Nanoscale investigation of deformation characteristics in a polycrystalline silicon carbide

D. Zhang¹ · L. G. Zhao¹ · A. Roy¹ · Y.-L. Chiu²

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Abstract

In this paper, we study the mechanical behaviour of silicon carbide at the nanoscale, with a focus on the effects of grain orientation and high-dose irradiation. Grain orientation effect was studied through nanoindentation with the aid of scanning electron microscopy (SEM) and EBSD (electron backscatter diffraction) analyses. Mechanical properties such as hardness, elastic modulus and fracture toughness were assessed for different grain orientations. Increased plasticity and fracture toughness were observed during indentations on crystallographic planes which favour dislocation movement. In addition, for SiC subjected to irradiation, increases in hardness and embrittlement were observed in nanoindentations at lower imposed loads, whereas a decrease in hardness and an increase in toughness were obtained in nanoindentations at higher loads. Transmission electron microscopy (TEM) analyses revealed that the mechanical response observed at a shallow indentation depth was due to Ga ion implantation, which hardened and embrittled the surface layer of the material. With an increased indentation depth, irradiation-induced amorphization led to a decrease in hardness and an increase in fracture toughness of the material.

Keywords Silicon carbide · Nanoscale deformation · Focused ion beam · Irradiation damage · Fracture toughness

Introduction

Owing to a strong bonding of carbon and silicon atoms, silicon carbide (SiC) exhibits superior mechanical and chemical properties, with a wide range of applications in industry (e.g., microelectromechanical systems, automobile brake parts, protective armour and cutting tools). To understand the mechanical properties of SiC at the nanoscale, quasi-static nanoindentation tests have been carried out by many researchers. For instance, Yan et al. [1] conducted nanoindentation on single-crystal 6H-SiC using a Berkovich indenter to investigate substrate damage in nanoindentation. A long microcrack propagating into the substrate was observed beneath the deformed zone of the imprint as also observed in 4H-SiC [2, 3].

However, the cracks in 4H-SiC were either lateral or radial [4], as opposed to median cracks found in 6H-SiC [1], due to the different crystalline structures between 6H- and 4H-SiC. Dislocations, as well as a transition from single-crystalline to polycrystalline (with a grain size of 10 nm) phase, were observed under nanoindentation. However, no amorphous phase was observed as seen in nanoindentation of silicon [4]. In addition, Goel et al. [5] carried out a number of nanoindentation tests on single-crystal 4H-SiC, with the intention of studying the failure mechanism caused by dislocation activity and/or microcrack generation. Dislocations are associated with the onset of plasticity which happens when the maximum shear stress beneath the indenter exceeds the theoretical shear strength, whereas microcracks occur by cleavage fracture which requires the maximum tensile stress at the tip to exceed the cleavage strength. It was concluded by Goel et al. [5] that plastic behaviour was caused by dislocations rather than microcracks as the tensile stress beneath the tip was lower than the cleavage strength. Similarly, Zhao et al. [6] performed a series of nanoindentation tests on polycrystalline 3C-SiC. Cracks were not observed at an indentation depth of 1 µm, which implied the maximum tensile stress would not exceed the theoretical cleavage strength, and hence the pop-in event was solely caused by plastic deformation. Subsequent TEM

✉ L. G. Zhao
L.Zhao@Lboro.ac.uk

¹ Wolfson School of Mechanical, Electrical and Manufacturing Engineering, Loughborough University, Loughborough LE11 3TU, UK

² School of Metallurgy and Materials, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

analyses confirmed the formation of shear bands around the indenter tip, with dislocation pile-ups in the heavily deformed zone.

