Synthesis of Metastable Carbon-Silicon-Nitrogen Compounds by Ion Implantation

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The feasibility of carbon-silicon nitride formation (β-$Si_{1.5}C_{1.5}N_4$, the homologue of equilibrium β-Si_3N_4 or hypothetical β-C_3N_4) has been investigated by high dose N^+ implantation into polycrystalline β-SiC (cubic phase). Thin films were formed using 100 keV implantations with varying ion doses and target temperatures. X-ray diffraction with a position-sensitive detector and cross-sectional transmission electron microscopy revealed that the as-implanted surfaces contained ~0.1 μm 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.

Key words: Carbon-silicon nitride, ion-implantation, SiC

INTRODUCTION

The hardest known materials, diamond and cubic boron nitride (c-BN), are metastable under ambient conditions. The synthesis of metastable β-C_3N_4, the homologue of β-Si_3N_4, has fostered fervent interest since it was theoretically predicted to have a bulk modulus rivaling that of diamond.[1–4] Derivation of a scaling relationship and first-principles pseudopotential total-energy calculations predicted the bulk modulus of β-C_3N_4 to be in the range of 427 to 483 GPa (443 GPa for diamond) with a large cohesive energy of 5.8 eV/atom.

Several attempts have been made to synthesize carbon nitride by employing various deposition processes, pyrolysis or shock compression.[5–20] However, these have resulted in the formation of either nonstoichiometric (nitrogen-deficient) compounds or unidentified crystalline compounds (based on diffraction studies). The formation of a carbon-silicon-nitrogen compound, namely β-$Si_{1.5}C_{1.5}N_4$, is a plausible approach since β-Si_3N_4 is a well-established equilibrium phase, while β-C_3N_4 is still hypothetical, probably due to its extreme metastability.[21,22] Several groups have reported the synthesis of carbon-silicon-nitrogen compounds, but the concentration of nitrogen in SiC_xN_y compound was not higher than 40 at.%.[23–25]

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The present study was undertaken to synthesize stoichiometric β- or α-$Si_{1.5}C_{1.5}N_4$ compounds by transforming the β-SiC (cubic) phase (carbon in sp^3 bond configuration) with nitrogen implantation. The notations of β- and α-$Si_{1.5}C_{1.5}N_4$ are the same as β- and α-Si_3N_4 phases, having 14 and 28 atoms per hexagonal unit cell, respectively.[26] 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-$Si_{1.5}C_{1.5}N_4$ to approach a thermodynamically stable state, rather than a metastable state of hypothetical β- or α-C_3N_4.

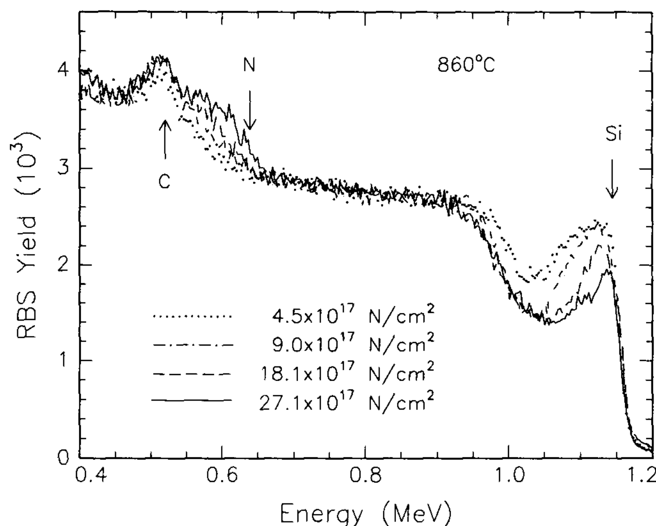

Fig. 1. Rutherford backscattering spectra for the dose dependence of the concentration profile in 100 keV N^+-implanted β-SiC samples at 860°C. These were measured by RBS with 2 MeV ^4He ions.

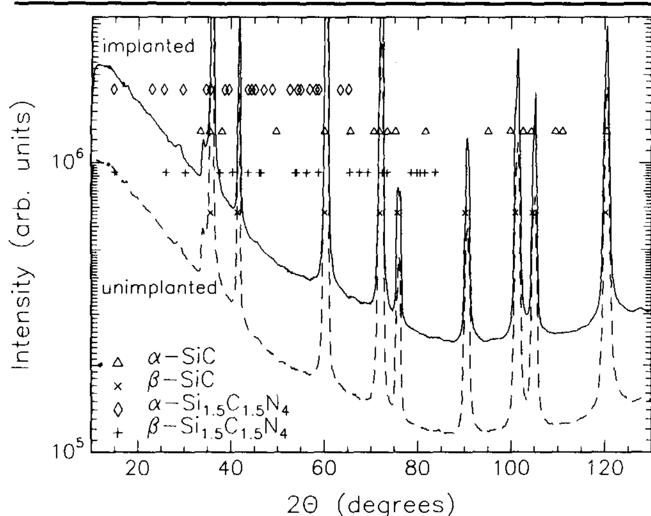

Fig. 2. X-ray diffraction of an unimplanted and a N^+-implanted β-SiC with a dose of 13.6 × 10^{17} N/cm² at 860°C (with CuK_α radiation: λ = 1.5418Å).

