

Deep Level Reduction in 4H-SiC Treated by Plasma Immersion

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Abstract. The carbon vacancy (V_C) is a lifetime-killer defect that hinders the correct functionality of 4H-SiC bipolar devices. Until now, different methods based on carbon interstitial injection, have been proposed, in order to reduce its concentration. However, if on one hand these methods effectively reduce the V_C concentration in the epilayer, on the other they cannot prevent the re-generation of V_C occurring during the manufacture of a p-i-n diode, e.g., p⁺ implantation and activation. In the following contribution, we employ PIII of B for the formation of the anode for a p-i-n diode. We show that by PIII, it is possible to simultaneously form a p⁺n junction with a low concentration of V_C in the drift layer.

Introduction

The doubly negative charge state of the carbon vacancy (V_C) gives rise to an electrically active level ($Z_{1/2}$) in the band gap of n-type 4H-SiC, at ~ 0.65 eV below the minimum of the conduction band (E_C). It is known to possess a negative-U behavior and behaves as a recombination center, thus limiting the charge carriers' lifetime [1]. Being of technological relevance, especially for the development of bipolar devices, several methods for its removal have been found in the past.

Storasta et al. [2] found that implantation of a thin layer of C and subsequent annealing ($\sim 1600^\circ\text{C}$) is effective in removing $Z_{1/2}$. Later, Hiyoshi et al. [3] showed that the same effect can be achieved by oxidation, at temperatures above $>1000^\circ\text{C}$. A model for the depth of V_C removal as a function of the (oxidation) time was proposed by Kawahara et al.. Another method for $Z_{1/2}$ removal was proposed by Ayedh et al. by performing low temperature annealing in a C-rich environment, e.g., by the use of a C-cap [4]. All of these methods rely on the injection of carbon interstitials (C_i) that, having a rather low migration barrier in n-type SiC [5], can diffuse and then recombine with V_C .

An issue common to the earlier mentioned methods is that, if a p-i-n diode needs to be manufactured, p⁺ implantation and activation, e.g. for junction termination extension or anode formation, leads to the generation of V_C . In fact, ion implantation is known to give rise to several defects, including V_C [6] and heat treatments above 1600°C also lead to the re-generation of V_C [7].

This leads to the following question: once the V_C has been removed, is there a way to form a p⁺ region (anode) without regenerating it? Or, in other words, is it possible to manufacture an anode without increasing the V_C concentration?

In order to answer this question, we carried out an electrical characterization study of n-type 4H-SiC epilayer, treated by plasma immersion ion implantation (PIII). PIII is a common technology in the Si industry and studies of PIII treated SiC were carried out by Biondo et al. [8], in the past.

Experimental Details

Two sets of n-type 4H-SiC epitaxial layers, 5 or 100 μm thick, with a net-donor concentration (N_d) of 2×10^{15} or 10^{14} cm^{-3} , respectively, were subject to 5 kV BF_3^+ (dose 10^{15} cm^{-2}) PIII treatments at room temperature and in vacuum. Prior and after PIII treatments, samples were cleaned by Piranha solution, rinsed in de-ionized (DI) water, dipped in HF and again rinsed in DI water. A C-cap was then formed on the samples for B-activation at 1600°C for 30 min in Ar atmosphere using a resistive furnace. The C-cap was removed by O_2 ashing at 200°C . After another round of cleaning, ohmic

contacts were formed on the epilayer surface by a Ti/Al stack, sintered for 1 min at 1000°C. The backside contact was formed by using Ag paste.

Another set of samples were implanted at 500°C with Al, using multiple energies (dose 10^{15} cm^{-2}) for the formation of box-profile. After forming a C-cap, samples were annealed for 30 min at 1700°C. C-cap removal, cleaning and ohmic contact deposition are the same as for the PIII samples.

