size was reduced to ~0.4-0.6 μm depending on the concentration of SPSA (Fig. 2(b)). As we add DPSA, the grain size was reduced to ~0.3-0.5 μm (Fig. 2(c)).

We then tested effect of the self-annealing caused by SPSA in a Cu/Co bilayer. Figure 3 shows the bilayer of 1 μm thick Cu on top of 1 μm thick Cu film before (Fig. 3(a)) and after (Fig. 3(b)) annealing at 400 °C for 30

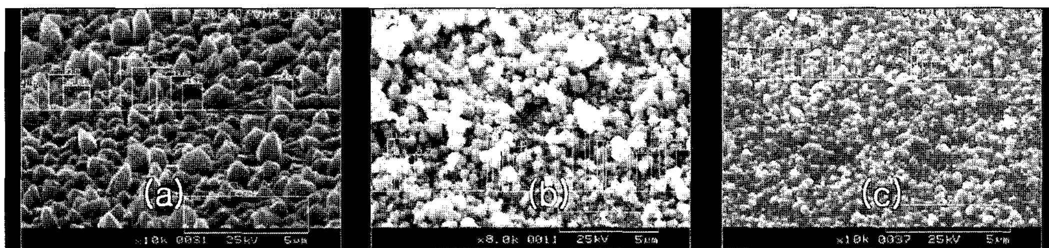

Fig. 2. Surface grains prepared by electroplating at high potential with pure electrolyte only (a), with ~5 mmol/L of SPSA in the electrolyte (b), and with ~5 mmol/L of DPSA in the electrolyte (c).

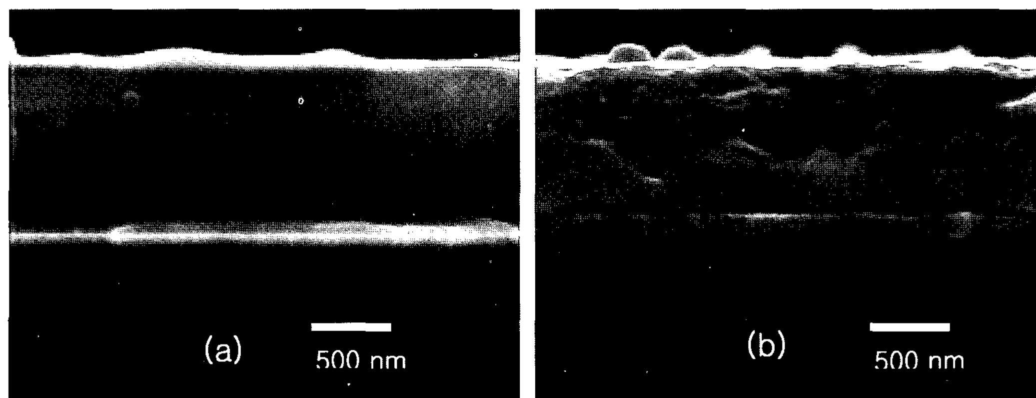

Fig. 3. Cu-Co bilayers before (a) and after (b) annealing at 400 °C for 30 minutes.

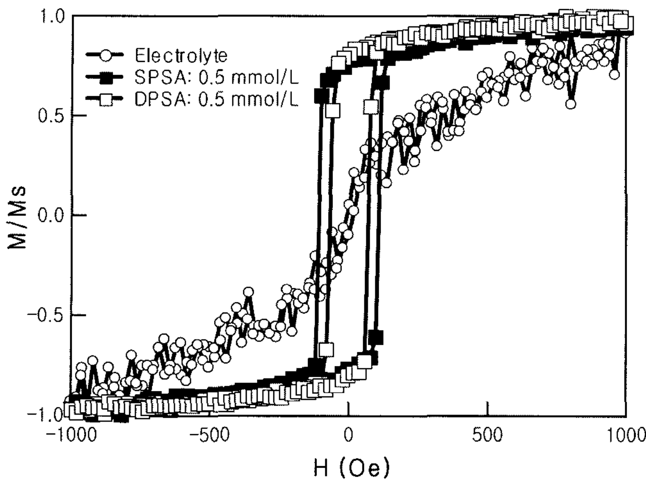

Fig. 4. Magnetization of Cu-Co multilayers prepared with pure electrolyte (open circles), with SPSA (closed squares), and DPSA (open squares) as the field was applied in the plane of the layers.

