Physical and bonding characteristics of N-doped hydrogenated amorphous silicon carbide films grown by PECVD and annealed by pulsed electron beam

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Abstract. Nitrogen-doped amorphous silicon carbide films were grown by a plasma enhanced chemical vapour deposition (PECVD) technique. The actual amount of nitrogen in the SiC films is determined by Rutherford backscattering spectrometry (RBS). For irradiation experiments we use electron beams with a kinetic energy 200 keV, a pulse duration of 300 ns, and a beam current of 150 A/cm². It is found that with increased nitrogen doping and following activation of dopants the resistivity of the amorphous SiC films is substantially reduced.

1. Introduction

High-temperature circuit operation from 350°C to 500°C is desired for use in aerospace applications (turbine engines and more electric aircraft initiative), nuclear power instrumentation, satellites, space exploration, and geothermal wells [1-2]. In addition to high-temperature applications, SiC has potential for use in high-power, high-frequency, and radiation-resistant applications [3]. For the application of amorphous SiC films in devices such as heterojunction bipolar transistors and photovoltaic cells, it is highly desirable to form amorphous SiC films with maximum conductivity and a well-defined bandgap. Highly pure, undoped SiC with a large energy gap exhibits insulating properties at normal conditions. However, the available materials are normally reported as having n-type conductivity due to unintentional doping with nitrogen or due to electrically active defects. N-doped SiC films have been prepared by various techniques, which include: chemical vapour deposition (CVD) at elevated temperatures [4], bias-assisted hot filament (CVD) [5], radio frequency plasma-enhanced CVD (PECVD) [6], microwave PECVD [7], electron cyclotron resonance PECVD [8], pulsed laser deposition [9], ion beam sputtering [10] and reactive magnetron sputtering [11]. Standard technologies for silicon device production, such as ion implantation at room temperature and the subsequent thermal annealing of radiation damage at moderate temperatures cannot be adopted because the radiation damage in SiC is extremely consistent. Very high temperatures are necessary for its annealing and to activate dopants. One way to overcome this problem is to perform high current pulse electron or ion beam irradiation instead of high temperature annealing.
The aim of this work was to investigate the properties of nitrogen-doped amorphous SiC films irradiated by pulse electron beams. The properties were investigated by RBS, ERD and IR measurement techniques. The current-voltage (I-V) characteristics of diodes made of doped and irradiated SiC films grown on silicon substrates were studied.

2. Experimental
Nitrogen-doped amorphous silicon carbide films were grown by plasma enhanced chemical vapour deposition (PE CVD) technique. All films were prepared on lightly doped n-type Si substrates (111). The films were deposited in a high frequency parallel-plate plasma reactor in which the frequency, the RF power and the substrate temperature were maintained at 13.56 MHz, 0.06 Wcm\(^{-2}\), and 350°C, respectively. Samples with different amount of N were achieved by small addition of ammonia NH\(_3\) into the gas mixture of silane SiH\(_4\) and methane CH\(_4\) which were directly introduced into the reaction chamber.

The actual amount of nitrogen in the SiC films was determined by Rutherford backscattering spectrometry (RBS). The hydrogen concentration was determined by the elastic recoil detection (ERD) method. For this purpose the \(^{3}\)He\(^+\) ion beam from a Van de Graaff accelerator at JINR Dubna was applied. The energy of 2.4 MeV was chosen. The target was tilted at an angle of 15° with respect to the beam direction and the recoiled protons were measured in forward direction at an angle of 30°.

The samples were irradiated in combined small pulse ion-electron source which consisted of high voltage accelerating generator, vacuum diode, vacuum and diagnostic systems. The negative polarity of the pulse voltage of Marx-Arkad’ev high voltage generator was used for production of the electron beam. For irradiation experiments we used electron beams with a kinetic energy 200 keV, a pulse duration 300 ns, and a beam current 150 A/cm\(^2\). The number of pulses was altered 20 pulses.

For electrical characterization of the SiC films vertical diode structures were formed on the prepared SiC/Si samples. Circular Au dots with a diameter of 0.5 mm and a thickness of 50 nm were evaporated after the cleaning procedure of SiC surface. Al served as large area back contact to Si substrate. The I-V characteristics of devices prepared from different SiC films were measured and evaluated.

3. Results and Discussions
The thickness and refractive index of the SiC films were measured by a Gaertner Ellipsometer. For technological conditions which represented by sample B2, the deposition rate was 12 nm per minute and refractive index was 2. For sample B3 the deposition rate and refractive index were practically the same.

A typical RBS spectrum of as deposited samples is shown in figure 1. The channel numbers at which steps occur correspond to those of carbon, silicon and nitrogen. A simulation of the RBS spectra was used to calculate the concentration of carbon, silicon and nitrogen. The depth scale conversion gives film thickness about 200 nm for both samples. After modeling, we can show from calculated results the presence of small amounts of oxygen but the concentrations of hydrogen in the SiC films are approximately 20 at%. In the case of sample B2 the concentration of silicon, carbon and nitrogen were 30, 35 and 10-11 at%, respectively. The concentration of Si, C and N in sample B3 were 30, 33 and 13-14 at%, respectively. There was no evidence of the substrate mixing into the films. Hydrogen was detected by means of elastic recoil detection.

