

SiC Quantum Dots in Si-Oxide Layer Fabricated by Double Hot-Si⁺/C⁺-Ion Implantation Technique

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Abstract

We experimentally studied SiC quantum nano-dots in Si-oxide layer fabricated by double hot-Si⁺/C⁺ ion implantation technique (Si⁺/C⁺-OX), comparing with SiC dots by single hot-C⁺ ion implanted oxide (C⁺-OX) and amorphous-Si layers (C⁺-aSi). STEM analysis shows that SiC dots were successfully formed in Si⁺/C⁺-OX. The Raman peaks of T- and D-bands of a-carbon (a-C), as well as TO-mode of Si-C vibration, are observed in Si⁺/C⁺-OX, which is the direct verification of SiC and a-C formation. We demonstrated that the maximum PL intensity I_{PL} of Si⁺/C⁺-OX is approximately 1.7 and 8.7 times larger than those of C⁺-aSi and C⁺-OX, respectively. The PL peak energy of Si⁺/C⁺-OX (2.5eV) is lower than that of C⁺-aSi (3.1eV). The I_{PL} of Si⁺/C⁺-OX shows the rapid increase after N₂ annealing, which is possibly attributable to the PL quantum efficiency enhancement of SiC dot.

I. Introduction

Using the self-cluster effects of ion-implanted C atoms in Si [1], 3C-SiC and hexagonal-SiC (H-SiC) nano-dots (diameter $R \approx 2$ nm) can be easily formed even in amorphous-Si layer (a-Si) as well as polysilicon (poly-Si) and crystal-Si (c-Si) by hot-C⁺-ion implantation technique [2], [3]. Thus, the crystal structure of Si is not essential for the SiC dot formation by hot-C⁺-ion implantation. We demonstrated the very large bandgap E_G (≈ 3 eV) (=peak PL-wavelength λ_{PL} of 400nm) and very strong PL emission I_{PL} in the near-UV/visible regions (>400 nm) from indirect-bandgap SiC dots, which is possibly attributable to free exciton recombination of excited electrons in SiC dots [4]. However, since the SiC dots with large E_G are embedded in Si layer with small E_G (≈ 1.1 eV), the SiC dot in Si layer is not a quantum dot, resulting in small PL quantum efficiency for visible Si-based photonic devices. Thus, it is strongly required to realize a quantum SiC dot embedded in much larger E_G material, such as SiO₂ with $E_G \approx 9$ eV, and thus the PL quantum efficiency of quantum SiC dots can be improved by band-to-band recombination of excited electrons.

In this work, we experimentally studied the SiC quantum dots embedded in SiO₂, using double hot-Si⁺/C⁺-ion implantation into a surface-SiO₂ (Si⁺/C⁺-OX) on bulk-Si. We successfully improved the PL intensity I_{PL} of quantum SiC dots in Si⁺/C⁺-OX, compared to those of single hot-C⁺-ion implanted oxide (C⁺-OX) and a-Si layers (C⁺-aSi). Moreover, an a-carbon (a-C) in C⁺-OX also showed very broad PL spectrum, as reported [5], but the I_{PL} was very weak.

II. Experiment Procedure

To form a SiC dot in surface-SiO₂ (SOX) layer, Si atoms as well as C atoms are required to coexist in SOX. SiC quantum dots in SOX were fabricated by double hot-ion implantations of Si⁺ (Fig.1-(I)(b)) and C⁺ ion (Fig.1-(I)(c)) into the SOX layer on (100) bulk-Si substrate at substrate temperature T (600°C) after forming 140-nm thick SOX (Fig.1-(I)(a)), using low and high hot-ion dose conditions of Si⁺ (D_S) and C⁺-ion doses (D_C) for Si⁺/C⁺-OX (Table-1). As a result, the peak concentrations of Si and C atoms at low dose conditions, simulated by Monte-Carlo simulator SRIM [6], are to be approximately 7×10^{21} and 5×10^{21} cm⁻³, respectively (Fig.2). Post N₂ annealing was carried out at annealing temperature $T_N = 1000^\circ\text{C}$ for various annealing time t_N ($0 < t_N \leq 60$ min), to poly-crystallize implanted Si atoms in SOX (Fig.1-(I)(d)), because a-Si can be poly-crystallized [3]. C⁺-OX structure was also formed in SOX (Fig.1-(II)(a)), using the single hot-C⁺ ion implantation (Fig.1-(II)(b)) and post N₂ annealing (Fig.1-(II)(c)). SiC dots in C⁺-aSi were also fabricated by hot-C⁺-ion implantation into a-Si layer [3].

