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Enhanced Surface Hardness in Nitrogen-Implanted Silicon Carbide

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Abstract

Preliminary studies have been performed on the feasibility of carbon-silicon nitride formation (β -Si_{1.5}C_{1.5}N₄, the homologue of equilibrium β -Si₃N₄ or hypothetical β -C₃N₄) by high dose N⁺-implantation into polycrystalline β -SiC (cubic). Thin films were formed using 100 keV implantations with varying ion doses in the range from 1.1×10^{17} to 27.1×10^{17} N/cm², and target temperatures between -196°C and 980°C. X-ray diffraction with a position-sensitive detector and cross-sectional transmission electron microscopy revealed that the as-implanted surfaces (up to 860°C) contained ~0.1 μ m thick buried amorphous layers. Rutherford backscattering spectroscopy showed that the peak concentration of nitrogen saturated up to approximately 54 at. % with increasing doses, suggesting formation of a new phase. Implantation to doses of 1.1×10^{17} and 2.3×10^{17} N/cm² at 980°C caused enhanced surface hardness compared to SiC.

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1. Introduction

There has been a continuous search for hard substances in materials research. The synthesis of metastable $\beta\text{-C}_3\text{N}_4$, the homologue of $\beta\text{-Si}_3\text{N}_4$, has fostered fervent interest since it was theoretically predicted to have a bulk modulus rivaling that of diamond [1,2]. The hardest known materials, diamond and cubic boron nitride (c-BN), are metastable under ambient conditions. Derivation of a scaling relationship and first-principles pseudopotential total-energy calculations predicted the bulk modulus of $\beta\text{-C}_3\text{N}_4$ to be in the range of 427 to 483 GPa, while the bulk modulus of diamond is 443 GPa.

Many attempts have been made to synthesize carbon nitride by employing various non-equilibrium processes: deposition, pyrolysis or shock compression [3-17]. However, these have resulted in the formation of either non-stoichiometric (nitrogen-deficient) compounds or unidentified crystalline compounds (based on diffraction studies). The formation of a carbon-silicon-nitrogen compound, namely $\beta\text{-Si}_{1.5}\text{C}_{1.5}\text{N}_4$, is a plausible approach since $\beta\text{-Si}_3\text{N}_4$ is a well-established equilibrium phase, while $\beta\text{-C}_3\text{N}_4$ is still hypothetical, probably due to its extreme metastability [18]. Several groups have reported the synthesis of carbon-silicon-nitrogen compounds, but the concentration of nitrogen in the SiC_xN_y compounds was not higher than 40 at. % [19-22].

The present study was undertaken to synthesize stoichiometric β - or $\alpha\text{-Si}_{1.5}\text{C}_{1.5}\text{N}_4$ compounds by transforming the $\beta\text{-SiC}$ (cubic) phase (carbon in sp^3 bond configuration) with nitrogen implantation. The notations of β - and $\alpha\text{-Si}_{1.5}\text{C}_{1.5}\text{N}_4$ are the same as β - and $\alpha\text{-Si}_3\text{N}_4$ phases, having 14 and 28 atoms per hexagonal unit cell, respectively [23]. With added nitrogen in SiC

phase, silicon atoms may maintain carbon-to-nitrogen bonds in sp^3 configurations, instead of sp^2 hybrids. This effect may cause β - or α - $\text{Si}_{1.5}\text{C}_{1.5}\text{N}_4$ to approach a thermodynamically stable state, rather than a metastable state of hypothetical β - or α - C_3N_4 . The β - or α - $\text{Si}_{1.5}\text{C}_{1.5}\text{N}_4$ phases with 57.14 at. % N would arrange atoms so as to form a network of sp^3 -bonded C and Si, linked by three-fold-coordinated N atoms. Silicon and carbon atoms may be chemically disordered in the β - or α -phase hexagonal structure, causing some local strains. The nucleation and growth processes of this feasible metastable phase will depend on the structural defects induced by ion irradiation, and could be controlled by ion energy, dose rate and substrate temperature.

2. Experimental Procedure

The substrates were chemical-vapor-deposited silicon carbide (polycrystalline with $\sim 5 \mu\text{m}$ grain size) with $10 \times 10 \times 1 \text{ mm}$ in size, and polished to a mirror finish (with $1 \mu\text{m}$ diamond paste) before any implantation. X-ray diffraction performed on the as-received substrates confirmed that they were mainly β -phase SiC (cubic) and had less than 1% of α -phase SiC (hexagonal).

