The Unusual Structure of Tungsten-doped Electrochemically-grown Alumina Films Detected by MeV Ion Scattering

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MeV Ion scattering has revealed a surprising periodic incorporation of anionic residue in anodically-grown alumina films which may provide important ramification of the properties of these films.

Alumina films are important in passivation, as receptors for dyes, coatings, and adhesives and in microelectronics as dielectrics, diffusion barriers or insulator structures. These films are also used as models for alumina based catalysts.[1] Recent evidence shows that electrochemically-grown films have a duplex nature where the outer region of the film contains species derived from the anions present in solution.[2,3] The presence of these 'anions' in the outer region of the alumina films can play a major role in defect structure[4] and electronic properties[5] which are extremely important to the above applications. The latter has recently been shown by Sharp *et al.*[6] Evidence from scanning transmission electron microscopy (STEM) suggests that the entire film is amorphous before dehydration but only the outer zone remains amorphous after drying, for example in the STEM electron beam.[7] Work by Wood and co-workers[2] suggests this outer region to be uniformly impregnated with the 'anion' when tungstate is incorporated based on electron-micrographs and *X*-ray emission data. In our work to discover the means and mechanisms of amorphous phase stabilization for formation of planar catalyst supports, we have found using α- and argon-backscattering that the distribution of incorporated species is non-uniform.

Anodic oxide films were grown galvanostatically at a current density of 150 mA cm^{-2} from nitrogen purged 0.15 M borate buffer solutions (pH 8.4), which were either 1 or 0.1 M in $Na_2WO_4 \cdot 2H_2O$, on highly polished aluminium discs. Film growth was continued until a cell voltage of 72 V was obtained. Taking a film growth rate[5] of 14 Å/V yields a film thickness of approximately 1000 Å.

With the view of ascertaining whether foreign metal based species could be incorporated into alumina films as a result of prior aluminium alloy formation, two types of aluminium were used. A commercial grade containing a low concentration of manganese and copper and a high purity form (99.999%, Alfa Ventron Corp.) were chosen.

Rutherford backscattering[8] data pertaining to these films were obtained using either a variable energy cyclotron, with a collimated 40 MeV Ar^{4+} ion beam (Texas A & M) or a Van der Graff accelerator, employing a collimated beam of 2 MeV He^{2+} ions (Rio de Janeiro).

Results of the backscattering experiments are shown in Figures 1 and 2. In Figure 1, a typical Ar^{4+} backscattering spectrum is shown for an alumina film grown in the presence of tungstate on ultra high purity aluminium. It is first noted that the concentration of tungsten decays as one moves into the interior of the alumina film. This concentration decay is, however, not monotonic but shows a strong periodic structure. Figure 2 shows the results of α-backscattering on a similar sample. This sample of aluminium contained Mn and Cu components. It was chosen to investigate the possible alternative method of incorporation of alloy components in the alumina film. The backscattering spectrum shows several features. The same periodic structure as observed in Ar^{4+} data is evident. In addition, the complementary periodic structure is seen in the aluminium oxide spectrum: where tungsten species are at a maximum concentration aluminium ions are at a minimum concentration. This strongly supports a layer type concentration profile for tungsten species in the outer region of the films. As shown in Figure 2, the main tungsten containing layer is less than half of the alumina layer thickness. It is also noted that the sharp rise of the Mn high-energy onset indicates that no Mn-oxide species are incorporated in the alumina film. The Mn seen is contained solely in the metallic aluminium.

These results show the advantage of using both heavy ion and α-backscattering where the fine structural detail is more evident in the former. The latter, however, supplies a more complete picture of the entire thin film. This periodic fluctuation of 'anion' incorporation has not, to our knowledge, been previously observed.

