Extended Abstracts of the 2014 International Conference on Solid State Devices and Materials, Tsukuba, 2014, pp996-997

Nitrogen Doping of 4H-SiC by Excimer Laser Irradiation in Liquid Nitrogen

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Abstract: Nitrogen (N) doping of 4H-SiC is performed by irradiating KrF excimer laser in liquid nitrogen. It is found that N is doped as deeply as 1 μm into the bulk of 4H-SiC, which is in contrast to the phosphorus (P) doping in phosphoric acid solution where P is doped as shallowly as a few tens nm. N concentration at the surface is a high as 4×10^{21} cm^{-3}. A pn junction diode fabricated by using this N doping technique shows turn-on at -2.8 V, which is reasonable for a pn diode of 4H-SiC where conventional recombination dominates current.

1. Introduction

Silicon carbide (SiC) is highly promising for producing high-voltage switching devices that have significantly lower losses than devices made of Si. However, to fully utilize the material property of SiC, it is necessary to develop a process technology, such as local doping to form pn junctions and low-resistance contacts to a metal. Ion implantation can be used for doping of SiC. However, in marked contrast to ion implantation of Si, ion implantation of SiC requires hot implantation at about 800 °C followed by high-temperature annealing at about 1700 °C to minimize implantation-induced damage and to electrically activate the implanted species [1-3]. This high-temperature process generates crystallographic defects such as segregation of carbon (C) atoms at the surface from the bulk of SiC [3,4]. Therefore, there is a strong need to develop a new technology for impurity doping of SiC.

Recently, we reported that phosphorus (P) and aluminum (Al) can be doped into 4H-SiC by KrF excimer laser irradiation in phosphoric acid solution [5-7] and aqueous solution of aluminum hydroxide [7, 8]. However, doping depths of these species is limited to ~40 nm even with increasing the laser fluence or the shot number. As a result, pn junction diodes fabricated using this technology showed current enhanced by the surface recombination. To fabricate junctions where conventional bulk recombination determines the current, deep doping of dopant atoms is desirable. In this study, we report deep and high density nitrogen (N) doping of 4H-SiC by KrF excimer laser irradiation in liquid nitrogen.

2. Experimental

Fig. 1 depicts the experimental setup used for the laser doping in liquid nitrogen. The sample was 4H-SiC, composed of a 1.8-μm-thick p-type epitaxial layer (1.3×10^{17} /cm^3 Al doped) on n$^+$-type 4H-SiC [0001]. The sample chip was immersed in liquid nitrogen. A KrF excimer laser (Gigaphoton Inc. wavelength: 248 nm; pulse-duration:55 ns, repetition:100 Hz) was irradiated on the 4H-SiC. The laser spot shape was rectangular with the size of 130 μm × 330 μm. The laser shot number was 1000 shots.

After the laser doping process, the sample chip was exposed to oxygen plasma to remove a carbon contamination generated by the laser irradiation. Then, Ti/Al was sputter-deposited subsequently on the surface to form an ohmic contact to the un-irradiated p-type epitaxial layer. The deposited Ti/Al layer was patterned on the undoped region by photolithography and wet etching. Finally, the sample chip was annealed at 1000 °C for 2min in N_2 ambient to form the Ti/Al alloy for ohmic contact to the p-type epitaxial layer.

3. Results and Discussion

Dopants depth profiles

Fig. 2 shows depth profile of N doped in 4H-SiC by irradiating 1000 shots at the fluence of 4.0 J/cm^2. The depth profile was measured using secondary ion mass spectroscopy (SIMS). In the figure, depth profile of P doped by irradiating 1000 shots at 3.7 J/cm^2 in phosphoric acid solution was also plotted. We can clearly see that N is doped as deeply as 1 μm from the surface, while P doped region is as shallow as a few tens nm. The concentration of N is as high as 4×10^{21} /cm^3 which is sufficiently high to produce an n$^+$ layer in 4H-SiC.

Thermal diffusion coefficient of N atom in 4H-SiC is reported as ~ 5×10^{-12} cm^2/sec at 2450 °C [9]. Accounting our laser irradiation condition (duration:55 ns, shot number:1000 shots), if the above diffusion constant holds, the N diffusion length is estimated to be 0.33 nm. This depth is considerably smaller than the observed depth distribution. In Fig. 2, in addition to depth profile of N, depth profiles of Si and C signal intensity measured by SIMS are also plotted. We can see that C intensity is significantly decreases towards the surface in the region about 0.3 μm deep where N concentration is high. This C depression suggests that a high density of C vacancies is generated near the surface. At the 0.1 μm depth, for example, the C density is decreased down to ~75% of the bulk intensity, which indicates that C depression is as high as 1.2×10^{22} /cm^3.