All samples were then characterized by C-V, I-V, at room temperature, and by Fourier transform deep level transient spectroscopy (FT-DLTS) in the 100-650 K temperature range. We employed a reverse bias (V_R) ranging between -1 to -10 V, a filling pulse (V_P) of +1 V by the duration of 1 ms. Electrical pulse was also substituted by an optical pulse. This was done to detect minority carrier traps (MCTS or minority carrier transient spectroscopy) and carried out by illuminating the front side of the sample with UV light (355 nm, 100 ms). The illuminated area was larger than that of the ohmic contact.

Some of the PIII treated samples were also characterized by secondary ion mass spectroscopy (SIMS) in order to detect the concentration depth profile of B, before and after heat treatments.

Results and Discussion

Fig.1 shows the concentrations of B (PIII) and Al (implanted), together to the net-donor concentration profiles. In agreement with previous results in the literature, PIII results in a rather shallow profile, extending up to a depth of $\sim 50 \text{ nm}$. In addition, since the PIII profile consists of non-monoenergetic species, it results in an implanted profile which is different from that of a typical ion implant. It can be noted that a dose of 10^{15} cm^{-2} results in a maximum B concentration of 10^{19} cm^{-3} .

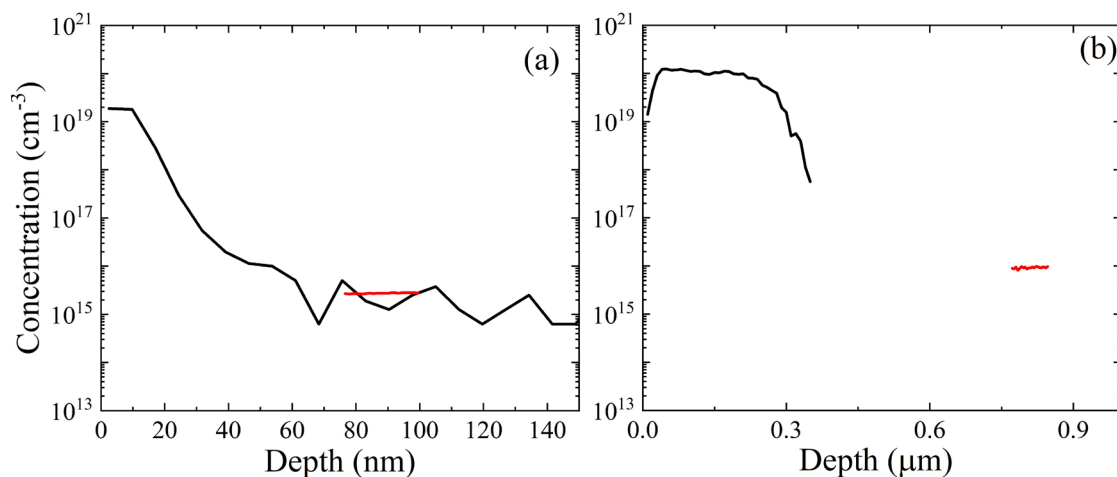


Fig.1. Concentrations of the (a) B PIII profile and (b) Al ion implantation profile. The former was measured by SIMS, the latter was calculated by a Monte Carlo simulation. The red solid lines represent the net-donor concentration measured by C-V.

Fig.2 shows the DLTS spectra of the as-grown, Al implanted and PIII treated samples. As it can be seen, the $Z_{1/2}$ ($1.5 \times 10^{11} \text{ cm}^{-3}$) and (hints of) the $EH_{6/7}$ levels can be found (fig.2(a)). The $Z_{1/2}$ ($8 \times 10^{12} \text{ cm}^{-3}$) is also found in the Al implanted samples (fig.2(b)). In this case, a presence of a negative DLTS peak can also be seen at $\sim 150 \text{ K}$, related to a level located at 0.2 eV above the valence band maximum, E_V ($2.3 \times 10^{13} \text{ cm}^{-3}$). A negative peak indicates the presence of a minority carrier trap. Although no minority carriers are injected during the DLTS measurements, such negative peaks can be present in the case of a graded junction [9]. The DLTS spectrum of the PIII sample (fig.2(c)) does not reveal the presence of the V_C . On the contrary, four levels are found, at 121 K, 190 K, 380 K and 490 K. These can be identified as the OF1 ($8.4 \times 10^{11} \text{ cm}^{-3}$), OF2 ($6 \times 10^{11} \text{ cm}^{-3}$), ON1 ($1.5 \times 10^{13} \text{ cm}^{-3}$) and ON2 ($7 \times 10^{12} \text{ cm}^{-3}$). The ON2 is known to be the overlap of two contributions ON2a and ON2b [10].

