Evidence for a hydrogen-related defect in implanted p-type 4H-SiC

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Abstract. 200 keV hydrogen implantation was performed in order to investigate the formation of electrically active hydrogen-related defects in Al-doped 4H-SiC epitaxial layers. Samples were annealed in the 100–1200 °C temperature range for 15 min and capacitance–voltage (C–V) profiling was employed to study the passivating effects of hydrogen. Eight electrically active hole traps have been found by means of deep level transient spectroscopy (DLTS) and the study of their thermal stability, as well as their depth profiles, revealed the possible formation of an electrically active hydrogen-related center.

Contents

1. Introduction 2
2. Experimental details 2
3. Results and discussion 3
4. Conclusions 6
Acknowledgments 6
References 6

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1. Introduction

The outstanding physical and chemical properties of silicon carbide (SiC), make it suitable for a huge number of applications aimed for harsh environments where more traditional semiconductors, like Si or GaAs, have limited or no functionality. However, as for any other semiconductor, the presence of impurities and defects influences the optical and electrical characteristics of SiC.

As one of the most common impurities in SiC and being the simplest atom of all, hydrogen has always attracted the interest of scientists. A great number of studies on the properties of hydrogen have been performed by incorporating hydrogen by either low-energy implantations (300 eV) [1] or plasma treatment [2]. It was found that hydrogen is mobile at low temperatures and very effective in passivating both boron (B) and aluminium (Al) on a micrometre scale [1, 2] by forming neutral H–Al and H–B complexes [3] whose dissociation energies have been studied in detail by Janson et al [4].

On the contrary, few studies on the properties of hydrogen implanted at higher energies can be found in the literature. Energetic protons, as well as electrons, are responsible for the degradation and malfunction of satellite on-board electronics because they can yield the formation of electrically active centers in the bandgap.

It is known that implantation (or irradiation) induced defects are efficient hydrogen traps which hinder its diffusion [5] and give rise to H-related complexes which are stable up to 900 °C [6]. However, if hydrogen is trapped by defects, e.g. implantation or irradiation induced defects, this poses a still unanswered question: are there any electrically active hydrogen-related defects?

Up to now, the only investigations on high-energy hydrogen implantation aimed to study the electronic properties and presence of electrically active H-related defects were carried out on n-type SiC epilayers [7, 8] but not on p-type material due to the difficulties of depositing suitable ohmic contacts. Also, in our previous work [9], we have investigated the properties of deep centers, as a function of the implantation temperature, in hydrogen double implanted p-type 4H-SiC, but due to the nature of the implantations, the detection of a possible hydrogen-related defect was of difficult actuation.

In this study, we investigated the presence of electrically active defects generated after 200 keV hydrogen implantation in Al-doped 4H-SiC and we report on the effects of implantation on the deactivation of doping in the region close to the surface, for annealing temperatures up to 300 °C. The presence of eight deep levels is also reported and their nature is discussed on the basis of previous results found in the literature. For two deep centers, the possible involvement of hydrogen is studied by analyzing their thermal stability and depth profiles.

2. Experimental details

The starting material was Al-doped p-type 4H-SiC epitaxial layers, grown on p-type substrates and purchased from Cree. The net acceptor concentration and thickness were Na ∼ 1 × 10^{16} cm^{-3} and 10 µm, respectively. A Ti/Al/Ni layer deposited on the backside of the samples by evaporation and sintered at 1000 °C was employed as ohmic backside contact. The epilayers were then implanted with 200 keV hydrogen (dose 1.5 × 10^{12} cm^{-2}) and a mean projected range of 1.1 µm was obtained according to Monte Carlo simulations [10]. The epilayers were annealed in the 100–1200 °C temperature range for 15 min, and after every heat treatment,
Figure 1. Comparison among the implanted hydrogen profile, as obtained by SRIM2003 and the net acceptor concentration profiles after implantation and heat treatments at 300, 900 and 1000 °C.

