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Enhancement of ODMR Contrasts of Silicon Vacancy in SiC by Thermal Treatment

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Abstract. We demonstrated the enhancement of the optically detected magnetic resonance (ODMR) contrast of negatively charged silicon vacancy (V_{Si}^-) in SiC by thermal treatment. To create a high density of V_{Si}^-, Proton Beam Writing (PBW) was conducted. After annealing at 600 °C, the ODMR contrast showed the highest value in the investigated temperature range. At lower irradiation fluence, despite no significant change was observed in terms of V_{Si}^- PL intensity, the improvement of the ODMR contrast was observed. Considering defect energy levels and annealing behavior previously reported, it was deduced that the improvement of the ODMR contrast was caused by the reduction of other irradiation-induced defect centers, such as EH3 center.

Introduction

Quantum technologies provide future applications like quantum cryptography, quantum computer and quantum sensors, which are expected to be beyond the limit of applications based on classical mechanics. Extensive researches have been conducted to realize these applications. Color centers with unique features such as great photo-stability, spin addressability and ease of device integration are one of the promising candidates as a building block for quantum technologies. Quantum states of the color centers are extremely sensitive to the outer circumstances like temperature and magnetic field. Besides, those sizes are as small as atoms, which leads to atomic-level spatial resolution. These two factors make color centers desirable for quantum sensing applications. Diamond nitrogen-vacancy (NV) center [1] is the leading candidate as it shows optical spin addressability and long spin coherence time even at room temperature.

Silicon carbide (SiC) has also been intensively explored in this regard and some of the promising color centers were previously reported [2-4]. Among them, negatively charged silicon vacancy (V_{Si}^-) can show NV center-like ideal optical and spin properties. Moreover, from the viewpoint of semiconductor material, both well-developed growth and device fabrication techniques are available in the case of SiC, which is of advantage in terms of device integration. Therefore, selecting SiC as a host material is beneficial for realizing practical devices. Proton beam writing (PBW), which is a direct lithographic technique, has been demonstrated to create V_{Si}^- ranging from singles to millions at a selected volume [5-7]. Combining mature SiC device fabrication processes and the defect-engineering techniques is extremely competitive for device integration.

Quantum sensors are based on the optically detected magnetic resonance (ODMR) which gives information about spin sublevels sensitively responding to the outer circumstances. In the case of color center-based magnetometry, the sensitivity is proportional to $C/\Delta\nu$, where C is the contrast of the ODMR signal and $\Delta\nu$ is the linewidth [8]. As V_{Si}^- has more than an order of magnitude lower C compared with NV center, both ODMR contrast and linewidth should be optimized to achieve as the same sensitivity as that of NV center. In addition, the enhancement of V_{Si}^--PL intensity caused by thermal annealing was previously demonstrated in literature [3,4,9,15]. In this paper, we investigated the effect of thermal annealing on the ODMR signal contrast obtained from V_{Si}^{-}s created by proton beams.

Experimental

A 25 μm thick n-type epitaxial 4H-SiC layer with a doping concentration of 5×10^{14} cm^{-3} (Si face, 4° off) was used in this study. The microbeam patterning was conducted using the 3 MV single-ended accelerator at TIARA, QST Takasaki [10]. We conducted microbeam patterning to 9 samples. V_{Si}^{-}s were incorporated into the epi-layer by PBW using 0.5 MeV focused proton beams with a diameter of 1 μm. Irradiation fluences are 1×10^{6} H^{+}/spot and 1×10^{7} H^{+}/spot, which are corresponding to 1×10^{14} H^{+}/cm^{2} and 1×10^{15} H^{+}/cm^{2}, respectively. The projected range of protons was estimated to be ~4 μm by Monte Carlo calculation (SRIM [11]). Each sample was annealed for 30 min at temperature ranges from 100 to 800 °C in vacuum.

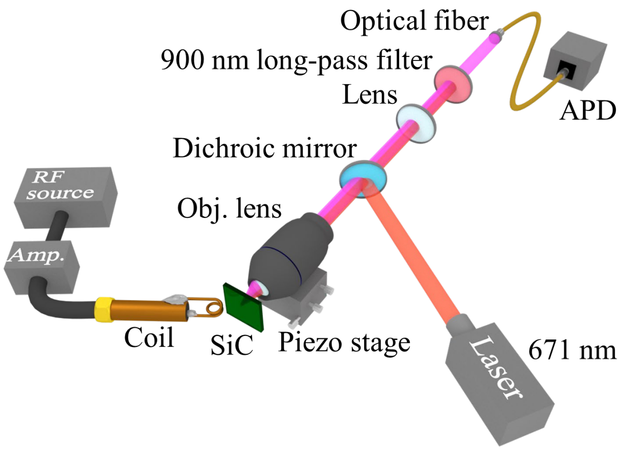

Fig. 1. The experimental setup for the ODMR measurement. A loop coil was used for the radio wave exposure.

