



## Room temperature ferromagnetism induced by N-ion implantation in 6H-SiC single crystal

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### ABSTRACT

6H-SiC single crystal implanted with N<sup>+</sup> ions with an energy of 160 keV and a dose of  $1 \times 10^{17} \text{ cm}^{-2}$  at room temperature was analyzed by atomic force microscopy (AFM), positron annihilation lifetime spectroscopy (PALS) and superconducting quantum interference device (SQUID). AFM analysis results show the morphological characteristics of degraded implanted sample. PALS analysis indicated the main defect type was silicon vacancy ( $V_{\text{Si}}$ ) and the concentration of  $V_{\text{Si}}$  increased in the SiC after N ion implantation. SQUID results showed that N-implanted 6H-SiC sample exhibits room-temperature ferromagnetic (RTFM) behavior. It is demonstrated that room temperature ferromagnetism can be obtained by metal-free doping. The possible mechanism of ferromagnetic order was briefly discussed.

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### 1. Introduction

Diluted magnetic semiconductors (DMSs) are actively pursued as one of the functional semiconductors, taking advantage of the spin degree of freedom for the realization of spintronics. As a kind of most important DMSs, SiC holds great potential for power devices under high temperature, high-frequency, and radiation environments [1]. Ion implantation is an efficient way to prepare DMSs and many groups have reported the magnetic properties of transition metal (TM)-implanted SiC [2,3]. However, the origin of ferromagnetic order was disturbed by the uncontrolled precipitation or secondary phase formation. For clarifying microscopic origin of magnetic properties, non-metal implantation to trigger ferromagnetism in SiC DMSs is desirable. Nitrogen, as a non-magnetic element has roughly the same atomic radius as carbon [4]. Nitrogen ion implantation has an advantage in excluding a contribution from the uncontrolled magnetic clusters. Doping nitrogen can facilitate the development of long-range magnetic order, which has been reported in some publications [5,6]. It has been theoretically predicted that N doped SiC exhibits ferromagnetism [7]. However, little attention has been paid to the magnetic properties of SiC implanted with N experimentally.

In this paper, we report the morphology, defect types and magnetic characteristics of the N-implanted 6H-SiC. It is

demonstrated that room temperature ferromagnetism can be obtained by N implantation.

### 2. Experimental

Semiconducting one-side polished n-type 6H-SiC (0001) single crystal from the KMT Corporation (Hefei, China) was implanted with N<sup>+</sup> ions with an energy of 160 keV and a dose of  $1 \times 10^{17} \text{ cm}^{-2}$  at room temperature. The size of 6H-SiC single crystals is about  $5 \times 5 \times 0.5 \text{ mm}^3$ . During implantation, the wafer was tilted 7° from the normal to minimize the channeling defect. The wafer was subsequently rapid thermal annealed at 850 °C for 10 min under the protection of flowing N<sub>2</sub>. The morphology, defect types and magnetic characteristics of the un-implanted and implanted samples were studied by AFM, PALS and SQUID magnetometer, respectively.

### 3. Results and discussion

The popular stopping and range of ions in matters (SRIM) program is widely used in implantation experiments for simulating the ion concentration profile and displacements per atom (dpa) distribution [8,9]. According to the SRIM simulation [10], the projected range of the ions is about 240 nm. Fig. 1(a) shows a calculated depth profile for the N implantation. The simulated dpa (displacements per atom) depth profile was shown in Fig. 1(b). The most implantation damage is essentially centered at about 350 nm top layer from the surface and a dpa level of 25 as the damage peak was observed.

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The morphological change was studied by AFM. All the images were measured over an area of  $5 \times 5 \mu\text{m}^2$ . The surface of un-implanted SiC reveals faint ridges and random scratches caused by the polishing process as shown in Fig. 2(a). This sample exhibits a relatively smooth surface morphology with a root mean square (RMS) value of 0.65 nm. Fig. 2(b) shows that the implanted sample has a rough surface with a RMS value of 1.45 nm, showing a much rough surface morphology than the un-implanted sample. The RMS values increased after N implantation, similarly to Cu implanted GaN [11], which may be attributed to the damage caused by implantation process.

