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A broad chemical and structural characterization of the damaged region of carbon implanted alumina

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ABSTRACT

As candidate materials for future thermonuclear fusion reactors, isolating ceramics will be submitted to high energy gamma and neutron radiation fluxes together with an intense particle flux. Amorphization cannot be tolerated in ceramics for fusion applications, due to the associated volume change and the deterioration of mechanical properties. Therefore, a comprehensive study was carried out to examine the effects of carbon beam irradiation on polycrystalline aluminium oxide (Al_2O_3), a ceramic component of some diagnostic and plasma heating systems. Complementary techniques have allowed a complete chemical and structural surface analysis of the implanted alumina. Implantation with 75 keV, monoenergetic carbon ions at doses of 1×10^{17} and 5×10^{17} ions/cm^2 was performed on polished and thermally treated ceramic discs. The alumina targets were kept below 120 °C. The structural modifications induced during ion irradiation were studied by the GXRD and TEM techniques. Under these conditions, alumina is readily amorphized by carbon ions, the thickness of the ion-beam induced disordered area increasing with the ion dose. Matrix elements and ion implanted profiles were followed as a function of depth by using ToF-SIMS, indicating the maximum concentration of implanted ions to be in the deeper half of the amorphous region. Ion distribution and chemical modifications caused in the Al_2O_3 substrate by carbon irradiation were corroborated with XPS. The amount of oxygen in the vicinity of the implanted alumina surface was reduced, suggesting that this element was selectively sputtered during carbon irradiation. The intensity of those peaks referring to Al–O bonds diminishes, while contributions of reduced aluminium and metal carbides are found at the maximum of the carbon distribution. TEM observations on low temperature thermally annealed specimens indicate partial recovery of the initial crystalline structure.

1. Introduction

Ion implantation is a common technique for the modification of surface and near-surface characteristics of materials, by means of atomic and nuclear collisions. It is often used to emulate the damage occurring during ion bombardment inside on a fusion reactor. Most of the literature concerns studies with low-fluence ion interactions in single crystals, concluding correlations between radiation damage and the modified properties [1]. Defects induced during ion implantation on functional ceramics will cause different near-surface microstructure and therefore modify the physical properties of the initial materials.

Ion implantation in ceramics is of considerable interest, since some of these materials will be used on the future fusion reactors under intense particle fluxes and high energy radiation fields. Alumina ceramics will have applications as general electrical insulator components and optical or RF windows in heating and current drive, and diagnostic systems [2]. During reactor operation, materials close to the fusion plasma will be subjected to low energy (eV to 100 keV) ion and neutral particle bombardment generated during neutron reactions and erosion of nearby vacuum surfaces and devices. In particular, the alumina-based insulators will be subjected to carbon particle deposition and/or implantation originating from the SiC and CFC materials included in the divertor system [3]. The energetic carbon particles will deposit most of their energy at or very near the surface, producing high levels of local ionization, atomic displacement, and sputtering.

Modification of the electrical properties of alumina with carbon has been previously investigated [4]. A dramatic increase in conductivity was observed when carbon impurities were present in concentrations higher than 0.5 wt%, due to a percolation effect at

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the grain boundaries. Other work demonstrated that bulk conduction could be inhibited by adding commercial carbon glassy microspheres which act as impurity traps at grain boundaries [5]. However all these studies relate to massive carbon contamination in the alumina bulk. The potential electrical and dielectric degradation after superficial damage and contamination with conducting carbon particles needs to be assessed. As part of a further study, it is the aim of this paper to analyse the effects of carbon implantation on the crystalline structure and the chemistry of polycrystalline sintered alumina samples. Grazing incidence X-ray diffraction (GXRD), X-ray photoelectron spectroscopy (XPS), cross-section transmission electron microscopy (TEM) and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) techniques were used to determine the chemical and structural surface modifications of implanted alumina as a function of carbon ion dose.

2. Experimental procedure

Fully densified sintered samples were fabricated by Sumitomo JPAA from alpha-alumina powders. Prior to implantation, the alumina was cut as 30 mm in diameter and 3 mm thick rods, mechanically polished to a flat mirror finish (Ra 20 nm) and then thermally etched in air at 1525 C for 30 min to relax any induced mechanical damage and to reveal the microstructure morphology. The processed alumina discs were used as the implantation targets, although one was retained as a control sample and not implanted.

Carbon implantation was then performed using the Whickham 200 keV implanter at the School of Engineering of the University of Sussex (UK). The 75 keV C^+ ion implantations were carried out using two different ion doses (1×10^{17} and 5×10^{17} ions/cm^2). To ensure temperatures below 120 °C during irradiation, the samples were clamped onto a water-cooled aluminium plate and ion current densities were kept below 10 μA/cm^2. Following ion implantation, samples were submitted to the different analytical techniques.