Silicon carbide has been proposed as a potential structural material for nuclear reactor cores, particularly for the next-generation fusion power plants which require higher mechanical strength, thermal stability and irradiation resistance [7]. The lifespan of a component in the nuclear reactor core ranges between 5 and 40 years [8, 9]. In order to study irradiation damage in SiC, accelerated tests are often recommended. Ion implantation technique is an alternative method to study irradiation damage in materials within a relatively short period of time. Helium ions were implanted into 4H-SiC in the work of Barbot et al. [10], and amorphous layers were observed beneath the surface exposed to helium ions. Such irradiation-induced amorphization was reported to cause an increase in fracture toughness due to the formation of microcracks which dissipate the strain energy. However, in the work of Park et al. [11], it was claimed that fracture toughness was independent of the irradiation dose. The contradicting results indicated that the effect of irradiation on the mechanical property of SiC was not fully understood. On the other hand, although ion implantation experiments could emulate the harsh environment in a nuclear reactor core, the irradiation dose for most experiments was quite low (0.1–10 dpa) due to relatively low fluence [10, 12]. For instance, the fluence was found to be $2.05 \times 10^{11} \text{ cm}^{-2}$ after 5-month exposure time which is two to three orders less than that of the focused ion beam (FIB). Although nuclear irradiation is different from FIB, the damage mechanism is similar. Here, high-energy ions or neutrons penetrate into the material and knock out the lattice atoms, leading to the formation of point defects, volumetric swelling and/or amorphization. Therefore, FIB has been used, as an alternative to a neutron source, to study the irradiation damage of structural materials, including 4H-SiC [13] and 6H-SiC [14]. However, there is a lack of quantitative data on the variation of mechanical property for SiC subjected to irradiation damage.

The applications of SiC span all length scales; therefore, it is of great importance to understand the mechanical behaviour of the material at the nanoscale. Most studies to date focus on single-crystal SiC at small length scales with limited research in polycrystalline bulk SiC. In this paper, a series of nanoindentation tests were carried out for a better understanding of the mechanical behaviour of polycrystalline SiC at the nanoscale, focusing on the grain-orientation effect and fracture mechanism of the material. In addition, high-dose irradiation damage was also studied for the material, where FIB was used to bombard ions onto the sample. Nanoindentation tests were

performed on both virgin and FIB-irradiated areas to quantify the change of material properties due to irradiation. In addition, SEM and TEM analyses were carried out to characterise the effect of FIB irradiation on the microstructural change of the material.

Experimental details

Material and specimen preparation

The material used in this study is 6H-SiC produced by SAINT-GOBAIN by pressureless sintering of submicron silicon carbide powder at a temperature in excess of 2000 °C. The sintered sample has a density of 3.10 g/cm^3 and a fine-grain microstructure with grain size ranging from 4 to 10 μm . The as-received silicon carbide tiles were of hexagonal shape with a side length of 27 mm and a thickness of 4 mm. Smaller samples were cut from these tiles using a diamond blade fitted on the Accutom 5 machine, and then hot mounted using polyfast resin for SEM examination. The mounted samples were then ground using Struers Piano plates (grit 220 to 1200), followed by a polishing procedure using polishing plate/cloths with a diamond slurry of 9 μm , 3 μm and 1 μm , consecutively. The grinding took a few minutes until the surface was flat with a consistent scratch pattern. Polishing was then carried out to remove all surface damage. Between each polishing step, the sample was washed in an ultrasonic bath to remove any potential contaminations, i.e. large diamond particles. Each polishing step took more than 1 h and as a result, a smooth mirror finishing surface was accomplished with a surface roughness (R_a) of 9–18 nm.

FIB irradiation

An area of $800 \times 800 \mu\text{m}^2$, of the polished sample, was exposed to FIB radiation. The process was carried out using an FEI NanoLab 600 DualBeam machine which uses Ga ion as the beam source. The voltage and current used were 30 keV and 20 nA, respectively. The diameter of the ion beam spot for the selected energy output was 427 nm. The ion beam was directed on the sample, at a location each time without overlap. The FIB duration was calculated as the time required for introducing the desired dose of 100 dpa, as suggested by Zinkle and Busby [15] for structural materials in future nuclear reactors. According to Was [16], the rate of radiation damage, R_d , may be calculated by:

$$R_d = N \int \varphi(E) \sigma_D(E) dE \quad (1)$$

where N is the atomic density, $\sigma_D(E)$ is the energy-dependent displacement cross-section for a particular material

and $\varphi(E)$ is the energy-dependent particle flux. The unit of R_d is displaced atoms/cm³-second. The dpa/s can be calculated by dividing R_d with the atomic density (N). Assuming the energy output is constant, the dpa/s can be obtained by:

$$\frac{\text{dpa}}{s} = \varphi \frac{\text{displacement}}{\text{ion} \cdot \text{cm}} \frac{1}{N} \quad (2)$$