The ion beam size was about 6 mm in diameter, and was swept across the $10 \times 10 \text{ mm}$ sample. Nitrogen ions at 100 keV with a beam current of $220 \mu\text{A}$ (instantaneous dose rate of $\sim 5 \times 10^{15} \text{ N/cm}^2 \cdot \text{s}$) were implanted into β -SiC to various doses in the range from 1.1×10^{17} to $27.1 \times 10^{17} \text{ N/cm}^2$, and irradiation temperatures between -196°C and 980°C . Nuclear and electronic stopping powers are approximately 10 and $50 \text{ eV/\AA}$, respectively, estimated from TRIM calculations [24]. The synthesized thin films of the as-implanted substrates were characterized by x-ray diffraction using a 120° curved-position-sensitive detector with low ($\sim 5^\circ$)

incident angle. Rutherford backscattering spectroscopy (RBS) with 2 MeV ^4He ions was conducted for compositional analysis of the as-implanted surface.

To characterize the microstructures and phases formed upon implantation, transmission electron microscopy (TEM) was used extensively. The as-implanted surfaces were prepared for plan-view and cross-sectional observations with the 200 keV field-emission Hitachi HF2000 TEM. For the cross-sectional TEM studies, two $\sim 2.5 \times 5.0$ mm rectangular pieces were glued face to face, and several thin wafers (typically 0.6 mm) were sliced. One of the typical $\sim 2.0 \times 2.5 \times 0.6$ mm cross sections was polished from both sides up to a final polish with 1 μm diamond paste. The ~ 100 μm thick sample was dimpled using 2-4 μm diamond paste to an approximate thickness of 25 μm . The two foil sections held together were glued on a Cu grid so as to leave the interface exactly at the center of the grid hole. Further thinning was achieved by Ar ion milling (typically at 4 keV and 1 mA) during which the foil was cooled by thermal contact with a metal cable immersed in liquid nitrogen, to minimize any possible ion-beam-induced phase transformations. For the chemical identification of the implanted area, the Noran ultra-thin window energy-dispersive spectrometer (EDS) attached to the TEM was used.

Hardness test of ion-implanted thin films was performed with a low load nanoindentation instrument. The nanoindenter (Mechanical Properties Microprobe), manufactured by Nano Instruments Inc., continuously monitored load and depth during loading and unloading of a diamond tip. Since the depth measured during indentation included both plastic and elastic displacements, the elastic component was subtracted from the data to obtain hardness. Motion of the specimen stage in the x-y plane was also precisely controlled, within 2 μm of any chosen point on the specimen. Nine separate indentation traces were used for the reproducibility of tests

for each sample.

3. Results and Discussion

Ion doses in the range from 1.1×10^{17} to 27.1×10^{17} N/cm² were incorporated into polycrystalline β -SiC. The Rutherford backscattering spectra (RBS) in Fig. 1 show a saturation of the nitrogen peak concentration for ion doses higher than 9.0×10^{17} N/cm² at 860°C. This is an indication of a new phase formation in the C-Si-N compound.

A quantitative analysis of the RBS data by a RUMP computer simulation [25] shows that the peak concentration of nitrogen in β -SiC varied from 8.8 to 51.0 at. % for the ion doses of 1.1 to 27.1×10^{17} N/cm² at 860°C (Table 1). Sputtering itself may not be enough to cause a concentration saturation of about 51 at. % nitrogen: With a sputtering yield of 0.2 atom/ion for SiC (upper limit) [24,26], the highest dose used (27.1×10^{17} N/cm²) would remove roughly 0.06 μ m of the surface.

The effect of irradiation temperature and ion dose on the peak nitrogen concentration is shown in Table 1. At the dose of 18.1×10^{17} N/cm², the amount of nitrogen incorporated into β -SiC decreases slightly from 53.5 to 50.5 at. % N with increasing temperatures (from -196°C to 860°C). Scanning electron microscopy (SEM) studies gave evidence that there were regions of cracks at the free surface for the high temperature implantations, while the cracking density for the liquid-nitrogen temperature implantations was reduced. Cracking (surface roughness) as well as ion-beam-enhanced diffusion with increasing irradiation temperature may have caused the temperature dependence of nitrogen concentrations. The actual concentration of nitrogen in

the buried layer may be higher than that measured by RBS, since any interface roughness will smear out the RBS spectrum. Interface roughness may result from the effects such as surface cracks, trapped bubbles below the implanted layer, sputtering surface morphology, etc.