A home-built confocal microscope (CFM) was used to obtain photoluminescence (PL) mapping of V_{Si}^{-} under a 671 nm laser excitation with a laser power of 0.3 mW. Figure 1 shows the confocal setup for the PL mapping and the ODMR measurement. For the confocal measurements, PL was collected through a 100× objective with a numerical aperture of 0.85 and filtered by 830 and 900 nm long-pass filters (LPF). The signals were detected by a Si avalanche photodiode (APD). For the ODMR experiment, a loop coil for radio wave exposure was placed close to the sample. We confirmed that the position deviation of the loop coil did not affect ODMR contrast since fluctuation of radio wave power significantly changes the ODMR contrast [12].

To analyze PL spectra, a HORIBA LabRAM HR Evolution spectrometer was used. A 532 nm excitation laser was focused onto a spot (1 μm diameter) of the sample and PL was collected through a 100× objective with a numerical aperture of 0.9. PL ranging from 540 - 1050 nm was obtained to extract information from not only V_{Si}^{-} but also other luminescent defect centers. All measurements were performed at room temperature.

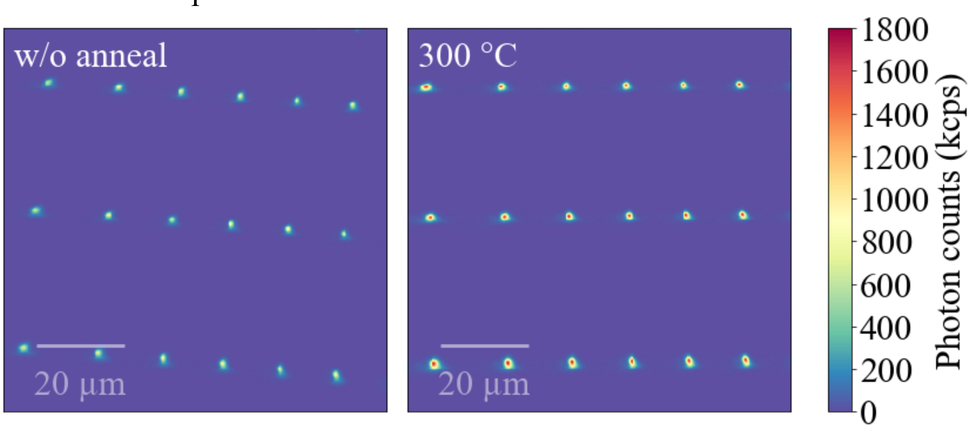

Fig. 2. Confocal maps of the proton (1×10^{7} H^{+}/spot) irradiated SiC epi layer excited by a 671 nm laser with a power of 0.3 mW filtered by 830 nm and 900 nm LPFs.

Results and Discussion

Figure 2 shows the confocal PL maps for the proton (1×10^7 H^+/spot) irradiated spot with and without annealing at 300 °C. PL intensity at the irradiated spots were increased after annealing. To figure out which defects contribute to PL intensity, we investigated their PL spectra. The result is depicted in figure 3. At a shorter wavelength, an emission peak at around 650 nm was observed. This peak went up as annealing temperature increased. After the highest peak for annealing at 700 °C, the peak showed a decrease when annealed at 800 °C. Considering this PL behavior and the emission wavelength, we assigned this PL emission was mainly from $C_{Si}V_C$ [3].

At longer wavelength, an emission peak around 900 nm was observed, which is caused by V_{Si}^- [13]. Figure 4 shows PL intensity as a function of annealing temperature obtained from samples irradiated with 1×10^6 and 1×10^7 H^+/spot. Different PL behavior was confirmed with respect to

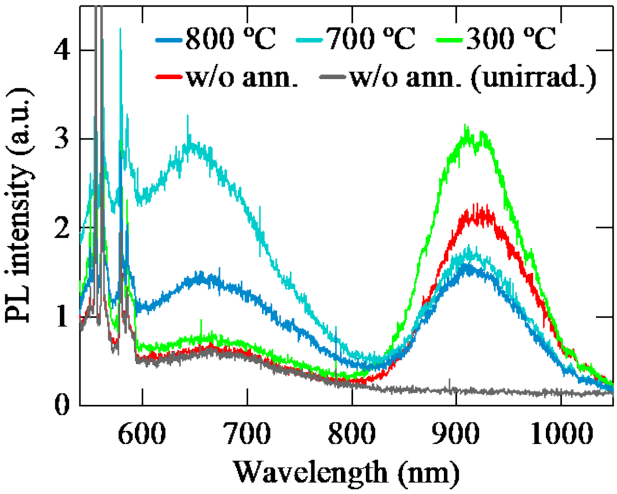

Fig. 3. PL spectra of 1×10^7 H^+/spot irradiated regions excited by 532 nm laser. The gray line is an unirradiated region without annealing.