where flux, φ , is the number of ions emitted on a certain area in 1 s (ions/cm² s). The second term is the displacement per ion per unit length and provided by Stopping and Range of Ions in Matter (SRIM) [17] software which was used for calculations of irradiation dose in this study. For the Ga ion source, each ion brings one charge to the surface when the FIB bombards the sample. One ion has a charge of 1.602×10^{-2} C which means it requires 6.242×10^{18} ions to give one coulomb charge. Here, the ion beam flux can be calculated by:

$$\begin{aligned} \text{Flux } (\varphi) &= \frac{\text{Current (A)} \times 6.242 \times 10^{18}}{\text{beam Cross-sectional Area}} \\ &= \left(\frac{\text{No. of ions}}{\text{cm}^2 \cdot \text{s}} \right) \end{aligned} \quad (3)$$

According to SRIM, the molecular density of SiC is 9.64×10^{22} atoms/cm³ and the displacement per ion per cm is 2.73×10^8 . Therefore, to reach the desired dose of 100 dpa, the needed exposure time was calculated as 0.4 ms for each ion beam spot based on Eqs. (2) and (3). During the experiment, the area was not completely irradiated due to the circular shape of the ion beam (Fig. 1 (a)). However, the area of a single ion beam spot was only $3.9 \times 10^{-3} \mu\text{m}^2$ which was negligible. In addition, the damage caused by the ion beam may spread over the neighbouring areas due to collisions between Ga ion and lattice atoms. For instance, SRIM simulation showed that the surrounding area was also affected for samples bombarded by 20,000 Ga ions (Fig. 1 (b)). In the SRIM simulation, the Ga ion was made to collide with the

sample one by one from a virtual source with no beam diameter. While, in the real FIB experiments, the ion beam diameter was 427 nm and several-order more ions would be bombarding the sample, thus reducing the uncovered area to a level which can be practically neglected. As can be seen in Fig. 2 (a), the FIB-irradiated area can be seen from the contrast difference. A zoomed-in SEM image is also presented in Fig. 2 (b), which shows the boundary between FIB-irradiated and virgin areas.

Nanoindentation setup

Nanoindentation experiments were carried out using a NanoTest 600 machine (Micromaterials Ltd Wrexham, UK) which has a maximum displacement resolution of 0.05 nm. Berkovich indenter with a tip radius of 400 nm was used for the experiments. Since the material used was polycrystalline 6H-SiC, the grain orientation effect must be studied. In order to distinguish which grain was indented, electron backscatter diffraction (EBSD) mapping was carried out using a high-resolution field emission gun scanning electron microscope (FEGSEM), as shown in Fig. 3. The voltage used in obtaining the EBSD map was 20 kV, and the specimen was tilted to an angle of 70°. The grain orientation was determined from the Euler angles (φ_1 , ϕ , φ_2) measured during the EBSD process and converted to Miller indices using:

$$\begin{pmatrix} u & r & h \\ v & s & k \\ w & t & l \end{pmatrix} = \begin{pmatrix} \cos\varphi_1\cos\varphi_2 - \sin\varphi_1\sin\varphi_2\cos\phi & \sin\varphi_1\cos\varphi_2 + \cos\varphi_1\sin\varphi_2\cos\phi & \sin\varphi_2\sin\phi \\ -\cos\varphi_1\sin\varphi_2 - \sin\varphi_1\cos\varphi_2\cos\phi & -\sin\varphi_1\sin\varphi_2 + \cos\varphi_1\cos\varphi_2\cos\phi & \cos\varphi_2\sin\phi \\ \sin\varphi_1\sin\phi & -\cos\varphi_1\sin\phi & \cos\phi \end{pmatrix} \quad (4)$$

where uvw , rst and hkl are related to rolling, transverse and normal directions, respectively. In this study, EBSD analysis was carried out from the perspective of a normal direction (ND) and the Euler angles were transferred to miller indices

Fig. 1 (a) Schematic diagram of the sample exposed to the ion beam and (b) SRIM simulation of ion beam penetration and the irradiated area

Fig. 2 SEM images of (a) overall FIB-irradiated area and (b) boundary of FIB-irradiated area and virgin area ($\times 15,000$ magnification)

hkl . The Miller indices (hkl) were then transferred to Miller-Bravais indices ($hkil$) with $i = -(h+k)$.

