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ESR characterization of activation of implanted phosphorus ions in silicon carbide

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Abstract

Phosphorus ion implantations of 6H-SiC in the mean phosphorus concentration of the implanted layer of $\sim 1 \times 10^{18}$ cm^{-3} were performed both at multi-fold energy between 9 and 21 MeV and at 340 keV. In the high-energy implantations at room temperature, 400, 800 and 1200 °C and in the 340 keV implantations at 800 °C, electron spin resonance spectra arising from isolated shallow phosphorus donors have been observed after post-implantation annealing at 1650 °C, but were not observed in as-implanted state.

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1. Introduction

Silicon carbide (SiC) is a promising material for electronic devices of high-frequency, high-power, high-temperature applications and for those used in a harsh environment. One of key issues for developing SiC devices is to establish the technology of the selective area doping. In SiC, due to the difficulty of doping by thermal diffusion, ion implantation is a potential method of introducing dopant atoms in the device fabrication process. Ion implantation doping of SiC is much more complicated than that of silicon. Formation of amorphous layer by excessive accumulation of radiation damages might cause polytype transition upon thermal annealing. Implantation-induced defects, both those formed as radiation damages and secondary ones formed by migration of defects during thermal annealing might be stable up to rather high-temperatures.

In addition to nitrogen, which is unintentionally incorporated during the crystal growth, phosphorus acts as a shallow donor [1,2]. To improve the doping efficiency by varying the conditions of ion implantation and those of post-implantation annealing, microscopic characterization of implanted phosphorus ions as well as that of implantation-induced defects is important. We have applied electron spin resonance (ESR) method to elucidate at microscopic level the thermal behaviour of implanted ions and radiation damages. To characterize the electric activation of phosphorus ions, it

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is critically important to observe the ESR signals from the phosphorus shallow donors. In the ESR method, identification of phosphorus related centers, for both phosphorus in the shallow donor state and phosphorus involved in paramagnetic defects such as phosphorus-vacancy complexes, is based on the observation of the hyperfine interaction of ^{31}P nucleus ($I = 1/2$, natural abundance 100%).When the donor concentration is sufficiently high, a single line spectrum instead of the two lines split by the ^{31}P hyperfine interaction is observed as a result of exchange interactions among the donor electrons. In such a single-line spectrum, it is not obvious to identify that the spectrum is arising from the shallow phosphorus donors. Thus, we used a low dose to attain an average phosphorus concentration of the implanted layer of $\sim 1 \times 10^{18}$ cm^{-3}.

2. Experimental

Samples used were n-6H-SiC crystals (Nippon Steel Corp., $N_A - N_D = \sim 10^{17}$ cm^{-3}). For high-energy implantations, a rectangular plate ($3 \times 10 \times 1.5$ mm^3) was irradiated using a 3 MV tandem accelerator with phosphorus ions (5×10^{13} cm^{-2} at each of nine stages of energy from 9 to 21 MeV). The dose rate at each energy step was from 5×10^{10} to 1×10^{11} cm^{-2} s^{-1}. By using a multi-fold implantation, the number of phosphorus atoms implanted can be increased without increasing the average phosphorus concentration. The target temperatures were room temperature (RT), 400, 800 and 1200 °C. For 340 keV phosphorus ions implantation (the dose of 2×10^{13} cm^{-2} and the dose rate of 1.8×10^{11} cm^{-2} s^{-1}) at 800 °C, rectangular plates ($3 \times 10 \times 0.22$ mm^3) were used. All implantations were carried out along the [0 0 0 1] axis. Post-implantation annealing was performed at 1650 °C for 30 min in Ar atmosphere by using a RF-heating system. Temperature increased from RT to 1000 °C for 10 min and from 1000 to 1650 °C for 4 min. After annealing, temperature decreased to RT in 90 min.

The ESR spectra were recorded on a Bruker ESP300 X-band spectrometer by using an Oxford Instrument ESR-900 to control the sample temperature. For ESR measurements, a single plate glued on a high-purity silica-glass rod was used in the case of the MeV implantations, and four slices were stacked into a high-purity silica-glass tube in the case of the 340 keV implantation. The signal intensity was estimated by double integration of the first derivative signal.

3. Results and discussion

3.1. Radiation damages

Before implantations, ESR spectra of shallow nitrogen donors [3,4] were strongly observed. ESR spectra taken in the as-implanted state of n-6H-SiC after high-energy implantations are shown in Fig. 1. Since the substrate used contains $\sim 10^{17}$ cm^{-3} of nitrogen, and since the thickness of the implanted layers relative to the thickness of our samples is small, the signals of the shallow nitrogen donors dominate over those of implantation-induced defects in a normally obtained ESR spectrum of the first derivative form of the absorption. To compare the concentrations of the radiation damages produced among the samples implanted with high-energy phosphorus ions at various temperatures, it is convenient to use the absorption spectra obtained by integrating the first derivative form in which the area underneath the curve corresponds to the number of spins (Fig. 1). The concentration of the ESR-active defects observed in the as-implanted state decreases with the increase of the implantation temperature (T_i).