The β- or α-$Si_{1.5}C_{1.5}N_4$ phases with 57.14 at.% N would arrange atoms so as to form a network of CN_4 and SiN_4 tetrahedra, linked at the corners by threefold coordination of N atoms. The nucleation and growth processes will depend on the structural defects induced by ion irradiation and could be controlled by ion energy, dose rate, and substrate temperature.

EXPERIMENTAL PROCEDURE

The possible formation of β- or α-$Si_{1.5}C_{1.5}N_4$ has been studied by ion-implantation as a non-equilibrium process. The substrates were polycrystalline silicon-carbide (~5 μm grain size), chemical vapor deposited SiC of 10 × 10 × 1 mm size and polished to a mirror finish (with 1 μm 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 × 10 mm sample. Nitrogen ions at 100 keV with a beam current of 220 μA (instantaneous dose rate of ~5 × 10^{15} N/cm²·s) were implanted into β-SiC to various doses up to 27.1 × 10^{17} N/cm² and irradiation temperatures up to 860°C. Nuclear and electronic stopping powers are approximately 10 and 50 eV/Å, respectively, estimated from TRIM calculations.[27] The synthesized thin films of the as-implanted substrates were characterized in detail by low angle (~5°) x-ray diffraction using a 120° curved-position-sensitive detector. 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-2000 TEM microscope. For the cross-sectional TEM studies, two ~2.5 × 5.0 mm rectangular pieces were glued, and several thin wafers (typically 0.6 mm) were sliced. One of the typical ~2.0 × 2.5 × 0.6 mm cross sections was mounted on a stainless-steel cylinder using low temperature epoxy and then hand polished from both sides up to a final polish with 6 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 ion-beam induced phase transformations. For the chemical identification of the implanted area, an ultra-thin window energy-dispersive spectrometer (EDS) was used.

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 at 860°C. 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. This is an indication of a new phase formation in the C-Si-N compound. Sputtering itself may not be enough to cause a concentration limit of about 51 at.% nitrogen. With a sputtering yield of 0.2 atom/ion for SiC (upper limit),[27,28] the highest dose used (27.1 × 10^{17} N/cm²) removes roughly 0.06 μm of the surface.

A quantitative analysis of the RBS data by a computer simulation[29] 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 I). The RBS data analysis also revealed that the thin films formed by 100 keV N^+ implantation contained a continuous buried layer centered at a depth of ~0.15 μm from the surface. The longitudinal statistical spread (ΔR_p : half-width at 60% maximum) was calcu-

lated to be between 0.04–0.11 μm, depending on the nitrogen dose.

The effect of irradiation temperature and ion dose on the peak nitrogen concentration is shown in Table I. It is seen that the amount of nitrogen incorporated into β-SiC decreases slightly from 53.5 to 50.5 at.% N with increasing temperatures (from −196 to 860°C) at the dose of 18.1 × 10^{17} N/cm². 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. Some smearing in the RBS measurements may have resulted from cracking (surface roughness) with increasing irradiation temperature and may have caused the temperature dependence of nitrogen peak concentrations.

For all the implanted samples shown in Table I, 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, as seen in Fig. 2. 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 ≈ 1.9Å^{-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, as shown in Fig. 3.

Figure 4 shows the cross-sectional TEM image of SiC implanted at 860°C with 9.0 × 10^{17} N/cm². Several distinct layers are visible. 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 ~0.1 μm thick amorphous layer where the nitrogen concentration is the highest. Diffraction studies showed a diffuse ring, which was very weak (probably because the layer was not thinned enough by differential sputtering during ion milling). The layer below the continuous amorphous zone contains bubbles which are characteristic of high dose implantation.[30]

It is not clear why crystalline phases are not formed by ion irradiation at high temperatures. Displaced lattices (structural defects) caused by the ion beam with approximately 10 eV/Å nuclear stopping power may cause ion-beam enhanced diffusion at 860°C. At a dose rate of ~5 × 10^{15} N/cm²·s (220 μA beam current on a spot size of 28 mm²), successive collision cascades of ~100Å in diameter occur at ~0.3 ms intervals.[31,32] Diffusion lengths of structural defects having an 1 eV activation enthalpy are approximately 3,000Å within ~0.3 ms at 860°C, assuming that a prefactor for diffusivity is ~10^{-1} cm²/s.[33] For ion-beam-induced solid-phase epitaxial growth in Si, an enhanced regrowth rate is expected at implantation temperatures above ~250°C with a similar dose rate and nuclear stopping power.[34] Further TEM studies are required to identify whether any small-size crystalline precipitates are embedded in amorphous C-Si-N matrix.

