THE EFFECT OF HYDROGEN/ DEUTERIUM INTRODUCTION ON PHOTOLUMINESCENCE OF 3C SiC CRYSTALS

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ABSTRACT

The effect of the incorporation and annealing of deuterium in 3C-SiC on its photoluminescence is reported. A 3C-SiC crystal has been implanted with 100 keV deuterium and subsequently annealed at temperatures between 1015 °C and 1220 °C for 1 to 5 minutes. SIMS depth profiles indicate hydrogen is strongly trapped by defects generated through ion bombardment, but a gradual damage repairing occurs during annealing. Photoluminescence was measured with 488 nm Ar laser excitation for sample temperatures from 89 K to 400 K. The PL peak wavelength of 540 nm at room temperature has shifted to 538 nm at 89 K. The peak PL intensity decreases with measurement temperature while its full width at half maximum (FWHM) exhibits an increasing trend. PL data were taken at five annealing stages. The post-implantation peak PL intensity and its integrated area increase initially with annealing temperature and time. After the final annealing at 1218 °C for 2 minute, PL intensity and its integrated area exhibit a decrease in level.

INTRODUCTION

SiC is a wide and indirect bandgap material suitable for high power, high frequency, and high temperature semiconductor devices, and as a substrate for III-V nitride epitaxial growth. High quality 3C-SiC have, in addition, a relatively highly efficient photoluminescence. Thus 3C-SiC has potential of being used for optical devices. However, atomic hydrogen may be introduced into device during processing stage, it can then passivate shallow and deep level impurities, thus affect the device luminescence and performance [2-4]. As a result, the effect of hydrogen on photoluminescence is of interest for making 3C-SiC a reliable optical device.

EXPERIMENT

The sample used for this experiment is a vapor phase grown 3C-SiC crystal. This single crystal has been grown from the thermal decomposition of methyltrichlorosilane (MTCS-CH_3SiCl_3) at the Baikov Institute. The SiC growth was carried out in a high flow of H_2 on a resistively heated graphite rod at temperatures ranging from 1650 °C to 1750 °C [7]. This unintentionally doped crystal appears yellow under normal light and emits green luminescence at 540 nm (2.3 eV) when excited by Ar laser. X-ray rocking curves of the <111> peak were obtained with a linewidth of 12.3 arc-sec [7]. This is the smallest value reported to date for any polytype of SiC. Incorporation of hydrogen in 3C-SiC was obtained through ion implantation. Deuterium ions were implanted in 3C-SiC crystal at 100 keV to a dose of 2 x 10^{15} cm^{-2}. The sample was subsequently rapid thermal annealed (RTA) five times under ultra high purity (UHP) N_2 at temperatures up to 1220 °C with durations from 1 to 5 min: 1st anneal - 1015 C for 1 min, 2nd anneal - 1092 °C for 1 min, 3rd anneal - 1213 °C for 1 min, 4th anneal - 1220 °C for 5 min, and 5th anneal - 1218 °C for 2 min. Photoluminescence (PL) and secondary ion mass spectrometry (SIMS) measurement were performed. The PL was measured as a function of temperature range from 89 to 400 K. We used 488 Ar laser excitation with an average beam power of 28 mW. The deuterium profiles were measured by SIMS using a Cs^+ ion beam. The SIMS depth profiling was quantified using ion implanted standards.

RESULTS

Fig. 1 shows the general trend of the PL of the 3C SiC crystal after the final (5th) anneal as a function of measurement temperature. The peak PL intensity decreases with increasing temperature while the FWHM becomes larger. The peak emission wavelength is blue shifted from a wavelength of 540 nm at room temperature to 538 nm at 89K. After implantation with deuterium, the PL intensity is greatly reduced. After the first three anneals the sample has recovered 50 to 60 % of its pre-implanted PL intensity. There is only a slight increase of PL after the 4th anneal. However, the PL intensity after the 5th anneal is actually reduced. This is shown in Fig. 2 for room temperature PL measurement. Hydrogen displays strong interaction with the implantation-induced defects and forms stable hydrogen-defects complexes [8]. The reduced

