

Electrodeposition of Cobalt Nanowires

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Received December 6, 2012, Accepted December 28, 2012

We developed an electroplating process of cobalt nanowires of which line-widths were between 70 and 200 nm. The plating electrolyte was made of CoSO₄ and an organic additive, dimethyldithiocarbamic acid ester sodium salt (DAESA). DAESA in plating electrolytes had an accelerating effect and reduced the surface roughness of plated cobalt thin films. We obtained void-free cobalt nanowires when the plating current density was 6.25 mA/cm² and DAESA concentration was 1 mL/L.

Key Words : Cobalt, Electroplating, Nanowire, Additive, Super-fill

Introduction

Metal nanowires have been widely studied for application in semiconductor devices and MEMS (Micro Electro-Mechanical System) elements. Nanowires of magnetic materials such as nickel, iron, cobalt, and alloys of them are one of the most widely investigated structures because of their possible applications in high density magnetic recording media, sensor elements, and building blocks in biological transport systems.¹⁻⁶ Typical fabrication methods have been chemical vapor deposition, physical vapor deposition, and electrodeposition. Electroplating is particularly interesting because of the unique merits such as low production cost, high purity of the products, and high throughput. One of the simplest methods to fabricate metal nano-structures using electroplating is the so-called “template-assisted electroplating” which makes use of porous membranes such as anodized aluminum oxide (AAO) disks, polycarbonate filter membranes, and diblock copolymers.⁷⁻⁹ This method is cost effective and can be used for mass production of nanowires with controlled geometry and morphology.¹⁰

Cobalt nanowires have large crystalline anisotropy due to their hexagonal close packed (hcp) structure, high coercivity, and large squareness, which are favorable properties for magnetic data storage devices and MEMS elements. We have previously reported the structural and magnetic properties of cobalt nanowires prepared by template-assisted electrodeposition into polycarbonate membranes.¹¹ While the template-assisted electroplating has been successful in producing nanowires of favorable magnetic properties, the wire arrays aligned vertically inside of a supporting matrix have limitations in being integrated into devices. Therefore, most devices of complicated geometry and various dimensions are fabricated by lateral deposition method. Indeed, lateral electroplating of copper has been employed for fabrication of damascene interconnect structures in semiconductor industry since mid 1990's. In this process, plating electrolyte

contains CuSO₄, H₂SO₄, and HCl. In order to enable fast plating speed at the bottom than at the top of the patterns, *i.e.* super-fill process, an organic additive set usually made of 2 or 3 species of organic chemicals are added to the plating electrolyte.¹²⁻¹⁹ Organic additives are categorized as accelerators and suppressors depending on their roles in plating process. An accelerator enhances charge transfer contributing to the reduction of metallic ions and increases current density at a specified plating voltage. A suppressor usually is a polymer reducing current density during deposition. Saccharine and polyethylene glycol are widely used as an accelerator and a suppressor, respectively, for metal electroplating. Their role in electroplating has been reported previously.^{16,18}

In this work, we have studied a method of filling Co in damascene structures of which line widths were between 70 and 200 nm. By making use of an appropriate additive, dimethyldithiocarbamic acid ester sodium salt (DAESA), we demonstrated a void-free gap-fill of narrow inlaid features.

Experimental

Physical vapor deposition method was used to prepare seed layers or working electrode consisting of 10-nm thick Ti and 20-nm thick Cu. The crystalline orientation of the Cu seed layer was principally Cu(111), with the remainder being Cu(100). The plating electrolyte was composed of 120 g/L of CoSO₄·7H₂O and 45 g/L of H₃BO₃ in distilled water.²⁰ Galvanostatic plating was carried out using the conventional three terminal method.²¹ Plating current density was 5-20 mA/cm² and the thickness of the deposit was controlled by adjusting the plating time. The effect of organic additives on plating current density was characterized using a commercial cyclic voltammetry system (QL-10, ECI Technology).²² Concentration of DAESA was below 20 mL/L. During the plating, the electrolyte was agitated with a magnet bar at 150 rpm. The film thickness was controlled to 400-500 nm for the blanket wafers and was 50-500 nm for the trench patterns of damascene structure. Electrolyte composition and plating condition are summarized in Table 1.

