ESR study on hydrogen passivation of intrinsic defects in p-type and semi-insulating 4H-SiC

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Hydrogen is an important element in the manufacturing process of semiconductor devices. For instance, hydrogen atoms can combine with defects and impurities in semiconductors, enabling us to control electronic properties of semiconductors. In silicon and diamond, hydrogen-vacancy complexes were found by electron-spin-resonance (ESR) spectroscopy [1,2]. In SiC, however, the same types of defects have not been found, despite vacancy defects are also present in SiC. Recently, it was found that a high-temperature annealing in H_2 ambience drastically increases a carrier lifetime of *p*-type 4H-SiC [3]. Furthermore, the enhanced carrier lifetime was reversibly decreased to its original value by high-temperature annealing in Ar ambience [3]. These results indicate that hydrogen atoms passivate or de-passivate lifetime killing defects in *p*-type 4H-SiC [3]. However, the microscopic entity of the lifetime killing defect is not clear yet.

In this work, we study the hydrogen passivation of intrinsic defects in *p*-type or semi-insulating 4H-SiC substrates by means of ESR. In *p*-type 4H-SiC, dominant intrinsic defects are already known: positively-charged carbon vacancy ($V_C(+)$, the EI5/6 centers) [4] and positively-charged carbon antisite-carbon vacancy pair ($C_{Si}V_C(+)$, the HEI9/10 centers) [5]. These defects are expected to become a lifetime killing defect of *p*-type 4H-SiC. We therefore examined the hydrogen passivation and de-passivation of these defects by observing their ESR signals.

The samples used in this study were semi-insulating 4H-SiC substrates which included the EI5/6 centers and the HEI9/10 centers, as similarly to *p*-type substrates. Their defect densities are in the order of 10^{14} cm^{-3}. The substrates were thinned to 180 μm by chemical mechanical polishing, to introduce hydrogen atoms into the whole substrate. The Si face of the substrate was subjected to high-temperature annealing at H_2 ambience at 500 to 1000ºC for 20 min. This hydrogen-annealing procedure is the same as that used for passivating the lifetime killing defects in *p*-epitaxial layers [3]. ESR spectra of the substrates before and after H_2 annealing were measured at 4.2 K to room temperature under an optimum microwave excitation.

Figure 1 shows ESR spectra of the base substrate (before H_2 annealing) for magnetic field // [0001]. The substrate shows the EI5/6 signal of $V_C(+)$, the HEI9/10 signals of $C_{Si}V_C(+)$, and unidentified signals (we name them "HEI7/8"), as shown in the figure. These signals have different microwave-saturation behaviors and different temperature dependences. Thus, we could experimentally separate ESR signals into two components (EI5/6 and HEI7/8 + HEI9/10) by changing a microwave power and temperature. Further lower temperatures (< 50 K) and with photo excitation, neutral divacancies ($V_{Si}V_C(0)$, the P6/7 centers [6]) were also detected in our substrates. Accordingly, we could examine the hydrogen passivation of four types of intrinsic defects (EI5/6, HEI7/8, HEI9/10, and P6/7).

Figure 2 shows hydrogen-induced changes in the ESR spectra. The signal intensities greatly decreased after H_2 annealing at 600ºC, indicating the hydrogen passivation of the intrinsic defects. We found that the EI5/6 signal is reduced by about 10%, while the HEI7/8 + HEI9/10 component is significantly reduced by about 90%. The relative changes in the ESR signals after H_2 annealing are plotted in Fig. 3, as a function of annealing temperature. Obviously, the hydrogen passivation differently affects each defect. For EI5/6, it is less effective and does not work above 700°C. On the contrary, for HEI7/8 + HEI9/10, it works much more drastic and is maximized above 700°C. This striking difference will be attributed to the different passivation form (either Si-H or C-H) of each defect. We will interpret details of the hydrogen-passivation effect of each defect as well as a relationship to the lifetime killing defect, based on more detailed data.

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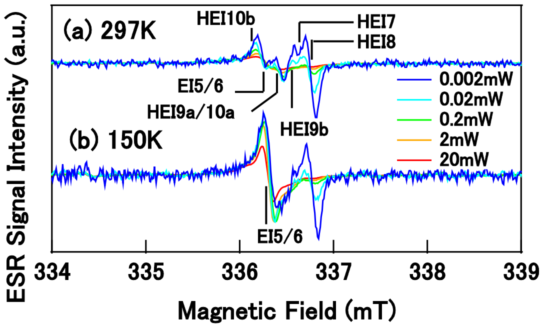

FIG. 1. ESR signals of the base substrate at different microwave powers and temperatures.

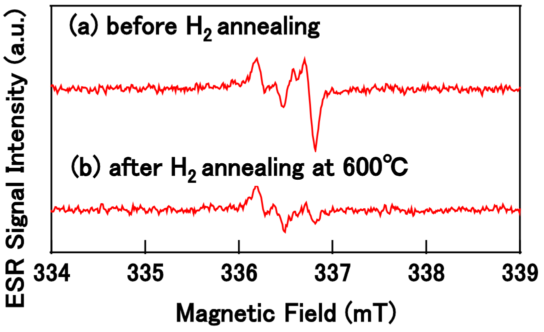

FIG. 2. Hydrogen passivation of ESR centers by H_2 annealing.
Both ESR spectra were measured at room temperature.

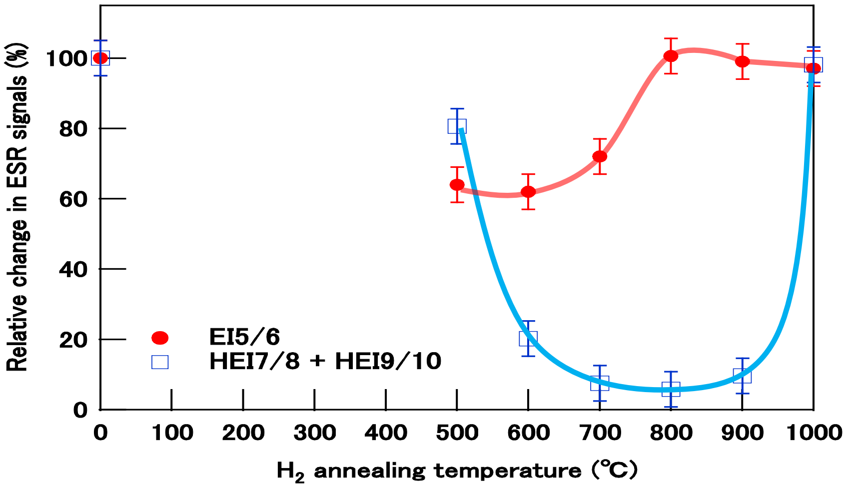

FIG. 3. Hydrogen passivation of the intrinsic defects as a function of H_2 annealing temperature.
“100%” represents ESR signals equal to those in the base substrate.