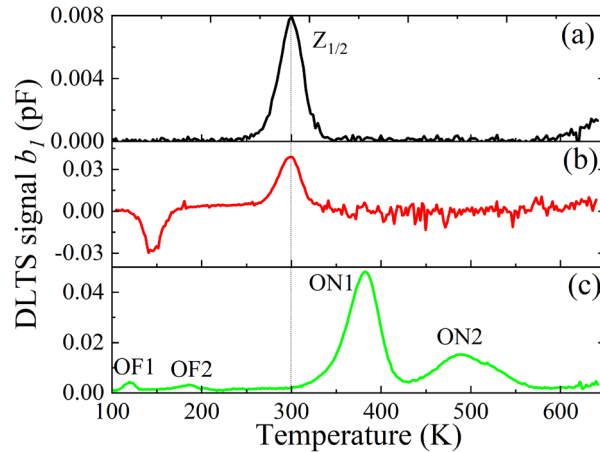


Fig.2 DLTS results of the (a) as-grown, (b) Al implanted and (c) PIII treated samples. The time period width was set to 0.2 s.

The MCTS spectra are shown in fig.3. As it can be seen, two peak can be found in the as-grown material, the B-acceptor ($E_V+0.30$ eV, 7×10^{13} cm $^{-3}$) and the D-center ($E_V+0.60$ eV, 8.3×10^{12} cm $^{-3}$), respectively (fig.3(a)). In the Al-implanted samples (fig.3(b)), the B-acceptor (2×10^{14} cm $^{-3}$) and D-center (6×10^{13} cm $^{-3}$) are also found, together to a shoulder peak located at ~ 150 K (9×10^{13} cm $^{-3}$). Similar results are obtained for the PIII sample (fig.3(c)), for which the B-acceptor, shoulder peak and D-center have concentrations of 2×10^{14} cm $^{-3}$, 7×10^{13} cm $^{-3}$, 3.5×10^{14} cm $^{-3}$.

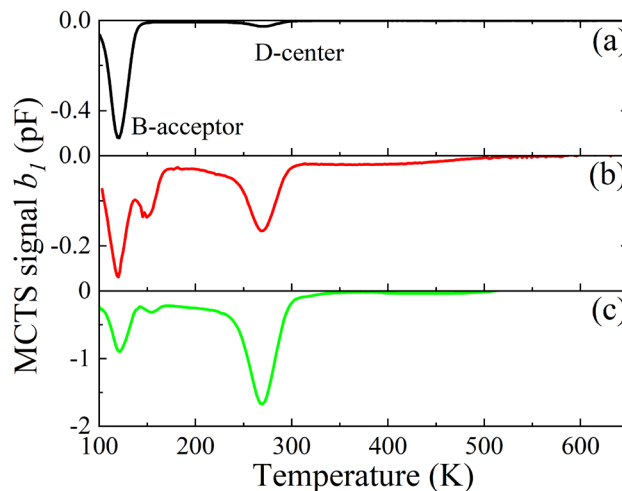


Fig.3. MCTS of the (a) as-grown, (b) Al implanted and (c) PIII treated samples. The period width was set to 0.2 s and the optical pulse to 100 ms.

We carried out a V_R dependence measurement of the levels detected in the PIII treated sample (not shown). We observed no change in the ON1 and ON2 concentration, by increasing V_R from -1 to -5 V. However, a shift in the temperature position of the OF2 is reported. Double correlation DLTS (DDLTS) measurements (not shown) showed that the emission rates of OF1, OF2, ON1 and ON2 do not have any dependence on the electric field, in agreement with the literature [10].