S. M. K. is a visiting Fulbright Professor from Hecetepe

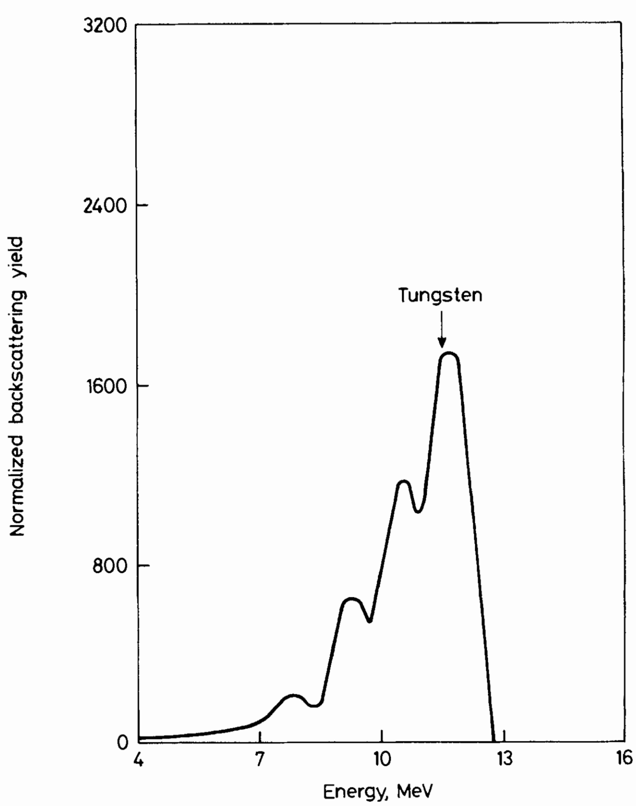

Figure 1. 40 MeV Ar^{4+} Backscattering spectrum of an alumina film formed in 1 M $Na_2WO_4 \cdot 2H_2O$ borate buffered solution. Note the strong periodic variation in the tungsten concentration from the outer (high energy side) portion of the film.

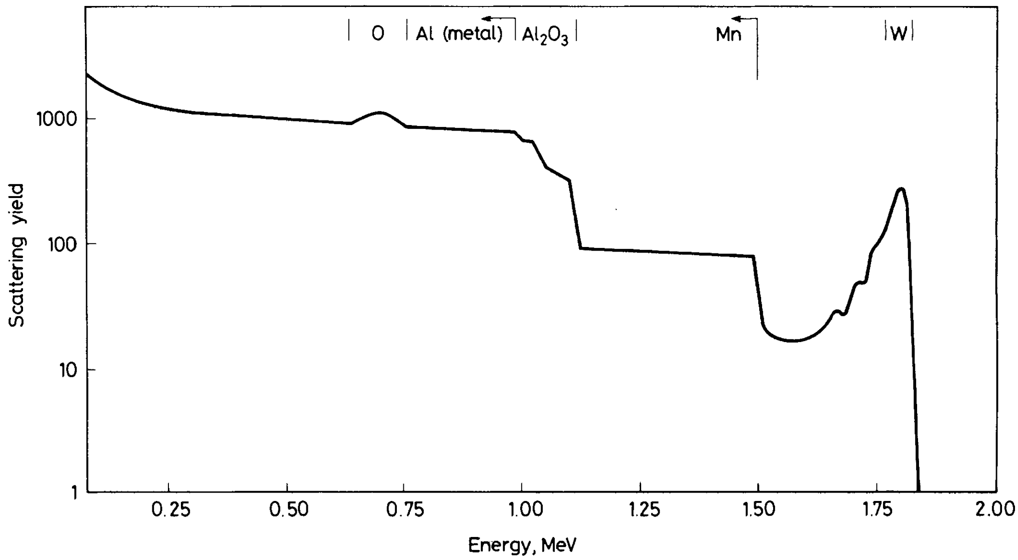

Figure 2. 2 MeV He^{2+} Backscattering spectrum of an alumina film grown on an aluminium alloy in 1 M $Na_2WO_4 \cdot 2H_2O$ buffered solution. The same periodic structure in the W and Al_2O_3 spectra can be seen.

University, Ankara, Turkey. The Center for Energy and Mineral Resources, Texas A & M University, generously supported D. L. C. in this work. Support for this work to C. V. B. L. by CNPq of Brazil and to E. A. S. by the U.S. National Science Foundation is gratefully acknowledged.

Received, 18th June 1984; Com. 845

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