GXRD was used to analyse the crystalline modifications of unimplanted and implanted samples. The experimental conditions on the Philips ẊPert MPD diffractometer were copper radiation, Kα (λ = 0.15405 nm) and 0.5° grazing angle for all the samples. At 0.5°, the best peak definition of penetration depth ratio is obtained. The sub-surface region analysed by the X-rays is thick, but the changes within the implanted layer will be observed, since 90% of the diffracted radiation comes from the material volume located on the first 1100 nm in depth, in agreement with Donnet [6].

Cross-section TEM specimens were prepared after thermal evaporation of a thin W layer (about 6 nm), to protect the implanted alumina surface grains from aggressive ion thinning. The W-coated implanted surfaces were then glued face-to-face, sectioned perpendicular to the irradiation surface and thinned by means of mechanical dimpling and cooled ion milling (Ar^+ ions, 5–8° milling angle). Thinning continued until perforation occurred at the W–W interface. The specimens were examined using a TEM (Philips TECNAI 20T) operating at 200 kV and equipped with an energy dispersive X-ray spectrometer (EDS).

Compositional analysis was performed on a ToF-SIMS type ION-TOF IV instrument. Sputter etching of the surface was accomplished with a beam of 2 keV Cs^+ ions (target current of 125 nA; incidence angle of 45°), rastered over a 300 μm × 300 μm area. A pulsed beam of 25 keV Bi^+ ions, scanned over a 50 μm × 50 μm region and centred within the sputtered area, was used to generate secondary ions for analysis in negative ion mode. A high current beam of low energy (<20 eV) electrons was employed for charge compensation. Mass resolution was higher than 6000. Depth values were provided by measuring the sputter crater using a Wyko NT1100 interferometer.

XPS experiments were performed using a Perkin–Elmer PHI 5400 spectrometer incorporating a MgKα source. Typical operation conditions were: X-ray gun, 15 kV, 20 mA; pass energy, 17.5 eV for high resolution spectra; 1 mm diameter beam size. The spectrometer was calibrated using copper, gold and silver standards. Energies were determined by referencing to the C 1s peak at 284.8 eV. Depth profiles were acquired by etching the exposed surface with a 3 keV Ar^+ gun. The estimated sputtering rate was 6 Å/min.

3. Results and discussion

A software simulation based on the Monte Carlo technique (SRIM 2006 [7]) was used to calculate the distribution and range of implanted carbon ions. For energies and doses similar to the experimental conditions, a slightly asymmetric Gaussian ion distribution is obtained. According to this model 90% of the carbon ions are implanted between 100 and 180 nm from surface, with a maximum density at 130 nm and a maximum depth of about 220 nm.

The initial experimental approach to ion-induced modifications in the alumina implanted targets was attained studying the crystalline phase evolution using XRD. Since the ion range was estimated to be about 200 nm, a grazing incidence angle of 0.5° was used during pattern registration. The unimplanted spectrum shows the diffraction peaks of the alpha-alumina phase (Fig. 1). A non-linear decrease in intensity of the crystalline peaks was the characteristic feature of both ion irradiated targets when are compared to the unimplanted sample (Fig. 1). No new peaks were registered, indicating that no new phases were formed. No peak broadening or maxima displacement of the best resolved peaks was observed, the loss of intensity being the only macroindicator of near-surface lattice disorder. The analytical study, discussed below, allow us to look deeply into the chemistry and microstructure modifications of an alumina sub-surface bombarded with a light ion-beam.

The SEM study shows the unimplanted ceramic sample consisting of equiaxed grains in which several intra and intergranular pores are seen. The calculated mean grain size (7 μm) was unal-

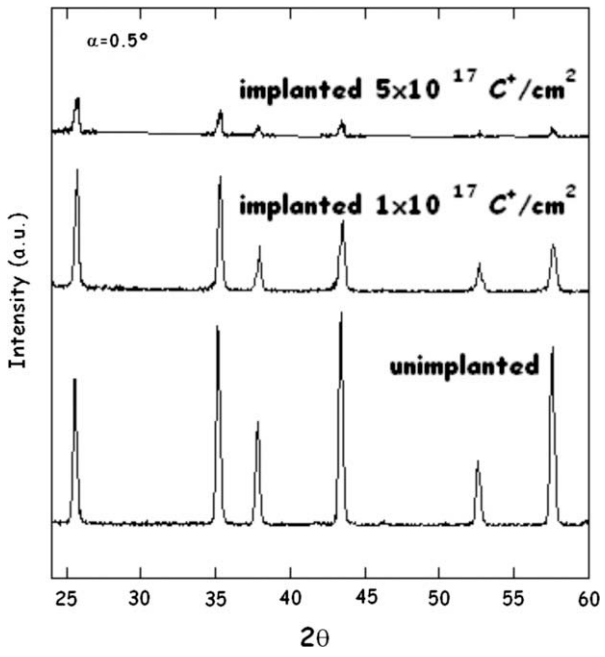

Fig. 1. X-ray diffraction patterns of the C^+ implanted alumina targets. Spectra were registered with a grazing incidence angle of 0.5°. The unimplanted pattern is also plotted for comparison.