Magnetic Field Effect on Electrodeposition of Copper Nanowire Arrays

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Introduction

Copper nanowire array was potentiostatically electrodeposited into 100 or 200 nm nano-sized pore of PC filter, based on Searson's technique [1]. The transient current was monitored at the cathodic potential of –400 mV vs. Teflon coated Cu wire conventional reference electrode. The significant difference was illustrated between the transient current variation for cathode over anode (C/A) and anode over cathode (A/C) configurations [2]. A kind of natural convection may be induced even in such a nano-sized pore. Now that, the magnetic field of 5 T is superimposed to induce a micro MHD effects.

Experimental

The electrolytic cell of C/A configuration is demonstrated in Figure 1. A/C configuration is also tried. One side of a polycarbonate filter surface with 200 or 100 nm sized pores was sputtered with Pt-Pd alloy. The thickness of sputtered layer was roughly 100 nm. It works as a cathode substrate, when a pore is filled with 0.6M $CuSO_4$– 5mM H_2SO_4 aqueous solution. Most experiments were carried out with a potentiostatic method. A Teflon coated Cu wire was used as a conventional reference electrode. It was faced to the cathode surface with 3 mm distance. The electrolytic cell was sometimes installed in a strong magnetic field provided by the cryocooled superconducting magnet at the High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University, Japan. Figure 1 also shows the direction of the applied magnetic field.

Results and Discussion

The transient variation of cathodic current is shown in Figure 2. When the electrodeposition at –400 mV vs. Cu/Cu^{2+} reference electrode is started onto the cathode facing upward in the bottom of 200 nm nanopores (A/C), the current rapidly decreases from 1.5 to 0.6 mA within 10 seconds in Stage I. It slightly increases over 230 to 260 seconds in Stage II, quickly rises up to 1.0 mA around 300 seconds (Stage III) and is thereafter saturated at such a value (Stage IV). The C/A configuration shows a similar behavior to that for A/C except for Stage II and IV. The current slightly decreases with time over 300 seconds (Stage II). It shows a small peak around 380 seconds, followed by further decreasing with time in Stage IV.

Stage I must correspond to the transition from the nucleation to the ionic mass transfer-controlling mode characterized in Stage II. These nano-sized pores are once filled up with Cu to introduce an increased effective surface area in the pore. The current suddenly increases in Stage IV through Stage III. The ionic mass transfer rate should be enhanced by Bernard convection above an upward facing cathode (A/C), while the diffusion mechanism prevails for C/A in Stage IV. The transient current difference in Stage II between both configurations may be referred to the induction of a kind of natural convection accompanied with Cu electrodeposition even in such a nano-sized pore. The difference diminished with a smaller diameter of pore.

If the magnetic field is applied perpendicularly to the electric field vector, MHD flow should be induced. Figure 2 also shows the transient current when the electrolytic cell with A/C configuration was installed in the 5 T magnetic field. When the strong magnetic field was applied, the cathodic current was 0.3 mA larger than that without magnetic field from Stage II to IV, and the transient time of Stage II was about 50 seconds shorter. It shows that the ionic mass transfer rate in the nano-sized pore was significantly enhanced by MHD flow.

Summary

PC filter can be reasonably employed as a template to process the metal nanowire electrodeposited in aqueous electrolyte solution. A strong magnetic field is effective to enhance the ionic mass transfer rate accompanying Cu electrodeposition even in such a nano-sized pore. Superposition of stronger magnetic field may provide a unique technique for the materials processing for nanostructured devices.

References

[1] T.M.Whitney, et al., *Science*, **261,** 1316 (1993)
[2] Y. Konishi et al, *Extended abstract of MPND2001*, p145 (2001)

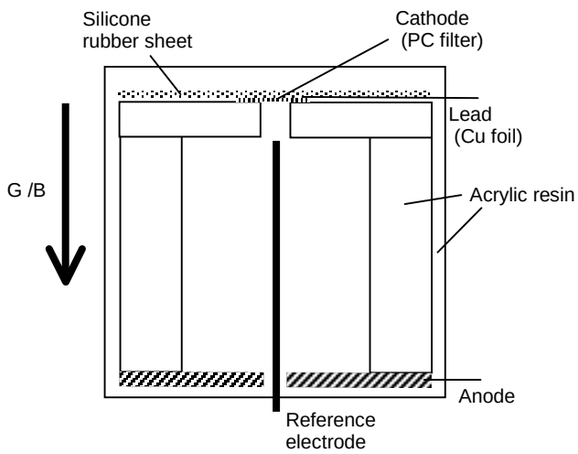

Fig.1: Schematic illustration of electrolytic cell (C/A configuration).

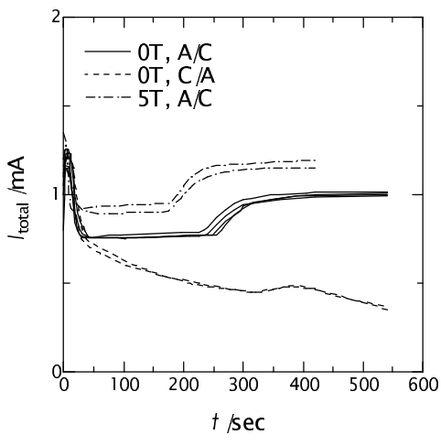

Fig. 2: Transient behavior of cathodic current
(200 nm-sized pore).