PL and Raman properties of three structures (Table-1) were measured at room temperature, where the excitation laser energy and diameter were 3.8eV and 1μm, respectively. The PL spectrum in the wide range of λ_{PL} from the UV to NIR regions was calibrated using a standard illuminant.

III. Results and Discussions

A. Material Structures of Si⁺/C⁺-OX and C⁺-OX

Since SiC dots are local Si-rich areas in SOX, SiC dot areas in HAADF-STEM image for Si⁺/C⁺-OX shows bright areas. Actually,

STEM image shows that many SiC dots with $R \approx 2$ -4nm (bright areas encircled in Fig. 3) are successfully observed below the 30nm depth from the SOX surface, whose C content in the SiC-dot layer is estimated to higher than 2at.% (Fig.2). However, in Si layer, SiC-dots were not formed, because of very low C-content (<1.5 at.%) (Fig.2).

It is noted that UV-Raman analysis of Si⁺/C⁺-OX (Fig.4) shows the strong two peaks of the T-band around 1100cm⁻¹ [7] and D-band of C-C vibration and no G-band peak, which suggests that a-C in Si⁺/C⁺-OX mainly consists of diamond-like carbon (sp^3 site) [5]. However, the TO-mode (I_{TO}) of Si-C vibration is very weak, compared with those of C⁺-aSi.

Moreover, with increasing the ion dose, the Raman intensities I_R of both T- and D-bands increase, and especially the D-band intensity enhancement is much larger than the T-band enhancement (Figs. 5(a) and 5(b)). Moreover, all I_R -peaks decrease with increasing t_N under low ion dose conditions in $t_N \leq 30$ min (Fig. 5(b)), whereas I_D , I_T , and I_{TO} peaks at high dose conditions are almost independent of t_N . Thus, at low ion dose conditions, it is possible that a-C area reduces after N₂ annealing.

On the other hand, C⁺-OX shows the typical Raman spectrum of a-C including the G-band of graphite (sp^2 site) (Fig.6). The I_D of Si⁺/C⁺-OX is much smaller than that of C⁺-OX, which indirectly suggests that some C atoms of Si⁺/C⁺-OX bind to Si atoms, resulting in SiC dot formation. However, the TO mode of Si-C vibration cannot be observed in C⁺-OX, as expected.

B. PL Properties of Si⁺/C⁺-OX and C⁺-OX

Firstly, we discuss the PL properties under low ion dose conditions. We successfully demonstrated that the PL intensity I_{PL} of Si⁺/C⁺-OX is much larger than that of C⁺-aSi, and the peak PL energy E_{PH} exhibits a red-shift from approximately 3.1eV of C⁺-aSi to 2.5eV (Fig.7). The broad PL of C⁺-OX is also observed, but the PL intensity is one order of magnitude smaller than that of Si⁺/C⁺-OX even under the same D_C (Fig.7).

The I_{PL} of Si⁺/C⁺-OX is remarkably enhanced after N₂ annealing (Fig.8), and drastically increase with increasing t_N under $t_N \leq 30$ min. As a result, the maximum I_{PL} of Si⁺/C⁺-OX is approximately 1.7 and 8.7 times larger than those of C⁺-aSi and C⁺-OX, respectively. The I_{PL} enhancement factor ΔI_{PL} compared with I_{PL} at $t_N = 0$ amounts to approximately 9.5 at $t_N = 30$ min, which is much larger than the ΔI_{PL} of C⁺-aSi (2.8) and C⁺-OX (2.2). The I_{PL} of Si⁺/C⁺-OX negatively correlates to the I_R of C-C and Si-C vibrations (Fig.5(b)), which suggests that the PL quantum efficiency of SiC dots increases after N₂ annealing. In addition, the I_{PL} of C⁺-OX is still lower than the I_{PL} of Si⁺/C⁺-OX in spite of increasing t_N , which indicates that the I_{PL} of a-C in C⁺-OX is much smaller than that of SiC dots.

