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Capacitance spectroscopy study of deep levels in Cl-implanted 4H-SiC

G. Alfieri and T. Kimoto

I. INTRODUCTION

Nowadays, one of the biggest challenges of the SiC industry is supplying affordable material of very high crystalline quality. Standard growth techniques, such as chemical vapor deposition (CVD), allow growth rates ranging between 5 and 10 μm/h which are time consuming and not economically viable because high-voltage devices rely on very thick epilayers (~100 μm). In order to overcome this problem, it was shown1−4 that the use of chlorinated precursors can effectively increase growth rates up to 170 μm/h (Ref. 5) yielding good quality epilayers, without stacking faults.5 Additionally, the increase of the flow rate results in the formation of Si droplets, which, if not flushed away from the growth chamber, will eventually come into contact with the crystal surface giving rise to defects in the epilayers. To the contrary, by introducing Cl in the reactor in the form of HCl, CHxCly, SiHxCly, Cl can bind to Si and prevents the formation of the above mentioned droplets. This allows the increase of the flow rate resulting in an increase of the growth rates.

However, similarly to the case of H, which is present in the precursor gases and can be incorporated in SiC, also Cl can be incorporated in SiC during growth.5,6 Even if the detected concentration is close to, or below, the detection limit (~10¹⁴ cm⁻³),7 the possibility that Cl atoms are incorporated in the 10¹¹−10¹² cm⁻³ range cannot be excluded. This raises the question of whether or not Cl impurities give rise to electrically active defects, as is the case with H. The presence of electrically active levels in the band gap (E_GAP) is a matter of extreme importance in device technology because they can act as charge carriers’ traps and harm the correct functionality of devices. However, despite the importance of this topic, scarce experimental and theoretical information is present in the literature.

La Via et al.1 have shown by deep level transient spectroscopy (DLTS) that both the Z₁/₂ and EH₆/₇ levels are present in n-type 4H-SiC grown by using HCl as a precursor and that new deep levels, related to Cl, are not observed, at least in the 10¹³ cm⁻³ range. Subsequently, by employing density functional theory (DFT), it was found that Cl preferably occupies a C-site rather than a Si-site and behaves as a triple donor.9 Furthermore, Cl easily binds to Al, giving rise to a very thermally stable complex defect, while it repels N (which is a donor itself).10 The donor character of Cl and Cl-related complexes10 can explain why the use of chlorinated precursors does not harm the net-donor concentration11 but cause the saturation of the net-acceptor concentration.12

In the following, we present a DLTS study on Cl-implanted n- or p-type 4H-SiC epilayers, annealed in 100−1800 °C temperature range, in order to shed the light on the possible presence of Cl-related electrically active defects in 4H-SiC.

II. EXPERIMENTAL DETAILS

We employed n- or p-type 4H-SiC epilayers doped with N or Al, respectively (Nᵣ≈Nᵢ≈7−8×10¹⁵ cm⁻³). Epilayers were implanted with 700 keV Cl, which resulted in a mean projected range of 0.5 μm from the surface13 and with a dose of 5×10¹⁵ cm⁻². Samples underwent an isochronal (15 min) annealing series in the 100−1800 °C temperature range (annealing step of 100 °C) in an Ar atmosphere. Heat treatments below 1000 °C were carried out in a rapid thermal annealing furnace (RTA) while for higher temperatures, a chemical vapor deposition chamber was employed. A carbon cap was deposited on the epilayer surface for temperatures above 1100 °C in order to minimize the effects of surface decomposition which was later removed by a dry oxidation process (1 h at 800 °C).14 After each annealing step, samples were dipped in HF for 10 min, and Au or Ti Schottky diodes were formed on the surface of n- and p-type 4H-SiC epilayers, respectively, by thermal evaporation. For p-type samples, ohmic contacts...
were formed on the backside of the as-grown samples, by depositing a Ti/Al/Ni tri-layer sintered for 10 min at 1000 °C.