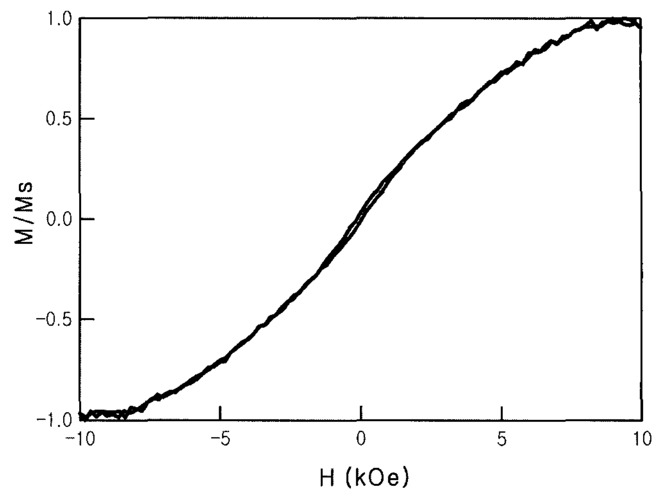

Fig. 5. Magnetization of Cu-Co multilayers prepared with SPSA as the field was applied perpendicular to the plane of the layers.

minutes. We can easily see that the annealing has made the Cu grains grow to the thicknesses of the thin films. However, the growth of Co by the annealing is not as distinct as in Cu.

Figure 4 shows VSM (vibrating sample magnetometer) measurement results of [Cu(1 nm)/Co(1 nm)] × 100 at room temperature as we applied the magnetic field in the plane of the layers. The open circles were obtained from a multilayered film plated with electrolyte only. It is close to one of paramagnets and we think this sample does not have separated Cu- and Co-layers. Instead, it seems to have mixture of Co grains in Cu matrix. A striking difference can be seen as we add SPSA and DPSA. Closed squares are obtained from a multilayer electroplated with an electrolyte containing ~0.5 mmol/L SPSA. Open squares are obtained similarly with ~0.5 mmol/L DPSA. Compared with that prepared with pure electrolyte, they clearly show ferromagnetism. We think that the additives reduce the grain size during deposition and separate the Cu/Co interfaces distinctly. Consequently, Co layers are well separated from the Cu layers. As we apply the magnetic field perpendicular to the planes, the multilayers prepared with pure electrolyte show similar superparamagnetic behavior, while those made with the additives show saturation magnetization at ~10 kOe, as shown in Figure 5. This saturating field is lower when it is compared with the demagnetizing field of Co thin film, $4\pi M \sim 17$ kOe. It can be explained as follows: The EDX (energy dispersive x-ray analysis) result of a thin film prepared with a similar method [15] showed that the Co layer had ~25% of Cu. Considering the Cu contained in Co layers, we expect lower magnetization and reduced demagnetizing field. It has been known that the magnetization of Co-Cu alloy decreases linearly in proportion to the Cu concentration and the relation is known as $dM/dC \sim -1.6$ per added Cu, where C is the Cu concentration [16, 17]. Considering ~25% of Cu concentration and the resulting ~40% reduction of the magnetization, the demagnetizing field of ~10 kOe agrees well with the prediction.

4. Conclusions

We have utilized organic additives in the electrodeposition of thin Cu/Co multilayers. DPSA and SPSA changed the properties of Cu/Co multilayered thin films. They showed super-paramagnetic behavior when plated with electrolytes only. However, they turned to ferromagnets by adding ~5 mmol/L of SPSA or DPSA. It seemed that the additives reduced the grain size of the thin films and made the layer interfaces distinct and, therefore, changed the magnetic properties.

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