ENHANCEMENT OF OXIDATION RESISTANCE OF SILICON CARBIDE BY HIGH-DOSE AND MULTI-ENERGY ALUMINUM IMPLANTATION

ZUNDE YANG,* HONGHUA DU,** MATTHEW LIBERA,* STEPHEN P. WITHROW,**
LUIS M. CASAS*** AND RICHARD T. LAREAU***

*Stevens Institute of Technology, Hoboken, NJ 07030

**Oak Ridge National Laboratory, Oak Ridge, TN 37831

***Army Research Laboratory, Fort Monmouth, NJ 07703

ABSTRACT

High-dose and multi-energy aluminum implantation of α -SiC (0001) was carried out to achieve a broad aluminum distribution extending from the sample surface to a depth of approximately 350 nm. Oxidation resistance of the implanted crystals was studied in 1 atm flowing oxygen at 1300°C. Aluminum implantation resulted in a 45% improvement in the oxidation resistance of α -SiC as compared with unimplanted crystals due to the formation of structurally dense mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) in the oxidation scale.

INTRODUCTION

Surface modification of ceramics by ion implantation is a fruitful area of research for the prospects of improving their surface-sensitive mechanical properties including wear resistance, hardness, and fracture toughness [1-3]. A ceramic surface can also be so tailored as to favor the conditions for enhanced surface-sensitive chemical properties such as oxidation and corrosion resistance. The potential of ion implantation to improve the oxidation stability of silicon-based ceramics such as silicon carbide and silicon nitride has been demonstrated [4,5].

Aluminum implantation of silica-forming ceramics offers excellent prospect to enhance their oxidation and corrosion resistance. Thermodynamically speaking, preferential formation of alumina and/or mullite is possible upon oxidation of these ceramics implanted with aluminum [6]. From the transport and environmental stability standpoint, alumina has much lower oxygen diffusivity values [7] and is far less susceptible to corrosive attack in a hostile environment than silica [8]. Mullite is also expected to be superior to silica in this regard. In addition, the incorporation of Al-O bond structure enhances the network connectivity and refractoriness of silica in environments containing network modifiers such as alkali and alkaline earth cations [9].

Recently, we reported the effect of high-dose and mono-energy aluminum implantation on the oxidation stability of SiC [5]. Aluminum implantation was shown to result in a 19% improvement in the oxidation resistance of β -SiC as compared with unimplanted crystals. The enhanced oxidation resistance was attributed to the formation of an oxidation scale consisting of a mullite-rich center layer sandwiched by an outer and an inner layer of silica. The layered-configuration of the oxidation scale resulted from the Gaussian-like distribution of aluminum around the projected range, which is typical of mono-energy implantation. A broad distribution of high aluminum concentration obtainable by high-dose and multi-energy implantation is expected to result in far greater an improvement in the oxidation resistance of SiC. This work

*To whom correspondence should be addressed.

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was carried out to evaluate the degree of enhancement of the oxidation resistance of SiC that the approach of high-dose and multi-energy aluminum implantation could achieve.

EXPERIMENTAL

4H polytype single crystal α -SiC (000 $\bar{1}$) fabricated by the Acheson furnace method was polished to a mirror surface finish with 0.25 μm diamond paste. The crystal was sequentially implanted with aluminum using an Extrion accelerator to $3.1 \times 10^{17}/\text{cm}^2$ at 196 keV, $1.2 \times 10^{17}/\text{cm}^2$ at 120 keV, $8.4 \times 10^{16}/\text{cm}^2$ at 72 keV, and $5.0 \times 10^{17}/\text{cm}^2$ at 36 keV. The beam current varied from 5 μA to 60 μA and the sample temperature was maintained at around 500°C during implantation. Earlier work indicated that implantation at this temperature can effectively eliminate amorphization of the SiC by promoting in-situ dynamic annealing and lattice recovery [11]. Elemental depth profiling of the implanted sample was performed by Auger electron spectroscopy (AES) using a Perkin-Elmer PHI 660 scanning Auger microprobe at an electron-beam energy of 3 keV with 2-keV Ar^+ sputtering.

Oxidation of the aluminum-implanted α -SiC crystals was conducted in 1 atm dry oxygen flowing at 500 SCCM at 1300°C for 282 min. Unimplanted samples were also oxidized simultaneously for comparison. The thickness of the oxidation scale on the implanted sample was determined by cross-sectional transmission electron microscope (XTEM) using a Philips CM20FEG microscope at an acceleration voltage of 200 kV. The thickness and refractive index of the oxide formed on the unimplanted sample were measured using a Rudolph AutoEL ellipsometer. The structural and chemical characteristics of the aluminum-implanted samples after oxidation were also studied by the CM20FEG microscope. Selected-area diffraction (SAD) and energy dispersive x-ray analysis (EDX) were carried out in conjunction with XTEM.

RESULTS AND DISCUSSION

Shown in Fig. 1 is the AES elemental depth profile of the aluminum-implanted SiC crystal. The relative sensitivity factors (RSF) for Si, C and Al are 0.350, 0.148, and 0.047 respectively. The RSF values for Si and C were calculated based upon the stoichiometry of bulk SiC. The RSF value for Al was obtained from the Perkin Elmer instrument handbook. As depicted in this figure, high-dose and multi-energy implantation resulted in a broad aluminum distribution extending from the surface to a depth of about 350 nm. The aluminum concentration at the sample surface is 20 at.%. It reached 30 at.% at around 190 nm. The relatively high aluminum background in the bulk SiC is a result of high signal noise, which could arise from sample charging in pure SiC. It is noted that computer simulation using the PROFILE CODE [10] suggested that the high-dose and multi-energy implantation should produce a relatively uniform aluminum distribution of 20 at.% down to approximately 240 nm. One reason for the discrepancy in aluminum composition is a lack of standard and the use of the published RSF value for Al. The discrepancy in the depth is being investigated using XTEM.

