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Nitrogen Ion Implantation and Thermal Annealing in SiC Single Crystal

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The interrelationship among implantation induced defect density, carrier activation rate, substrate temperature during nitrogen implantation and post annealing in 6H-SiC has been clarified. Several kinds of defect, whose energy for repairing of lattice damage depends on the substrate temperature during implantation, was observed. The complex defect composed of the interstitial carbon and the substituted nitrogen produces localized electronic state and a redundant unoccupied level in the band gap. This complex defect model is proposed firstly as the origin of the low carrier activation rate in nitrogen implanted SiC.

1. Introduction

Silicon carbide (SiC) is an expectable material for high temperature operation electron devices, high power transistors and high frequency devices because of its large bandgap (2.9eV for 6H-SiC), large critical electric field which is one order magnitude larger than that of silicon, large saturated electron velocity and high thermal conductivity.[1] For realizing these SiC electron devices, selective doping process have to be developed. However, thermal diffusion process for impurity doping used in silicon process is not available at suitable temperature in SiC process because of a very low diffusion coefficient of impurity in SiC bulk.[2] As one of the solution to achieve selective doping in SiC, high temperature ion implantation has been studied.[3][4] Nevertheless high temperature ion implantation technique has been considered as one of the expectable candidate for impurity doping into SiC, the details of the implantation phenomena in SiC such as relationship between carrier activation rate and annealing condition are not clear compared to that in silicon. The purpose of this paper is to clarify the interrelationship among implantation induced defect density, carrier activation rate, substrate temperature during nitrogen implantation and post annealing in 6H-SiC.

2. Experimental

Nitrogen molecule ions ($^{14}N_2^+$) were implanted into 6H-SiC p/p$^+$ wafer with epitaxial layer doped with aluminum of $1\times10^{16}cm^{-3}$ and thickness of $10\mu m$ at several temperatures up to 800℃, followed by furnace annealing at 1000 or 1300℃ for 10min in Ar. For the sample to measure the implantation induced defect, 300 keV, $^{14}N_2^+$ were implanted with a dose of $1\times10^{15}cm^{-2}$. For the sample to measure carrier density by Hall measurement, $^{14}N_2^+$ were implanted at 800℃ through a 30nm silicon dioxide thermally grown using a multiple implant sequence to make a uniform density profile (junction depth was 300nm). The implantation induced defect of the 6H-SiC substrate was measured by 1.5MeV He$^+$ Rutherford back scattering (RBS) spectrometry. The defect density, which is defined by the concentration of lattice disorder, were derived from fitting spectrum simulated based on the multiple scattering model to the RBS spectrum.[5]

3. Results and Discussion

Fig.1(a) shows RBS spectrum of the 6H-SiC substrate in which nitrogen was implanted at room temperature. Fig.1(b) shows defect density profiles derived by fitting simulation to RBS data and SIMS profile of nitrogen. In the Fig.1, the maximum defect density (D_{max}) as implantation was 19at.%. The depth of maximum defect density as implantation was 90% of the depth of maximum nitrogen density. After the post annealing at 1300℃ for 10min, the D_{max} decreased to 6.5at.%. By the annealing, nevertheless nitrogen profile was not changed, the depth of maximum defect density was changed. Fig.2(a) shows RBS spectrum of the 6H-SiC substrate in which nitrogen was high-temperature-implanted at several temperatures. Fig.2(b) shows defect density profiles and SIMS profile of nitrogen. The higher substrate temperature during implantation, the lower defect density