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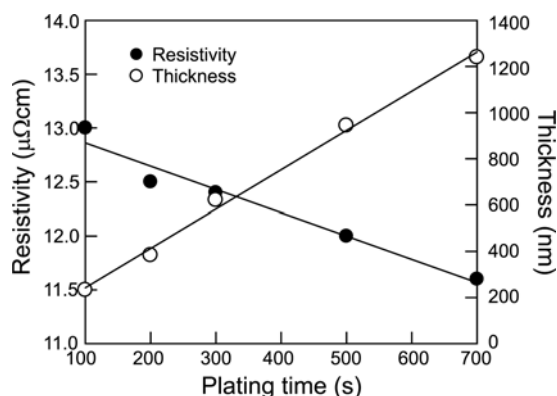
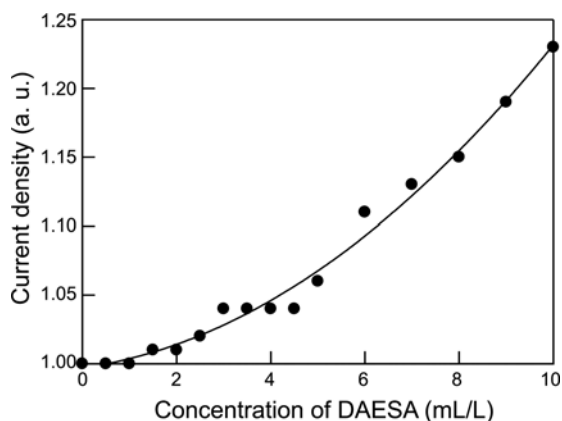
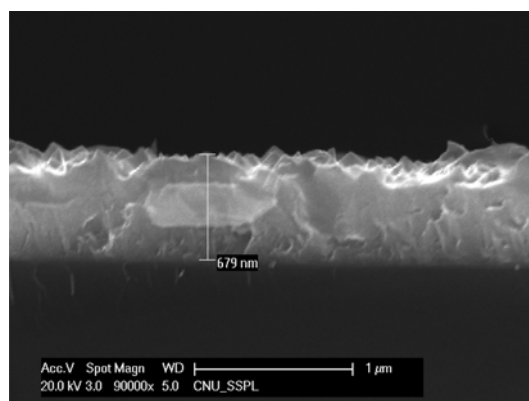
Table 1. Composition of the plating electrolyte and plating condition

| | |
|--------------------------------------|--------------------------|
| CoSO ₄ ·7H ₂ O | 120 g/L |
| H ₃ BO ₃ | 45 g/L |
| Current Density | -6.25 mA/cm ² |
| DAESA Concentration | 0.1-10 mL/L |

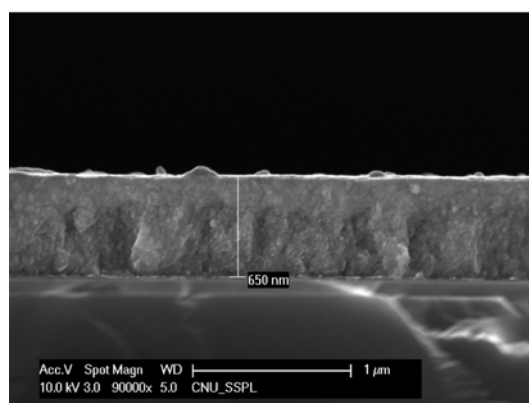
Surface roughness of the thin films was characterized by measuring the root mean square (rms) roughness of the sample over a scan area of 1.0 μm × 1.0 μm by atomic force microscopy (AFM). The electrical resistivity was measured using a 4-point probe resistivity measurement apparatus.

Results and Discussion

We varied the plating time and obtained thin films of different thickness. Figure 1 shows the changes of electrical resistivity and the film thickness of Co thin films when the plating current density was 6.25 mA/cm² and the plating time was varied from 100 s to 700 s. As the film thickness increased from 233 nm to 1240 nm, the electrical resistivity decreased from 13 μΩ·cm to 11.6 μΩ·cm, which is a typical behavior caused by the decrease in surface scattering of

**Figure 1.** Changes of the electrical resistivity and the film thickness depending on the plating time. The solid lines are fits to linear functions.**Figure 2.** Effect of DAESA on plating current density of Co. The solid line is a fit to an exponential function.