Electrical characterization was performed by capacitance-voltage (C-V) and Fourier-transform DLTS measurements.15 DLTS measurements were carried out in the 200-700 K temperature range, with a reverse bias of ±6 V (in order to cover the whole implantation range), a filling pulse to 0 V for 1 ms and a period width of 0.2 s. For annealing temperatures up to 400 °C, the highest DLTS temperature limit coincided with the annealing temperature.

III. RESULTS AND DISCUSSION

In Figs. 1(a) and 1(b), the results of the C-V measurements, for the as-grown and implanted n- and p-type 4H-SiC epilayers, are shown together with the implanted Cl and the total vacancies concentration profiles. The C-V profiles are obtained by changing the reverse bias up to 6 V (depletion width at 0 V ~ 0.4 μm) while the implanted Cl and total vacancies profiles are obtained from full-cascade SRIM simulations,13 in which the threshold displacement energies were set to 20 and 35 eV for C and Si, respectively. For n-type (Fig. 1(a)), the net-donor concentration (Nd) profile in the as-implanted sample is located well beyond the implanted zone, at a depth ranging between 0.8 and 1.3 μm. Subsequent heat treatments do not result in a significant donor reactivation closer to the implanted Cl profile. However, after annealing at 1400 °C, the Nd is reactivated at ~0.6 ~ 0.7 μm from the surface (shadowed area of Fig. 1(a)) where implanted Cl atoms are present in the 1012 ~ 1014 cm−3 range. A similar behavior is observed in the p-type sample for which higher annealing temperatures (1700 °C) are needed for the net-acceptor concentration (Na) to be reactivated close to the Cl implanted profile. The lower concentration of Cl, with respect to that of either Nd or Na, rules out the possibility that Cl itself may be responsible for the passivation of either N or Al. Furthermore, in the n-type material, it would be difficult for Cl to bind to N due to Coulombic repulsion.10 Instead, the absence of enhanced Nd (or Na) signal in the implanted region may be due to the presence of compensating centers generated by implantation. As shown in Fig. 1, the total vacancy concentration is approximately ~3 × 1017 cm−3 and silicon vacancies (Vs) that are present in a negative (positive) charge state in the upper (lower) half of the band gap of 4H-SiC,16-18 can be a cause for donor (acceptor) compensation. A similar analysis can be done for carbon vacancies (VC) which, contrary to Vs, have a higher thermal stability.19 In addition, the formation of doping related complexes, arising after implantation, cannot be excluded: For instance, after implantation, N atoms can decorate Vs yielding Vs(NC) (Ref. 20) which gives rise to an acceptor level in the upper half of the band gap and is thermally stable up to 2000 °C, while Al atoms can form Al(Cl) which yields a donor level in the lower half of the band gap and has also a high thermal stability (1700 °C).21

Fig. 2 shows the DLTS spectra obtained in as-grown material and after annealing at 700, 1400, 1800 °C for n- and p-type 4H-SiC. In as-grown n-type 4H-SiC (Fig. 2(a)), the Z1/2 (concentration 2 × 1013 cm−3) and EH4/7 (12 × 1013 cm−3) are detected while, for p-type, we have found the D-center (~1012 cm−3). After implantation (Fig. 2(b)), two levels are found in n-type 4H-SiC. The broad DLTS peak at 400 K (3 × 1015 cm−3) is identified as the EDT level22 and a peak at ~575 K (~1015 cm−3), at 1.34 eV below the minimum of the conduction band (EC), and labelled Cl1 which has not been reported earlier in the literature. In p-type material, we found one level labeled CI2 (2 × 1012 cm−3) at 0.51 eV above the maximum of the valence band, Ev, and another one identified as the UK2 center (2.5 × 1012 cm−3).23 Heat treatments at 1400 °C (Fig. 2(c)) results in the detection of the Z1/2 (5 × 1014 cm−3) and EH6/7 (75 × 1014 cm−3) levels, for the n-type 4H-SiC epilayer, while the EH4 is not detected at this annealing stage because it anneals out after 1200 °C.24 We note that the EH6/7 level may have been overlapping with the Cl1 level and becomes clearly visible only after the annealing of Cl1. For this reason, we considered the spectrum at 1400 °C as the final annealing stage from which we subtracted the DLTS signal of the 700 °C annealed sample. The result of

![Fig. 1](https://example.com/fig1.png)

**Fig. 1.** Implanted Cl and total vacancies profiles plotted together with the (a) net-donor (Nd) and (b) net-acceptor (Na) concentration, in the as-grown, as-implanted and 900, 1400, and 1700 °C annealed epilayers.