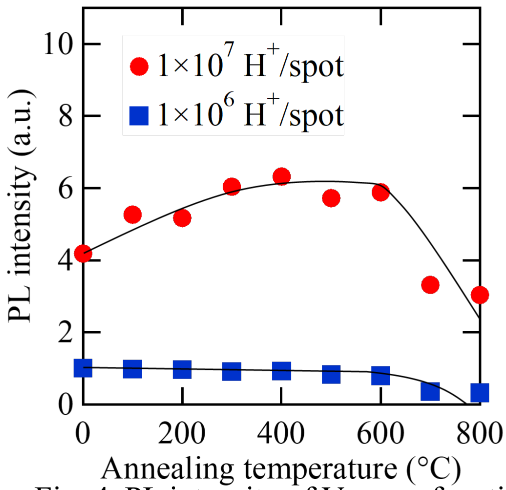

Fig. 4. PL intensity of V_{Si}^- as a function of annealing temperature. The lines are guides to the eye.

irradiation fluences. For a fluence 1×10^6 H^+/spot, PL intensity was almost constant for annealing temperature up to 600 °C, then started decreasing at higher temperatures. On the other hand, for a fluence 1×10^7 H^+/spot, PL intensity increased and kept the maximum value at 300 - 600 °C, then decreased at higher temperatures. This trend agrees with the previous report about 1×10^{15} cm^{-2} of proton-irradiated 4H-SiC [9]. According to our previous studies [5,6], PL intensity of V_{Si}^- is proportional to a proton fluence up to 3×10^6 H^+/spot and then starts deviating from the linear relationship (toward degradation). These results indicate that the sample with an irradiation fluence of 1×10^7 H^+/spot had enough other radiative and/or nonradiative centers to degrade PL emission while no significant other defects were influencing on PL emission in the sample with irradiated 1×10^6 H^+/spot. In the experiment, 1×10^7 H^+/spot showed 4.2 times higher PL intensity than 1×10^6 H^+/spot under the without-annealing condition, which roughly agreed with the previous study [6]. Therefore, PL enhancement happened for the sample of 1×10^7 H^+/spot due to a reduction of such defects by annealing whereas 1×10^6 H^+/spot did not show such a behavior. Wang *et al.* recently demonstrated that the increase of PL intensity even for less irradiated V_{Si}^- (1×10^{14} cm^{-2}) [14]. The discrepancy may be caused by a difference epi-layer used (such as crystalline quality, the concentration of unintentional and/or intentional impurities and the kind) for each experiment. Thereby, the number of defects and the kind created by the proton beam should be different, which could affect the healing of defects. From the reason, different healing behavior was observed. The reason for the decrease at more than 600 °C annealing was attributed to the conversion of V_{Si} into carbon antisite vacancy pair ($C_{Si}V_C$) [3,15].

Figure 5 shows zero-magnetic-field ODMR spectra obtained from the proton-irradiated (1×10^7 H$^+$/spot) spot with and without annealing at 600 °C. The normalized ODMR signals were fitted by Lorentzian function. The ODMR peak was observed at around 70 MHz, which corresponds to the zero magnetic field splitting for V_{Si}^- [4]. The ODMR contrast: C = ΔI/I×100 (I is PL intensity) became larger with increasing annealing temperature up to 600 °C as shown in Fig. 6. A similar trend was observed for both 1×10^6 H$^+$/spot and 1×10^7 H$^+$/spot. At the temperature of 600 °C, the ODMR contrast showed the maximum value, 1.6 times larger than that for an as-irradiated sample in both irradiation conditions. This will lead to 1.6 times greater sensor sensitivity. However, the ODMR contrast started decreasing at the annealing temperature of more than 600 °C. This behavior was caused by a decrease of the number of V_{Si}^- as shown in Fig. 4.