An interesting feature illustrated in Fig. 1 is the varying extent of Si depletion/C enrichment in the implanted region compared with stoichiometric SiC. Similar results were reported in the studies of β -SiC implanted with aluminum and chromium [6,11,12]. Silicon sublimation and surface graphitization were shown to occur during vacuum annealing of single crystal α -SiC above 1000°C [13]. The compositional variation in Fig. 1 can therefore be attributed to migration of elemental silicon, which resulted from the rupturing of the Si-C bonds in SiC, to

the sample surface and subsequent sublimation and/or sputter removal into the vacuum environment during hot implantation. The excess carbon is present as free carbon and/or aluminum carbide from the thermodynamic standpoint [6] and based upon the mono-energy implantation results [11]. It is expected that majority of the aluminum implants remain in elemental form in the implanted region due to the high aluminum concentration and low degree of carbon enrichment. Detailed phase analysis of the implanted crystal is being pursued using x-ray photoelectron spectroscopy and XTEM.

Figure 1. AES elemental depth profile of aluminum-implanted α -SiC.

The sample surface became optically rough after oxidation. Fig. 2 is an XTEM image of the oxidized sample. The region between the two arrows corresponds to the oxidation scale formed. The band below of dark contrast is the implanted region which was not oxidized. SAD analysis indicated that the implanted α -SiC remained crystalline, consistent with earlier experimental observations [11]. The sparse and irregular light spots are artifacts introduced during XTEM sample preparation.

The thickness of the oxidation scale on the aluminum-implanted α -SiC crystal is approximately 250 nm according to XTEM. In contrast, the oxide on the unimplanted crystal is 458 nm thick as determined by ellipsometry. The ellipsometry measurement yielded a refractive index of 1.468 for the oxide, which is characteristic of silica. These results indicate that high-dose and multi-energy aluminum implantation led to a 45% improvement in the oxidation resistance of α -SiC, far exceeding that resulting from mono-energy implantation [5].

The oxidation scale grown on aluminum-implanted α -SiC clearly represents an excellent oxygen diffusion barrier compared with silica. As shown in Fig. 2, the oxidation scale consists of an outer layer of phases mostly of relative dark contrast (region a), a homogeneous center layer of light contrast (region b), and an inner layer with precipitates of darker contrast uniformly dispersed in a phase of lighter contrast (region c). Region a is crystalline with high silicon and

aluminum contents as indicated by the SAD pattern and EDX spectrum shown respectively in Figs. 3(a) and 3(b). Oxygen in the oxidation scale was not revealed in Fig. 3(b) due to the insensitivity of EDX to relatively light elements. It can be deduced that mullite is the crystalline constituent of the oxidation outer layer from the SAD and EDX analyses and the documented oxidation studies of sialon, a silicon-based ceramic with high aluminum content [14,15].

Figure 2. XTEM image of aluminum-implanted α -SiC after oxidation. The bar corresponds to a length of 200 nm.

Figure 3. (a) SAD pattern and (b) EDX spectrum from region **a** in Figure. 2.

Shown respectively in Figs. 4(a) and 4(b) are the SAD pattern and EDX spectrum from the oxidation center layer (region **b**) in Fig. 2. This region is amorphous in nature and contains no

detectable aluminum. These experimental results indicate that silica is the main constituent in this region. In contrast, the oxidation inner layer (region c) is a continuous silica phase which contains uniformly dispersed fine mullite precipitates. The morphological feature of the oxidation scale seems to indicate significant segregation of aluminum toward the oxidizing surface during the early stage of oxidation, which leads to formation of an aluminum-rich oxidation outer layer, i.e. mullite. The segregation resulted in a region beneath the oxidation growth front gradually depleted in aluminum, which was subsequently oxidized to silica. It is not yet clear why aluminum segregation was confined in the near surface region since further oxidation resulted in the formation of both silica and mullite. It seems unlikely that atomic mobility of aluminum would vary so drastically in the implanted region.

Figure 4. (a) SAD pattern and (b) EDX spectrum from region **b** in Figure 2.

The formation of a coherent and protective mullite layer was shown to be responsible for the superior oxidation resistance of sialon as compared with silicon nitride [14,15]. The improvement of the oxidation resistance of β -SiC by mono-energy aluminum implantation was also attributed to the formation of a mullite-rich oxidation center layer [5]. Mullite formed, particularly in the outer-most region of the oxidation scale has hence acted as a good oxygen diffusion barrier during oxidation of the high-dose and multi-energy implanted α -SiC crystals. It played a critical role in retarding the mass transport of oxygen through the oxidation scale toward the reaction interface.

CONCLUSIONS

High-dose and multi-energy aluminum implantation resulted in a broad distribution of aluminum of high atomic content in α -SiC crystal. The oxidation resistance of SiC was greatly improved, which can be attributed to the formation of mullite in the outer region of the oxidation scale. Further studies are being carried out to better understand the detailed structural and chemical characteristics of the implanted and oxidized samples and the corresponding evolution mechanisms.

The outcome of this research has a broader implication in that enhanced oxidation/corrosion resistance of silicon-based ceramics can be achieved through aluminum surface modification not only by ion implantation, but also by other surface processing techniques such as laser surface alloying and chemical vapor co-deposition. Aluminum surface modification is also expected to increase the wear resistance of silicon-based ceramics in sliding and rolling contact in high-temperature oxidative environments due to the enhanced surface chemical durability and the formation of oxidation layers of better tribological characteristics than silica.

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