The RBS data analysis also revealed that the thin films formed by 100 keV N^+ implantation contained a buried layer centered at a depth of $\sim 0.15 \mu\text{m}$ from the surface, consistent with the TRIM simulations [24]. The longitudinal statistical spread (ΔR_p : half-width at 60% maximum) was calculated to be between $0.04\text{--}0.11 \mu\text{m}$, depending on the nitrogen dose, as shown in Table 1. It is however not clear why the incorporated nitrogen amount in SiC (calculated by the peak concentration multiplied by the longitudinal spread ΔR_p) from Table 1 is not proportional to the nitrogen dose. Some fraction of nitrogen atoms in the ion-beam modified SiC and bubble layer may depart the substrate by ion-beam-induced diffusion or through various possible cracks.

Figure 2(a) shows the cross-sectional TEM image of SiC implanted at -196°C with $18.1 \times 10^{17} \text{ N/cm}^2$. Several distinct layers are visible. The top layer is a $\sim 0.15 \mu\text{m}$ thick continuous amorphous layer, confirmed by micro-diffraction. The layer below the continuous amorphous zone contains bubbles which are characteristic of high dose implantation [27]. The next layer shows another amorphous layer ($\sim 0.06 \mu\text{m}$ thick), on top of the SiC substrate.

Figure 2(b) is from N^+ -implanted SiC at 860°C with $9.0 \times 10^{17} \text{ N/cm}^2$. The top layer containing mainly Si and C is visible with small crystalline and amorphous regions confirmed by micro-diffraction. Below this top layer is a $\sim 0.08 \mu\text{m}$ thick amorphous layer where the nitrogen concentration is the highest. The layer below the amorphous zone contains bubbles, and is followed by a $\sim 0.07 \mu\text{m}$ thick amorphous layer, similar to the image in Fig. 2(a) of the

low-temperature implanted SiC.

For all the implanted samples shown in Table 1, glancing angle x-ray diffraction with a 120° curved-position-sensitive detector showed no new crystalline peaks other than those from β - and α -SiC substrate. Plan-view TEM diffraction studies from a N^+ -implanted SiC substrate with a dose of 18.1×10^{17} N/cm² at 860°C showed a diffuse peak at $k \approx 1.9 \text{ \AA}^{-1}$ for the scattering wave vector ($k = 4\pi \sin\theta / \lambda$ where θ is the scattering angle and λ is the electron wavelength), in addition to the diffraction spots from β -SiC and α -SiC.

Diffraction studies by cross-sectional TEM from the buried amorphous layers showed diffuse rings. However, these were very weak, probably because the layer was not thinned enough due to differential sputtering during ion milling. In addition, sample preparation for the cross-sectional TEM was quite difficult, since the buried layer by high-dose ion implantation was under high compressive stress. The inner diffraction ring was very obscure due to the direct beam from the micro-diffraction. The scattering vector for the outer diffuse peak was observed at $k \sim 5 \text{ \AA}^{-1}$. Further detailed studies are required to confirm diffraction patterns from these buried amorphous layers as well as the top crystalline layer (shown in Fig. 2(b)).

It is not clear why amorphous phases still exist even by ion irradiation at 860°C. Displaced lattices (structural defects) caused by the ion beam with approximately 10 eV/Å nuclear stopping power may cause ion-beam enhanced diffusion. At a dose rate of $\sim 5 \times 10^{15}$ N/cm²·s (220 μ A beam current on a spot size of 28 mm²), successive collision cascades of $\sim 100 \text{ \AA}$ in diameter occur at ~ 0.3 ms intervals [28,29]. Diffusion lengths of structural defects having an 1 eV activation enthalpy are approximately 3,000 Å within ~ 0.3 ms at 860°C, assuming that the

prefactor for diffusivity is $\sim 10^{-1} \text{ cm}^2/\text{s}$ [30].