![Fig. 2](https://example.com/fig2.png)

**Fig. 2.** DLTS spectra of the n- and p-type 4H-SiC epilayers annealed for 15 min at (a) as-grown, (b) 700 °C, (c) 1400 °C, and (d) 1800 °C. The signal of the DLTS spectra of the as-grown n-type material is multiplied by 100. The black broken line represents the DLTS peak of the Cl1 level obtained from the subtraction of the spectrum detected after annealing at 700 and 1400 °C annealed n-type 4H-SiC samples.
the difference between the two DLTS spectra is shown by the broken line in Fig. 2(b) which may correspond to the real DLTS peak of the $Ci1$ level. For the $p$-type epilayer, the $Ci2$ and $UK2$ levels are still present, and a new level is found at ~430 K and identified as the $IM7$ level ($\sim 10^{13}$ cm$^{-3}$). After the last annealing step (1800 °C, Fig. 2(d)), the $Z1/2$ and $EH6/7$ are still detected in the $n$-type sample, and three new levels arise, labeled $Ci3$, $Ci4$, and $Ci5$ at 0.37 eV (1.4 $\times$ $10^{13}$ cm$^{-3}$), 1.06 eV (2.4 $\times$ $10^{13}$ cm$^{-3}$), and 1.3 eV (3.4 $\times$ $10^{13}$ cm$^{-3}$) below $EC$, respectively. For $p$-type samples, while the $UK2$ and $IM7$ are annealed out, the $Ci2$ is found to be persistent even after annealing at 1800 °C and at the same time two other levels arise: One is labeled $Ci6$ at 0.97 eV (2.3 $\times$ $10^{12}$ cm$^{-3}$) above $EC$, and the other one is identified as the $IM8$ energy level ($8 \times 10^{12}$ cm$^{-3}$). A summary of the levels detected in the present study can be found in Table I.

Of all the levels, presently found in $n$-type 4H-SiC epilayers, the $Z1/2$, $EH6/7$ and $EH4$ have been reported earlier in a number of studies. It is well known that the $Z1/2$ possesses a negative-$U$ behavior and that its nature may be related to that of a carbon vacancy (V$_C$). The broad $EH6/7$ is thought to be related to the $Z1/2$ center; Both $Z1/2$ and $EH6/7$ are present in either as-grown or irradiated/implanted material, share the same annealing behavior, and their concentration is reduced when carbon interstitials, $Ci$, are injected into the epilayer. However, since these three levels have concentrations in the $10^{13}$ cm$^{-3}$ range, the involvement of $Ci$ in their microscopic structure may be more plausible. In fact, their detection coincides with the reactivation of $N_d$ at 0.6 – 0.7 µm below the epilayer surface, and although neither theoretical nor experimental studies are present on $Ci$ diffusion, the in-diffusion of $Ci$ atoms at these temperatures cannot be excluded.

Much less is known on the nature of the traps detected in $p$-type 4H-SiC. The $UK2$, $IM7$, and $IM8$ have all been reported earlier. The $UK2$ was found in either electron irradiated or hydrogen implanted material, while the $IM7$ and $IM8$ were detected in hydrogen implanted samples. The $UK2$ was associated to a carbon-related complex and the $IM7$ to an Al-related complex, while no hypothesis on the nature of the $IM8$ level has been put forward yet. The level labeled $Ci2$ was found in the as-implanted material, and for this reason, the participation of $Ci$ in its microscopic structure can be ruled out. On the contrary, since the $Ci1$ level has similar temperature position and thermal stability (both levels anneal out below 1700 °C) of those of the $IN8$ level found by Kawahara et al., we believe that $Ci1$ and $IN8$ levels may belong to the same defect. The $Ci3$ and $Ci4$ levels have a close energy position to that of the $P3$ and $RD1$ levels found in $He^+$ implanted 4H-SiC (Ref. 34), but since they have a different annealing behavior (both $P3$ and $RD1$ anneal out at 1400 °C), they are more likely to have different origins. Analogously to the $Ci3$ and $Ci4$, also for the $Ci5$ not much can be said on its microscopic nature. However, since these three levels have concentrations in the $10^{13}$ cm$^{-3}$ range, the involvement of $Ci$ in their microscopic structure may be more plausible. In fact, their detection coincides with the reactivation of $N_d$ at 0.6 – 0.7 µm below the epilayer surface, and although neither theoretical nor experimental studies are present on $Ci$ diffusion, the in-diffusion of $Ci$ atoms at these temperatures cannot be excluded.

