

A Compensation Mechanism for Semi-Insulating 6H-SiC Doped with Vanadium*

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Abstract: A model is presented to describe a compensation mechanism for semi-insulating 6H-SiC grown with the intentional doping of vanadium. Because we found nitrogen to be the principal shallow donor impurity in SiC by secondary ion mass spectroscopy (SIMS) measurements, semi-insulating properties in SiC are achieved by compensating the nitrogen donor with the vanadium deep acceptor level. The presence of different vanadium charge states V^{3+} and V^{4+} is detected by electron paramagnetic resonance and optical absorption measurements, which coincides with the results obtained by SIMS measurements. Both optical absorption and low temperature photoluminescence measurements reveal that the vanadium acceptor level is located at 0.62eV below the conduction band in 6H-SiC.

Key words: 6H-SiC; semi-insulating; vanadium doping; compensation; vanadium acceptor level

PACC: 6170W; 7155

CLC number: TN304.2

Document code: A

Article ID: 0253-4177(2008)02-0206-04

1 Introduction

Semi-insulating SiC single crystals are gaining importance as substrate for high frequency electronic devices based on both SiC and GaN^[1]. However, growth of high purity semi-insulating SiC substrates is difficult due to the poor control of residual impurities associated with the high-temperature growth environment. As a result, most SiC crystals are conducting due to contamination of either nitrogen donors or boron acceptors introduced in the ambient and graphite parts^[2]. Semi-insulating properties in SiC are achieved by compensating all residual shallow donors or acceptors with the doping of vanadium^[3,4]. As an amphoteric impurity in SiC^[5], vanadium substitutes for Si sites in three possible charge states: positive V^{5+} ($3d^0$), neutral V^{4+} ($3d^1$), and negative V^{3+} ($3d^2$), and therefore, produces the donor and acceptor levels in p- and n-type SiC samples, respectively. There is a consensus that the vanadium donor level (V^{5+}) resides near the middle of the band gap in 6H-SiC, at approximately 1.35eV below the conduction band^[6]. The acceptor level (V^{3+}) is closer to the conduction band, but its location has not yet been unambiguously determined. Studies indicate that the acceptor level is located at 0.6 ~ 0.8eV below the conduction band^[7,8].

Since vanadium can act as donor or acceptor in SiC, the compensation mechanism is determined by whether the residual background is p type or n type. Temperature-dependent Hall or resistivity measurements can be used to determine the activation energy of impurities^[9,10]. However, the measurements may be inaccurate due to the difficulty in making good ohmic contact on high-resistivity samples.

In this paper, a compensation mechanism for semi-insulating 6H-SiC doped with vanadium is investigated by secondary ion mass spectrometry (SIMS), electron paramagnetic resonance (EPR), optical absorption (OA), and photoluminescence (PL) measurements. The last two measurements are also used to determine the location of the vanadium acceptor level in 6H-SiC.

2 Experiment

The vanadium-doped semi-insulating 6H-SiC crystals were grown by the physical vapor transport (PVT) process at the 46th Research Institute, CETC without intentional doping. The resistivity of the sample is as high as $10^5 \Omega \cdot \text{cm}$. A CAMECA-ims-4f SIMS instrument with a 10.5keV O_2^+ primary ion beam was used to investigate the impurities concentrations. The EPR spectra were recorded on a Bruker ER200-SRC X-band spectrometer equipped with a liquid nitrogen

* Project supported by the National Natural Science Foundation of China (No. 60376001), the Key Research Foundation of the Ministry of Education (No. 106150), and the Xi'an Applied Materials Foundation (No. XA-AM-200607)

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Received 6 August 2007, revised manuscript received 29 August 2007