Since both the linewidth and the microwave power dependence of the intensity of an ESR signal often strongly depend on the temperature, the response from a particular ESR center might be effectively suppressed by choosing an appropriate measurement condition. In the crystal lattice of 6H-SiC, there are three inequivalent sites (a hexagonal site h and two quasi-cubic sites k_1 and k_2) for each of silicon and carbon. The spectra shown in Fig. 1 were taken at the temperature and with the microwave power where the signal intensity of the shallow nitrogen donors on the quasi-cubic sites of carbon increased with the increase of the microwave power, while the signal of the shallow

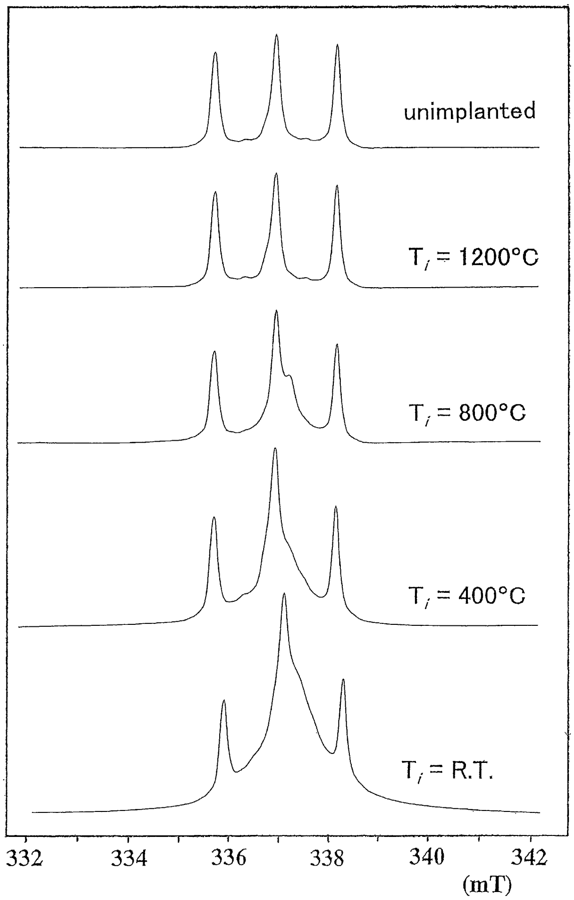

Fig. 1. ESR spectra of *n*-6H-SiC implanted with high-energy phosphorus ions at various temperatures. Absorption spectra were obtained by integration of the spectra obtained in the first derivative form (60 K, $B\|[0001]$, microwave frequency (ν) 9.46 GHz, microwave power (MP) 2×10^{-3} mW, amplitude of 100 kHz field modulation (MA) 2×10^{-2} mT).

nitrogen donors on the hexagonal site of carbon was broadened.

3.2. Phosphorus shallow donors

The ESR spectrum of *n*-6H-SiC which was annealed at 1650 °C after the implantation of the high-energy phosphorus ions at 800 °C is shown in Fig. 2. Each of the two spectra labeled P_a and P_b consists of two-lines arising from ^{31}P hyperfine structure. The P_a and P_b spectra, which were originally observed in 6H-SiC in which phosphorus had been introduced by neutron transmutation of ^{30}Si [4–9], are associated with the isolated shallow phosphorus donors on the quasi-cubic silicon sites [4,9]. The ESR parameters obtained from the angular dependence of the line positions of P_a and P_b ($A_{\|}/g_e\beta_e = 5.50$ mT, $A_{\perp}/g_e\beta_e = 5.42$ mT for P_a, $A_{\|}/g_e\beta_e = 5.09$ mT, $A_{\perp}/g_e\beta_e = 5.09$ mT for P_b at 30 K) agree with those reported. The ESR spectrum from the isolated shallow phosphorus donor on hexagonal silicon site [9] could not be resolved, being hidden underneath the strong central line of the nitrogen shallow donor spectra.

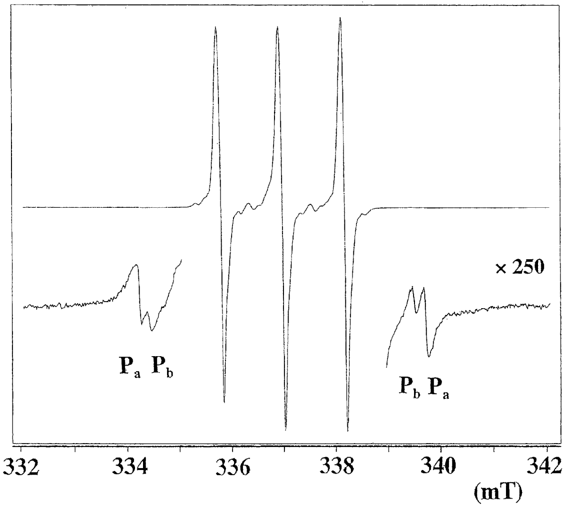

Fig. 2. ESR spectra of of *n*-6H-SiC implanted with high-energy phosphorus ions at 800 °C with subsequent annealing at 1650 °C (80 K, $B\|[0001]$, $\nu = 9.46$ GHz, MP $= 2\times10^{-1}$ mW, MA $=$ 4×10^{-2} mT).