To gain insight into the defect types produced by ion-implantation, positron annihilation lifetime spectroscopy measurements have been performed. A lifetime spectrum is a linear combination of exponential functions corresponding to different annihilation sites. The lifetime spectra contain at least  $10^6$  events and were analyzed using the program package LT 9.0 [12]. The fitted two positron lifetimes  $\tau_1$ ,  $\tau_2$ , and the intensity value ( $I_1$ ,  $I_2$ ) of the corresponding positron lifetime for the samples are shown in Table 1. It is obvious that the lifetimes  $\tau_1$  and  $\tau_2$  are independent of implantation behavior within the allowed range, showing the same defect type in the samples. The lifetime  $\tau_1$  is found to show

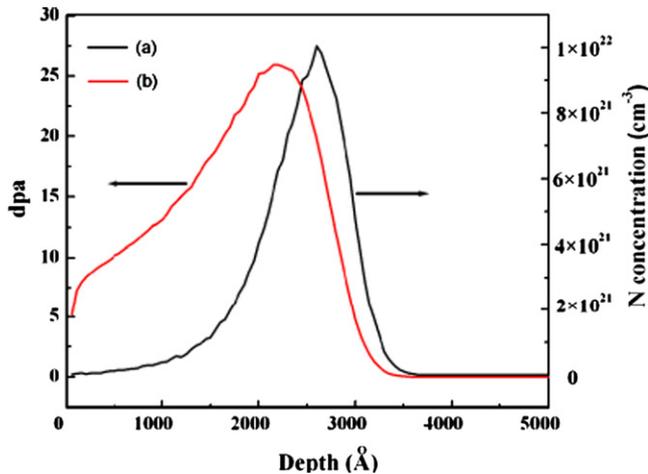


Fig. 1. Calculated: (a) N concentration profile and (b) depth distribution of displacements per atom for the implanted sample.

almost constant value ( $\approx 170$  ps). This value is in agreement with the positron lifetimes at silicon vacancy defect ( $V_{\text{Si}}$ ) in 6H-SiC single crystal [13]. Consequently, the lifetime  $\tau_1$  is attributed to positron trapping at  $V_{\text{Si}}$ . The lifetime value of  $\tau_2$  can correspond to positron lifetime of vacancy clusters, according to the theoretical calculation [14]. After implantation, the  $I_1$  value become larger, revealing the increasing concentration of  $V_{\text{Si}}$ . While the  $I_2$  value decreases after implantation, indicating the concentration of vacancy clusters decreases. N may prefer to fill the C vacancies in vacancy cluster due to the similarity between N and C atoms. Hence the vacancy clusters begin to collapse and shrink, bringing the concentration of vacancy clusters decreases and that of the  $V_{\text{Si}}$  increases. Moreover,  $V_{\text{Si}}$  may also be created by implantation damage high energy particles knock silicon atoms out of the 6H-SiC lattice.

The magnetization as functions of magnetic field ( $M-H$ ) curve at 5 K and 300 K for the implanted SiC single crystal (subtracted the diamagnetic background of the SiC substrate and a plastic straw used for the samples mounting) was displayed in Fig. 3. The magnetic fields were applied parallel to the sample plane.  $M-H$  curves of the un-implanted SiC single crystal were also measured for the purpose of comparison. Note that the un-implanted SiC shows diamagnetism (DM). It is observed that the implanted SiC single crystal exhibits a clear ferromagnetism loop at 5 K. Even at 300 K, hysteresis loop can still be observed, indicating that the implanted SiC single crystal has RTFM property. The saturation magnetization of implanted sample at 5 K is about  $8.5 \times 10^{-4}$  emu/g, which is larger than that of the neutron irradiated 6H-SiC [15].

For the ferromagnetism origin in N implanted 6H-SiC, possible explanations could be as follows. The possible TM-related clusters or secondary phase could be excluded owing to the non-metal implantation. The absence of N-related secondary phases confirmed by the high resolution XRD (not shown) has also ruled out

Table 1  
The positron lifetimes for the samples.

| Parameters    | Un-implanted     | Implanted        |
|---------------|------------------|------------------|
| $\tau_1$ (ps) | $164 \pm 3$      | $175 \pm 2$      |
| $I_1$ (%)     | $47.46 \pm 0.82$ | $63.93 \pm 0.68$ |
| $\tau_2$ (ps) | $391 \pm 5$      | $405 \pm 6$      |
| $I_2$ (%)     | $46.10 \pm 0.82$ | $31.79 \pm 0.69$ |

