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Creation and Functionalization of Defects in SiC by Proton Beam Writing

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Abstract. Proton beam writing (PBW) a with 1.7 MeV proton micro beam was carried out into high purity semi-insulating 4H-SiC bulk substrates. Luminescent defects created in the SiC were investigated at room temperature using a confocal laser scanning microscope. A peak around 900 nm associated with the silicon vacancy was observed for the irradiated SiC without any post-implantation processing such as annealing. The overall depth profile of photon counts detected from irradiated areas is in good agreement with simulated vacancy depth profile. This suggests that the silicon vacancy can be applied as an ion tracking detector. In addition, since the silicon vacancy is known as a single photon source with a spin that can be controlled at room temperature, PBW is expected to be a useful tool to fabricate spin qubits.

Introduction

The silicon vacancy (V_{Si}), divacancy ($V_{\mathrm{Si}}V_{\mathrm{C}}$) and carbon antisite carbon vacancy ($C_{\mathrm{Si}}V_{\mathrm{C}}$) defects in silicon carbide (SiC) are known to act as single photon sources (SPSs), and their luminescence properties can be controlled at room temperature (RT) [1-4]. In addition, in our previous studies [5,6], we found that bright fully polarized SPSs can be created near the surface of SiC (3C-, 4H- and 6H), although the atomic structure of these particular SPSs has not yet been identified. These results indicate that SiC is a good host material for SPS which can be operated at RT. Since SPSs are vital for quantum spintronics and quantum photonics applications, the development of fabrication processes of these defects and understanding their quantum optical properties are of great importance. Ion irradiation is one of the most useful tools to create luminescent defects in materials. In particular, micro/nano ion beams can be used to form SPSs at a certain location with micro/nano meter precision. Proton Beam Writing (PBW) is known as a direct lithography technique using focused micro-ion-beams of MeV protons [7-9]. Since proton beams can create crystal damage (displacement of atoms at lattice sites), PBW is expected to be a powerful tool to create SPSs in certain locations. In addition, if bright SPSs are introduced by ion incidence, the radiation induced SPSs can be applied as an ion tracking detector [10]. However, the creation of crystal defects which act as SPS in SiC using PBW has not yet been clarified. In this study, SPSs created in SiC by PBW are discussed.

Experimental

The samples used in this study were commercially available high purity semi-insulating (HPSI) 4H-SiC bulk substrates (Si-face). PBW was carried out at a microbeam line connected with the 3 MV single-ended accelerator at TIARA, QST Takasaki [11]. The samples were organic-cleaned and their native surface oxide was removed by hydrofluoric acid etch before PBW. The pattern shown in Fig. 1 was drawn on the samples at RT using a 1.7 MeV proton beam with a beam diameter of ~1 μm. The same pattern but different proton fluences between 1×10^8 and 1×10^{16} /cm^2 were employed by controlling proton beam current and irradiation time (*e.g.* beam current was around hundred fA, and irradiation time was from μsec to hundred sec). Thus, the fluence was estimated by multiplying the beam current by the irradiation time. After PBW, the photoluminescence (PL) was measured at RT using a confocal laser scanning microscope (CFM) system with an excitation laser at 532 nm. Before PL measurements, no annealing step was carried out.

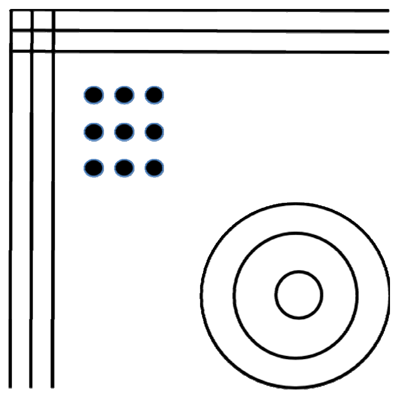

Fig.1. PBW pattern

Results and Discussion

Figure 2 shows confocal PL maps obtained with HPSI 4H-SiC irradiated with 1.7 MeV-protons at fluences of (a) 1×10^8 and (b) 1×10^{16} /cm^2. In addition to the 9 (3×3) irradiated areas resulting in the central isolated PL spots, other features were also written with the PBW technique including circles (partially shown in Fig. 2 (a)) and two horizontal and one vertical lines shown in Fig. 2 (b). Since the fluence of 1×10^8 /cm^2 means that only one proton was used to create each of the spots in the 3x3 grid, the obtained result suggests that one ion incidence can be detected by the observation of luminescent defects using confocal PL measurements. However, it should be mentioned that the fluence of 1×10^8 /cm^2 is not very accurate in this study because the proton fluence was estimated by multiplying the beam current by the irradiation time. To discuss the detection limit of incident protons, further studies are necessary. Comparing Fig. 2 (a) with (b), photon counts are greater for the sample irradiated at 1×10^{16} /cm^2 than for the 1×10^8 /cm^2 sample indicating that the defect concentration of the former is considerably greater, as expected.