On the other hand, it has been reported that N substitutes C sites while P substitutes Si sites in 4H-SiC [10]. It has also been reported that the formation energy of Si vacancy (8.2 eV) is higher than that of C vacancy (5.3 eV) in 4H-SiC [11]. These activation energies indicates that Si vacancies less than C vacancies are generated. From these knowledge and experimental results obtained in this study, it is strongly suggested that the fast diffusion of N is a result of enhanced diffusion by C vacancies.

Diode I-V curves

Fig. 3 shows I-V curves of the pn junction diode fabricated by N doping in liquid nitrogen or P doping in phosphoric acid. Formation of ohmic contacts with the Ti/Al electrode to the p-type epitaxial layer was confirmed by I-V between two Ti/Al electrodes. The N doped diode can deliver much higher current in the forward direction than the P doped diode. This is considered to be owing to reduced resistance in the doped region. The N doped diode shows a triple threshold characteristic. The first threshold is recombination current in the depletion region, which gives similar amount of current in the reverse direction. The second one could be due to turn on of the diode at the un-passivated peripheral region. The third one is the turn on of the main diode produced by the N doping. The turn-on voltage of the N doped diode is ~ -2.8 V. This indicates that, although the recombination-generation current need to be reduced, the N doped diode behaves as a conventional junction diode where current are determined by the bulk recombination process like diode fabricated by using ion implantation [12,13].

4. Conclusion

Doping of N atoms into 4H SiC by KrF excimer laser irradiation in liquid nitrogen has been demonstrated. It can introduce N atoms as deeply as 1 μm from the surface with concentration as high as 4×10^{21} cm^{-3} near the surface. Depth profile strongly suggests that diffusion in solid state takes place. However, the diffusion speed is extremely higher than the one expected from the reported diffusion constant. This high speed diffusion is probably due to enhancement by C vacancies generated by laser irradiation. This new doping technology can produce pn junction diode with fairly good rectifying characteristic where currents are determined by recombination process.

Acknowledgements

We are grateful to Prof. Tatsuo Okada for his useful discussion. We also thank to Gigahoton Inc. for providing the excimer laser. This work was supported by JSPS KAKENHI Grants, 25289105 and 26420309.

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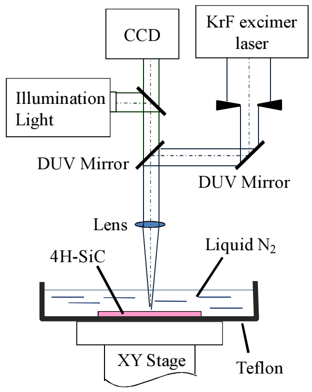

Fig. 1. Schematic illustration of the experimental set up for KrF excimer laser irradiation in liquid nitrogen.

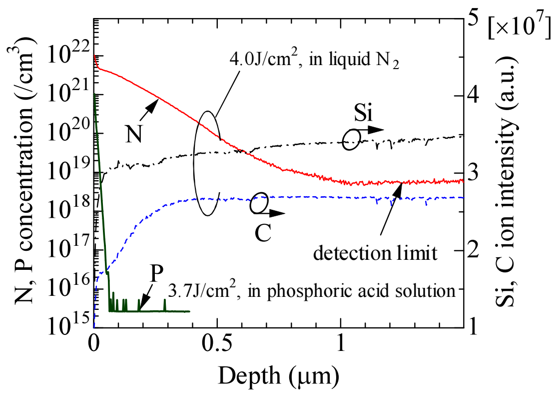

Fig. 2. Depth profile of N and P doped by irradiation in liquid nitrogen and phosphoric acid, respectively, measured using SIMS. Signal intensity profile of Si and C obtained from the N doped sample were also plotted.

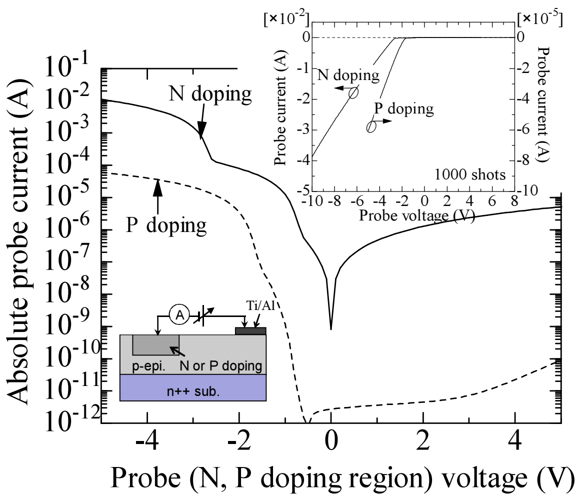

Fig. 3. Forward and reverse I-V characteristics of N doped and P doped junction diodes. The inset shows linear scale plots.