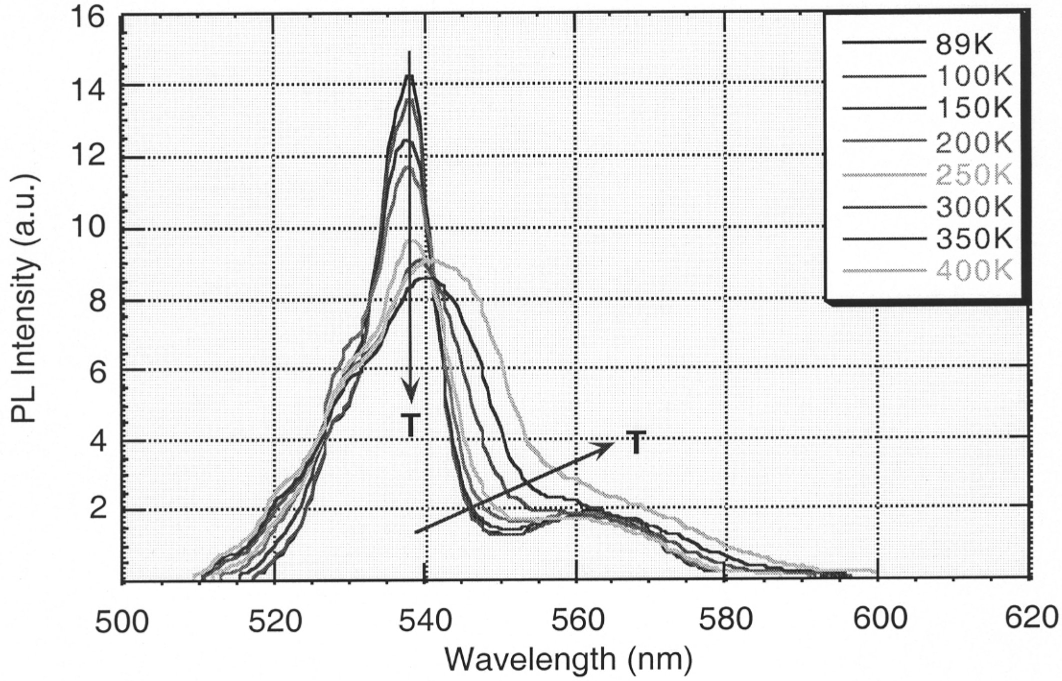

Fig. 1 General trend of photoluminescence as function of temperature for the ^{2}H implanted 3C-SiC after the 5th anneal.

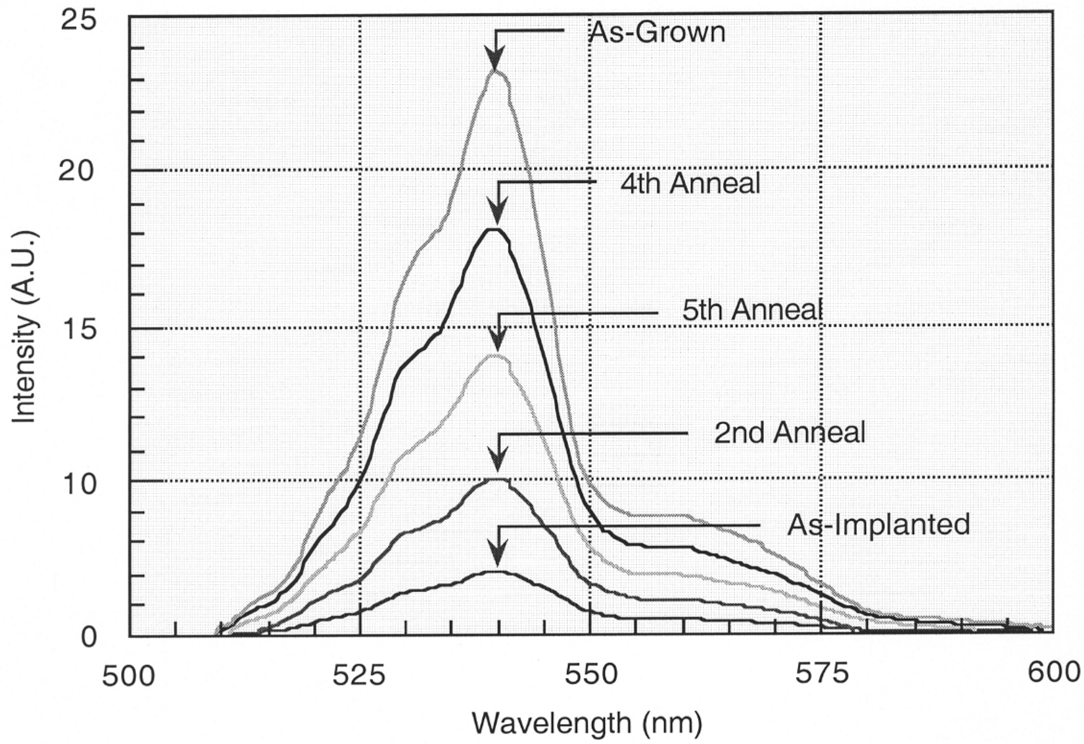

Fig. 2 Room temperature PL for pre- and post- annealing conditions.