Ti Schottky diodes were prepared by thermal evaporation of Ti on the epilayer. Thermal annealings have been performed in Ar ambient. Samples were characterized by deep level transient spectroscopy (DLTS) [11] in the 150–750 K range, and for heat treatments up to 400 °C, the higher temperature limit for the DLTS was the same as the annealing temperature, to avoid any unintentional annealing during the measurement. The reverse bias voltage was set to 18 V to cover the whole implantation peak.

The net acceptor concentration was monitored by capacitance–voltage (C–V) measurements, and depth profiling measurements were carried out to estimate the concentration of deep levels as a function of depth [12].

3. Results and discussion

In figure 1, the isochronal annealing behavior of the net acceptor concentration after implantation, and heat treatments at 300, 900 and 1000 °C is shown, measured by C–V. For comparison, the hydrogen implanted profile as obtained from SRIM2003 is also displayed. Right after implantation, no C–V signal can be detected from the surface to a depth of 0.8 µm. A similar effect was reported after low-energy hydrogen implantation and attributed to the passivating effects of hydrogen [1].

However, in the present study, the role of implantation induced defects cannot be neglected. It is suggested that the observed effect may be due to the combined actions of both hydrogen passivation and doping compensation. In fact, the role of implantation-induced defects is much more evident in the 1.0–1.4 µm region, where the hydrogen implantation profile peak maximum is located. In this region, where the implantation damage is higher, hydrogen is trapped by defects [6] reducing its passivating effects. As we move close to the surface and the amount of implantation induced damage decreases, hydrogen passivation becomes more effective.
Figure 2. DLTS spectra (period width 0.2 s, filling pulse 1 ms) of (a) as-implemented 300, 400, 600 and (b) 700, 900, 100 and 1200 °C annealed 4H-SiC. In all cases, the time step was 15 min.

Heat treatments at 300 °C result in the reactivation of Al doping close to the surface whereas Achtziger et al [1] obtained partial reactivation after annealing at ∼250°C under reverse bias conditions. Further annealing at 900 and 1000 °C yields a slight increase of the net acceptor concentration and a shift of the profile toward the surface. As Samiji et al [2] have reported, Al-reactivation close to the surface corresponds to Al-passivation deeper in the epilayer due to in-diffusing hydrogen atoms which form new Al–H complexes, and this may explain the observed drop in the net-acceptor concentration after annealing at 300 °C.

In figure 2, the DLTS spectra after implantation and after different heat treatments are shown. In figure 2(a), right after implantation a single DLTS peak labeled H1 is found at $T \sim 260$ K and located 0.22 eV above the valence band $E_v$ (concentration $\sim 9 \times 10^{13}$ cm$^{-3}$). After annealing at 300 °C hints of a broad peak can be noted for $T \sim 600$ K, and only after a further heat treatment at 400 °C could this DLTS peak be completely resolved and labeled H2 ($E_v + 1.17$ eV). Moreover, at this stage, a new peak arises at $T \sim 320$ K whose energy position ($E_v + 0.28$) and temperature position agree well with the one of the UK2 center [13]. These levels are still present after annealing at 600 °C while another level labeled H3 ($E_v + 1.52$ eV) was also found. In figure 2(b), it can be seen that annealing treatment at 700 °C yields the presence of two new peaks, one of which located at $T \sim 220$ K that, according to previous data found in the literature, we identified as the UK1 center [13], and the H4 level which could not be completely resolved. Heat treatments at higher temperatures (900 and 1000 °C), cause an increase in concentration of these levels and lead to the detection of two new levels, one identified as the IM7 center [9] and the other one labeled H5 ($E_v + 0.82$ eV). A summary of the detected DLTS levels is reported in table 1.