The scattering wave vectors for the plausible β- and α-$Si_{1.5}C_{1.5}N_4$ phases are estimated from the experimental lattice parameters of β- and α-Si_3N_4[26], and theoretical parameters of β- and a-C_3N_4.[1–4,7,8] These calculated values are shown in Fig. 2 (symbols + and ◇). A weight factor is incorporated into the calculation, considering that the lattice constant of β-SiC (4.35Å) is not simply the average of the lattice constants of silicon (5.430Å) and diamond (3.567Å). It also assumes that silicon and carbon atoms are chemically disordered in the β-and α-phase hexagonal structures. Both from plan-view and cross-sectional transmission electron microscopy diffraction studies, the scattering wave vectors from diffuse amorphous peaks were approximately 1.9Å^{-1}.

Table I. Nitrogen Peak Concentrations Obtained by RBS Measurements at Various Ion Doses and Implantation Temperatures

Temp. (°C) Dose (10^{17}N/cm²)	-196	375	600	750	860
1.1					8.8%
2.3					18.3%
4.5	37.1%				37.1%
9.0	53.1%				48.6%
13.6					50.5%
18.1	53.5%	51.7%	52.7%	50.4%	50.5%
27.1					51.0%

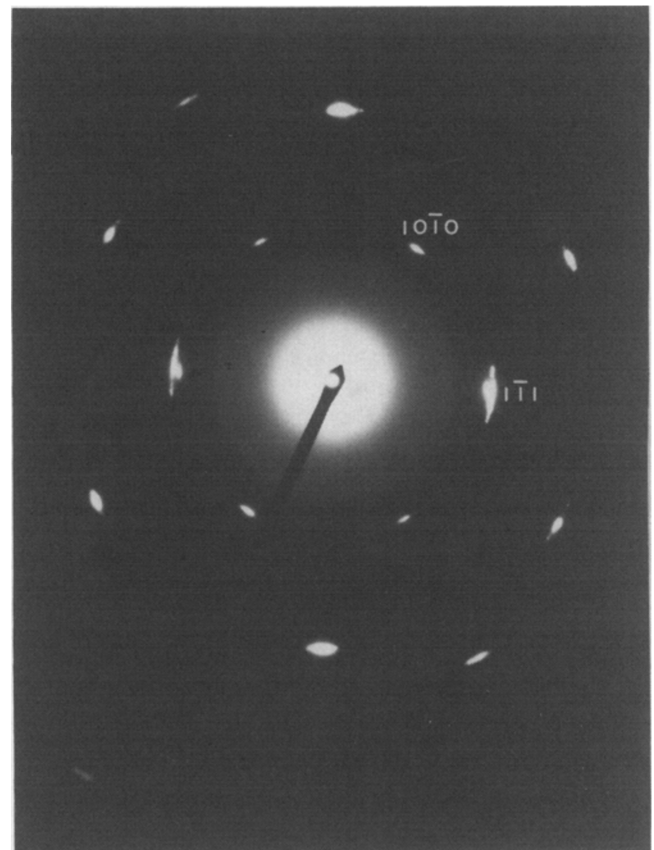

Fig. 3. Selected area diffraction pattern by TEM from a nitrogen-implanted SiC substrate with a dose of 18.1 × 10^{17} N/cm² at 860°C. The zone axes for α- and β-SiC are [0001] and [$\bar{1}$23], respectively. A diffuse ring is inside the sixfold (10$\bar{1}$0) peaks from α-SiC.

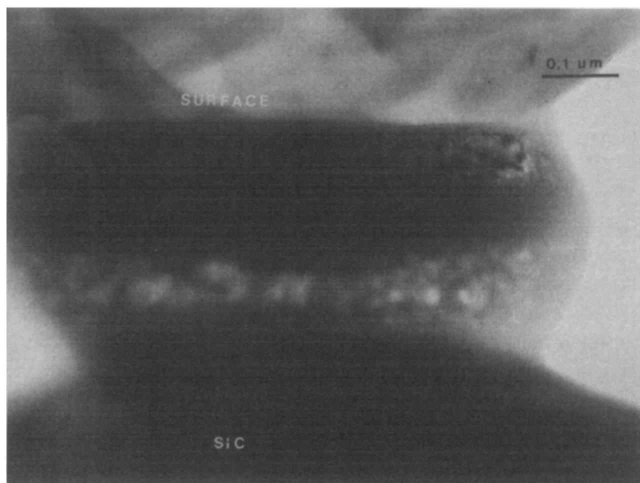

Fig. 4. Cross-sectional TEM micrograph from a nitrogen-implanted SiC substrate with a dose of 9.0×10^{17} N/cm^2 at 860°C.

CONCLUSIONS

The feasibility of β- or α-$Si_{1.5}C_{1.5}N_4$ phases has been investigated by high dose N^+ implantation into β-SiC. Our preliminary results indicate the possibility of metastable carbon-silicon nitride, based on saturation of nitrogen peak concentrations with increasing ion doses. Further structural identifications are required, and formation of crystalline phase should be investigated. 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 understand the challenging synthesis of superhard β- and α-C_3N_4 phases.

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