Secondly, we discuss the hot-ion dose dependence of PL properties of Si⁺/C⁺-OX.

In spite of increasing D_C , the I_{PL} of Si⁺/C⁺-OX is reduced, which is approximately 85% of that at low D_C (Fig.9(a)). However, the PL spectrum line shape is independent of D_C (Fig.9(a)). In addition, the t_N dependence of the I_{PL} improvement of Si⁺/C⁺-OX at high D_C is very slow, and the maximum I_{PL} improvement can be achieved at $t_N = 240$ min, whereas the peak- t_N under low D_C is only 30min (Fig.9(b)). Thus, it is strongly required to optimize the hot-ion dose to improve the I_{PL} of Si⁺/C⁺-OX.

IV. Conclusion

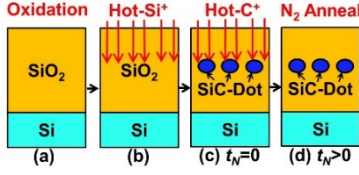
In this work, we experimentally studied SiC quantum dots in SOX fabricated by the double hot-Si⁺/C⁺ implantation into an oxide layer. We demonstrated very strong PL intensity of Si⁺/C⁺-OX in the UV/visible regions, compared with that of C⁺-aSi and C⁺-OX. Since a semiconductor layer is not essential for forming Si⁺/C⁺-OX, Si⁺/C⁺-OX technique is very promising for low-cost visible photonic devices.

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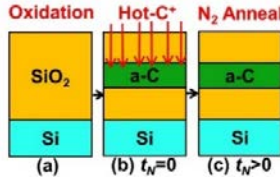
References: [1] T.Mizuno, JJAP 57, 04FB03, 2018. [2] T.Mizuno, Abst. SNW, p.121, 2018. [3] T.Mizuno, JJAP 58, SBBJ01, 2019. [4] J.Fan, *Silicon Carbide Nanostructures* (Springer), 2014. [5] Rusli, JAP 80, 2998, 1996. [6] J.F.Ziegler, <http://www.srim.org/>. [7] C. Casiraghi, Phys. Rev. B 72, 085401, 2005.

Structures	D_S ($\times 10^{16} \text{cm}^{-2}$)	D_C ($\times 10^{16} \text{cm}^{-2}$)
$\text{Si}^+/\text{C}^+-\text{OX}$	6	4
	10	6
C^+-OX	0	4
C^+-aSi	0	4

Table-1 Hot-ion dose conditions for three structures.



(I) $\text{Si}^+/\text{C}^+-\text{OX}$



(II) C^+-OX

Fig.1 Fabrication steps for (I) $\text{Si}^+/\text{C}^+-\text{OX}$ by double hot- Si^+/C^+ -ion-implantation into SOX and (II) C^+-OX by single hot- C^+ -ion-implantation into SOX. In (I), after (a) forming 140-nm thick SiO_2 on (100) bulk-Si substrate, (b) hot- Si^+ -ions and (c) the following hot- C^+ -ions were implanted into the SOX layer at $T=600^\circ\text{C}$. (d) Post N_2 annealing was carried out at $T_N=1000^\circ\text{C}$ for annealing time t_N . (II) shows that C^+-OX is also fabricated by the same processes for $\text{Si}^+/\text{C}^+-\text{OX}$ without hot- Si^+ -ion implantation of (I)-(b).

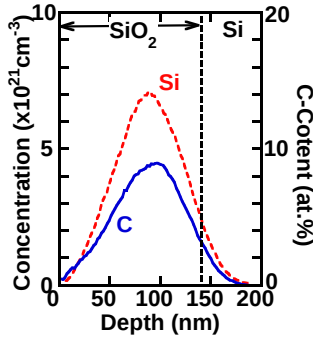


Fig.2 Implanted Si (dashed line) and C atom (solid line) depth profiles simulated by SRIM [6], where $D_S=6 \times 10^{16} \text{cm}^{-2}$, $D_C=4 \times 10^{16} \text{cm}^{-2}$, and $T=25^\circ\text{C}$. The left and right vertical axes show the concentration and C-content, respectively.

