Ionic Transport in Anodically Oxidised Al/Ta Layers during the Growth of Metal-Oxide Nanostructures

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Recent study has shown that anodic processing of a specimen consisting of a layer of aluminium deposited upon a layer of tantalum (Al/Ta) results in the formation of self-organized arrays of metal-oxide 'nanocolumns' in the alumina pores [1]. In the present study, we have justified experimentally and described conceptually the model of ionic transport and film growth during the anodic process.

Experimental samples were Al/Ta (250/100 nm) metal bilayers sputtering-deposited onto Si wafers. The processing resulted in initial growth of porous anodic alumina film (Fig. 1a), followed by uniform penetration of the alumina pores by columns of tantalum oxide at the commencement of high voltage reanodising (Fig. 1b). The growth and field-assisted dissolution of the nanostructured anodic oxides were studied by SEM, XPS and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

It was found that the penetration of the alumina pores is assisted by relatively higher Pilling-Bedworth ratio for the tantalum oxide of the columns (3.5) and unusually high transport number for outwardly migrating Ta^{5+} ions (0.5). The width of the columns is almost three times the diameters of the corresponding alumina pores. At the commencement of columns growth, the ionic current flows not only through regions of tantalum oxide but also



Fig. 1 SEMs of an anodically oxidized Al/Ta bilayer (a) before reanodising, (b) after reanodising,(c) after selective dissolution of the alumina film

through outer regions of the alumina cell walls, having relatively lower ionic resistivity due to being contaminated by electrolyte-derived species. While the columns grow up, onethird of the cell wall thickness dissolves into the forming electrolyte with a few percent incorporation of alumina into the column material. The findings reveal clearly that the relatively big diameters of the columns are mainly due to the penetration of the alumina cell walls by a displacement process, not by the inherent plasticity in amorphous anodic oxides.

In-depth understanding of the growth mechanism could be

efficient in extension to some other high-melting-point metals, such as Nb, W, Mo for the synthesis of corresponding metal oxide nanostructures.

[1] A. Mozalev, M. Sakairi, H. Takahashi, J. Electrochem. Soc. 151 (2004) F257