(a)



(b)

Figure 3. Cross-sectional view of the plated Co thin films: (a) a thin film plated without DAESA in the electrolyte and (b) a thin film plated with 10 mL/L of DAESA in the electrolyte.

transport electrons.

The organic additive, DAESA, employed in the experiment exhibited an accelerating effect. Figure 2 shows the effect of DAESA on plating current density of Co. As the concentration of DAESA in the electrolyte increased from 0 to 10 mL/L, plating current density increased exponentially up to 22%. This property is very similar to the role of SAPS (Saccharine-*N*-3-propanesulfonic acid, sodium salt) in Ni electroplating.²³ In addition to being an accelerator, DAESA reduced the surface roughness of plated Co thin films. As shown in Figure 3, as we added DAESA in the plating electrolyte, the surface roughness of the plated Co thin films was significantly reduced. Figure 4 shows the quantitative changes in rms roughness of plated Co surfaces; as the concentration of DAESA increased from 0 to 10 mL/L, the roughness was reduced from ~21 nm to ~4 nm. Further increase of DAESA concentration to 20 mL/L resulted in slight increase in the surface roughness.

Gap-fill performance of the plating electrolyte has been extensively tested by changing the plating current density and the concentration of DAESA. While the surface roughness was lowest with 10 mL/L of DAESA concentration, void-free gap-fill of 70-200 nm line-widths was obtained when DAESA concentration was 1 mL/L and the plating

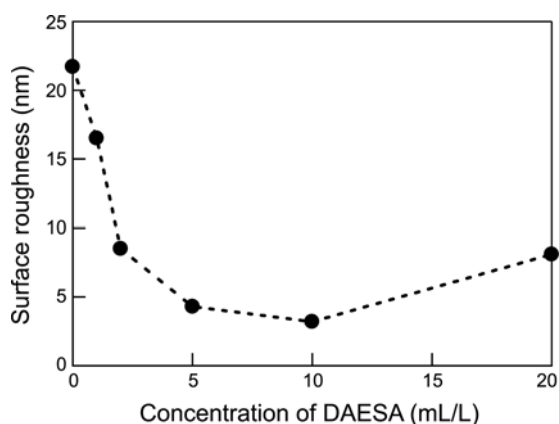


Figure 4. Reduction of the surface roughness of plated Co surfaces by DAESA.

current density was 6.25 mA/cm^2 . Figure 5 shows time evolution of the gap-fill process of 70 and 200 nm line-widths between 10 and 100 s after startup of the electroplating under the optimized plating conditions. The SEM images are significantly blurred because of the interaction between electronic spin and the magnetic moments of Co. The successful gap-fill could be clearly demonstrated after coating the surface with Pt and polishing the side-walls with FIB (Focused Ion Beam), as can be seen in Figure 6. While the surface roughness was lowest and plating current density was relatively high when the concentration of DAESA was

10 mL/L, optimum condition for the gap-fill was obtained when the DAESA concentration was 1 mL/L. It can be explained in terms of preferential coverage of the additives and the resulting difference in the plating speed between top and bottom surfaces of trenches. When both an accelerator and a suppressor are employed for deposition of 200-500 nm wide trenches, suppressor elements adheres at the top surface and prohibits electrodeposition while the accelerator molecules

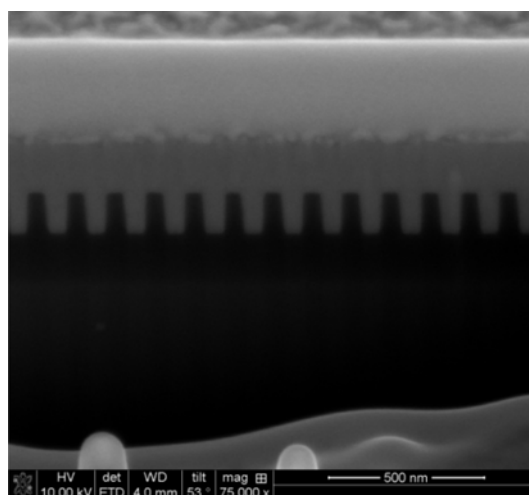


Figure 6. SEM micrograph of the 70 nm line-widths after coating of Pt on the surface of plated Co nanowires and polishing with FIB.

