Creation of Color Centers in SiC PN Diodes Using Proton Beam Writing

Yoji Chiba^{1,2,a}, Yuichi Yamazaki^{2,b*}, Takahiro Makino², Shin-ichiro Sato², Naoto Yamada², Takahiro Satoh², Kazutoshi Kojima³, Sang-Yun Lee⁴, Yasuto Hijikata¹, and Takeshi Ohshima²

¹Saitama University, Saitama 338-0825, Japan

²National Institutes for Quantum and Radiological Science and Technology (QST), Takasaki, Gunma 370-1292, Japan

³National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8568 Japan

⁴Center for Quantum Information, Korea Institute of Science and Technology (KIST), Seoul, 02792, Republic of Korea

E-mail: ^achiba@opt.ees.saitama-u.ac.jp, ^byamazaki.yuichi@qst.go.jp *Corresponding Author

Keywords: Color center, pn diode, Proton beam writing, Electroluminescence, Optically detected magnetic resonance

Abstract. We demonstrated that silicon vacancy (V_{Si}) can be created in SiC pn junction diode by proton beam writing (PBW) without degradation of the diode performance. The V_{Si} showed the same specific emission for both optically and electrically excitation, which suggests that electrically controllable V_{Si} was created. In addition, optically detected magnetic resonance (ODMR) signal was successfully detected from optically excited V_{Si} at room temperature. This result suggests that V_{Si} introduced into the device by PBW still maintain spin manipulating capability, which is an important step toward realizing SiC devices internally equipped with a V_{Si} -based quantum sensor.

Introduction

Silicon vacancy (V_{Si}) defect in Silicon Carbide (SiC) is a color center that acts as single photon source (SPS) enabling quantum communication with complete confidentiality and quantum sensing for detecting local information such as magnetic and electric field, and temperature [1-3]. In the field of color center study for quantum technologies, the nitrogen-vacancy center in diamond [4] has attracted increasing attention as a leading candidate because of its brightness and addressability. However, for diamond, it is quite difficult to grow high-quality intrinsic and doped crystalline layers and fabricate devices. In contrast, SiC has well-developed growth technologies as well as sophisticated device fabrication processes such as ion-implantation, etching and metal contact. In recent years, specific centers such as silicon vacancy (V_{Si}) [5], carbon antisite – carbon vacancy pair (C_{Si}V_C) [6], divacancy (V_CV_{Si}) [7] and SiO₂/SiC interface defects [8] have been found as SPSs. Among them, V_{Si} is the most promising SPS in SiC from the viewpoints of brightness, luminescence stability and spin manipulation at ambient condition. Combining V_{Si}-based quantum sensor and SiC devices will provide new value such as diagnostics during device operation. In addition, since V_{Si} has a half-integer spin (S = 3/2) and near infrared emission band, these features also make living-bodysensing-applications, such as high-precision magnetometry and thermometry, desirable.

In order to realize practical quantum sensors, V_{Si} is required to introduce at not only whole area [9] but also desired positions depending on demands. Proton beam writing (PBW) is known as a direct lithographic technique using focused micro-ion-beams of MeV protons. In previous studies, it has been revealed that V_{Si} can be created in SiC [10-12]. In this paper, we demonstrated the creation of V_{Si} at certain locations of in-plain SiC pn diodes by employing PBW, and electrically controlled luminescence from V_{Si} .

Experimental

Figure 1 shows the schematic of a SiC pn $(p^+p^-n^+)$ junction diode used in this study. The diodes were fabricated on a p-type epilayer grown on n-type 4H-SiC substrates (Si face). The thickness and the doping concentration of the epilayer were 5.6 μ m and 1.5×10^{16} cm⁻³, respectively. Al and P implantation at 800 °C was performed to form p⁺ (2.0×10^{20} cm⁻³) and the n⁺ (5.0×10^{19} cm⁻³) regions, respectively. Activation annealing was carried out at 1800 °C for 5 min in Ar atmosphere. Finally, an Al electrodes were formed onto the p⁺- and n⁺-type regions by a lift-off process.