In order to determine any possible involvement of hydrogen in the detected levels, the thermal stability and depth profiling have been examined. It is known that hydrogen-related defects and its complexes are stable for temperatures up to 900 °C [6], therefore their associated
Table 1. Labeling, values of the energy position (above $E_v$), capture cross section and condition for detection, for the eight detected traps.

| Trap label | Energy position (eV) | Capture cross section (cm$^2$) | Comments |
|------------|----------------------|-------------------------------|----------|
| H1         | 0.22 ± 0.05          | $\sim 5 \times 10^{-16}$     | Stable up to 600 °C |
| H2         | 1.17 ± 0.06          | $\sim 6.5 \times 10^{-15}$   | Stable at least up to 1200 °C |
| H3         | 1.52 ± 0.09          | $\sim 8.4 \times 10^{-14}$   | Detected after 600 °C anneal |
| H4         | —                    | —                             | Stable at least up to 1200 °C |
| H5         | 0.82 ± 0.08          | $\sim 2.5 \times 10^{-16}$   | Detected after 1000 °C anneal |
| UK1        | 0.28 ± 0.03          | $\sim 4.4 \times 10^{-19}$   | Stable at least up to 1200 °C |
| UK2        | 0.58 ± 0.01          | $\sim 6.3 \times 10^{-16}$   | Idem     |
| IM7        | 0.79 ± 0.03          | $\sim 5.7 \times 10^{-19}$   | Idem     |

DLTS peak should anneal in this temperature range. The UK1 and UK2 defects have been detected after electron irradiation [13] and were associated to a complex involving carbon, whereas the IM7 defect was instead related to carbon interstitial clusters (C$_i$) [9]. It can be seen that all the detected levels display a high-thermal stability up to 1200 °C, therefore only H1 and H3 are the most likely candidates for a possible participation of hydrogen in their microscopic structure. In order to find any evidence for the presence of hydrogen the atomic structure of H1 and H3, we performed depth-profiling measurements of these two centers.

In figure 3, we show the results of such measurements performed after implantation and annealing at 400 and 600 °C, for the H1, H2 and H3 levels, respectively, and compared with the simulated hydrogen profile. It is known that the depth distribution of implanted hydrogen has a small width and a symmetrical distribution around the peak maximum position [12]. Our measurements show that the concentration distribution of the H1 level is narrow, located at $\sim 1.1 \mu$m, in the region close to the implantation peak, with a small skewness toward the surface indicating the presence of a possible diffusion mechanism [14]. The depth position of the H1 level is also consistent with the data reported in figure 1 where it is shown that, for the as-implanted sample, the $C$–$V$ signal could only be detected deeper than 0.8 $\mu$m. This provides strong hints for the possible participation of the implanted hydrogen in the microscopic nature of the H1 level. On the contrary, the depth distribution of the H3 level is more shallow and broader than the one of the H1 level and is similar to the depth distribution of the H2 level, which is stable for temperatures higher than 900 °C and cannot be associated with hydrogen. For this reason, the involvement of hydrogen in the structure of the H3 level can be ruled out.

Obviously, the exact atomic nature of the H1 level could not be determined because DLTS alone is not suitable for obtaining such information but theoretical studies, performed on defect-free [15] and irradiated SiC [16], can be helpful in order to get some useful hints about the nature of the detected levels. After irradiation, or implantation, self-interstitials anneal out at relatively low temperatures while a consistent number of vacancies is present and hydrogen binds more tightly to a silicon vacancy ($V_{Si}$) than to a carbon vacancy ($V_{C}$) [16]. If we assume that a $V_{Si}$ complex can be involved in the microscopic structure of the H1 defect, a level lying 0.32 eV above $E_v$ was predicted for the $V_{Si}$ + H center [15], 0.1 eV higher than the energy position of the H1 level. In contrast, Prezzi et al [17] have shown that a hydrogen dimer bound to

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a carbon anti-site (C$_{Si}$H$_2$) is the best candidate to explain the nature of a set of hydrogen-related photoluminescent lines in H-rich 4H-SiC and thus may be a more suitable choice for the identification of the H1 level.

However, additional work is being pursued and a comparative study between hydrogen-implanted and deuterium (D)-implanted SiC could yield further indications on the annealing kinetics, and thus on the exact nature of the H1 center.

4. Conclusions

In conclusion, we studied the electrically active defects in 200 keV hydrogen-implanted p-type 4H-SiC and we detected eight deep levels. The nature of these levels was discussed in the light of previous data reported in the literature. By studying both the thermal stability and their depth profiles, we identified one center (H1: $E_v + 0.22$ eV) which may involve the participation of at least one hydrogen atom.

Acknowledgments

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