With a similar dose rate and nuclear stopping power, an enhanced regrowth rate is expected at implantation temperatures above $\sim 260^\circ\text{C}$ from ion-beam-induced solid-phase epitaxial regrowth in Si [31]. (A comparable threshold temperature would be expected in SiC for the ion-beam induced regrowth kinetics, since structural defects controlling interfacial motion are created by ion beams). However, further TEM studies are required to identify irradiation-temperature dependence for the crystalline and amorphous phase formations.

Surface hardness was obtained by nanoindentation for SiC implanted at 980°C with doses of 1.1×10^{17} , 2.3×10^{17} and $4.5 \times 10^{17} \text{ N/cm}^2$ (10, 20 and 40 at. % nitrogen, respectively), as shown in Fig. 3. Since the depth measured during indentation induced both plastic and elastic displacements, the elastic component was subtracted from the data to obtain the hardness [32]. The apparent surface hardness from the 1.1×10^{17} and $2.3 \times 10^{17} \text{ N/cm}^2$ implantation is enhanced by approximately 20% at the indentation depth of $0.075 \mu\text{m}$, compared to the unimplanted SiC [19,20]. However, nitrogen implantation with a dose of $4.5 \times 10^{17} \text{ N/cm}^2$ at 980°C made SiC slightly softer (Fig. 3). Also, the surface hardness of SiC implanted with a dose of $9.0 \times 10^{17} \text{ N/cm}^2$ at 860°C was only 10 GPa (not shown in the figure). This reduction in hardness may result from the formation of bubbles below the Si-C-N compound with high ion dose. Further studies are required to correlate the microstructures (phases) with the enhanced surface hardness.

4. Conclusions

Preliminary experiments on the feasibility of β - or α - $\text{Si}_{1.5}\text{C}_{1.5}\text{N}_4$ phases have been performed by high-dose N^+ -implantation into β -SiC. These results indicate the possibility of metastable carbon-silicon-nitride formation, based on saturation of nitrogen peak concentrations with increasing ion doses. Further structural identifications are required, and formation kinetics of crystalline phase should be investigated in connection with the enhanced surface hardness. Issues related to nucleation/growth processes and stability/metastability need to be understood to successfully synthesize new metastable materials. These studies will also prove valuable to understanding the challenging synthesis of superhard β - and α - C_3N_4 phases.

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Table 1. Nitrogen peak concentration in at. %, and projected range R_p and longitudinal spread ΔR_p in μm , at various ion doses and implantation temperatures. These values were calculated from the RBS measurements.

Temperature ($^{\circ}\text{C}$)	-196	375	600	750	860	980
Dose (10^{17} N/cm 2)						
1.1					8.8 % 0.16 (0.04)	10.0 % 0.16 (0.04)
2.3					18.3 % 0.16 (0.04)	22.1 % 0.16 (0.04)
4.5	37.1 % 0.16 (0.05)				37.1 % 0.17 (0.05)	37.3 % 0.17 (0.05)
9.0	53.1 % 0.17 (0.06)				48.6 % 0.15 (0.09)	
13.6					50.5 % 0.15 (0.09)	
18.1	53.5 % 0.15 (0.10)	51.7 % 0.15 (0.09)	52.7 % 0.15 (0.10)	50.4 % 0.15 (0.10)	50.5 % 0.15 (0.09)	
27.1					51.0 % 0.14 (0.11)	

Figure Captions

Fig. 1. Rutherford backscattering spectra for the dose dependence of the concentration profile in 100 keV N^+ -implanted β -SiC samples at 860°C. These were measured by RBS with 2 MeV ^4He ions.

Fig. 2. (a) Cross-sectional TEM micrograph from a N^+ -implanted SiC substrate with a dose of $18.1 \times 10^{17} \text{ N/cm}^2$ at -196°C . (b) High-temperature implanted SiC with $9.0 \times 10^{17} \text{ N/cm}^2$ at 860°C.

Fig. 3. Nanoindentation results from high-temperature (980°C) implanted SiC with doses of 1.1×10^{17} , 2.3×10^{17} and $4.5 \times 10^{17} \text{ N/cm}^2$, and from an unimplanted SiC.

Fig. 1

Fig. 2(a)

Fig. 2(b)

Fig. 3