It had been estimated that the enhancement of PL intensity due to the annealing effect would contribute to the improvement of the ODMR contrast. However, since we did not observe any enhancement in PL intensity for a fluence 1×10^6 H$^+$/spot, it is certain to say that there are other factors contributing to the ODMR contrast. One of the possible factors is a reduction of other paramagnetic defects by annealing. The less paramagnetic defects in the proximity of V_{Si}^-, the less decoherence for V_{Si}^- spins, which can lead to higher ODMR contrast. Kasper *et al*. demonstrated that V_{Si}^- coherence time increases as annealing temperature up from 200 to 500 °C [16]. Non-paramagnetic defects can also be a candidate for spin killer defects. Both optical excitation of V_{Si}^- from the ground to excited states and spin-dependent transition from excited to meta-stable states are key phenomena of the ODMR. If energy levels of radiative and/or nonradiative centers are located to that of V_{Si}^- nearby, the photo-excitation and its relaxation will be impeded, leading to a decrease of the ODMR contrast. A Monte Carlo simulation proposed that recoveries of carbon interstitials and carbon vacancies occur at relatively low temperature ranges of 400 - 700 °C [17]. In Ref. 18, annealing effects for electrically active defects in 4H-SiC incorporated by 160 keV electron beams were investigated using deep level transient spectroscopy (DLTS) and minority carrier transient spectroscopy (MCTS). The result showed that the defect concentration of EH1 and EH3 centers, which were tentatively assigned as carbon interstitials, decreased at the temperature of more than 400 °C. Their defect levels are positioned at 0.41 and 0.71 eV below the conduction band minimum, respectively [18]. As for V_{Si}^-, its ground state energy level was calculated to be 0.9 eV above the valence band edge [19]. As for EH3 center, its energy level could be energetically located close to V_{Si}^-, 671 nm excitation laser is possible to excite electrons from V_{Si}^- ground state to EH3 level, which results in a reduction of spin polarization rate of V_{Si}^-. We deduce this center to be one of the killer defects for the ODMR of V_{Si}^-. In addition to that, other radiative centers increase a baseline of the ODMR spectrum. Considering the low ODMR contrast of V_{Si}^- (less than ~1 %), the ODMR signal could be buried in the higher baseline for larger other radiative defects. This indicates a decrease in a net ODMR contrast.

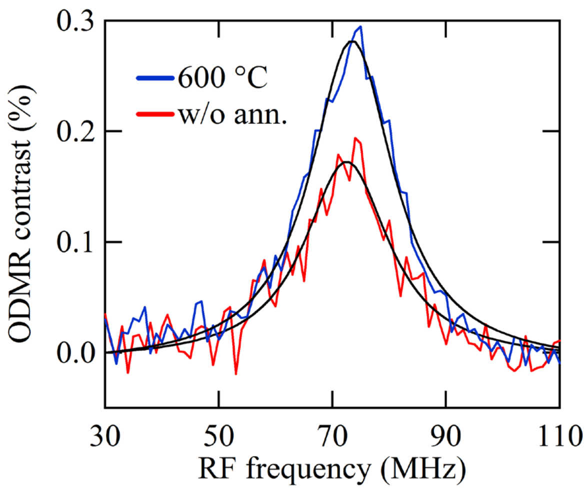

Fig. 5. ODMR spectra obtained from V_{Si}^- under zero magnetic field.

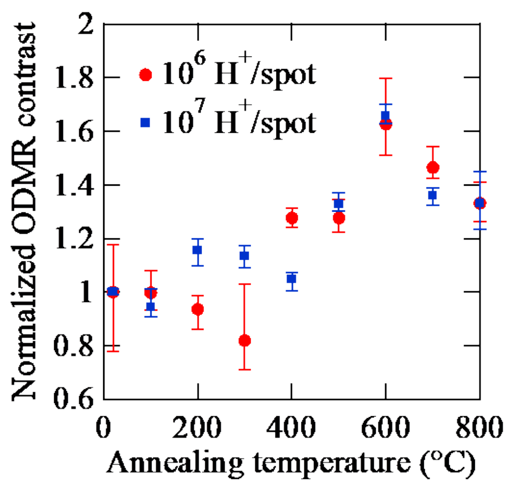

Fig. 6. Experimental result of ODMR contrast as a function of annealing temperature.

Summary

We investigated the effect of post-irradiation thermal annealing on the ODMR contrast of V_{Si}^- in SiC. Highly localized and high-density V_{Si}^-s were created using a PBW technique. At a fluence of 1×10^7 H^+/spot, the PL intensity for V_{Si}^- showed enhancement after the annealing process. On the other hand, at an irradiation fluence of 1×10^6 H^+/spot, the PL intensity did not show an enhancement. Unlike the PL behaviors, the improvement of the ODMR contrast was observed after annealing for both fluences. At the annealing temperature of 600 °C, the ODMR contrast showed the maximum value, 1.6 times higher than that for the as-irradiated sample in both irradiation conditions. We deduce the improvement of the ODMR contrast to be a reduction of other radiative centers, which impede the optical spin polarization rate of V_{Si}^-, with increasing annealing temperature. The ODMR contrast improvement by moderate annealing temperature will be a basic technique to enhance performances of V_{Si}^--based quantum sensors.

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