Since fig.2(c) shows that PIII treatments can remove V_C , we performed a series of measurement to find out how deep in the epilayer such V_C are removed. To do this, lowly doped samples were characterized employing a $V_R = -10$ V. After the first measurement, ohmic contacts were removed from the epilayer surface and reactive ion etching was carried out to etch ~ 10 μm of epilayer. Measurements were repeated after cleaning and deposition of new ohmic contacts. This procedure was repeated several times. The results of the measurements are shown in fig. 4. As it can be seen,

low levels of V_C are detected up to a depth of $\sim 25 \mu\text{m}$. Possibly, longer annealing times, even employing lower temperatures as suggested by Ayedh et al. [4], might result in the removal of $Z_{1/2}$ much deeper in the epilayer.

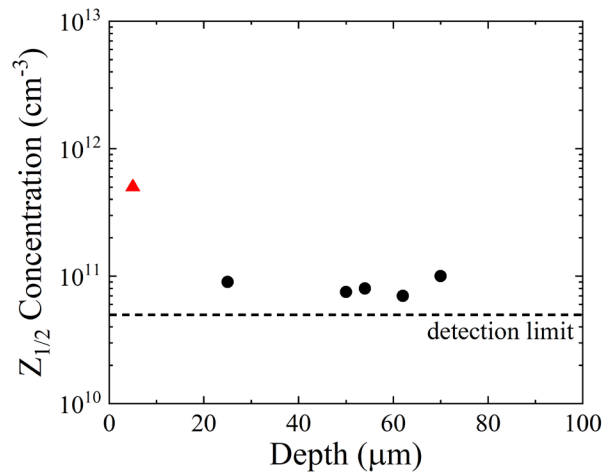


Fig.4. Concentration of the $Z_{1/2}$ level as a function of the depth, in an as-grown or PIII treated $100 \mu\text{m}$ thick epilayer. Red triangle represents the as-grown concentration of $Z_{1/2}$.

As our results show, by PIII and subsequent annealing it is possible to obtain a p^+n junction and, at the same time, to remove V_C . As previous results in the literature have shown, V_C removal occurs due to the recombination of C_i with V_C . This is true also in the present case, as the presence of ON1 and ON2 levels is related to C_i injection [2, 3]. However, unlike previous works in the literature, neither C-layer is present, nor oxidation is performed. In order to explain the V_C reduction, we note that PIII can lead to strain in the implanted region, due to the presence of interstitial species, e.g., Bi [11]. In addition, it was shown that strain build up can be correlated to the presence of primary defects, e.g. interstitials and vacancies [12]. For these reasons, it can be speculated that such strain might be responsible for the creation of a surplus of C_i which, during high temperature annealing, are injected in the epilayer.

Lastly, the role of F remains to be discussed. Although SIMS was performed to check only the B concentration, it can be thought that a substantial concentration of F can also be present. The electronic properties of halogen species in SiC were subject of few theoretical studies that showed that such elements should behave as donors when in substitutional sites [13, 14]. However, interstitial F (F_i) was found to form a shallow acceptor level in 4H-SiC [14]. For this reason, it can be thought that F can contribute to the p^+ activation, when BF_3^+ PIII is employed for doping purposes in 4H-SiC. Not much can be said regarding the effects of post-implantation annealing temperature (1600°C) on the diffusion of F, as no studies on the topic can be found in the literature. However, if the diffusivity of F is comparable to that of Cl, then the PIII F atoms might not be affected by annealing [15].

Summary

To conclude, it was found that by PIII of BF_3 of n-type 4H-SiC, and subsequent annealing, it is possible to form a p^+n junction, with a rather low concentration of V_C in the drift layer. DLTS measurements showed that no V_C related electrically active levels could be found, up to a depth of $\sim 25 \mu\text{m}$. The mechanism of V_C removal is due to C_i injection in the epilayer. This is due to the possible build up of strain in the PIII region which leads to the formation of interstitials.

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