Journal of Magnetics 11(3), 119-122 (2006)

Interface between the Electroplated Copper-cobalt Thin Films and the Substrate

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(Received 19 July 2006)

We electroplated copper-cobalt thin films on a silicon substrate, which had 150 nm thick copper seed layer. The adhesion between the two metallic layers could be increased by utilizing a proper organic additive, pulse plating technique, and high temperature annealing. The thin films exhibited columnar growth of the deposits and enhanced adhesion. This is attributed to the grain growth mechanism introduced by the additive and annealing.

Key words : electroplating, Copper, Cobalt, thin film, interface

1. Introduction

For decades, electroplating technique has been in use for the fabrication of various magnetic materials and devices. It has advantages of simple system configuration and low production cost while maintaining relatively high purity of the deposits. However, conventional electroplating techniques have their own limitations on fabricating sophisticated structures such as sub-micron sized alloys and multilayers and on ensuing required properties. In order to overcome the technical barriers, there have been various attempts.

One of the them was to use the pulse plating technique, where the plating voltage was varied between two or more values [1, 2]. This has an advantage of changing the diffusion lengths of the metallic ions in the electrolyte and has demonstrated a capability of reducing contaminants in the deposit layers when producing multilayered structures. Others include reverse pulse plating and repetitive pulse train method. They have demonstrated capability of fabricating narrow wires and thin multilayers [2, 3].

Another kind of technical improvement involves specific organic additives in the electrolytes. The role of additives in the metallic micro- and nano-structures has been studied by both electrochemical and engineering points of view [4]. Depending on their roles in the plating electrolyte, organic additives are categorized as accelerators and suppressors. An accelerator, when included in an electrolyte, enhances charge transfer and contribute to reduction of M^{++} to M^{+}, where M is a metallic element. A suppressor, on the other hand, reduces the plating current density and slows down the deposition rate. Most additives have specified roles, either an accelerator or a suppressor, for each electrolyte. Additives can also alter the grain growth mechanism and, thereby, cause the variation of the micro-structure of the deposits [5]. The effect of proper additives on fabrication of Cu interconnects was to reduce the grain size during the deposition and a rapid growth of the grains, termed as “bamboo structure”, by annealing afterwards [6].

An interesting additive we have employed in this work is Dimethyl-dithiocarbamic acid (DPSA). It is an unique additive for Cu and Co depositions in the sense that at the concentrations between 0.1 and 1 mmol/L, the relative accelerating effect on Cu and Co varies significantly. By adjusting the concentration of DPSA in the plating electrolyte of Cu and Co, the relative content of the two metals could be controlled as low as a few tenths of percent [5, 7]. At higher concentrations it works as a strong accelerator for both Cu and Co.

The pulse plating technique and an appropriate organic additive individually have demonstrated significant technical improvements for development of various devices. However, there still exists another technical difficulty: the interface between the working electrode or, so-called, the seed layer and the deposits. Weak adhesion between the two layers resulted in failure of the electrical connections prior to and during the characterization and operation. In this work, we have introduced the pulse plating technique and a favorable

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additive, i.e. DPSA, at an appropriate concentration to the electrodeposition of thin Cu-Co layer on Cu seeds and observed improvement of adhesion.

2. Experimental

The substrate was n-type Si(100) with ~1 nm of natural SiO_2 layer on the surface. A 150 nm thick Cu layer was vacuum deposited on it for use as a working electrode. The electrical resistivity was ~2 μΩ·cm and the rms (root mean square) roughness was ~1.5 nm.

We made use of two kinds of electrolytes. The first one (ELYT) consists of inorganic chemicals; $CoSO_4$, $CuSO_4$, H_3BO_3, and HCl [8]. The relative content of Cu and Co ions was adjusted to ~1:10 to achieve low surface roughness. The second one (ADDT) is basically identical with ELYT except that it contains 0.48 mmol/L of DPSA.

Electroplating was carried out using a 20 mL cell and three electrodes: a Ag/AgCl reference electrode, a platinum plate working as a counter electrode, and the 150 nm thick copper seed as a working electrode [9]. A potentiostat (SI1286, Solartron) was used as a power supply. With the system the plating voltage for Cu was 0.29 V and that for Co was 0.95 V, respectively. The pulse width and duration time for 0.29 V was 9 s and 10 s, respectively, and those for 0.95 V was 1 s and 10 s, respectively. The current density was 1×10^{-4} - 5×10^{-4} A/m^2 and the deposition rate was 1-2 nm/s. Film thickness was controlled by adjusting the number of the pulses and was later confirmed with an SEM.