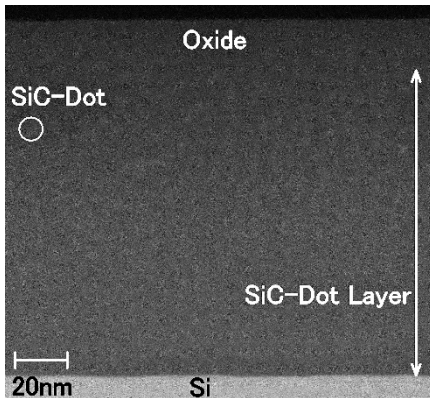


Fig.3 HAADF-STEM images of the cross section of SiC dots (bright areas) encircled in SOX of $\text{Si}^+/\text{C}^+-\text{OX}$, where $D_S=6 \times 10^{16} \text{cm}^{-2}$, $D_C=4 \times 10^{16} \text{cm}^{-2}$, and $t_N=10 \text{min}$. SiC dots in SOX are the Si rich area, resulting in the bright areas in HAADF-STEM image. Many SiC dots are formed below 30nm depth from the SOX surface shown as an arrow of SiC-Dot Layer.

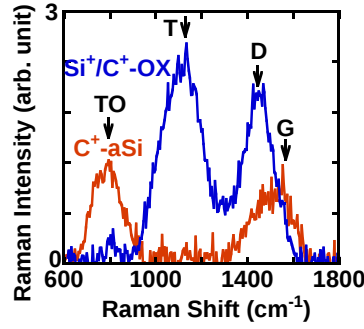


Fig.4 Raman spectra of $\text{Si}^+/\text{C}^+-\text{OX}$ (blue line) at $D_S=6 \times 10^{16} \text{cm}^{-2}$ and C^+-aSi (brown line), where $D_C=4 \times 10^{16} \text{cm}^{-2}$ and $t_N=0$. The arrows of $\text{Si}^+/\text{C}^+-\text{OX}$ show the D and T bands of C-C vibration, and the arrows of C^+-aSi show the G band of C-C vibration and the TO mode of Si-C vibration.

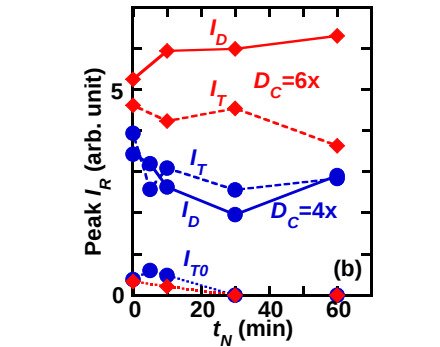
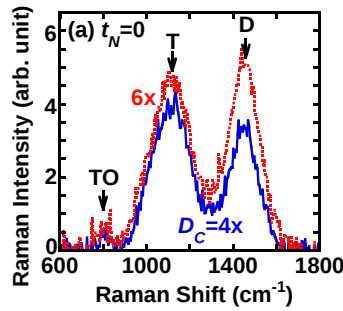


Fig.5 (a) D_C dependence of Raman spectra of $\text{Si}^+/\text{C}^+-\text{OX}$ under low ($D_S=6 \times 10^{16} \text{cm}^{-2}$ and $D_C=4 \times 10^{16} \text{cm}^{-2}$ (solid line)) and high ion dose conditions ($D_S=1 \times 10^{17} \text{cm}^{-2}$ and $D_C=6 \times 10^{16} \text{cm}^{-2}$ (dotted line)), where $t_N=0$. (b) t_N dependence of I_D (solid lines), I_T (dashed lines), and I_{TO} peaks (dotted lines) under low (circles) and high ion dose conditions (rhombi). At low ion dose, both I_D and I_T decrease after N_2 annealing at $t_N \leq 30 \text{min}$. I_{TO} also decreases and is almost zero at $t_N \geq 30 \text{min}$.