luminescence of 3C-SiC by deuterium implantation is believed to be caused by a H atom bonded to a C atom at a Si vacancy [1]. It was reported that in III-V nitride materials, upon annealing at temperature higher than 400 °C, the hydrogen is dissociated from the complex. The hydrogen does not leave the crystal at this temperature but probably associates with other hydrogen atoms to form molecules and larger clusters. At much higher temperature (> 800 °C in GaN), these clusters outdiffuse from the sample [5]. A similar process might occur in 3C-SiC crystals. Splitting of the H atom from the Si-C-H complex and subsequent associative recombination of H atoms to form H_2 molecules may account for the 60% recovery of PL intensity.

Diffusion of hydrogen is observed in the implanted area via SIMS depth profiling. The surface concentration of hydrogen before annealing is 1×10^{17} cm^{-3} and its peak concentration of 1×10^{20} cm^{-3} is at the depth of 0.8 μm. Hydrogen SIMS depth profiles are shown in Fig. 3 for two conditions: the as-implanted sample and after the 3rd anneal. After the 3rd anneal, the following salient differences are observed: 10× increase of surface concentration, a 4× decrease in peak concentration, a shift in the peak depth slightly closer to surface, a 3× reduction in total hydrogen dose remaining in crystal. Hydrogen is strongly trapped by defects generated through ion bombardment, but a gradual damage repairing occurs during annealing [9-10]. Although substantial increase in PL intensity was observed after RTA, annealing up to 1092 °C did not measurably alter the deuterium profile, whereas annealing at 1220 °C reduced the ^{2}H peak concentration to ~2.3×10^{19} cm^{-3}.