After careful calibration and sample preparation, nanoindentation tests with loads of 30 mN, 60 mN and 100 mN were carried out on the virgin sample. For these load levels, a constant rate of 1 mN/s was used, and a 10-s dwell time was imposed at the peak load. The tests were performed in a temperature-controlled lab, and the gap between each indent was sufficient to avoid the interference of the residual stress field due to prior indents. A schematic of the indentation pattern is shown in Fig. 4, where the indents made at 400-mN load were used as reference points to locate indents made at 30-, 60- and 100-mN loads during SEM examinations. To quantify the effect of irradiation exposure, low-load nanoindentation (1 and 3 mN) was carried out on both virgin and FIB-irradiated areas of the same sample. In this case, the loading rate was chosen to be 5% of the peak load per second. For instance, for 1 mN, the loading rate was set as 0.05 mN/s. A 4×4 matrix was set for both 1- and 3-mN

indentations. In addition, high load nanoindentation (30, 60 and 100 mN) was also carried out to study the effect of irradiation on the material behaviour, including the fracture properties, at a larger depth. In this case, 20 indents were made for each load level and the loading condition was controlled to be the same as that used for nanoindentations on virgin area, including the loading rate, dwell time and temperature.

Results and discussion

Force-displacement response for sample as-received

The force-displacement curves obtained from nanoindentation tests at 30-, 60- and 100-mN loads for the as-received sample are shown in Fig. 5. It can be seen that the initial portion of the loading segment is consistent across the three load levels, i.e. the grain orientation effect

Fig. 3 EBSD map of the indentation area

Fig. 4 The schematic of the indentation pattern

was not obvious at small load levels. With an increase in load, the force-displacement curves start to differ due to differences in the grain orientation. The hardness and reduced elastic modulus for each experiment were calculated using the Oliver and Pharr method [18]. The elastic modulus of the specimen was determined based on contact mechanics with known mechanical properties of the diamond indenter ($E = 1140$ GPa, $\nu = 0.07$) [19–21]. Figure 6 shows the comparison of Young's modulus (E) and hardness (H) obtained from the three load levels. It can be seen that both H and E reduce with increasing load due to the indentation size effect.

SEM and EBSD characterisation of the as-received sample after nanoindentation

The mechanical response was different for different indentation locations even at the same load (Fig. 5) due to a difference in local grain orientation. To assess the grain orientation effect, EBSD mapping was performed for the sample after nanoindentation. Figure 7 shows a selected grain, with two indents made at 60-mN load. Black triangles indicate these locations in Fig. 7 (b). Based on the EBSD map and the inverse pole figure (IPF), the orientation of the selected grain is neither a basal (0001) plane nor a pyramidal ($10\bar{1}1$) plane. It has a Euler angle of (61.1, 39.0, 32.7) which corresponds to

(0.3399, 0.4198, 0.8415) in Miller indices and (0.3399, 0.4198, -0.7598 , 0.8415) in Miller–Bravais indices for hexagonal crystalline material. Figure 7 (c) shows the force-displacement curves corresponding to the two imprints on the selected grain, which correspond well with each other.

Further EBSD analysis was carried out for indents with 60-mN load. Three indents were selected, each in a different grain. Figure 8 (a) is the IPF map indicating the orientation difference of the three grains. We observe that there were two grains with relatively similar orientation (shown in pink and light pink colours). The other indent was made on a grain which has a significantly different orientation from the other two. The corresponding force-displacement curves are shown in Fig. 8 (b) using the same colour and label as for the IPF. It can be seen that the initial stage of the loading coincides for all three curves which imply that the mechanical behaviour within the elastic region is similar. A difference in the force-displacement response was observed from the point of elastic-plastic transition until the peak load. For the two similar grains (#. 1 and #. 2), the difference of force-displacement response was much smaller when compared with that between grains #1 and #3. For the same load level, a deeper penetration was made for grain #3 when compared with that for grain #1 and #2. We notice that the orientation of grain #3 was close to a prismatic crystallographic plane, with a normal direction of $\langle 12\bar{1}0 \rangle$, on which dislocations were reported [22, 23],

Fig. 5 Force-displacement curves for 30-, 60- and 100-mN indentations made on the as-received sample

Fig. 6 Average hardness and elastic modulus obtained from indentations made on the as-received sample

Fig. 7 (a) EBSD map with IPF, and (b) image and (c) the force-displacement curves of the two imprints made on the same grain under 60-mN load

leading to more plastic deformation and a larger displacement/penetration.