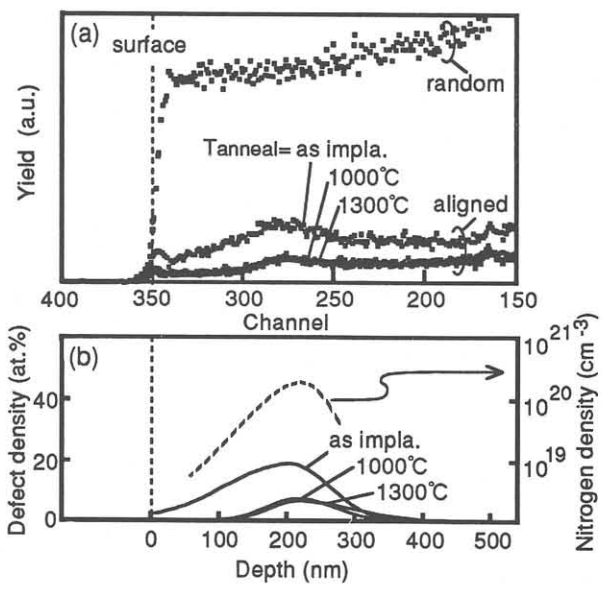

Fig.1 (a) RBS spectrum of nitrogen implanted 6H-SiC without elevating substrate temperature during implantation. (b) Defect density profiles and SIMS profile of nitrogen. $^{14}N_2^+$ ions were implanted with a dose of $1\times10^{15}cm^{-2}$ at 300keV.

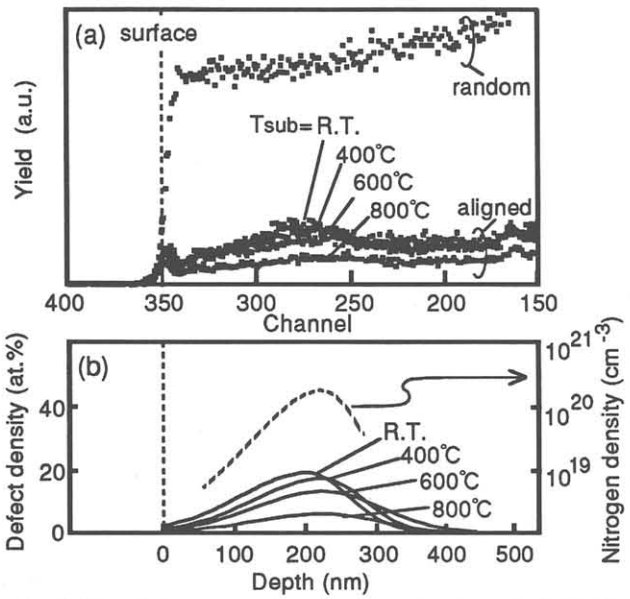

Fig.2 (a) RBS spectrum of nitrogen implanted 6H-SiC with elevated substrate temperature during implantation. (b) Defect density profiles and SIMS profile of nitrogen. $^{14}N2^{+}$ ions were implanted with a dose of $1\times10^{15}cm^{-2}$ at 300keV.

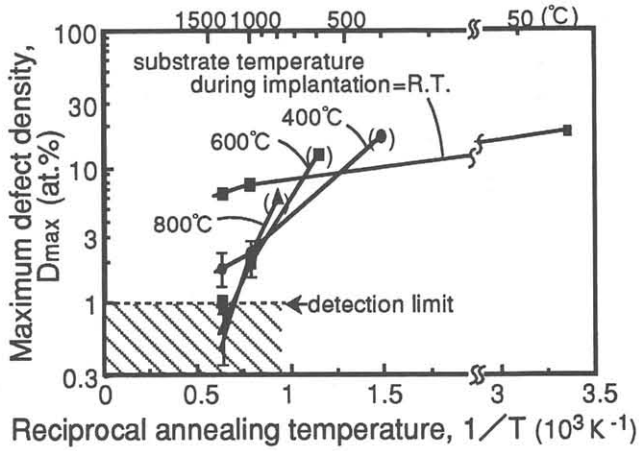

Fig.3 Relationship between maximum defect density and reciprocal post annealing temperature. Parameter is the substrate temperature during implantation. The plots parenthesized were substituted temperature during implantation for annealing temperature.