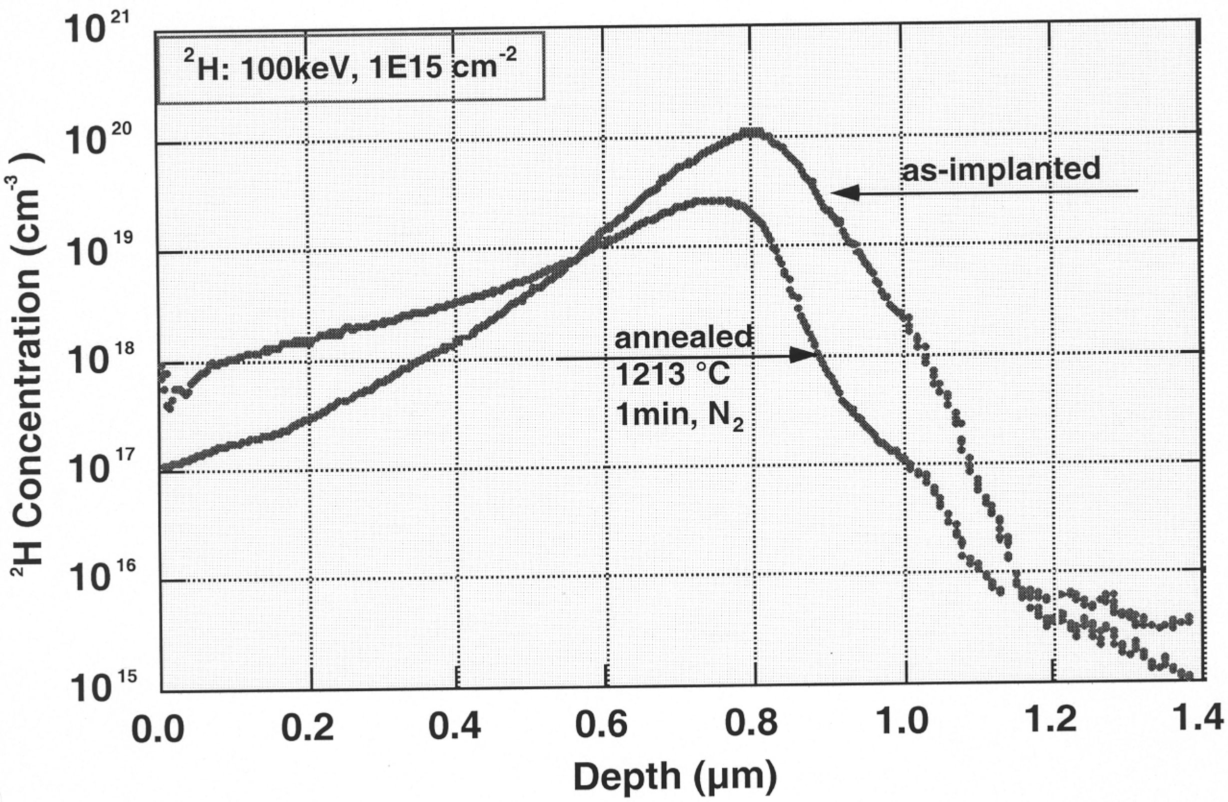

Fig. 3 SIMS depth profiles of the 3C-SiC crystal: as-implanted and after the 3rd anneal.

The peak PL intensity and its integrated area increase initially with annealing temperature and time. The peak and integrated PL are plotted in Figs. 4 and 5 versus measurement temperature at five annealing levels. The peak PL uniformly decreases with increasing measurement temperature. The temperature dependence of the integrated PL is more complex, exhibiting both increasing and decreasing intensity. A clearer picture emerges if peak and integrated PL are plotted against the cumulative thermal exposure ("budget") of the sample. As shown in Figs. 6 and 7, both the peak and integrated PL level drop sharply after implantation. Annealing succeeds in bringing the level back, but is not able to produce the pre-implantation level. After a constant PL level is reached, further annealing actually reduce the PL intensity.

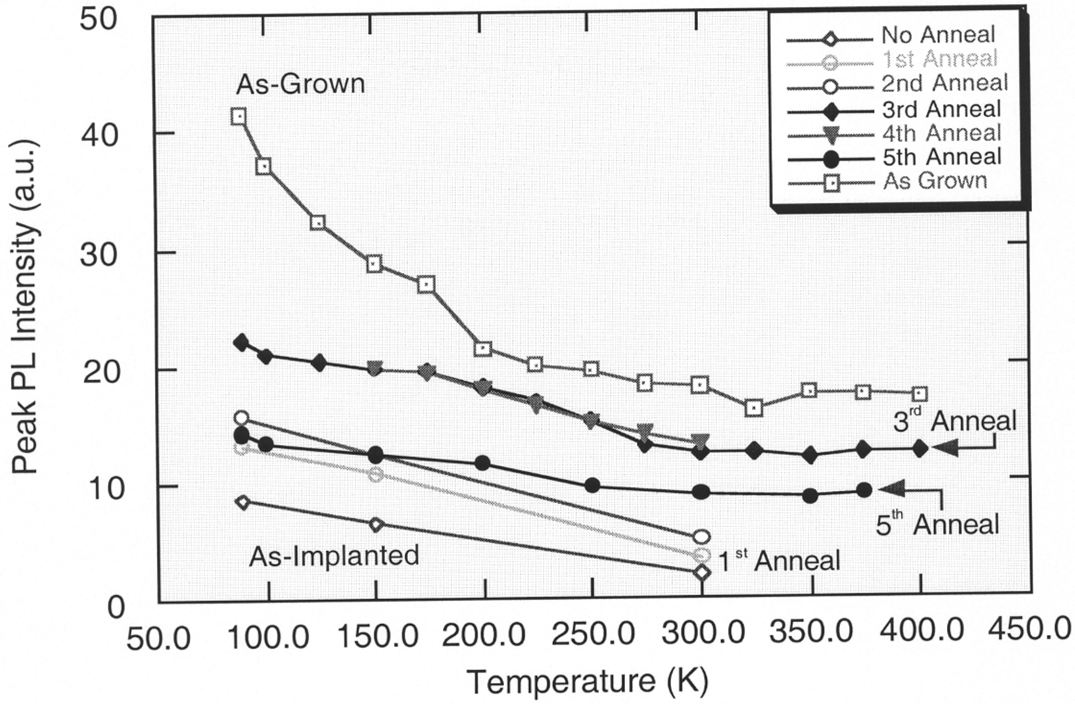

Fig. 4 Peak PL intensity (at 538 - 540 nm) as a function of measurement temperature for pre- and post- annealing conditions.