To create V_{Si} in the pn diodes, PBW was carried out using the 3MV single-ended accelerator at TIARA, QST Takasaki [13]. Sample was irradiated with protons (H⁺) at a beam diameter of ~ 1 µm at an energy of 0.5 MeV at room temperature. The range of H⁺ was estimated to be ~ 4 µm from the sample surface using SRIM simulation [14]. 41×41 dot pattern was drawn into the diodes. Irradiation fluences were varied from 1×10^4 - 1×10^6 H⁺/dot ($1.3\times10^{12} - 1.3\times10^{14}$ H⁺/cm²). Although the current-voltage (I-V) characteristics slightly degraded at the highest fluence of 1×10^6 H⁺/dot after PBW process as shown in Fig. 2, this device characteristic was acceptable for proceeding to the CFM measurement.

Photoluminescence (PL) and electroluminescence (EL) were measured using a home-built confocal scanning microscope (CFM). The excitation lasers at wavelengths of 532 and 671 nm were used to optically excite V_{Si} to obtain PL mapping and spectra, respectively. EL measurement was conducted applying forward bias to sample under constant current conditions. Unnecessary luminescence was cut by 808 and 594 nm long pass filters for mapping and spectrum measurements, respectively. For optically detected magnetic resonance (ODMR) measurements, in addition to laser, a radio frequency (rf) field for magnetic resonance was radiated from an gold thin wire over the sample as shown in Fig. 1. An external magnetic field was applied to the sample by a permanent magnet with changing a distance along c axis. In this study, the orientation of magnetic field was set to be perpendicular with respect to c-axis of SiC crystal ($\theta = 90^{\circ}$) in order to minimize deviation of resonance frequencies due to misalignment of θ while changing the distance. It is noted that resonance frequencies changed and additional allowed transitions appeared when magnetic field was applied with $\theta \neq 0^{\circ}$ [15]. The sample was placed in immersion oil for collecting photo- or electroluminescence more efficiently during measurements. All measurements were conducted at room temperature.



Fig. 1. Schematic of the SiC p-n $(p^+p^-n^+)$ junction diode. An Au thin wire was placed over the sample in order to radiate a rf field for the ODMR measurements.



Fig. 2. I-V characteristics before and after PBW ($1 \times 10^6 \text{ H}^+/\text{dot}$).

Results and Discussion

Figure 3 (a) shows the confocal PL mapping of the pn diode upon irradiation of 1×10^5 H⁺/dot. The luminescent pattern was clearly observed as designed by PBW except at Al electrode regions. Figure 3 (b) shows the EL mapping, exactly the same measurement area shown in Fig. 3 (a). In Fig. 3 (b), we also observed EL from the same positions as PL mapping. It is noted that for EL only V_{Si} located in the current path (mainly at the central region between electrodes) can be excited by current, resulted in partial luminescent pattern. A peak centered around 900 nm was observed for both PL and EL spectra as shown in Fig. 4, which was in good agreement with the previous report [1]. These results suggest that electrically controllable V_{Si} were successfully created at desired positions. A pronounced luminescence observed along the p⁻n⁺ junction region for EL was caused by D₁ defects [5].

For verifying possibility of spin manipulation of electrically excited V_{Si}, ODMR measurements were performed. Firstly, optically excited V_{Si} was subjected to the measurement to confirm resonance frequencies as a function of magnetic field strength. Figure 5 shows ODMR spectra of optically excited V_{Si} as a function of magnetic field. The ODMR line was observed around v = 70 MHz at zero magnetic field, corresponding to zero-field splitting of V_{Si} [14]. We estimate all the small peaks around 70 MHz are attributed to experimental noise signals. Applying a magnetic field, the ODMR line was split by the Zeeman effect. We compared experimental results and theoretical expectation of resonance frequencies. From the spin Hamiltonian for S = 3/2 system, $H = g_e \mu_B \mathbf{B} \cdot \mathbf{S} + D[S_z^2 - S(S + I)/3]$ [14], theoretical resonance frequencies were calculated as shown in Fig. 6 in the case of $\theta = 90^\circ$.