In SiC, the deformation response in indentation depends on the grain orientation and related slip system activity within the grains. 6H-SiC has a hexagonal close-packed (HCP) crystal structure, and the basal plane is the favourable slip plane for slip activity with slip occurring in the $\langle 11\bar{2}0 \rangle$ direction. To initiate slip, a critical resolved shear stress is required for a slip system which may differ significantly across slip systems. Therefore, SiC with different grain orientations may behave differently under the same load conditions. In the present work, when the indentation was made on the prismatic plane (indent #3 in Fig. 8), which was also one of the crystallographic planes in 6H-SiC, more plastic deformation was observed at indent #3 in comparison with locations such as indents #1 and #2. Indent #1 was made on $(0.3399, 0.4198, -0.7598, 0.8415)$

plane (i.e. not a rational crystal plane), and experienced less plastic deformation. Here, a fracture could occur when the applied stress was sufficiently high in the absence of preferred slip systems to allow for plastic deformation.

For the experiment with 100-mN load, two indents, made on different grains (grain A and B), were selected for direct comparison (Fig. 9). The IPF map shows that the two grains have a significant misorientation. The SEM image in Fig. 10 shows no crack (primary or secondary) formation due to indentation on grain A. For indentation made on grain B, cracks can be clearly seen at the three corners of the imprint. However, it may be argued that for indentation on grain B, the possible presence of voids in the immediate vicinity of the imprint may lead to the nucleation and propagation of cracks. The imprint sizes (tip to corner length) of indents on grain A and B are 1.73 and 1.76 μm, respectively. The difference was

Fig. 8 Inverse pole figure for 3 selected grains and the corresponding force-displacement curves

marginal, which implies the existence of a void has a negligible influence on the imprint. Therefore, the major reason for cracking in grain B was probably the grain orientation which

prohibits dislocation movement, thereby leading to a stress build-up and eventual crack generation. In contrast, for grain A, the grain orientation may be favourable for the dislocation

Fig. 9 EBSD map with IPF and two indents made on a single grain

Fig. 10 SEM images of imprints made on (a) grain A and grain B (b) under 100-mN load

nucleation and movement, and therefore under the same load, the stress leads to plastic slip thereby avoiding fracture.

Force-displacement response for FIB-irradiated sample

Lower load level

As shown in Fig. 11, at lower loads (1–3 mN), the FIB-irradiated sample showed a harder response than the virgin sample. The hysteresis loops show that the unloading segment of the curves was close to the loading segments, which indicates limited plastic work and deformation. In contrast, the force-displacement curves for the virgin sample indicate larger plastic work and deformation.

The average E and H were plotted in Fig. 12, where the FIB-irradiated sample showed higher values than the virgin sample. This increase of hardness or embrittlement is observed in metallic materials, including NiAl–Mo alloys [24], tungsten [25] and Fe–Cr alloys [26], after irradiation. This is attributed to the irradiation-induced point defects which act as barriers to dislocation movement. For irradiated ceramic materials, an increase in hardness and elastic modulus has been rarely observed; instead, most studies report a drop in hardness which was attributed to the irradiation-induced amorphization of the material. In contrast, a study of nanoindentation on SiC coating (59-μm thick) [27] showed an increased hardness and elastic modulus after irradiation, which was attributed to the irradiation-induced point defects that impeded the movement of dislocations. In this study, the observed

Fig. 11 Force-displacement curves for 1- and 3-mN indentations on both virgin and FIB-irradiated samples

Fig. 12 Comparison of hardness and elastic modulus for indentations made on virgin and FIB-irradiated samples

behaviour at lower loads (1 to 3 mN) was most likely due to Ga ion implantation on the surface [28, 29], which hardened the surface layer of the material by obstructing dislocation movement.