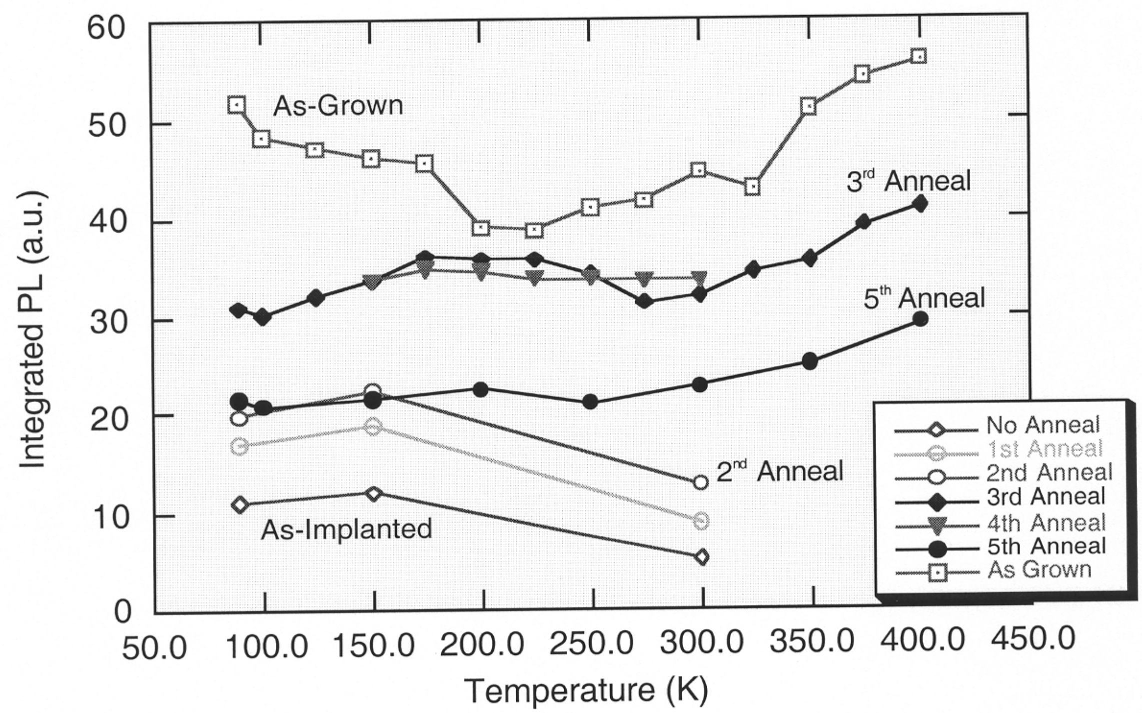

Fig. 5 Integrated PL intensity as a function of measurement temperature for pre- and post- annealing conditions.