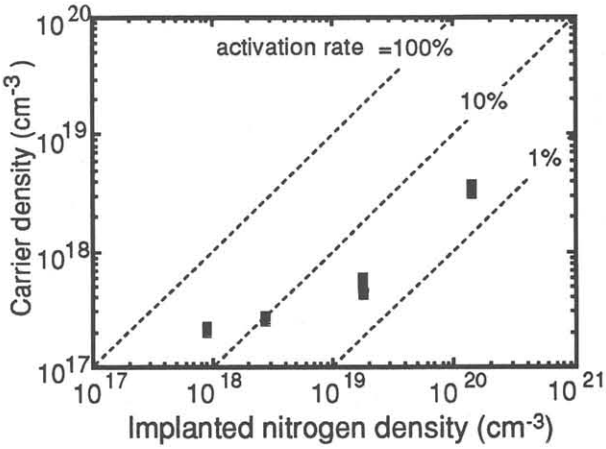

Fig.4 Carrier density in 6H-SiC as a function of implanted nitrogen density. The substrate temperatures were selected as 800℃ for implantation and 1300℃ for post annealing.

in the substrate. The Dmax introduced by 800℃ implantation was 6%. This value is similar to the value of room temperature implantation, followed by 1300℃ annealing. Fig.3 shows relationship between Dmax and reciprocal post annealing temperature (1/T). The defect introduced by implantation at more than 600℃ was removed below the detection limit of RBS. The higher substrate temperature during implantation, the larger gradient of Dmax−1/T line. This result suggests that several kinds of defects, whose energy for repairing of lattice damage depends on the substrate temperature during implantation, are introduced by high temperature implantation.

Fig.4 shows carrier density of 6H-SiC measured by the hall measurement as a function of implanted nitrogen density. The activation rate was 2.6% under the condition that the implanted nitrogen density was $1.4\times10^{20}cm^{-3}$. The activation rate calculated by Ruff as donor level was 100meV was 4.5%.[6] Though defect density is low enough unable to detect by RBS measurement, the experimental activation rate is lower than the calculated one and depends on implanted nitrogen density.

In order to investigate the reason of the low experimental carrier activation rate in nitrogen implanted SiC, we have executed a first principles local-density functional calculation for the nitrogen impurity state. We have studied two problems: (I)Does a nitrogen atom substitute either on a silicon atom or a carbon atom?; (II) What effect does an interstitial atom ejected by an implanted nitrogen atom bring to the donor state? The calculation are performed on a cubic SiC crystal whose unit cell includes 64 atoms for the problem (I) and 65 atoms for the problem (II). The atomic configuration around impurity atoms is determined by a first principles molecular dynamics method (Car & Parrinello method [7]).

Firstly, we study the problem (I). Fig.5 and Fig.6 show the calculated partial charge density distribution around a nitrogen atom on the carbon site and on the silicon site, respectively. Because the charge density in Fig.5 spreads over the whole unit cell, a nitrogen impurity on the carbon site acts as a shallow donor. We can see from Fig.6 that a nitrogen impurity on the silicon site does not constitute a shallow donor state, because the charge density localizes around the nitrogen atom. To investigate the site dependence of stability of the nitrogen impurity, we have calculated the cohesive energy. The result is shown in Table 1. From this Table, we can get two results: (1)The nitrogen impurity is stable both on silicon site and on carbon site; (2)the nitrogen atom on the carbon site is more stable than that on the silicon site. From these calculations, we can conclude that the nitrogen impurity locates on the carbon site and constitutes a shallow donor state.