For samples implanted at RT, 400, 800 and 1200 °C, the P_a and P_b spectra were not observed before the annealing at 1650 °C but were observed after the annealing at 1650 °C. It is likely that the temperature of 1200 °C is not sufficiently high to activate phosphorus ions implanted. To compare the concentration of the isolated shallow phosphorus donors (the sum of P_a and P_b) among various implantation temperatures, the intensity of the signal of the shallow nitrogen is utilized as an internal standard. The relative ratio of concentration of the isolated shallow phosphorus donors for implantation temperatures RT, 400, 800 and 1200 °C was 1:0.8:1.5:0.8. We chose the dose to attain the average concentration of phosphorus in the implanted layer to be $\sim1\times10^{18}$ cm^{-3} by using

Monte Carlo simulation using TRIM. In this relatively low dose, the shallow phosphorus donors are observed after annealing at 1650 °C even in the case of the implantation at RT. In the implantation of the low dose, it was reported that the carrier concentration measured by the Hall-effect measurements did not differ significantly after annealing above ~1400 °C among the samples implanted at RT, 800 and 1200 °C [2].

The P_a and P_b spectra are observed when the unpaired electrons are bound to the phosphorus shallow donors. The absolute number of the phosphorus giving rise to the P_a and P_b spectra at 80 K was estimated by comparing the signal intensity with that of Cr^{3+} in ruby which was simultaneously measured by co-mounting with the sample on a glass rod. The ratio of the isolated shallow phosphorus donors on the two quasi-cubic sites (the sum of P_a and P_b) relative to the amount of the implanted phosphorus ions is estimated to be ~0.08 for the high-energy implantation at 800 °C. It is likely that most of the phosphorus ions implanted did not attain the configuration of the isolated shallow donors of neutral charge state.

The P_a and P_b spectra, which are arising from the implants driven into the required lattice sites, have been also observed in *n*-6H-SiC implanted with 340 keV phosphorus ions at 800 °C after the post-implantation annealing at 1650 °C (Fig. 3).

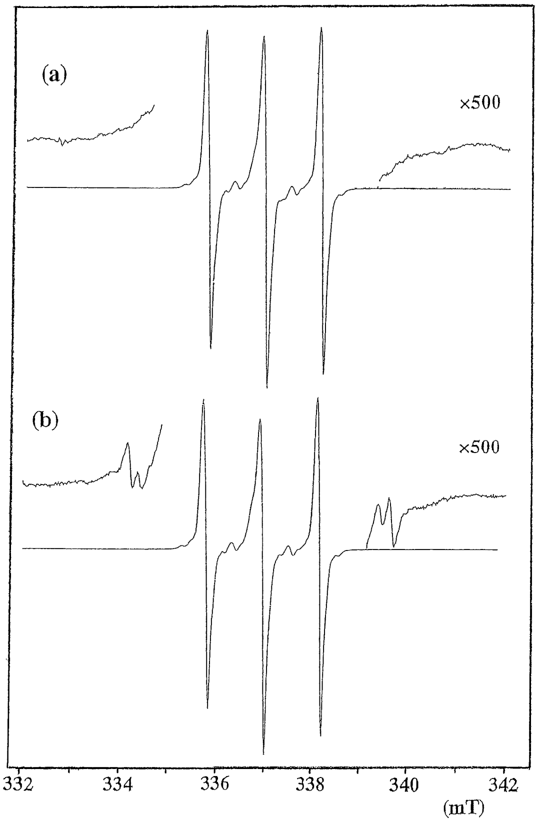

Fig. 3. ESR spectra of of *n*-6H-SiC implanted with 340 keV phosphorus ions at 800 °C. (80 K, $B_{\|}[0001]$, $\nu = 9.46$ GHz, MP = 0.2 mW, MA = 4×10^{-2} mT): (a) as-implanted, (b) after post-implantation annealing at 1650 °C.

4. Conclusion

Activation of phosphorus ions implanted into 6H-SiC has been studied in a low dose of the mean phosphorus concentration of $\sim 1 \times 10^{18}$ cm^{-3}. In both for high-energy (9–21 MeV) and for 340 keV phosphorus ion implantations, ESR spectra originating from shallow phosphorus donors at the quasi-cubic sites have been observed after the thermal annealing at 1650 °C. The concentration of the shallow donor did not vary significantly among the samples implanted at RT, 400, 800 °C and 1200 °C.

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