Higher load level

Force-displacement plots for indentations tests performed on the irradiated and virgin samples at 30-, 60- and 100-mN loads are shown in Fig. 13. The virgin samples show a stronger response than the irradiated samples. This was reflected in the depth of penetration under the same load level (30–100 mN), which was in sharp contrast to the trend observed at low load levels (Fig. 11). The overall E and H obtained from tests on the virgin area were greater than those for the FIB-irradiated area at same load levels. Figure 14 shows the comparison of E and H obtained from the two samples. The observable difference was believed to be caused by irradiation-induced amorphization (see “TEM and EDS analyses of FIB-irradiated sample”). Such irradiation-induced material degradation was proposed by Barbot et al. [10]. The experimental results indicated that, with an increase in imposed load (30–100 mN), the effect from irradiation-induced amorphization dominates the effect from Ga ion implantation, leading to an overall degradation of properties. It was worth noting that the elastic modulus difference reduced with an increase in load. For instance, at 30 mN, the modulus

difference was about 260 GPa; while for indentations made at 100 mN, the modulus reduced by about 130 GPa. A similar observation was made on comparing the hardness parameters. This was believed to be caused by the decreasing effect of the amorphous layer when the overall indentation depth increases (i.e., the influence of the substrate material increases).

In this study, we perform 15 indentation tests for both 1-mN and 3-mN loads (virgin and FIB-irradiated samples), 30 for both 30-mN and 60-mN loads (virgin sample) and 10 for 100-mN load (virgin sample). Additionally, 20 indentation tests were carried out on the FIB-irradiated sample at 30-, 60- and 100-mN loads. The results reported above are the average values (Figs. 6, 12 and 14). Standard deviations were also worked out for each case and the results are presented in Table 1 for both virgin and irradiated samples.

TEM and EDS analyses of FIB-irradiated sample

To verify the damage caused by FIB exposure, a FIB lift-out was performed on the damaged area. Different FIB currents were used for different stages of the lift-out process. Specifically, coarse milling was performed at 30-kV voltage and 20-nA current, followed by fine milling with 3-nA current. The final thinning was performed with a current decreasing from 1 nA to 100 pA to produce a lamella for TEM

Fig. 13 Force-displacement curves for 30-, 60- and 100-mN indentations on both virgin and FIB-irradiated samples

Fig. 14 Comparison of hardness and elastic modulus for indentations made on virgin and FIB-irradiated samples

Table 1 Standard deviations for hardness and Young's modulus averaged from series of nanoindentations made on both virgin and irradiated samples

Load (mN)	Virgin sample		Irradiated sample	
	<i>E</i> (GPa)	<i>H</i> (GPa)	<i>E</i> (GPa)	<i>H</i> (GPa)
1	1253.38 ± 151.17	159.86 ± 16.51	1211.82 ± 101.43	361.67 ± 72.14
3	940.14 ± 97.51	98.22 ± 7.76	988.62 ± 72.59	290.07 ± 45.97
30	890.06 ± 98.05	101.21 ± 1.94	632.34 ± 35.12	63.43 ± 1.24
60	723.51 ± 96.62	73.44 ± 1.37	574.73 ± 46.82	48.46 ± 1.86
100	674.01 ± 30.71	64.63 ± 1.13	570.33 ± 48.23	45.13 ± 1.93

examination. Figure 15 (a) shows the TEM image of the overall SiC lamella (the darker area in the figure was the protective Pt layer). In the enlarged image (Fig. 15 (b)), different layers can be clearly seen, i.e. the top Pt layer, the amorphized SiC layer and the substrate crystalline SiC. The boundary between each layer was easily distinguishable. The diffraction contrast (i.e., the cloudy pattern) below the amorphized layer was believed to be caused by FIB-induced defects or local stresses. Such diffraction contrast can only be found in crystalline materials [30], while the amorphized layer above the substrate shows no such diffraction contrast. We observe the thickness of each layer was uniform, suggesting that the FIB exposure method delivers a uniform ion flux (Fig. 15 (c)). In addition, selected area diffraction (SAD) was performed at a specific location (marked with a red circle in Fig. 15 (c)), and clearly indicated the crystalline characteristics of the substrate material (Fig. 15 (d)).