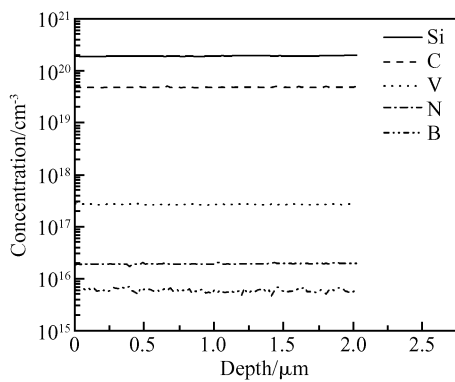


Fig. 1 SIMS results of the unintentionally doped semi-insulating 6H-SiC crystals doped with vanadium

continuous flow cryostat, typically at 77K. The optical absorption measurements were performed with a Bruker IFS-120HR Fourier transform infrared (FT-IR) spectrometer at 12K, equipped with a tungsten quartz-halogen source, a CaF beam splitter, and an InSb detector. Low temperature PL spectra were measured under excitation with a KIMMON He-Cd laser operating at a wavelength of 325nm. The sample was cooled to 10K by using a closed-cycle helium cryostat during the measurements.

3 Results and discussion

3.1 SIMS results

Figure 1 shows the SIMS measurements of the impurities concentrations. The results indicate that nitrogen and boron are the principal residual impurities, with a concentration of around 2×10^{16} and $6 \times 10^{15} \text{ cm}^{-3}$, respectively. Boron is usually assumed to be a contaminant in the starting material, while the nitrogen most likely comes from atmospheric contamination of the graphite furnace elements. The doping concentration of vanadium is about $2.8 \times 10^{17} \text{ cm}^{-3}$, which is lower than the maximum solubility of vanadium in SiC^[11], with the value of $(3 \sim 5) \times 10^{17} \text{ cm}^{-3}$. SIMS results reveal the presence of nitrogen in larger amounts than boron, so nitrogen is the principal electrically active shallow donor impurity in SiC. Since the concentration of nitrogen is over an order of magnitude less than that of vanadium, semi-insulating properties in 6H-SiC are achieved by compensating shallow nitrogen donors with the doping of vanadium: $[B] \leq [N]_{\text{residual}} \leq [V] \leq (3 \sim 5) \times 10^{17} \text{ cm}^{-3}$, and the Fermi level lies close to the vanadium acceptor level.

3.2 Electron paramagnetic resonance

EPR measurements were used to determine the

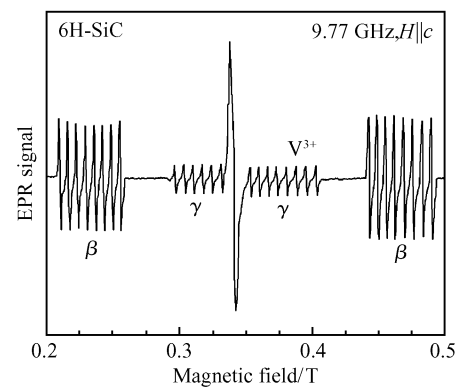


Fig. 2 EPR spectrum of the acceptor state V^{3+} in the vanadium-doped 6H-SiC samples measured at 77K, 9.55GHz and $H \parallel c$ (The hyperfine octets belong to the V^{3+} cubic sites (β, γ))

presence of the vanadium charge state and to estimate its compensation mechanism. The characteristic hyperfine octet structures of V^{3+} are clearly observed in EPR spectra at 77K, as shown in Fig. 2. The two sets of vanadium-related spectra can be distinguished, which are assigned to V_{Si} on the two quasi-cubic sites β and γ ^[12]. An additional EPR line in the center at $g = 2.0057$ is attributed to the nitrogen donor^[12].

The detection of the V^{3+} charge state suggests that the doped vanadium in SiC is electrically active, as a deep level impurity. The presence of V^{3+} is due to electron capture at neutral V^{4+} , which means that vanadium acts as a deep acceptor in 6H-SiC by compensating the residual shallow donor nitrogen. This result is in agreement with the compensation mechanism obtained from SIMS measurements.