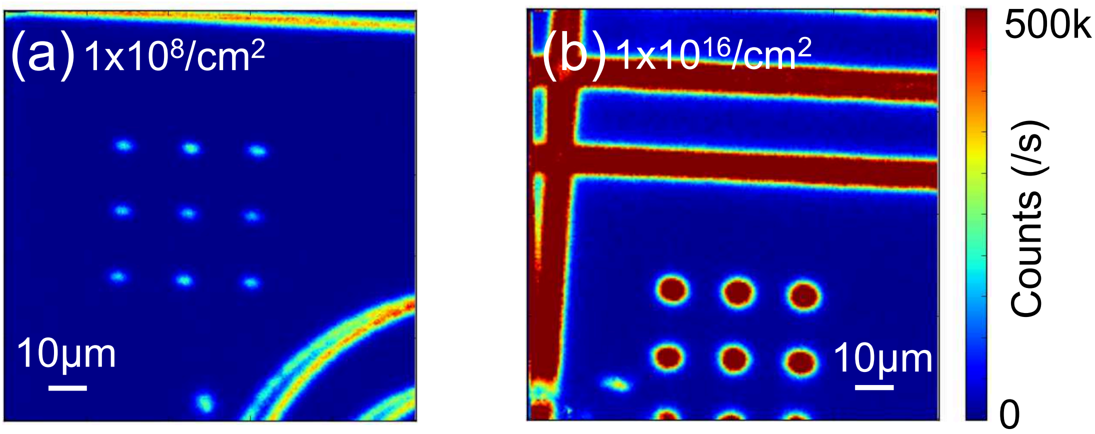

Fig.2. Confocal PL map for HPSI 4H-SiC irradiated with 1.7 MeV-protons at (a) 1×10^8 /cm^2 and (b) 1×10^{16} /cm^2 at RT.

To identify the defects observed by confocal PL mapping, PL spectra for irradiated areas were measured. Fig. 3 shows a PL spectrum obtained from an area irradiated with 1.7 MeV-protons at 1×10^{16} /cm^2. For comparison, a PL spectrum obtained from a non-irradiated area is also plotted in the figure. A PL signal centered at ~900 nm is observed in the irradiated area only. In a previous study [12], PL peaks labeled V1 (~ 860 nm) and V2 (~ 920 nm) for 4H-SiC were observed at low temperatures and concluded to originate from V_{Si} at *k*-sites and V_{Si} at *h*-sites, respectively. PL spectra were measured at RT in this study, and as a result, the zero phonon line cannot be observed owing to the phonon sideband. However, it can be concluded that the PL peak obtained in this study is associated with the V_{Si} defect in 4H-SiC. We would also like to mention that since the spin property of V_{Si} can be controlled at RT [3, 4], V_{Si} is expected to be applied to spin qubits which can be operated at RT similar to the nitrogen-vacancy centers in diamond [13-15].

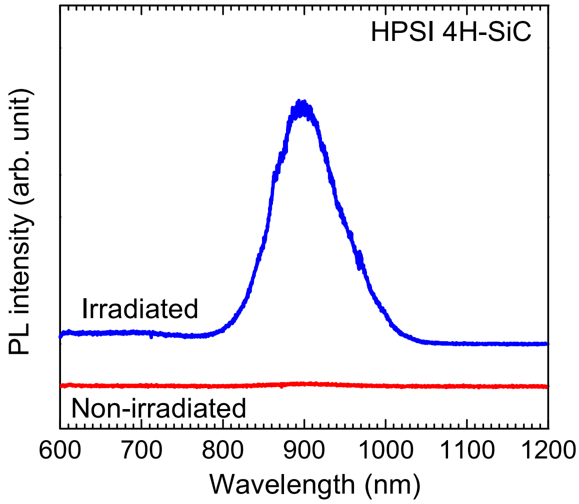

Fig.3. PL spectra obtained from irradiated and non-irradiated areas of HPSI 4H-SiC at RT.

Next, the distribution of V_{Si} along the depth direction is discussed. Figure 4 shows a confocal PL map along the depth direction for HPSI 4H-SiC irradiated with 1.7 MeV-protons at 1×10^{12}/cm^2. The PL map was obtained by changing the focusing point of the CFM from the surface. The values of depth experimentally observed by CFM were corrected using the refractive index of SiC (2.6). As shown in the figure, three bright linear shapes are observed along the proton tracks. This indicates that V_{Si} are created in SiC by proton irradiation, despite no subsequent thermal annealing being performed. For the precise creation of V_{Si} as well as the development of an ion tracking detector, it is important to understand the depth profile of V_{Si}. Figure 5 (a) shows the calculated Si vacancy depth profile in SiC irradiated with 1.7 MeV-protons and (b) photon counts obtained from proton irradiated area (1.7 MeV-protons at 1×10^{12}/cm^2) as a function of the distance from the surface. The Monte Carlo simulation code, SRIM [16] was used for the estimation of Si vacancy distribution. The number of vacancies increases with increasing distance from the surface, and a significant increase in the number of vacancies is observed around the projection range of 1.7 MeV-protons (24.7 μm) which is called the "Bragg peak". For the PL results shown in Fig. 5 (b), the photon counts also increase with depth, and a peak in the counts is observed around 21 μm. The tail of photon counts is observed in the deeper region than that of the calculated result. The discrepancy can be interpreted in terms that the simulation was done using amorphous SiC and crystal effects cannot be considered. Thus, ion channeling might occur, and as a result V_{Si} can be created in the deeper region than the estimated ion range. Although the experimental result is not exactly the same as the vacancy distribution calculated by the Monte Carlo simulation, it can be said that the overall feature for photon counts shows good agreement with the estimated vacancy