High temperature annealing was carried out using a RTA (rapid thermal annealing system, KVR-020, Korea Vacuum Technology). The rising time was 10-60 s, the annealing time was 30 min, and the falling time was 30-40 min.

3. Results and Discussions

We studied the magnetic property of the Cu-Co thin film using a VSM (Vibrating Sample Magnetometer, Model 7407, Lakeshore). Figure 1 is a typical magnetization behavior of a 100 nm thick Cu-Co thin film made with ADDT, when the magnetic field was applied parallel to the plane of the film. The coercivity was 2.0 ± 0.2 Oe. While a similar structure prepared with a vacuum deposition method exhibits lower coercivity after rapid thermal annealing at 200-500 °C [5], our films did not show considerable difference by the same thermal treatments. However, by annealing at 600 °C for 30 min, the specimen turned to non-ferromagnetic. It is known that annealing of the similar structures increases the grain size and turn to multi-domain structures and, as a result, coercivity becomes lower. In our samples, however, the grain size is larger than that prepared with vacuum method since DPSA contained in the electrolyte, ADDT, enhances the grain growth rate and enables larger grains [3]. Since the grains are large enough, the annealing did not cause further increase of the grains and, thereby, the magnetic properties did not exhibit any noticeable change. As for the paramagnetic behavior upon annealing above 600 °C, we think that the thin Cu and Co layers diffuse across the interface, completely mix together, and turn to super-paramagnetic. It needs further investigation to verify this property.

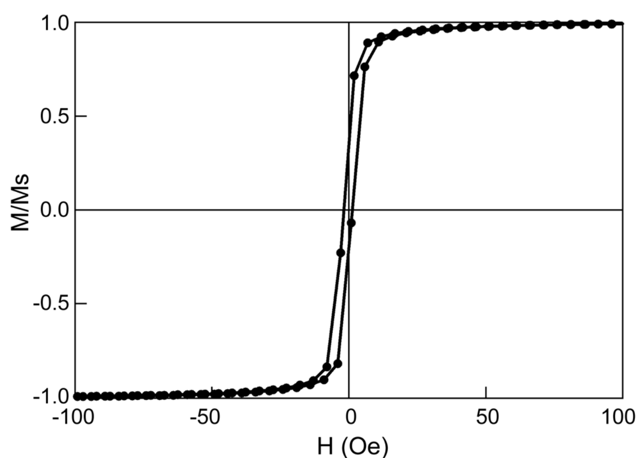

Fig. 1. Magnetization behavior of the ~360 nm thick Cu-Co thin film.

Structural and chemical analyses of the interface were performed by using a high resolution transmission electron microscope (HRTEM, JEOL JEM-2100F, 200 kV) equipped with an energy dispersive X-ray (EDX) spectrometer. Figure 2 is a TEM micrograph of a 500 nm thick Cu-Co film plated with ELYT. It shows that the thin film is mostly made of vertical columns of Co (bright) and partial thin layers of Cu (dark). EDX (Electron Dispersive X-Ray) analyses indicate that the Cu concentration was ~25%. This is a considerably higher compared with the electrolyte composition. This is due to the alternating plating voltage; when 0.29 V pulse is

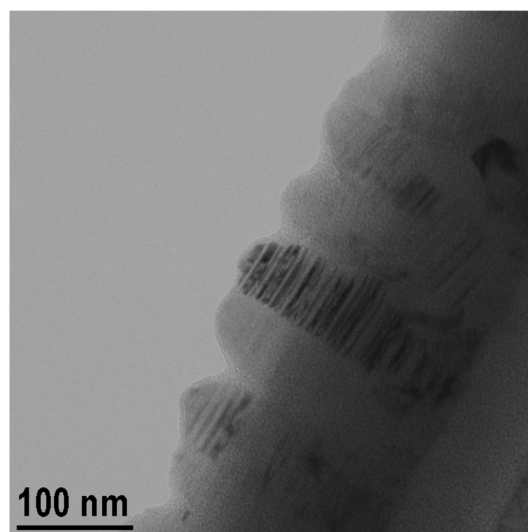

Fig. 2. TEM micrograph of an as-deposited Cu/Co thin film with ELYT: the dark area is Cu and the bright area is Co.