The EPR spectra of V^{4+} , which are usually detected at 4K^[13], are not shown here due to instrument limitations. More detailed measurements and analysis need to be performed in the future.

3.3 Infrared absorption

Figure 3 shows the near-IR optical absorption spectra of vanadium-doped 6H-SiC at 12K with a resolution of 0.3nm. Background absorption is stripped from the data before processing. Absorption peaks in the wavelength regions of 1300~1400nm and 1980~2080nm are observed, as shown in the dashed circles indicated by the arrows, which is attributed to V^{4+} and V^{3+} intra 3d-shell transitions, respectively^[14].

For further investigation, optical absorption spectra were measured in the wavelength regions of 1300~1400nm and 1980~2080nm with a resolution of 0.03nm, as shown in Figs. 4(a) and 4(b), respectively. OA measurements on 6H-SiC reveal the classical absorption spectrum of V^{4+} ($3d^1$). Figure 4(a) shows the peaks attributed to V^{4+} on the hexagonal site (α) and on the cubic sites (β and γ). In addition, two

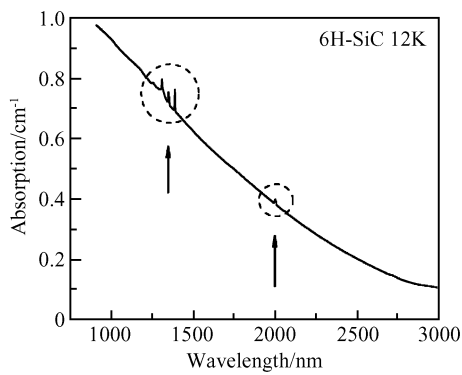


Fig. 3 Near-IR range optical absorption spectrum at 12K showing series of peaks in vanadium-doped 6H-SiC

peaks attributed to the vanadium acceptor level (V^{3+}) are also observed, as shown in Fig. 4 (b). Based on DLTS results showing high vanadium contamination and according to works done on III-V compounds^[15], these peaks should be correlated to the ${}^3A_2 \rightarrow {}^3T_2$ internal transitions of the V^{3+} center. The results indicate that the vanadium acceptor level is located at 0.60~0.62eV below the conduction band in 6H-SiC. The spectrum in Fig. 4 is the same as that reported in several papers^[8,12], is identified with vanadium atoms in 6H-SiC, and is the accepted IR signature of vanadium in 6H-SiC crystals.

Considering the impurities concentrations from the SIMS measurements, we can conclude from these two facts that: (1) vanadium is present in its $3d^1$

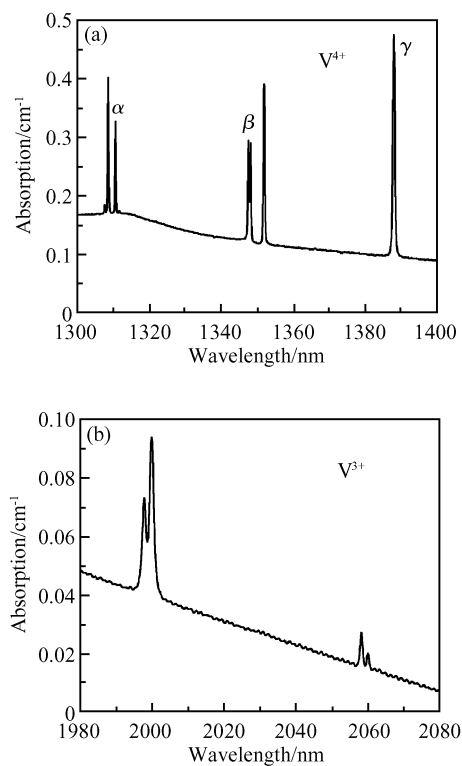


Fig. 4 FTIR absorption spectrum of V^{4+} (a), and V^{3+} (b) in the vanadium-doped 6H-SiC samples