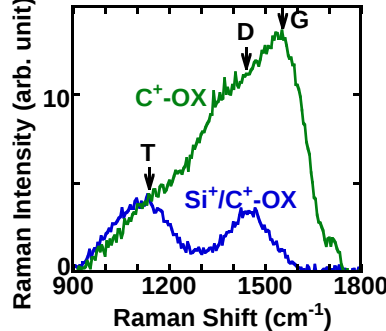


Fig.6 Raman spectra of $\text{Si}^+/\text{C}^+-\text{OX}$ (blue line) at $D_S=6 \times 10^{16} \text{cm}^{-2}$ and C^+-OX (green line), where $D_C=4 \times 10^{16} \text{cm}^{-2}$ and $t_N=0$. The arrows show the G (observed in only C^+-OX), D and T bands of C-C vibration.

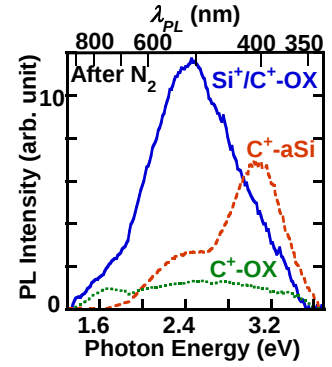


Fig.7 PL spectra of three structures of $\text{Si}^+/\text{C}^+-\text{OX}$ at $D_S=6 \times 10^{16} \text{cm}^{-2}$ (solid line), C^+-aSi (dashed line), and C^+-OX (dotted line) after N_2 annealing, where $D_C=4 \times 10^{16} \text{cm}^{-2}$. t_N of $\text{Si}^+/\text{C}^+-\text{OX}$, C^+-aSi , and C^+-OX are 30, 10, and 30min under the maximum I_{PL} conditions, respectively.

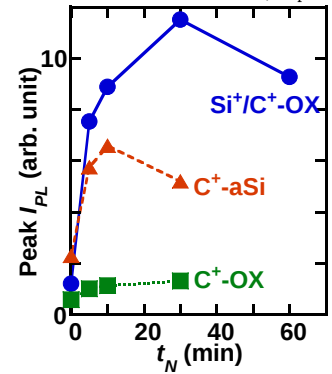


Fig.8 t_N dependence of peak- I_{PL} of $\text{Si}^+/\text{C}^+-\text{OX}$ at $D_S=6 \times 10^{16} \text{cm}^{-2}$ (circles), C^+-aSi (triangles), and C^+-OX (squares), where $D_C=4 \times 10^{16} \text{cm}^{-2}$.

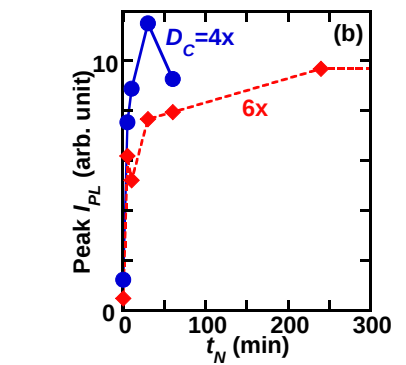
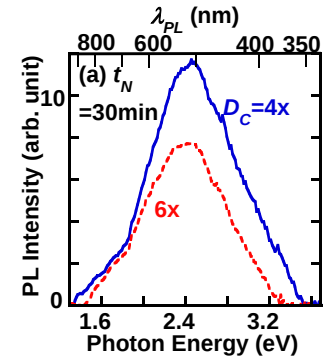


Fig.9 (a) D_C dependence of PL spectra under low ($D_S=6 \times 10^{16} \text{cm}^{-2}$ and $D_C=4 \times 10^{16} \text{cm}^{-2}$ (solid line)) and high ion dose conditions ($D_S=1 \times 10^{17} \text{cm}^{-2}$ and $D_C=6 \times 10^{16} \text{cm}^{-2}$ (dotted line)), where $t_N=30 \text{min}$. (b) t_N dependence of peak- I_{PL} of $\text{Si}^+/\text{C}^+-\text{OX}$ at low (circles) and high ion doses (rhombi).