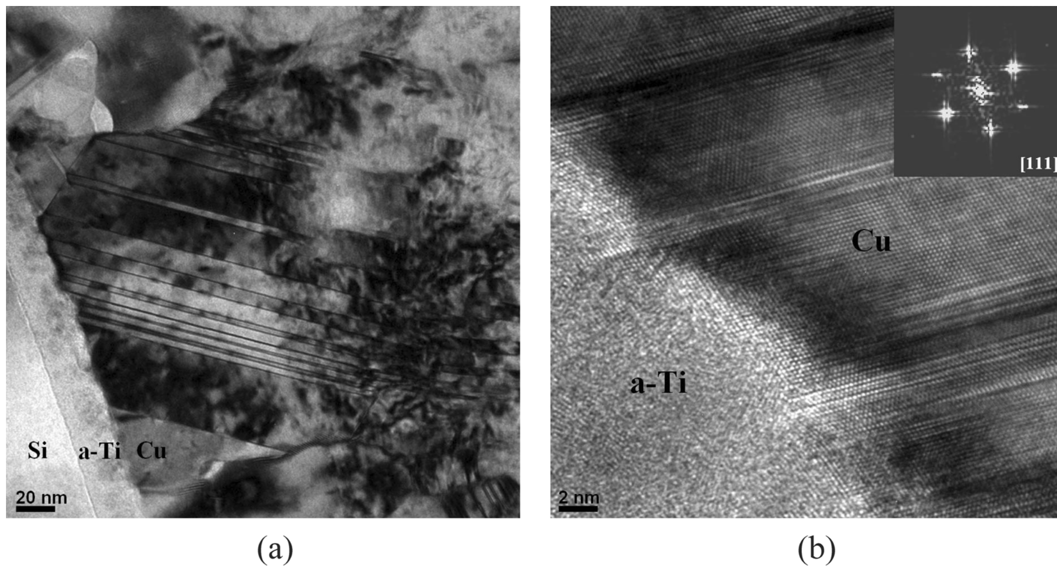

Fig. 3. TEM micrograph of the interface between Cu seed layer and substrate with DPSA after annealing at 500 °C for 30 min illustrating the vertical growth of the thin film: (a) Cu seed layer on Si(100) substrate and (b) high resolution TEM view of the interface between amorphous Ti layer and Cu seed layer.

applied, Cu is deposited and when 0.95 V is applied, Co and Cu are deposited simultaneously, resulting in higher concentration of Cu. Furthermore, since DPSA works as a strong accelerator for Cu, reduction of Cu^{++} could have been at higher rates [5]. It is also interesting to note that Cu deposits were embedded in the Co columns and has horizontal laminar structures. This is also caused by DPSA, which was demonstrated as a conformal growth in the electroplating process of Cu metallic interconnects [6].

Figure 3 shows the interface after annealing at 500 °C for 30 min. Figure 3(a) illustrates the grain growth by annealing. It shows that most of the grains grew by twin mechanism; a typical enlarged grains observed in the annealed Cu interconnects. The twining structure takes place when an appropriate organic additive is employed in the plating electrolyte [6]. Figure 3(b) is a high resolution TEM micrograph at the interface between the amorphous Ti layer and the Cu seed. The inserted fast fourier transform (FFT) of HRTEM image in Cu seed area shows that the grain growth started at the seed layer in the [111] direction of Cu. Furthermore, the vertical columns grew maintaining the crystalline structure of the seed layer. It clearly indicates strong adhesion of the deposits with the Cu seed. We have not observed a similar growth behavior when plated with ELYT. We think this unique adhesion is caused by DPSA in ADDT. The grain growth mechanism is caused by DPSA, which reduced the grain size of the deposits [10] during electrodeposition and enabled grains to grow to twin structures [6] upon high temperature annealing.

4. Conclusions

We made use of a proper organic additive and pulse plating technique to fabricate a thin Cu-Co layer on Cu seeds. The coercivity of electroplated thin films was larger than those prepared with vacuum deposition techniques and high temperature annealing did not change the behavior. This is attributed to the effect of the additive, i.e. DPSA, which increases the grain size during the electrodeposition. Since the deposits have large grains, annealing did not cause further increase of the grains and the magnetic property did not change. However, DPSA in the electrolyte and the following high temperature annealing enabled vertical growth of grains and strong adhesion of the deposits on the seed layer. We think the strong adhesion of the thin layer have shown the possibility of using it for fabrication of various magnetic structures of Cu and Co.

Acknowledgments

This work was in part supported by grant No. R05-2002-000-00626-0 from the Basic Research Program of the Korea Science & Engineering Foundation (KOSEF) and R11-1999-066-06002-1 from the Research Center for Advanced Magnetic Materials (ReCAMM) at Chungnam National University.

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