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Effect of Hydrophobicity of Cathode Template on Copper Filling Into Nanoholes by Electrodeposition

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Extended Abstract

The advantage of employing a supercritical carbon dioxide (sc-CO₂) fluid for electrodeposition of metal into highaspect ratio microholes has been reported in our previous study [1]. The feasibility of enabling this technique to fill metal into an array of nano-sized holes has also been confirmed [2]. However, the merit of sc-CO₂ electrodeposition seems dependent on the hydrophobicity of the electrode used. Thus, in this study, both hydrophilic and hydrophobic anodized aluminium oxide (AAO) templates were used as the cathode arrays and the efficiency of metal filling into the high-aspect ratio nanoholes was evaluated and compared.

Copper metal filling into heat-treated AAO nano-array holes was attempted by electrodeposition involving emulsified sc-CO₂ fluid, in comparison with that performed using conventional process at ambient pressure. The AAO template was likely hydrophobic in nature after being heat treated at 860 °C/24h. It had a dimension of about 5 um in thickness with an average hole-size of 60 nm and an aspect ratio of 83. Copper electrodeposition was conducted at 50 °C and at a pressure of 10 Mpa in an electrolyte consisting of 40 vol% of sc-CO₂ and 60 vol% of CuSO₄ aqueous solution. Both constant potential (-0.4 V_{Pt}, -0.5 V_{Pt}, -0.6 V_{Pt}) and constant current density (-10 mA/cm²) conditions were applied for metal filling. After electrodeposition, the extent of metal filling was examined using a scanning electron microscope (SEM) and a transmission electron microscope (TEM), both coupled with an energy dispersive spectrometer (EDS).

When as-anodized AAO template was used, a higher filling efficiency (in terms of cross section area percentage) was found in sc-CO₂ bath than in conventional bath. When heat-treated AAO template was used, copper filling into the high aspect ratio nano-holes could be successfully achieved by $sc-CO_2$ electrodeposition, while it was not possible in conventional bath. The advantage of $sc-CO_2$ electrodeposition over that of conventional process was mainly attributed to the change of hydrophobicity of AAO template induced by heat treatment.

Keywords: High Aspect Ratio Nano-Hole, Copper Electrodeposition, Anodic Aluminum Oxide, Hydrophobicity, Supercritical Carbon Dioxide Fluid.

References

- [1] Ch.-Y. Li, J.-J. Yang, W.-T. Tsai, Ch.-J. Lin, T.-F. Mark Chang, and M. Sone, "High aspect ratio micro-hole filling employing emulsified supercritical CO₂ electrolytes," *J. of Supercritical Fluids*, vol.109, pp.61-66, 2016.
- [2] W.-T. Tsai, J.-J. Yang, Ch.-L. Cheng, "Enabling high aspect ratio nano-hole metal filling by employing supercritical carbon dioxide electrochemical deposition," in *Proceedings of the World Congress on Recent Advances on Nanotechnology (RAN'16)*, Prague, Czech Republic, 2016.