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Phosphorus Doping of 4H-SiC by KrF Excimer Laser Irradiation in Phosphoric Solution

Akihiro Ikeda, Koji Nishi , Hiroshi Ikenoue and Tanemasa Asano

Graduate School of Information Science and Electrical Engineering, Kyushu University
744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan
Phone: +81-92-802-3732 E-mail: ikeda@ed.kyushu-u.ac.jp

1. Introduction

Silicone carbide (SiC) is a promising semiconductor for high-power devices due to its superior material properties; high breakdown field, high electron saturation velocity, and high thermal conductivity. To implement SiC power devices, pn junction must be formed in the SiC. However, ion implantation for impurity doping has several problems for the SiC. For example, while a high-temperature (~1700^{o}C) post-implantation annealing is required to electrically activate implanted species[1], it induces generation of crystallographic defects in the SiC, such as segregation of carbon atoms at the surface from the SiC bulk [2]. Therefore, development of new technology for local doping of SiC is highly demanded.

In this study, we investigate doping of phosphorus using KrF-excimer laser irradiation to 4H-SiC immersed in a phosphoric acid solution. The use of laser with chemically active environment for doping has been reported on the following two investigations: One is doping of Si by irradiating green (532 nm in wavelength) laser thorough a waveguide produced by a laminar flow of liquid containing chemicals [3]. The application of this technique to SiC is not straightforward because SiC is transparent for the green light. The other is the use of KrF-excimer laser irradiation to SiC in diborane gas [4]. Doping was possible using this technique but it limited the maximum doping concentration to 10^{18} cm^{-3}. In this paper, we demonstrate that our new method is able to dope phosphorous to the concentration over 10^{20} cm^{-3} and the doping depth is varied by changing the number of laser pulse shots.

2. Experimental

Figure 1 shows schematic illustration of the experimental setup for the investigation. The sample chip was placed in a glass petri dish filled with phosphoric acid solution at room temperature and irradiated with KrF excimer laser (Gigaphoton Inc.). The laser irradiation condition was as follows; the laser pulse repetition rate was 10 Hz, the pulse width was 55 ns, the laser fluence was 1.83 J/cm^2 per pulse, the number of the pulse shots was 10 or 100 shots, the laser irradiation area was 100 μm×1200 μm.

The chip used in this study consisted of an n-type 4H-SiC epitaxial layer on an n$^+$-type 4H-SiC substrate. The surface orientation of the epitaxial layer was 4° off Si-face. The doping concentration of nitrogen in the epitaxial layer was 1×10^{16} /cm^3, that corresponded to about 0.5 Ωcm. The thickness of the epitaxial layer was 3.5 μm.

3. Results and Discussion

Figure 2 shows surface morphology of the irradiated area with 100 laser shots, as was observed with scanning electron microscopy (SEM). We can recognize the irradiated area whose dimension is almost same as the laser spot size. The irradiated area with 10 laser shots showed much less change in surface morphology. Surface profiling revealed that a depression is formed in the irradiated area. The depth was less than 20 nm and about 130 nm for the 10 shots and 100 shots, respectively.

Figure 3 shows depth profiles of phosphorus measured with secondary ion mass spectroscopy (SIMS) for the irradiated areas of 10 laser shots and 100 laser shots. The measurement was carried out near the middle of each irradiated area. To investigate the effect of surface-adsorbed phosphoric molecules on the depth profiling, SIMS was

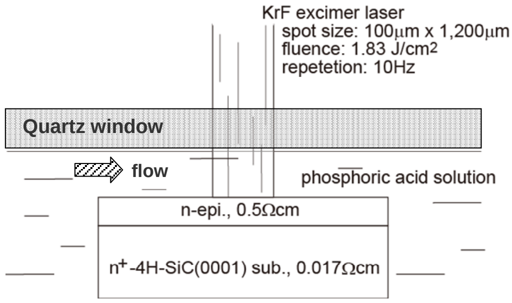

Fig. 1 Schematic illustration of experimental setup.

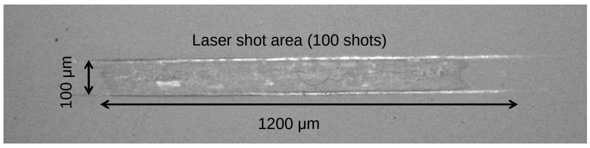

Fig. 2 Surface morphology of the area irradiated with 100 laser shots.

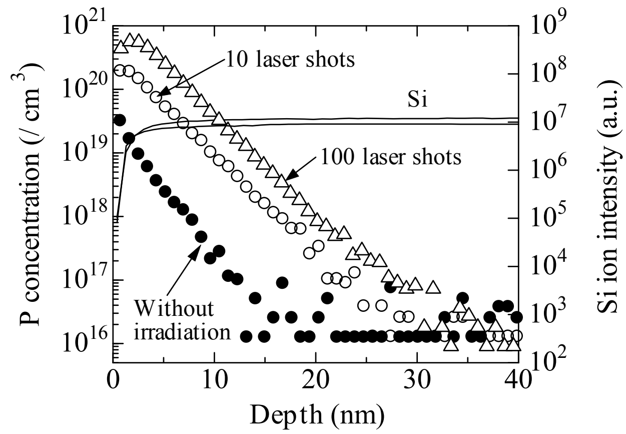

Fig. 3 Depth profiles of phosphorus concentrations measured with SIMS. Si ion intensity was also indicated for reference.

