Anomalous Morphology Evolution during Stress Relaxation of Cobalt Films due to Dissolution in Electrolyte Solutions

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Supplementary Materials

Experimental technique

1. Substrate Preparation

For ECD, the substrate must be conductive and inert to the electrolyte solution. Here, a 150μm thick glass slide (VWR international, Inc) was capped with a very thin amorphous NiTi layer with an underlying Cu/Cr bilayer. The Cu layer provided high conductivity for the whole substrate and hence avoided a non-uniform distribution of voltage on the substrate during deposition. The Cr seed layer was used to enhance adhesion to the glass substrate. The amorphous NiTi and Cu/Cr layers were prepared by magnetron sputtering at room temperature in a chamber with 10mtorr Ar gas. The final substrate was shaped into a piece of 6cm × 1cm by diamond scribe. The surface NiTi alloy was found to posse a layer of TiO_x by energy dispersion spectroscopy. Nevertheless, the electric current can still tunnel through this layer, which enables ion reduction. The oxide layer is inert to electrolyte solution when pH value is higher than 3. As the electric resistance between two ends of the substrate measured by multimeter was very small, the voltage drop along the substrate was ignored and the power distribution on the surface of the substrate was considerably uniform. The surface roughness of the substrate characterized by AFM was smaller than 5nm.

2. Electrochemical deposition

The deposition cell was made of Teflon and had a size of 8cm × 6cm × 4cm for containing solutions. The bottom of the cell was sealed with a quartz bottom cover that is

transparent to laser beam while minimizing the laser absorption. The basic electrolyte solution in this study was $CoSO_4$ dissolved deionized (DI) water. The concentration of $CoSO_4$ ranged from 0.01 to 0.1 mol/L. Additives, such as NaCl, were added to study the effects of different ions on the thin film growth. The pH values of the electrolyte solutions were between 4 and 7. The reference electrode was an Ag/AgCl electrode, which had an equilibrium potential 0.222V, with respect to the standard hydrogen electrode (SHE). A platinum plate with a size of 7cm×2cm acted as the counter electrode (anode). Before deposition, the platinum plate was cleaned by flame from a propane torch. The electrochemical deposition was controlled by an EG&G Princeton Applied Research Corporation model 263A potentiostat/galvanostat that was connected with a computer. To maintain a constant deposition rate, a constant current mode rather than a constant potential mode was employed during all depositions. The effective thickness of the growing film was determined by integrating the charge transferred during deposition, with the assumption of 100% cathode current efficiency.

3. Stress measurement

The stress was measured by cantilever bending technique (Fig. 1). The substrate and the counter electrode were mounted in a parallel fashion while the counter electrode was placed 1 cm above the substrate (working electrode/cathode). The substrate was about 1 cm away from the quartz cover. Before deposition, the laser spot was adjusted to localize in the center of the position sensitive diode such that the current signals were almost zero. Deposition and stress measurements were started after photocurrent signals maintained around zero for a few minutes. The data acquisition rate for stress signals was maintained at 10Hz. The photocurrent signals due to the bending of the substrate were converted to stress*thickness based on a pre-calibrated curve.