

Electrochemical Growth of Copper Nanowires Inside of Semiconducting TiO₂ Nanotubes

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Growth of metal/oxide nanowires inside of semiconducting nanotubes has several applications, such as: electrodes for energy storage and energy conversion devices, and sensors. Electrodeposition of nanowires within the oxide nanotubes requires fine-tuning of the electrolytic solution as well as other deposition parameters because of the very high aspect ratio, and the semiconducting nature of the nanotubes. Electrodeposition of copper within nano trenches (Damascene process) has been reported for electronic interconnect applications [1-3]. However, the aspect ratios of the trenches are lower than that of nanotubes and a seed metal barrier layer is present in the Damascene process that improves conductivity for copper deposition. Growth of metal nanowires by electrodeposition onto a large nanoporous surface of anodic aluminum oxide (AAO) has also been reported [4]. AAO is an insulator and one surface is metallized for growth of nanowires. Little work has been done in the area of electrodeposition of nanowires inside of semiconducting oxide nanotubes.

In the present study, growth of copper nanowires inside of TiO₂ nanotubes will be discussed. The TiO₂ nanotubes (length: 300-400 nm, and diameter: 70-110 nm) were prepared by anodization of a 0.2 mm thick Ti foil. The TiO₂ nanotubes were annealed in air at 450 °C to have a high electrical resistance. In order to facilitate the bottom-up growth of Cu nanowires, the base of the TiO₂ nanotubes were cathodically polarized to increase the conductivity locally. The base solution for copper deposition was CuSO₄ and H₂SO₄. The accelerator and inhibitor additives used in experimental trials were (0.5 to 2 mM) NaCl, (0.5 to 2 mM) NaF, (25-100 μM) bis(3-sulfopropyl) disulfide (SPS), (44-176 μM) ethylene glycol (EG), (44-176 μM) polyethylene glycol PEG, (50-200 picomolar) polyethyleneimine (PEI). These were added individually and in mixed groups to determine the electrochemical characteristics of each additive. The other experimental variations/parameters investigated were: temperature of the solutions, and stirring conditions (mechanical vs. ultrasonication).

Two cyclic voltammetry runs, using a Gamry Interface 1000 Potentiostat/Galvanostat were performed on each solution, one using TiO₂ and another using platinum as the working electrode. [Figure 1](#) gives an example of the extreme changes in the cyclic voltammetry with very small amounts of inhibitor and accelerator additions. Addition of PEI was observed to show a substantial effect in the solution on copper deposition. All depositions into TiO₂ nanotubes substrates were examined under a Zeiss Supra 35VP Scanning Electron Microscope

(SEM). As can be seen in [Figure 2](#) the copper was not completely filling the nanotube to start a bottom up deposition. The results of the various additions to the electrolyte solution and the mechanisms of electrodeposition within the semiconducting nanotubes will be discussed in detail in the presentation.

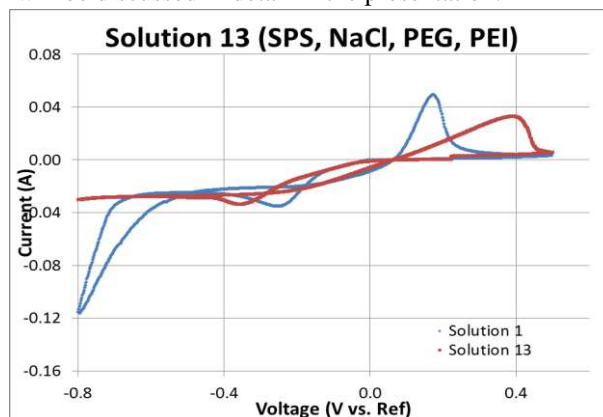


Figure 1: Cyclic voltammograms of copper electrolytic solution with and without additives (Solution 1: no additive; solution 13: with all additives).

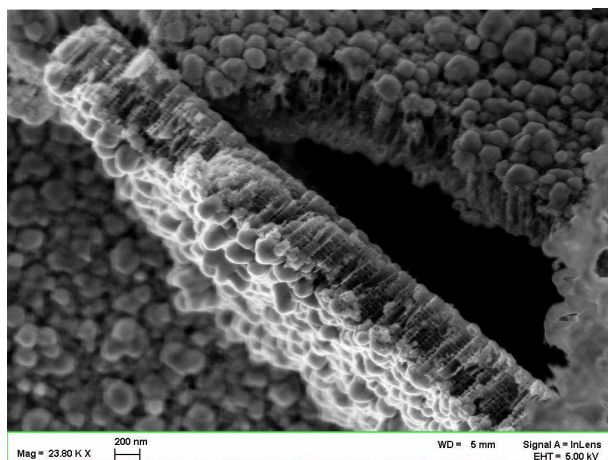


Figure 2: Cu deposition on TiO₂ with SPS and PEI additives (mag: X 24K)

References

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