The ERD analyses (figure 2) show that the amount of incorporated H for samples B2 and B3 were 20 and 19 at%, respectively. Figure 3 shows RBS spectra of the samples B2 and B3. Samples B2 and B3 were surface irradiated by 20 electron beam pulses with parameters E~200 keV, pulse duration 300 ns and j~150 Acm\(^{-2}\). From RBS spectra we show that the spectra are practically uniform and only region which represents the interface is various. There is the possibility that the thickness of the layers were changed after surface irradiation by pulsed electron beam. From modelling and calculating results, the influence of the surface irradiation on the thickness is very small-in the range of the
measured mistake. Infrared spectra of as deposited samples B2 and B3 showed that, there is no essential difference between the spectra of the two samples with different amount of nitrogen.

![RBS spectra](image1)

**Figure 1.** RBS spectra of SiC films deposited onto a silicon substrate for 2 MeV alfa particles detected at scattering angle of 170º.

![ERD spectra](image2)

**Figure 2.** The ERD spectra of recoiled hydrogen obtained with 2.4 MeV $^4$He$^+$. The concentration of hydrogen for samples B2 and B3 was 20 and 19 at%, respectively.

The films contain features typical for hydrogenated amorphous silicon carbide: the main band at 790 cm$^{-1}$ is related with the Si-C stretching modes, the C-H stretching band at around 2900 cm$^{-1}$ and the band around 2100 cm$^{-1}$ are assigned to Si-H stretching vibrations. The infrared spectra in figure 4 revealed the main absorption region between 400 and 2000 cm$^{-1}$. From the spectra we could determine the following vibration frequencies: 520 to 530 and 1090 to 1093 can be related to SiO$_2$, the higher wavenumber can be also related to Si-N bonds close to Si$_3$N$_4$ bonds; 944 to 950 and 1000 to 1005: they can be roughly related to Si-N bonds from Si$_3$N$_4$; 1260 to 1265: they can be related to C-N bonds; 606 to 610: it can be related to Si-C localized vibration normally found in Si due to C in single crystalline Si. The main phonon or vibration frequency is related to SiC and has the following characteristics determined from the reflection spectra: sample B2: center position 795 cm$^{-1}$, width 178 cm$^{-1}$; sample B3: center position 795 cm$^{-1}$, width 145 cm$^{-1}$. The non stressed phonon position of cubic
SiC is 796 cm\(^{-1}\). In amorphous material a shift to higher values indicate on recrystallisation or nucleation of small crystallites.

**Figure 3.** RBS spectra of SiC films: Samples B2 and B3 were surface irradiated by pulse electron beam (E~200 keV, j~150 Acm\(^{-2}\)).

**Figure 4.** IR spectra of SiC films deposited on silicon substrate. Differences of IR spectra between samples are very small.

Representative curves obtained from the I-V measurements of diodes from samples B2 and B3 with different nitrogen doped SiC films are compared in figure 5. Both samples B2 and B3 were exposed to the same pulse electron beam irradiation conditions (20 pulses). The diode currents at applied bias of 5 V were about 2 pA and 200 pA for samples B2 and B3, respectively. These results confirm the fact that samples B3 with higher nitrogen doping (i. e. with nitrogen content of 14 at\%) exhibit about two orders of magnitude higher conductivity (i. e. lower resistivity) compared to B2 (with nitrogen content of 10 at\%).
Figure 5. I-V characteristics of diodes prepared from samples with nitrogen-doped SiC films irradiated by 20 pulses of electron beam.

4. Conclusions
The RBS results showed the concentrations of Si, C and N in the films. The ERD results showed a concentration of hydrogen about 20 at%. IR results showed the presence of Si-C, Si-O, Si-N, Si-H, C-H and C-N specific bonds. It was observed that nitrogen incorporation during deposition produces doping of amorphous SiC films but their resistivity is fairly high. Therefore, the high current pulse electron beam irradiation was applied to activate the nitrogen dopands in the amorphous SiC films. The electrical conductivity was evaluated by means of I-V measurements of diodes prepared from two nitrogen-doped SiC films and the influence of nitrogen concentration was investigated. It was found that with increased nitrogen doping and following activation of dopants the resistivity of the amorphous SiC films was substantially reduced.

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References
[1] Brown I G 1993 J. Vac. Sci. Technol. A 11 1480
[2] Cusack D E, Glassen W M and Steglich H R 1994 Trans.of 2nd Int. High Temperature Electronics Conf. (HiTEC) 17
[3] Trew R J, Yan J B and Mock P M 1991 Proc. IEEE 79 598
[4] Bendeddouche A, Berjoan R, Beche E and Hillel R 1999 Surf. Coat. Technol. 111 184
[5] Gong Z, Wang E G, Xu G C and Chen Y 1999 Thin Solid Films 348 114
[6] Sachdev H and Sheid P 2001 Diamond Relat. Materials 10 1160
[7] Wu J Y, Kuo C T and Yang P J 2001 Mater. Chem. Phys. 72 245
[8] Gomez F J, Prieto P, Elizalde E and Piquerasa J 1996 Appl. Phys. Lett. 69 773
[9] Soto G, Samano E C, Machorro R and Cota L 1998 J. Vac. Sci. Technol. A 16 1311
[10] He Z, Carter G, and Colligon J S 1996 Thin Solid Films 283 90
[11] Berlind T, Hellgren N, Johansson M P and Hultman L 2001 Surf. Coat. Technol. 141 145