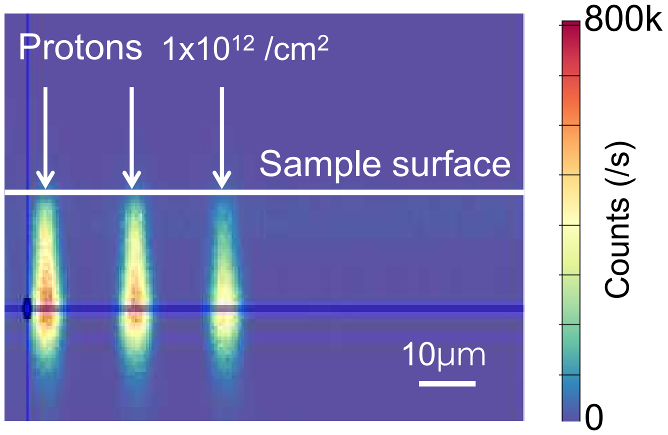

Fig.4. Confocal PL map along depth direction for HPSI 4H-SiC irradiated with 1.7 MeV-protons at 1×10^{12} /cm^2.

profile. This suggests that the V_{Si} can be used as an ion tracking detector. Since V_{Si} can be created by just ion incidence without any subsequent treatment such as high temperature annealing and chemical etching to samples, we can conclude that V_{Si} is regarded as promising candidate for an *in-situ* ion tracking detector.

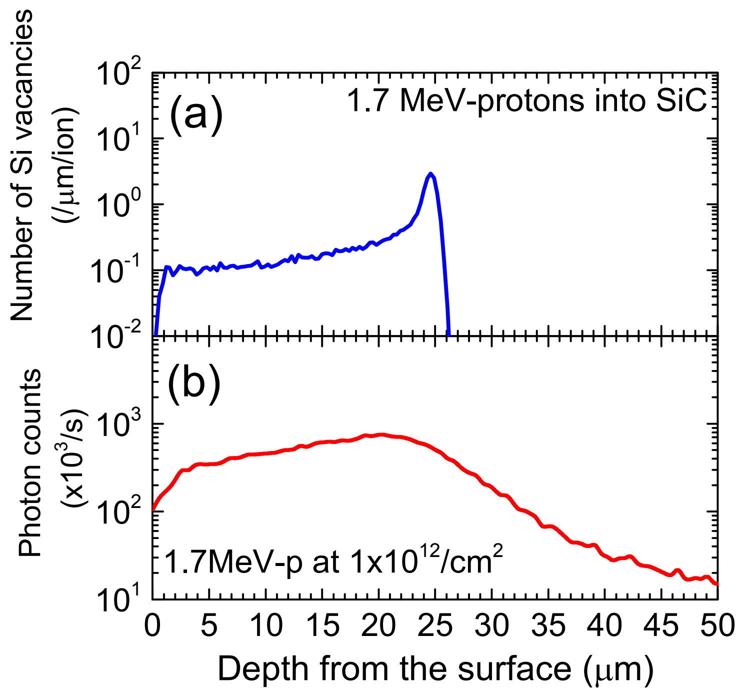

Fig.5. Depth profile of (a) Si vacancies introduced by 1.7 MeV-protons which is estimated using SRIM [16] and (b) Photon counts from HPSI 4H-SiC irradiated with 1.7 MeV-protons at 1×10^{12} /cm^2.

Summary

Luminescent defects created in commercially available high purity semi-insulating 4H-SiC bulk substrates by PBW using 1.7 MeV-protons were investigated at RT using a confocal laser scanning microscope system. As a result, a PL peak around 900 nm associated with V_{Si} was observed for the irradiated areas without subsequent treatment such as thermal annealing and chemical etching. The photon counts obtained from irradiated areas increased with proton fluence. The overall depth profile of the photon counts is in good agreement with simulated vacancy depth profile. This result suggests that V_{Si} can be used as an *in-situ* ion tracking detector. In addition, since V_{Si} is known as a single photon source of which spins can be controlled at RT, PBW is expected to be a useful tool for the fabrication of spin qubits.

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