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Hardness and friction of N_2^+ and Al^+ implanted B_4C

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Surfaces of boron carbide (B_4C) were implanted with 200 keV N_2^+ or 100 keV Al^+ ions to a dose of $8 \times 10^{17} cm^{-2}$. Ultralow load indentation via the Nanoindenter was used to determine the changes in surface hardness and elastic modulus following implantation. A pin-on-disk testing device in ultrahigh vacuum was used for measuring changes in friction and wear of the implanted disks. Results of hardness measurements show that the hardness of the nitrogen-implanted sample drops to about 58% of the unimplanted hardness, and that for the aluminum-implanted sample drops to about 52% of the unimplanted value. The elastic modulus also falls to approximately 62% of its unimplanted value for both implantations. Friction and wear studies conducted in UHV show an increase in friction of both implantations from 0.5–0.6 after one cycle to 0.8–1.1 after ten cycles. This is larger than the 0.17–0.25 values measured for pure B_4C. The wear is significantly reduced in the early cycles of the implanted samples relative to the unimplanted ones. The dramatic softening and improved wear behavior are probably due to the formation of an amorphous surface layer.

1. Introduction

Ion implantation is known to cause significant changes in the hardness, friction and wear behavior of many ceramic materials [1]. This can, in part, be ascribed to changes in the microstructure. Al_2O_3 becomes amorphous after high fluence implantation at room temperature or after lower fluences at 77 K [2]. MgO becomes amorphous after implantation with Ti to a fluence of 8×10^{16} cm^{-2} [3]. The covalently bonded ceramics α-SiC and Si_3N_4 are easily amorphized at 300 K with moderate doses of 280 keV Cr^+ [4]. As a result of the amorphous structure, both the hardness and coefficient of friction have been found to be substantially reduced. Al_2O_3 implanted with 4×10^{16} Al^+/cm^2 (90 keV) and 6×10^{16} O^+/cm^2 (55 keV) at 77 K reduced the hardness of the amorphous material by 45% relative to that of the crystalline material [3,5] and lowered the coefficient of friction from 0.24 to 0.04 in pin-on-disk tests under a normal force of 0.49 N and a sliding velocity of 5 rpm. [6]. Implantation and amorphization of SiC with 2×10^{16} Cr^+/cm^2 (260 keV) at 300 K produced a softening of 40 to 50% relative to the crystalline material [6], and a drop in the coefficient of friction from 0.5 to 0.3 under a load of 10 N [6]. Hoiki et al. [5] found that the friction coefficient μ as a function of sliding cycle for SiC in contact with SUJ2 steel at a sliding velocity of 0.05 m/s and a normal load of 0.2 N, implanted with Ar^+ to 1×10^{16} cm^{-2} at 300 K, dropped from 0.6 to 0.15. Recently, DeKoven et al. [7] showed evidence for chemical and mechanical changes in B_4C after nitrogen implantation. Following a dose of up to 5.5×10^{17} N/cm^2 (100 keV) the B_4C pin wear scar experienced a 60% reduction in diameter compared to unimplanted B_4C, and the coefficient of friction showed a 200% increase for measurements made in air. Nastasi et al. [8] reported that in friction and wear studies of N-implanted Al_2O_3, SiC, TiB_2 and B_4C using a hardened chromium steel ball in air, friction drops of ~ 50% occurred for all the covalent ceramics. DeKoven and Hagans [9] reported a friction coefficient of ~ 0.25 for a clean B_4C surface in ultrahigh vacuum (UHV) following a mechanical conditioning step at 3×10^{-4} m/s. Nitrogen implantation of B_4C in UHV to a retained dose of 8×10^{16} cm^{-2} (10 keV) resulted in a coefficient of friction of 0.7–0.8 using a clean B_4C pin on an implanted flat.

The objective of this study is to determine the changes in hardness and the coefficient of friction for boron carbide (B_4C) as a function of implantation of N_2^+ and Al^+ to $8 \times 10^{17} cm^{-2}$, and to relate the observed changes to the chemical and structural effects of implantation.

2. Experiment

Boron carbide (B_4C) samples were hot pressed from a single lot of commercially available powder (ESK 1500, ESK Engineering Ceramics, New Canaan, CT) of average particle size ~ 1 mm. The powder was hot

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pressed in a graphite die at 2100 °C using a pressure of 35 MPa for 30 min. B_4C pins (5 mm radius, lapped to 1 μm finish) and flats (diamond polished to a 1 μm finish) were used for the friction experiments.