In order to find out more evidence on the nature of the $Ci2$, $Ci3$, $Ci4$, $Ci5$, and $Ci6$ levels, we analyzed the depth profiles of these traps and compared them with the $Ci1$-implanted distribution obtained by Monte-Carlo simulations. These levels were detected in $n$- and $p$-type samples that underwent the last annealing stage at 1800 °C, and depth profiles measurements were performed by changing the reverse bias voltage up to ±6 V. As it is shown in Fig. 3, the concentration of the $Ci2$ trap is found outside the implanted region, at a depth of 0.65 µm from the epilayer surface and has rather uniform depth distribution. The lack of a localized depth distribution close to the implanted $Ci1$ profile rules out the possible involvement of $Ci1$ in the microscopic nature of $Ci2$ and favors the identification of this defect as the $D$-center. The depth profiles of $Ci3$, $Ci4$, $Ci5$, and $Ci6$ display similar features: The concentrations of these traps show a rather steep increase of concentration for
localized distribution close to the Cl involvement of therefore, also for this trap, it can be concluded that the EV has been achieved. Second, although the measurements are decreasing depth, in contrast to the more gradual increase the maximum of the implantation peak, and for this reason, CiCVSi the case, two different charge states of the Ci and Cl found to arise after ClCVSi implantation and labeled or for a depth allstr of the EV depth profiles. Analogously to CI2, the depth profile of CI3 does not show a narrow and localized distribution close to the CI implantation peak; therefore, also for this trap, it can be concluded that the involvement of CI may be unlikely.

Regarding the CI4, CI5, and CI6 levels two scenarios are possible. First, the extrapolation of these depth profiles, toward the surface, may yield very high defect concentration for a depth ≤ 0.6 μm. This rules out the possibility of CI involvement but would explain why, even after heat treatments up to 1800 °C, no reactivation of either N2 or N is has been achieved. Second, although the measurements are not feasible for a depth ≤ 0.6 μm, the depth profiles of CI4, CI5, and CI6 may have a localized distribution around the maximum of the implantation peak, and for this reason, the involvement of CI would be possible. If this would be the case, two different charge states of the CI2V5 complex are very close to the energy level position of CI4 and CI5 while a CI interstitial (CI) level was predicted at EV + 0.96 eV, very similar to the energy position of the CI6 level.

IV. CONCLUSIONS

Twelve deep levels were detected in either n- or p-type 4H-SiC implanted with 700 keV CI. Of these, four levels are found to arise after CI implantation and labeled CI3, CI4, CI5 (in n-type 4H-SiC), and CI6 (in p-type). The involvement of CI in the microscopic nature of these defects was discussed in detail in the light of previous theoretical studies and of the results of a depth profile analysis. We conclude that the CI involvement is unlikely for the CI3 level, whose nature could be linked to the presence of implantation related defects, but it may be more plausible for the CI4, CI5, and CI6 levels.

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FIG. 3. Depth profiles of CI2, CI3, CI4, CI5, and CI6 levels found in either n- or p-type 4H-SiC epilayers implanted with CI and annealed at 1800 °C. The depth profiles of two dominant traps found in p-type 4H-SiC (EH0, Z1/2 is not shown) are reported for comparison. The implanted CI profile, as obtained by Monte-Carlo simulations, is also shown.