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The acceptor level for vanadium in 4H and 6H SiC

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Abstract

Electron paramagnetic resonance (EPR) and temperature-dependent Hall measurements were performed on seven different vanadium-doped semi-insulating SiC samples. Comparison of the EPR data and carrier activation energy suggests that the acceptor level for vanadium is 1.1 eV below the conduction band edge (E_c) in 4H SiC and within 0.86 of E_c in the 6H polytype. Photo-induced EPR results support the level assignments. However, analysis of the V^{4+} spectra in 4H samples suggests that the dominant vanadium EPR signal monitored in the 4H samples used for this experiment does not represent a simple isolated impurity. Rather, the results reflect a strained or complex defect.

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1. Introduction

Semi-insulating (SI) SiC is produced by limiting impurities during growth and compensation of residual donors or acceptors by means of intrinsic defects or extrinsic impurities. The intrinsic center that compensates the remnant amount of donors and acceptors is not known; however, vanadium is the impurity thought to provide the deep level for compensation in doped material. Although high-purity wafers are preferred for SiC-based homojunction devices where SiC is the active layer, vanadium doping remains a viable and less-expensive option for GaN-based devices where the GaN layer is grown on SiC substrates.

Temperature-dependent Hall or resistivity measurements of V-doped SI SiC often yield an activation energy (E_a) of 1.1 eV, although values up to 1.6 eV have also been measured [1]. To date, the species responsible for the 1.1 eV level is not known, but the 1.6 eV value is thought to be due to the vanadium donor ($V^{4+/5+}$) level. Electron paramagnetic resonance (EPR) spectroscopy is commonly used to identify intrinsic defects and impurities, and in combination with photo-excitation, may be used to determine a defect level. EPR measurements of Maier and coworkers provide the EPR signatures of V^{4+} and V^{3+} in 6H and 4H SiC, and photo-induced EPR measurements of p-type 6H SiC show that the neutral-to-positive transition (or, equivalently, $V^{4+/5+}$) at the hexagonal site is 1.6 eV above the valence band edge (E_v) [2]. Although no similar studies were reported for the negative-to-neutral ($V^{3+/4+}$) acceptor level, or the donor level at the cubic site, estimates from infrared photo-neutralization experiments suggest that the $V^{4+/5+}$ donor level for the cubic site in 6H SiC is 1.46 eV above E_v, and several studies indicate that the $V^{3+/4+}$ level is 0.82–0.80 eV and 0.66 eV below conduction band edge (E_c) of 4H and 6H SiC, respectively [3–5]. Some studies suggest that vanadium may couple to a second defect, forming a vanadium complex [3,6]. For example, theoretical studies suggest that a V–H pair in 4H SiC would have a donor and acceptor level at $E_v + 1.19$ and $E_c - 0.7$ eV, respectively [6].

In principle, the carrier activation energy determined by a Hall measurement reflects the Fermi level (E_f), which in semi-insulating material is expected to be near the electrical level of the defect responsible for compensation. A

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spectrum measured by EPR prior to illumination and below room temperature often represents the uncompensated charge state of a defect because the measurement detects centers with 'unpaired' electrons. Thus, EPR provides a means of identifying the defect that determines the location of E_f. To test the assignment, two criteria should be considered: (1) the concentration of a specific center must be similar to the concentration of uncompensated defects extracted from the Hall data and (2) the defect should have a photo-induced transition consistent with the carrier activation energy. Unfortunately, the first criterion cannot be tested in SI SiC because temperature-dependent Hall measurements do not exhibit carrier saturation within the temperature range available for measurement. Nevertheless, the second criterion can be used as a guide to judge the feasibility of various species as the primary compensating defect. Our work addresses the activations energies between 0.7 and 1.1 eV found in vanadium-doped 4H and 6H SiC. Several pieces of evidence suggest that these E_a values represent the defect level for $V^{3+/4+}$ in the different polytypes, but preliminary analysis of the EPR spectrum suggest that a complex, rather than isolated impurity, is responsible for the value obtained in the 4H polytype.