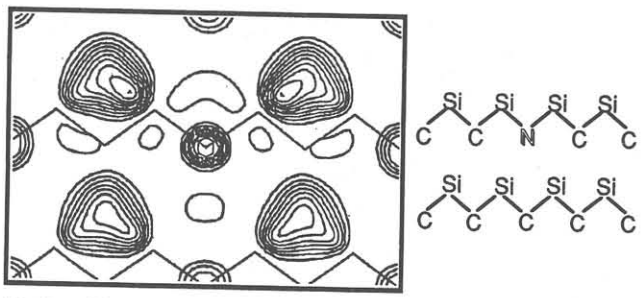

Fig.5 Partial charge density distribution in the (110) plane due to the donor state in SiC crystal model (64 atoms) in which one carbon atom is replaced by nitrogen atom.

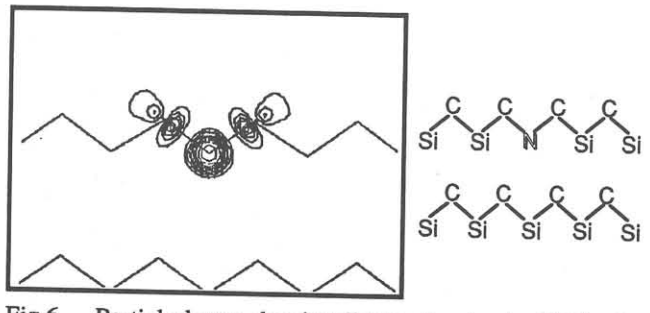

Fig.6 Partial charge density distribution in the (110) plane due to the donor state in SiC crystal model (64 atoms) in which one silicon atom is replaced by nitrogen atom.

Table 1 Calculated cohesive energy

substitutional type	cohesive energy Ecoh (eV/atom)
without nitrogen	6.88
nitrogen at carbon site	6.84
nitrogen at silicon site	6.78

Secondly, we study the problem(II). As the nitrogen impurity locates on the carbon site, an interstitial carbon atom will appear as a result of the nitrogen implantation. We investigate the effect of the interstitial carbon atom on the impurity state. The most stable position of the interstitial carbon atom is found to be the Si-C bond center site by the molecular dynamics calculation. Fig.7 shows the partial charge density distribution for the most stable atomic configuration. From this figure, we can see that the charge distribution due to the shallow donor, shown in Fig.5, disappears. We have studied also energy levels for this carbon-nitrogen complex defect, and this defect produces a redundant unoccupied level in the band gap, which traps a carrier generated by an isolated nitrogen donor. From these results, we can propose that the complex defect composed of the interstitial carbon and the substituted nitrogen is the origin of the low carrier activation rate in nitrogen implanted SiC.

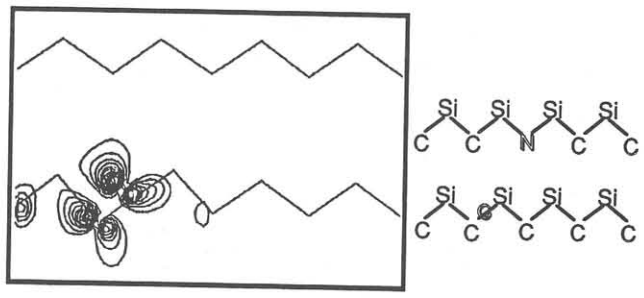

Fig.7 Partial charge density distribution in the (110) plane due to the donor state in SiC crystal model (64+1 atoms) in which not only substituted nitrogen atom but also interstitial carbon atom neighboring the nitrogen atom are positioned.

4. Summary

The interrelationship among implantation induced defect density, carrier activation rate, substrate temperature during nitrogen implantation and post annealing in 6H-SiC has been clarified. Several kinds of defect, whose energy for repairing of lattice damage depends on the substrate temperature during implantation, was observed. More than 600℃ is needed as a substrate temperature during nitrogen implantation in order to repair of defect below the detection limit of RBS after post annealing at 1300℃. The complex defect composed of the interstitial carbon and the substituted nitrogen produces localized electronic state and a redundant unoccupied level in the band gap. This complex defect model is proposed firstly as the origin of the low carrier activation rate in nitrogen implanted SiC.

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