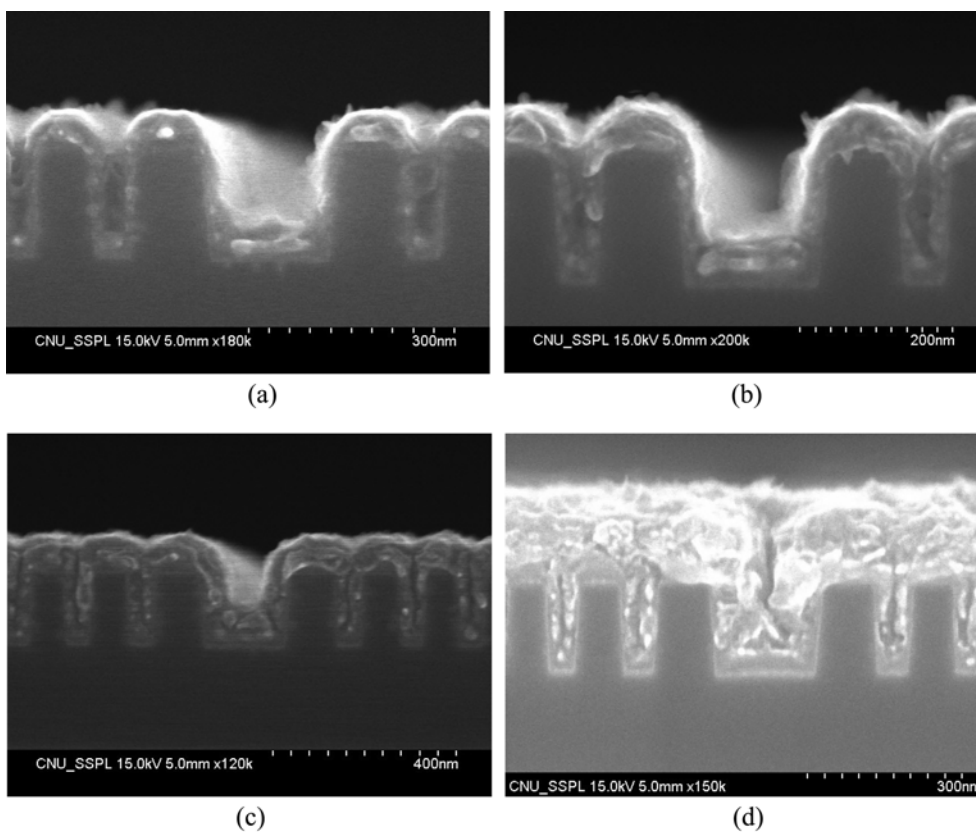


Figure 5. SEM micrographs showing the gap-fill process of 70 and 200 nm line-widths; (a) 10 s, (b) 20 s, (c) 50 s, and (d) 100 s after startup of electroplating.

are populated mostly at the bottom of the trenches and enhances the plating speed.^{15,16} Typical process window of accelerators is 2-5 mL/L and that of a suppressor is between 5-15 mL/L. The difference of plating speed enables super-fill or bottom-up fill process. In our case, a single accelerating agent with relatively lower concentration has been added to the electrolyte and a suppressing agent has not been employed. We think that lack of suppressor and low concentration of an accelerator maintained the appropriate difference in the plating speed between the top and bottom of the trenches and, therefore, superfill process has been accomplished. One of the weaknesses of this approach is the narrow process window; with other concentration of DAESA and different plating current density, voids were observed in the Co nano-wires.

Conclusion

We tested the effect of plating current density and an organic additive, DAESA, on the plating procedure of Co. DAESA had an effect of increasing the plating current density and reducing the surface roughness. By employing the plating current density of 6.25 mA/cm² and 1 mL/L of DAESA concentration, we demonstrated that Co nanowires with line-widths between 70 and 200 nm could be successfully fabricated. We think this method can be applied for electroplating of other materials with similar electrochemical properties such as nickel. The fabricated Co nano-wires could be used for nano-structured systems such as MEMS devices, sensing elements, and an alternative of copper interconnects.

Acknowledgments. This research work was supported by the National Research Foundation of Korea Grant (NRF-2011-0013323). The authors appreciate help of KCTECH for their supply of patterned wafers.

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