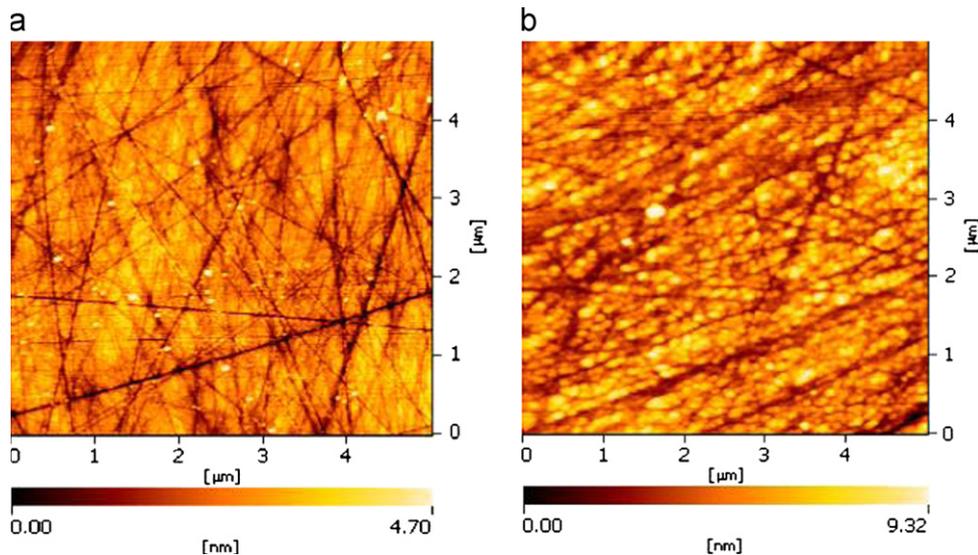


Fig. 2. AFM images of the (a) un-implanted SiC and (b) implanted SiC.

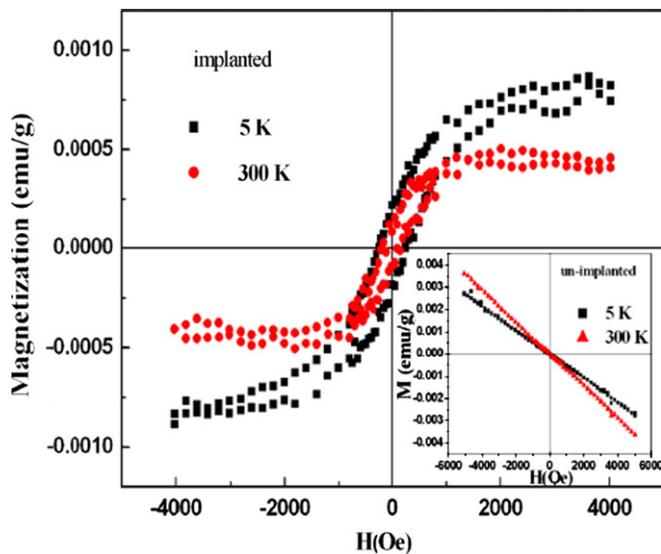


Fig. 3.  $M$ - $H$  curves of implanted SiC single crystal at 5 K and 300 K. Inset is the  $M$ - $H$  curves of the un-implanted SiC single crystal at 5 K and 300 K.

the possibility of FM due to extrinsic origin. Even though some tiny parasitic phases exist in the N-implanted SiC single crystal beyond the resolution limit of this technique, the N-C and N-Si compounds are all non-magnetic or diamagnetic [16,17]. In addition, an implantation technique is a clean process and can avoid the impurity contamination during the sample preparation [2,3]. Recently, defects were thought to be responsible for the origin of the FM property in implanted SrTiO<sub>3</sub> single crystal [18]. Zhao et al. [7] predicated that the  $V_{Si}$  can induce local magnetic moments and FM order by first principle computation. Therefore, we proposed that the  $V_{Si}$  defects play an important role in determining the FM order. In our case, un-implanted 6H-SiC single crystal has diamagnetic property though  $V_{Si}$  measured by the PALS was present in the single crystal, which indicates that vacancy-induced ferromagnetism can occur only if vacancy concentration exceeds a certain threshold value. Similar defects in threshold effect were also observed in the literature [15], in which the un-irradiated 6H-SiC containing divacancies shows diamagnetic behavior. Moreover, it is likely that N atoms occupied C site in SiC lattice since N atom has roughly the same atomic radius as C. Some incorporation of N atoms can give rise to the presence of a lone pair electron spin and then facilitate the development of the long range magnetic order [19,20]. In other words, it is speculated that the vacancy defects together with some substituted N atoms should jointly be responsible for the FM.

#### 4. Conclusion

In summary, the morphology, defects and magnetic characteristics of N-ion implanted 6H-SiC has been studied. N ion implantation of 6H-SiC single crystal can lead to the room-temperature ferromagnetism. It is speculated that the vacancy defects combined

with some substituted N atoms should jointly be responsible for the FM. We hope that our observations can lead to a better understanding in SiC-based DMSs by the implantation pathway.

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