Fig. 3. Confocal mappings for a proton irradiated $(1 \times 10^5 \text{ H}^+/\text{dot})$ SiC pn diode. (a) PL mapping upon excitation with laser power of 1.6 mW. (b) EL mapping upon excitation with forward current of 500 μ A.



Fig. 4. Normalized PL and EL spectra obtained from irradiated areas $(1 \times 10^5 \text{ H}^+/\text{dot})$.

Although all possible transitions ($\Delta m_s = \pm 1$, 2 and 3) are allowed in this condition, two resonances having high transition probability for ODMR out of 6 ones can be observed experimentally. The obtained resonance frequencies were accorded with these from theoretical calculation despite there was some deviation (< 10 MHz) probably caused by fitting to the spectra with low signal-to-noise ratio. We confirmed that more deviation and/or different trend appeared for other conditions ($0^{\circ} \le \theta < 90^{\circ}$). These results indicate that V_{Si} introduced into the device by PBW still maintain spin manipulating capability, which was ready to try spin manipulation using electrically excited V_{Si} .

Conclusion

We demonstrated the creation of electrically controllable V_{Si} in SiC pn junction diode by PBW. Both optically and electrically excited V_{Si} showed the same specific emission as well as that reported,



Fig. 5. ODMR spectra of optically excited $V_{\rm Si}$ (1×10⁶ H⁺/dot). A rf field of 20 dBm and magnetic field strength of 0, 0.4, 0.6 and 0.8 mT were applied. All peaks were fitted with the Lorentzian function without considering noise signals.



Fig. 6. ODMR spectra calculated using the spin Hamiltonian for $\theta = 90^{\circ}$. Thick lines indicate two resonances having high transition probability for ODMR in the condition. Red diamonds show experimental data obtained by the curve fitting.

which suggests that electrically controllable V_{Si}

was successfully created by PBW. ODMR signals were successfully detected from optically excited V_{Si} at room temperature. This result suggests that V_{Si} introduced into the device by PBW still maintain spin manipulating capability. We believe that it is an important step toward realizing SiC devices internally equipped with a V_{Si} -based quantum sensor.

Acknowledgement

This study was partially supported by JSPS KAKENHI 17H01056. We would like to appreciate Mr. Minh-Tuan Hoang, Prof. Dai Hisamoto and Prof. Mutsuko Hatano of Tokyo Institute of Technology for the advices on ODMR measurements.

References

- [1] P. G. Baranov, et al., Phys. Rev. B 83, 125203 (2011).
- [2] A. N. Anisimov, et al., Sci. Rep. 6, 33301 (2016).
- [3] T. Ohshima, et al., J. Phys. D: Appl. Phys., 51, 333002 (2018).
- [4] J. R. Maze, et al., Nature 455, 644 (2008).
- [5] J. R. Petta, et al., Science 309, 2180 (2005).
- [6] S. Castelletto, et al., Nat. Mater. 13, 151 (2014).
- [7] D. J. Christle, et al., Nat. Mater. 14, 160 (2015).
- [8] A. Lohrmann, et al., Nat. Commun. 6, 7783 (2015).
- [9] F. Fuchs, et al., Sci. Rep. 3, 1637 (2013).
- [10]H. Kraus, et al., Nano. Lett. 17, 2865 (2017).
- [11]T. Ohshima, et al., Mater. Sci. Forum, 897, 233 (2017).
- [12] Y. Yamazaki, et al., J. Mater. Res. 33, 3355 (2018).

- [13] TIARA, http://www.taka.qst.go.jp/tiara/tiara/index_j.php.
- [14] SRIM, http://www.srim.org/.
- [15] D. Simin, et al., Phys. Rev. Appl. 4, 014009 (2015).