2. Experimental details

Samples from several SI SiC wafers grown by physical vapor transport at Cree Inc. or by Northrup Grumman were characterized by temperature-dependent Hall and resistivity measurements, and EPR. The values for the vanadium concentration range between 4×10^{17} and $5\times10^{16}\,cm^{-3}$ as measured by secondary ion mass spectroscopy or as reported by the growers. Wafers were cut into $0.5\,cm^2$ pieces for the Hall measurements and $0.25\times0.5\,cm^2$ pieces for EPR. Samples for electrical characterization were oxidized at 1150 °C for 5 h to remove surface damage, and the oxide was removed with HF solution before measurement. The oxidation/etching process performed on selected EPR sample had no affect on the photo-EPR data; thus, some of the EPR data were obtained from as-grown samples. For the Hall samples, Ta/NiCr/W ohmic contacts were deposited in a van der Pauw configuration and annealed at 925 °C for 2 min in forming gas. The Hall data were acquired using a 0.8 T magnetic field and a guarded DC measurement system. A specially constructed furnace insert was used to heat the samples to temperatures of 1020 K.

For a variety of reasons, Hall effect measurements have rarely been reported for SI SiC. The lack of low-resistance ohmic contacts makes measurements difficult because the high resistance of the contacts leads to large RC time constants. In the work reported here, E_a was extracted from the data using least-squares fits that included the $T^{3/2}$ dependence of the density of states. In samples of main interest to the present work, those with $E_a < 1.2$ eV, conductivity type is reliably determined, so we report values with respect to E_c or E_v as appropriate. In the two cases with higher E_a, the value is near midgap, so the uncertainty in band edge does not significantly affect the conclusions.

X-band (9.5 GHz) EPR spectroscopy was performed at 4 K or room temperature in the dark and during illumination using a 250 W quartz–tungsten–halogen lamp and monochrometer. The samples were placed in a darkened EPR cavity at room temperature for at least 12 h prior to measurement to achieve stability. Defects were identified by their g-values and hyperfine parameters (A tensor) as is described in many texts [7]. Unfortunately, we cannot compare the total number of centers that change with photon energy because the absolute amount of vanadium is not measurable from these EPR spectra; however, much can be gleaned by examining the trends among different defects.

3. Results and discussion

The activation energy and dark EPR results are shown in Table 1 for both 4H and 6H SiC. In the 6H samples, the V^{4+} signal from the hexagonal site was below the detection limit of the spectrometer, so all data were obtained from spectra representative of the cubic site. The temperature dependence of the carrier concentration used to extract E_a values for the 4H sample 2 (unfilled circles) and 6H sample 2 (filled squares) are shown in Fig. 1. All samples with $E_a < 1.1$ eV exhibit n-type conduction. The solid line represents a fit to the data as described earlier. The EPR results shown in Table 1 indicates that both charge states of vanadium were observed only for samples with an E_a of 1.1 eV (4H) and <0.86 eV (6H). The simultaneous presence of the three-plus and four-plus charge states suggests that E_f is located near the $V^{3+/4+}$ level. Furthermore, assuming that E_a approximates the Fermi level, the data of Table 1 indicate that the acceptor level of vanadium is 1.1 eV below E_c in 4H SiC and within 0.86 eV of E_c in the 6 H polytype. The interpretation of E_a as E_f in the vanadium-doped samples is supported by the results of 6H sample 4, which exhibits only V^{4+} before illumination. In this case, the Fermi level should be close to the $V^{5+/4+}$ donor level. As seen in Table 1, sample 4 has an activation energy of 1.4 eV, within 0.1 eV of previously reported donor level energies for vanadium in 6H SiC [8]. Also note that the 4H sample with a 1.6 eV activation energy reveals only V^{4+} in the dark EPR measurement, consistent with the expected donor level in the 4H polytype [9].

Steady-state photo-induced EPR measurements support the acceptor level assignments indicated by Table 1. Figs. 2 and 3 illustrate the intensity of the V^{3+} (unfilled circles), V^{4+} (filled squares) and nitrogen (plus signs) signals in the 4H (6H) samples, relative to the intensity measured before illumination. For clarity, boron data are not shown because the trend in 4H and 6H SiC is the same. The relative intensity remains unchanged until 2.1 ± 0.1 eV when the boron signal begins to increase monotonically.