Implantations were conducted in a Varian model 400-10 ion implanter. Samples were mounted onto a copper block and implanted with either 200 keV N_2^+ (4–8 $\mu A/cm^2$) or 100 keV Al^+ (3–4.6 $\mu A/cm^2$) to a dose of $8 \times 10^{17} cm^{-2}$. Implantations were conducted in a vacuum of better than 9×10^{-7} Torr. Composition vs depth profiles were determined via Rutherford backscattering spectrometry (RBS) using 2.0 MeV He^+ ions at normal incidence with a detector at 165° to the incoming beam.

Hardness was measured using an ultralow load indenter, the Nanoindenter. On each sample, 15 indents were made on the unimplanted region and on the implanted region in a 3×5 square array at a spacing of 20 μm. Each indent was made under displacement control at a rate of 4 nm/s to a depth of 250 nm, yielding a set of load–displacement pairs every 5 nm. From these data, hardness was determined by dividing the load by the contact area of the indenter using the shape function given in ref. [10]. The elastic modulus was determined from stiffness calculated from the unloading portion of a series of loading-unloading segments. The hardness or modulus profiles of implanted surfaces are plotted as normalized hardness/modulus profiles, defined as the hardness/modulus of the implanted sample divided by that of the unimplanted sample.

Friction measurements were conducted in UHV ($< 1 \times 10^{-9}$ Torr) at room temperature using a novel pin-on-flat device attached directly to the preparation chamber. The load range was 0.10–0.15 N. The pin was moved in a linearly oscillatory motion over a 2×10^{-3} m track length at a speed of 3×10^{-4} m/s. Load, adhesion and coefficient of friction were digitally recorded as a function of time. Large area X-ray photoelectron spectroscopy (XPS) was used to investigate the boron carbide surfaces before making friction measurements.

3. Results and discussion

The RBS spectra of the N_2^+ and Al^+-implanted samples of B_4C are shown in figs. 1 and 2, respectively. Although the overlap of the N and C peaks in fig. 1 makes quantitative analysis difficult, modeling the implanted N as a Gaussian function with a peak at 190 nm and a FWHM of 130 nm yielded a good fit and a peak N concentration of 50 at.%, in good agreement with calculations using TRIM [11]. The Al implantation yielded a much more well defined and separated peak which was located at 120 nm with a FWHM of 165 nm, yielding a peak Al concentration of ~ 42 at.%, also in good agreement with TRIM calculations.

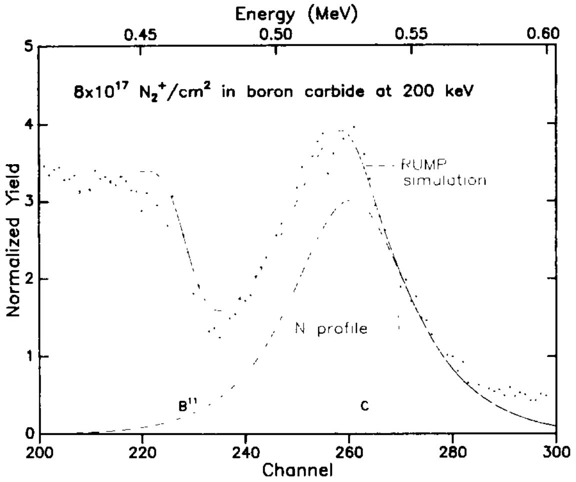

Fig. 1. RBS spectrum of B_4C implanted with 200 keV N_2^+ to $8 \times 10^{17} cm^{-2}$, using 2.0 MeV He^+ with a detector angle of 165°. The RUMP simulation is for a Gaussian distribution of N with a peak at 190 nm and a FWHM of 130 nm.

The normalized hardness profile shows that the hardness reaches a minimum of 58% for the N-implanted sample and 52% for the Al implanted sample at a distance of 50 nm from the surface, fig. 3. However, since the measured hardness is a function of the plasticity in front of the tip of the indenter, the minimum in the hardness profiles may have been reached at a depth shallower than 50 nm. Due to this limitation on depth resolution, the minima in the normalized profiles can be