In addition, high-resolution TEM (HR-TEM) was performed on the FIB lift-out using FEI Talos F200X machine to further study the irradiation damage in SiC. Figure 16 shows TEM images of the FIB damaged surface under high magnification (~ 1 million times). The ion radiation direction was perpendicular to the sample surface. Regions with darker contrast were seen near the surface, which was caused by Ga ion implantation. Such a layer was believed to be the reason for a harder response observed for low load indentation. Spatially further from the surface, irradiation-induced damage was observed as darkened areas. Fast Fourier transformation (FFT) was applied to the HR-TEM image, providing an enhanced contrast of the HR-TEM images by means of filtering and masking. A typical amorphous diffraction pattern (broad ring) can be seen however mixed with the diffraction pattern for crystalline material (Fig. 16). Diffraction patterns for the crystalline and amorphous Si should be clearly distinguishable, as shown in the work of Sternad et al. [31]. However, in the present study, the FFT images showed both types of diffraction patterns (i.e. crystalline and amorphous) which indicated the occurrence of partial amorphization (up to a depth of ~ 45 nm).

The force-displacement curves for low load (1 and 3 mN) indentation show an indentation depth ranging from ~ 20 to ~ 35 nm for the FIB-irradiated case. Therefore, we conclude that

the increase in hardness and elastic modulus was caused by the shallow Ga ion implanted into the material, while the partially amorphized layer was the cause for the degraded properties as measured from the experiment. EDS was further carried out on both the virgin and FIB-irradiated surfaces. As shown in Fig. 17, Ga element was seen in addition to C, Si and O on the irradiated surface, while no Ga was observed for the virgin sample.

Assessment of fracture toughness

Critical stress intensity factor, K_{IC} , also known as fracture toughness, is a property that describes the resistance of a material to fracture. It can be determined by the size of the cracks from indentation experiments; however, it may be affected by the type of cracks, e.g. radial, median, “half-penny” and the geometry of the indenter [32, 33]. For ceramics, most cracks are caused by tensile stress (mode I) with fracture toughness indicated by K_{IC} . The initial approach to determining the fracture toughness of carbide ceramics using Vickers indentation was proposed by Palmqvist [34, 35]. Crack-length-related fracture toughness model was proposed by Lawn et al. [36] as:

$$K_{IC} = k \left(\frac{E}{H} \right)^n \frac{P}{c^{3/2}} \quad (5)$$

where k is the calibration constant and c is the crack length from the centre of the imprint. The value of n was suggested to be 1/2, and the corresponding value of k is 0.016. While Anstis et al. [37] proposed that n and k had a value of 2/3 and 0.0098, respectively. As mentioned above, the model describes that the fracture toughness may be affected by the type of cracks, and Eq. (1) was valid for median-radial cracking in a homogenous brittle material. It may overestimate the fracture toughness for a tougher material in which only radial cracks develop. In addition, Laugier [35] developed an alternative expression for fracture toughness:

$$K_{IC} = x_v \left(\frac{a}{l} \right)^{1/2} \left(\frac{E}{H} \right)^{2/3} \frac{P}{c^{3/2}} \quad (6)$$

where x_v is a constant and found to be 0.015 for Vickers indentation, a is the distance measured from the imprint centre to corner, l is the crack length measured from the corner and $c = a + l$. For a Berkovich indenter, Ouchterlony [38] proposed a modified relation for the fracture toughness due to different cracking behaviours (three radial cracks for Berkovich indenter as opposed to four cracks for Vickers indenter):

$$K_{Ic} = x_b \left(\frac{a}{l} \right)^{1/2} \left(\frac{E}{H} \right)^{2/3} \frac{P}{c^{3/2}} \quad (7)$$

where the modifying factor $x_b = 1.073x_v$,

The SEM images of imprints made on virgin and FIB damaged areas are shown in Fig. 18 (a) and (b), respectively. The parameters needed for fracture toughness calculation were obtained from the image. The corresponding elastic modulus and hardness for selected imprints were obtained from force-displacement curves (“Force-displacement response for sample as-received”). The fracture toughness for the virgin and irradiated sample was calculated to be $2.39 \text{ MPa m}^{1/2}$ and $4.31 \text{ MPa m}^{1/2}$, respectively, as detailed below:

$$\begin{aligned} K_{Ic,v} &= 1.073 \times 0.015 \\ &\times \left(\frac{1.60 \times 10^{-6}}{0.95 \times 10^{-6}} \right)^{1/2} \left(\frac{684.6 \times 10^9}{65.8 \times 10^9} \right)^{2/3} \left(\frac{100 \times 10^{-3}}{2.55 \times 10^{-6 \frac{3}{2}}} \right) \\ &= 2.39 \times 10^6 \text{ Pa m}^{1/2} = 2.39 \text{ MPa m}^{1/2} \end{aligned} \quad (8)$$