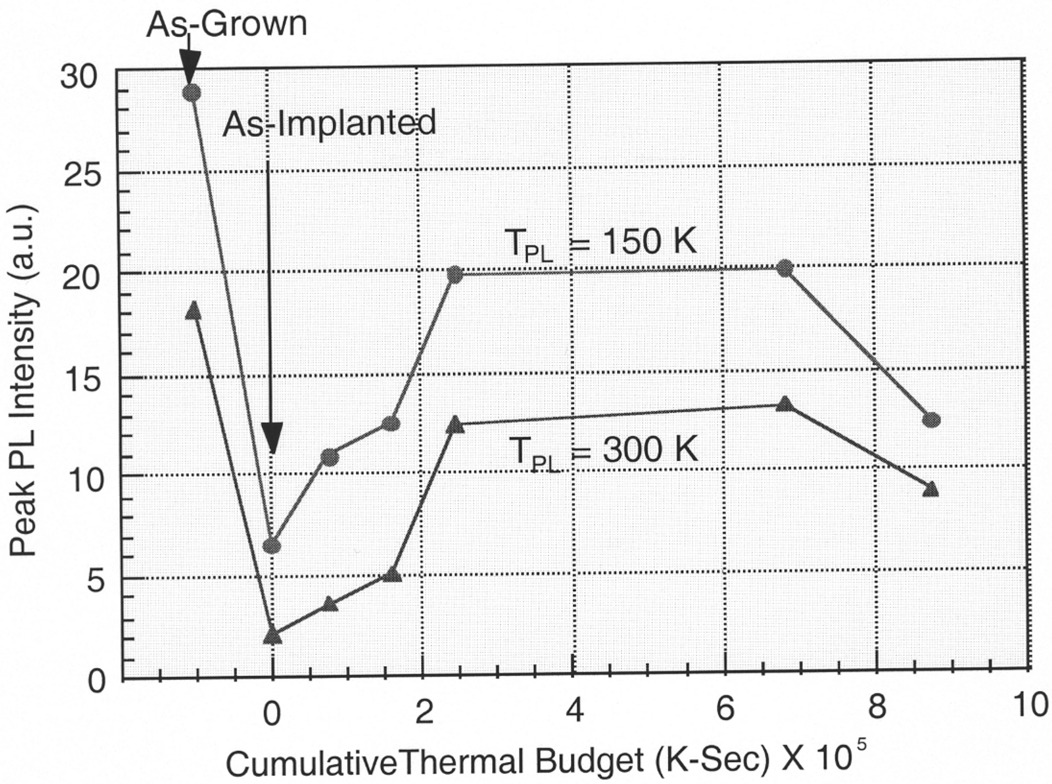

Fig. 6 Peak PL intensity as function of thermal budget for pre- and post- annealing conditions.

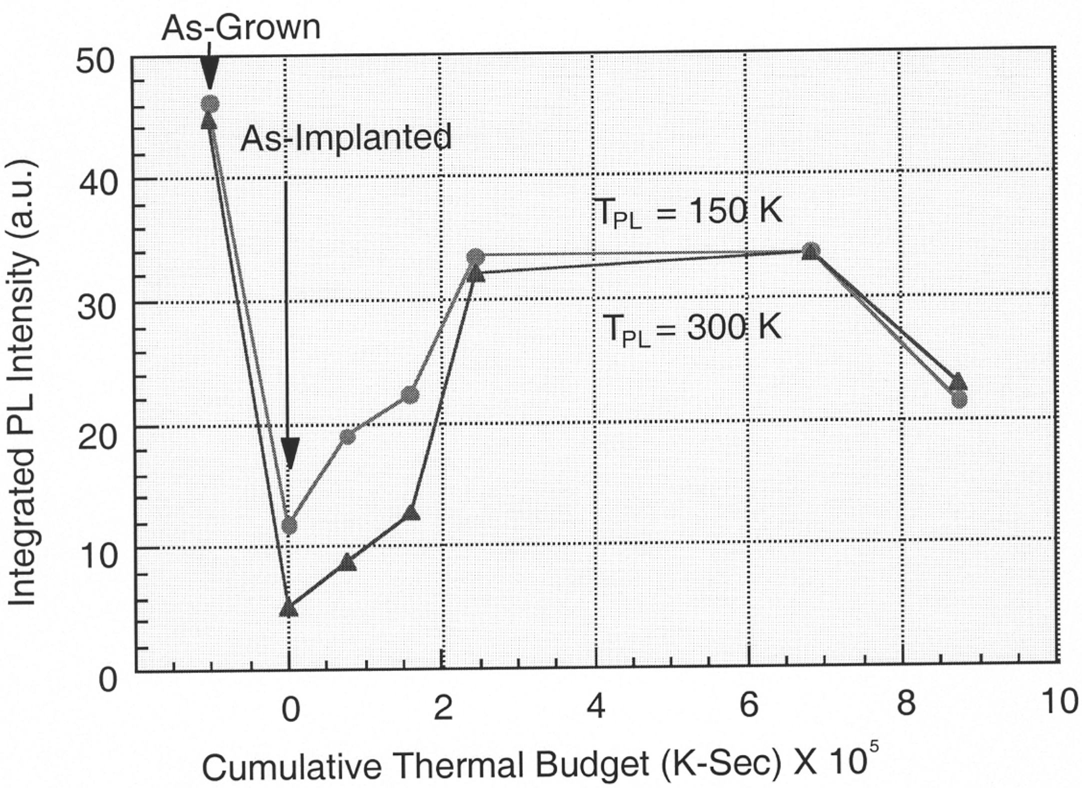

Fig. 7 Integrated PL intensity as function of thermal budget for pre- and post- annealing.

CONCLUSIONS

3C-SiC has the highest reported mobility of all SiC polytype and crystals luminescence strongly at room temperature. The hydrogenation of 3C-SiC has reduced the intensity of PL. Hydrogen atoms can passivate shallow acceptor and donor impurities as well as deep level defect. The reduction of PL intensity is probably due to the fact that hydrogen atoms are trapped by the implantation-induced defects and form stable hydrogen defect complexes. Subsequent annealing repaired the damage and diffused hydrogen atoms. Nonetheless, PL intensity did not fully recover back to the pre-implantation level. High temperatures are required to outdiffuse H in 3C (> 1200 °C) as compare to other SiC polytypes (< 900 C). This indicate that the thermal stability of the deuterium profiles in 3C materials is much higher than that of other SiC polytypes and other compound semiconductors.

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