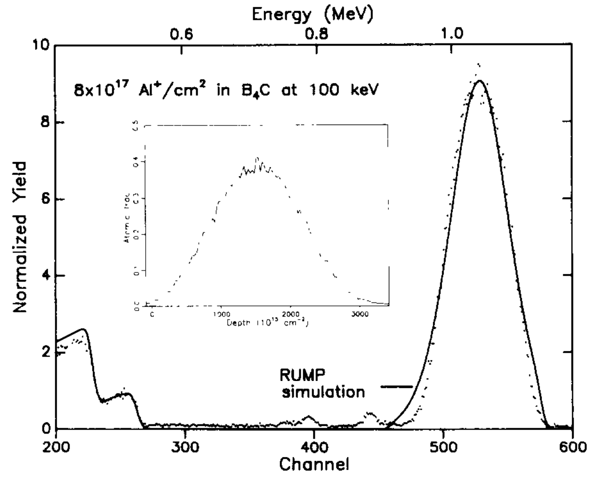

Fig. 2. RBS spectrum of B_4C implanted with 100 keV Al^+ to $8 \times 10^{17} cm^{-2}$, using 2.0 MeV He^+ with a detector angle of 165°. The RUMP simulation is for a Gaussian distribution of Al with a peak at 120 nm and a FWHM of 165 nm. The inset shows the atomic concentration profile of Al.

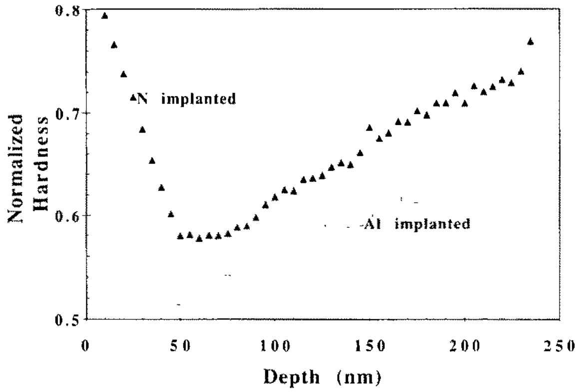

Fig. 3. Normalized hardness–depth profile of N-implanted and Al-implanted B_4C.

taken as limiting values with actual values at or below these levels. In both cases, the hardnesses rise rapidly to between 70 and 80% of the unimplanted material by 250 nm, indicating that the depth of the affected layer is of order 200 to 250 nm. This is to be compared with values of $R_p + \sigma$ of 245 nm for the N-implanted sample and 195 nm for the Al-implanted sample.

The normalized moduli follow trends very similar to that of the normalized hardness, fig. 4. The normalized modulus of the N-implanted sample is at a minimum of ~ 61% at 50 nm vs a minimum of ~ 62% at 50 nm for the Al-implanted sample. Both rise rapidly to between 80 and 90% of the unimplanted values by a depth of 225 nm.

The friction was measured in UHV using a "clean" B_4C pin contacting either an Al-implanted B_4C flat or a N-implanted B_4C flat. The flats were lightly sputtered prior to the friction studies in order to remove the thin layers of oxides and aliphatic carbon on the surface due to air exposure. There was no difference in the friction between the two implanted samples, but the measured values are distinctly different from the published values [9] for the clean and air-exposed surfaces measured in UHV. The friction measured for the implanted surfaces, however, showed a dependence on the number of linear oscillatory pin cycles over the selected 0.002 m distance. The friction started at 0.5–0.6 for the first several cycles and then monotonically increased up to 0.8–1.1 by the tenth cycle. The friction values for the ion-implanted surfaces are significantly higher than the friction measured for the atomically clean B_4C surfaces (0.18–0.25) measured using similar loads and sliding speeds [9].

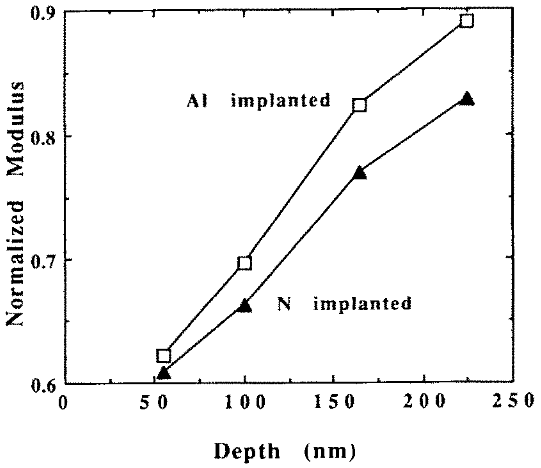

Fig. 4. Normalized modulus–depth profile of N-implanted and Al-implanted B_4C.