$$\begin{aligned} K_{Ic,FIB} &= 1.073 \times 0.015 \\ &\times \left(\frac{1.78 \times 10^{-6}}{0.53 \times 10^{-6}} \right)^{1/2} \left(\frac{567.8 \times 10^9}{48.9 \times 10^9} \right)^{2/3} \left(\frac{100 \times 10^{-3}}{2.31 \times 10^{-6 \frac{3}{2}}} \right) \\ &= 4.31 \times 10^6 \text{ Pa m}^{1/2} = 4.31 \text{ MPa m}^{1/2} \end{aligned} \quad (9)$$

The toughened response for the FIB-irradiated area was believed to be due to nucleation of microcracks which occur at irradiation-induced point defects. Such microcracks aid the dissipation of strain energy, thus increasing the fracture toughness [11]. Furthermore, indentation pile-ups were seen under SEM in Fig. 19 (a), but such features were not observed in nanoindentation experiments on the intact surface (Fig. 19

Fig. 15 TEM images of (a) the overall lamella and (b, c) different layers. (d) The diffraction pattern of the substrate material

Fig. 16 HR-TEM image of FIB-irradiated SiC

(b)). The surface profile was measured using an NPFLEX non-contact optical profiler. As observed in Fig. 19 (c), indentation pile-ups can be observed in the FIB-irradiated sample, while such pile-ups were not seen for the virgin sample (Fig.

19 (d)). A similar observation was found in 4H-SiC [10] and attributed to the net effect of irradiation-induced amorphization of the material. Bulk SiC impedes the amorphization of SiC leading to the formation of pile-ups.

Fig. 17 EDS analysis showing (a) no trace of Ga for intact SiC sample and (b) the existence of Ga element for FIB-irradiated sample

Fig. 18 SEM images of the imprint made under 100 mN for (a) virgin and (b) FIB-irradiated samples

The presence of pile-ups indicates more plastic deformation due to a softer response of the amorphized layer, which on the other hand enhances the fracture toughness of the material.

In this study, the virgin sample was sintered pressureless with different grain sizes and orientations, exhibiting the properties of crystalline materials. The irradiated sample

demonstrated different properties caused by the amorphization through ion implantation. Specifically, the virgin sample is polycrystalline 6H-SiC which behaves like most crystalline ceramics, and deforms plastically only when the resolved shear stress on certain slip systems such as basal and prismatic planes exceeds the critical value during

Fig. 19 SEM images of imprints made on (a) FIB-irradiated and (b) virgin samples with surface profile measurements (c and d)

indentation-induced deformation. Under Ga ion irradiation, the crystal structure is affected or even destroyed, resulting in amorphization. Therefore, surface pile-ups, as well as an increase in fracture toughness, were observed for the irradiated sample under indentation at a high load level. On the other hand, Ga ion implantation may also cause significant lattice distortion of the surface layer and thereby inhibit plastic deformation. Therefore, the irradiated sample had different mechanical responses under indentation at a low load level (shallow penetration), showing a harder response in comparison with the virgin sample.

Conclusion

Nanoindentation tests using Berkovich indenter have been carried out to analyze the mechanical response of polycrystalline 6H-SiC at the nanoscale. Grain misorientation influences the force-displacement response. Indentations made on the crystallographic planes which favoured dislocation movement showed a softer response. Additionally, SEM and EBSD analyses showed that crack initiation was affected by the grain orientation, and crack may not occur for indentations made on grains with orientations that were favourable to dislocation activities. In addition, for the sample exposed to FIB irradiation, a different response was observed in terms of force-displacement curves for different load regimes. For a lower load (1 and 3 mN) indentation, an improvement of properties was observed for hardness and the elastic modulus, but also with an increase in embrittlement. Such behaviour was attributed to Ga ion implantation, as confirmed by the EDS analyses. For higher load levels (30, 60 and 100 mN), reduced hardness and elastic modulus were observed. SEM and surface profile analyses showed indentation pile-up which was not observed for the virgin sample. The fracture toughness for the FIB-irradiated sample was found to be higher than that for the virgin sample. The increase of the fracture toughness, as well as reduction in mechanical property and indentation pile-up, was due to the irradiation-induced amorphization, as confirmed by TEM analyses.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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