THE EXAMINATION OF CALCIUM ION IMPLANTED ALUMINA WITH ENERGY FILTERED TRANSMISSION ELECTRON MICROSCOPY

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Ion implantation can be used to alter in the optical response of insulators through the formation of embedded nano-sized particles. Single crystal alumina has been implanted at ambient temperature with 50 keV Ca^+ to a fluence of 5×10^{16} ions/cm². Ion channeling, Knoop microhardness measurements, and transmission electron microscopy (TEM) indicate that the alumina surface layer was amorphized by the implant. TEM also revealed nano-sized crystals $\approx 7 - 8$ nm in diameter as seen in Figure 1. These nanocrystals are randomly oriented, and exhibit a face-centered cubic structure (FCC) with a lattice parameter of $0.409 \text{ nm} \pm 0.002 \text{ nm}$. The similarity between this crystallography and that of pure aluminum (which is FCC with a lattice parameter of 0.40 nm) suggests that they are metallic aluminum nanocrystals with a slightly dilated lattice parameter, possibly due to the incorporation of a small amount of calcium. Energy-filtered transmission electron microscopy (EFTEM) provides an avenue by which to confirm the metallic nature of the aluminum involved in the nanocrystals. Experiments were performed with a Gatan Imaging Filter (GIFTM) interfaced to a Philips CM30 TEM operated at 300 kV. The gain normalized images were 512×512 pixels in size, and were recorded with an exposure time of 1 second and an energy window of 5-eV. The component in the 15-eV loss images due to alumina valence excitation was estimated from adjacent loss images and subtracted².

Three single scattering energy loss distributions from material standards are shown in Fig. 2³. The valence-loss spectrum from Al_2O_3 (a) shows a large loss feature at ~ 25 eV. The plasmon loss spectrum taken from Al (b) shows an energy loss peak at ~ 15 eV. The Ca valence-loss spectrum (c) also exhibits a small feature at ~ 15 eV. A typical spectrum from the implanted sample contains major loss features at both 25 and 15 eV (not shown). This raises the possibility of the presence of calcia in the implanted region. However, the calcia valence-loss spectrum also contains a strong feature at ~ 40 eV. This 40-eV-loss feature is not evident in a typical spectrum from the implanted sample. A zero-loss image of the implanted sample is shown in Fig. 3a. A 15-eV-loss image, seen in Fig. 3b, indicates that the crystals contain metallic aluminum. In a 25-eV-loss image from the same region (Fig. 3c), the same features are slightly darker than the surrounding matrix. This image confirms that the particles are not alumina. Fig. 4 shows the oxygen "jump-ratio" image (post-edge divided by pre-edge) from an area similar to the area in Fig. 3. This type of image yields information similar to that of an elemental map in that the dark areas have a low ratio value which indicates a deficiency in the element of interest. Therefore, this image shows that the particle regions are oxygen deficient with respect to the matrix material. Figure 5 shows a calcium "jump-ratio" image which indicates that the particle regions are calcium deficient. The large "halos" around the particle positions may indicate calcium enrichment in the immediately surrounding matrix, however it may also be the result of focusing difficulties due to the low beam intensity at the high energy loss values (346-350 eV) required for imaging the Ca L2-3 edge.

EFTEM has confirmed that the aluminum present in the particles is metallic in nature, that the particles are oxygen deficient in comparison with the matrix material and that the particles are deficient in calcium, and therefore not likely to be calcia. The particles thus appear to be FCC Al (possibly alloyed with a few percent Ca) with a lattice parameter of 0.409 nm . A similar result was obtained for yttrium ion implantation into alumina⁴.

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