Fig. 5 shows the SEM photos of three scars on B_4C surfaces made in UHV. Fig. 5 (upper panel) shows the scar resulting from 20 pin cycles using atomically clean B_4C. Fig. 5 (lower two panels) show scars on the Al-implanted B_4C sample made using a clean pin after 60 cycles and one cycle, respectively. There is clearly a different morphology associated with each scar. The clean surface scar (fig. 5 (upper panel)) shows a very fine granular, cobblestone-like appearance, whereas the scar from the Al-implanted sample given 60 cycles shows evidence of grain pull-out and fracture. Although not shown, similar changes were observed in the N-implanted B_4C. However, the scar width following a single cycle (fig. 5 (lower panel)) is very smooth and narrow: 4–6 μm wide compared to 17–20 μm after 60 cycles and 60–70 μm for the clean B_4C sample.

The reason for the increase in friction for the Al and N implants compared to the unimplanted B_4C is not clearly understood. Since the wear scars in the implanted surfaces have a smoother appearance than those in the unimplanted surface, the actual contact area of the pin and flat for the former case could be significantly larger, leading to a higher coefficient of friction. Since in these studies the actual contact area is unknown, and morphological and chemical differences exist between these surfaces, it is difficult to intuitively predict how the friction would change after implantation. The dramatic softening and drop in modulus is consistent with other results in which amorphization has occurred [1–6] suggesting that this could be the case here. This softer surface with a low elastic modulus provides a more wear resistant film than the hard, brittle unimplanted B_4C sample, by preventing fracture and grain pull-out.

4. Conclusions

(1) Implantation of B_4C with 8×10^{17} Al^+/cm^2 (100 keV) or N_2^+/cm^2 (200 keV) resulted in a drop in the surface hardness of 48 and 42%, respectively, and a drop in the elastic moduli by about 38% for both implantations, possibly the result of amorphization.

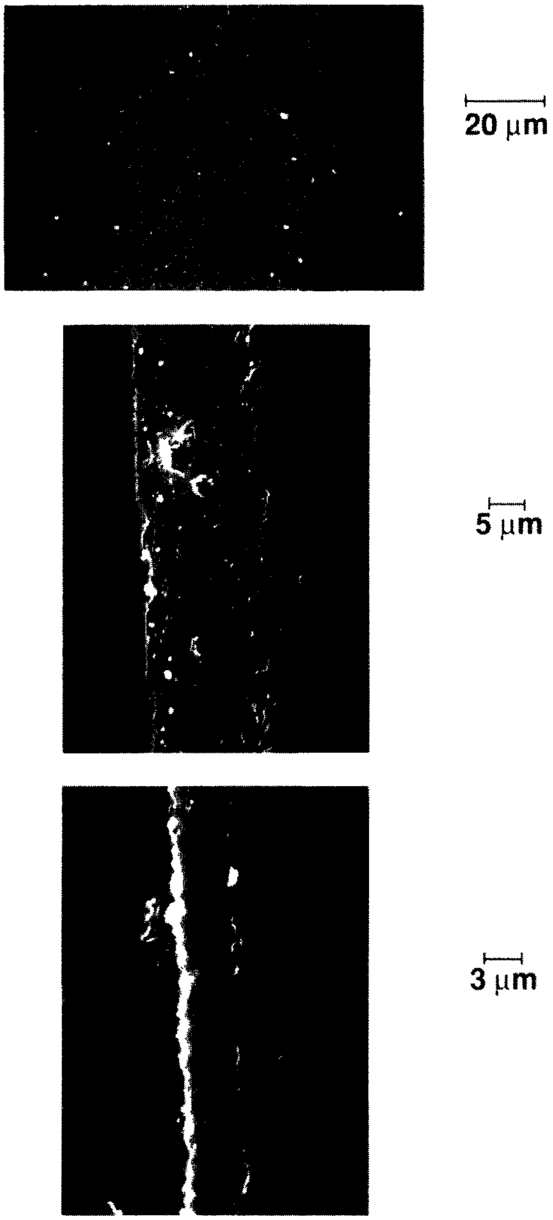

Fig. 5. Scanning electron micrographs of scars on B_4C surfaces made in UHV for pure B_4C after 20 pin cycles (upper panel) Al-implanted B_4C after 60 pin cycles (middle), and Al-implanted B_4C after 1 pin cycle (lower).

(2) The wear resistance of the implanted layers is significantly improved over unimplanted B_4C by the reduction in hardness and modulus, thus reducing grain pull-out and fracture until the implanted layer has been worn through.

(3) The friction coefficient of both the N- and Al-implanted samples measured in UHV increases from 0.5–0.6 after the first cycle to 0.8–1.1 after 10 cycles, compared to 0.17–0.25 for atomically clean B_4C.

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