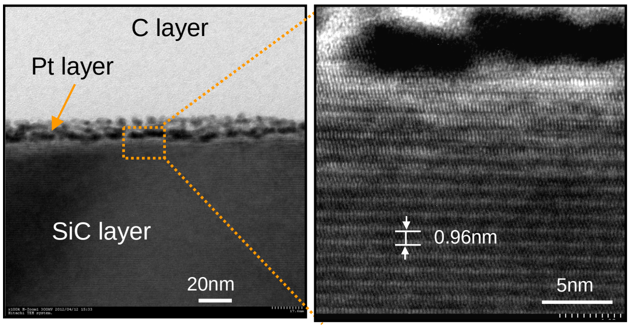

Fig. 4 Cross-sectional TEM micrographs showing the near surface area of the 4H-SiC irradiated with 100 laser shots. Pt coating was carried out to protect the surface from ion irradiation damage during sample preparation using focused Ga ion beam.

applied also to the un-irradiated area where phosphoric molecules adsorbed to the surface were not completely washed away by water rinse after irradiation. The measured profile was also plotted in Fig. 3. Comparison of these three profiles indicates that phosphorus concentration in the surface region is increased by the irradiation and that the concentration increases with increasing shot number of laser pulses, demonstrating doping of the SiC with phosphorus. The phosphorus diffusion coefficient was known to be very small in 4H-SiC even at high temperature. The phosphorus diffusion coefficient has been reported to be 4.18×10^{-19} cm^2/s at 2200 °C [5], which suggests that negligible amount of diffusion takes place. However, as shown in Fig. 3, phosphorus concentration increases with increasing number of laser shots. During the laser irradiations, the SiC surfaces might be heated up to near the SiC dissociation temperature (3100 K). Under such high temperature, laser-induced stresses due to the thermal expansion or electron excitation in the SiC might generate significant amount of vacancies near the SiC surface. The generation of vacancies may cause in-diffusion of phosphorus at the surface.

Figure 4 shows TEM images at the SiC surface with the 100 laser shots. The periodic stripe pattern was clearly observed in the SiC. The stripe pattern corresponds to bilayer stacking sequence of the 4H-SiC [6]. The unit size of the periodic stripe is deduced to be 0.96 nm as indicated in Fig. 4. This size is almost same as the height of unit cell (1.008 nm) of the bilayer stacking structure [7]. As observed in Fig. 4, the thickness of the bright layer was increased near the SiC surface. It indicates that the bilayer stacking sequence was changed. It was reported that heavily nitrogen doping induced stacking faults in 4H-SiC [5]. Therefore, the stacking sequence modification observed in our sample could be possibly induced by large strain due to the heavily phosphorus doping.

Figure 5 shows current-voltage (I-V) characteristics at the positions with and without the laser irradiation. The probing stylus for the I-V measurements was made of tungsten. The probes were directly contacted to the SiC surfaces. To remove the surface carbon layer induced by the laser irradiation, O_2 plasma ashing was carried out before the I-V measurements. The distance between the two probes was about 200 μm. The current measured by contacting the two probes outside of the irradiated area was only about 8 pA at 1 V. This small current is due to Schottky contacts

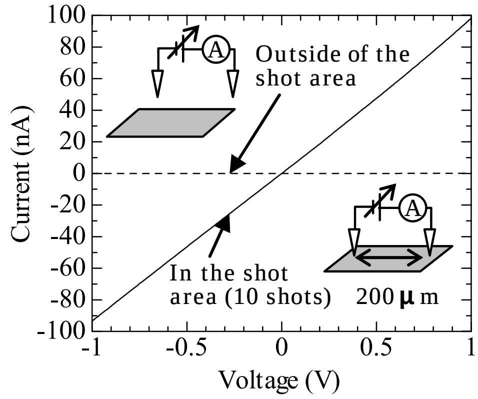

Fig. 5 Current-voltage curves measured by probing with two tungsten needles at the areas with and without the laser irradiation.

between the probes and SiC surfaces. On the other hand, the current measured by contacting the probes inside the irradiated area was about 100 nA at 1 V and follows linear ohmic characteristic. This fact indicates that doped phosphorus were activated electrically in the SiC.

4. Conclusion

A novel technique of doping SiC, excimer laser irradiation in a chemical solution, has been investigated. KrF excimer laser pulses were irradiated to the surface of 4H-SiC immersed in a phosphoric acid solution. Incorporation of phosphorus in the 4H-SiC has been observed. The surface concentration of phosphorus has been found to increase with the number of laser shots. No significant damage was observed in the lattice of the irradiated surface region. The irradiation remarkably improves the ohmic contact performance. These findings indicate that the technique is worth investigating further as a new doping technique of SiC.

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