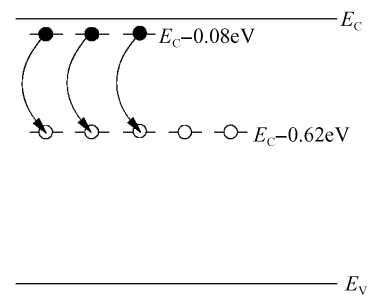


Fig. 5 Schematic diagram of compensation in semi-insulating 6H-SiC doped with vanadium

charge state, and (2) the sample is in equilibrium and the Fermi level must be pinned to the vanadium acceptor level. Since most electrons in 6H-SiC are captured by vanadium impurity, this leads to the neutral-to-negative transition of vanadium. Figure 5 shows the compensation process. The band edges of SiC and two major levels are shown: the nitrogen donor level located at 0.08eV below the conduction band and the vanadium acceptor level at $\sim E_C - 0.62\text{eV}$. Since the vanadium concentration is higher than that of uncompensated nitrogen, the electrons from the nitrogen donor will be trapped by the vanadium acceptor. During the near-infrared absorption measurements, the captured electrons are emitted from the vanadium acceptor level back to the conduction band. Thus, we conclude that the activation energy at $\sim E_C - 0.62\text{eV}$ is related to the vanadium acceptor level. The energy is similar to the value reported in many previous studies^[8,16].

3.4 Low temperature photoluminescence

To verify the location of the vanadium acceptor level in 6H-SiC, typical PL spectra of samples are measured at 10K, as shown in Fig. 6. A dominated peak is detected by PL measurements attribute to the internal transition of V^{3+} in 6H-SiC. The vanadium acceptor level is located at 0.62eV below the conduc-

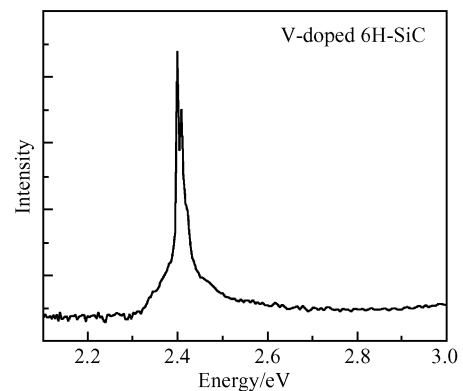


Fig. 6 Low temperature PL spectrum of the vanadium-doped 6H-SiC

tion band. These results coincide with optical absorption measurements discussed above.

4 Conclusion

A model for the compensation of intentionally vanadium doped 6H-SiC, which forms semi-insulating material, is developed. SIMS analysis indicates that nitrogen is the principal shallow donor impurity in SiC and partially compensates the vanadium, thus pinning the Fermi level to the vanadium acceptor level. EPR and optical absorption measurements indicate the presence of vanadium in different charge states in 6H-SiC. As V^{3+} and V^{4+} signatures can be detected separately by these techniques, the compensation mechanism for the formation of semi-insulating 6H-SiC with the doping of vanadium is determined, which coincides with the SIMS measurements. Both OA and EPR results match the results obtained from chemical analysis and electrical measurements in other studies. Optical absorption and low temperature PL measurements reveal that the vanadium acceptor level is located at 0.62eV below the conduction band in 6H-SiC.

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钒掺杂形成半绝缘 6H-SiC 的补偿机理*

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摘要: 研究了钒掺杂生长半绝缘 6H-SiC 的补偿机理. 二次离子质谱分析结果表明, 非故意掺杂生长的 6H-SiC 中, 氮是主要的剩余浅施主杂质. 通过较深的钒受主能级对氮施主的补偿作用, 得到了具有半绝缘特性的 SiC 材料. 借助电子顺磁共振和吸收光谱分析, 发现 SiC 中同时存在中性钒(V^{4+})和受主态钒(V^{3+})的电荷态, 表明掺入的部分杂质钒通过补偿浅施主杂质氮, 形成受主态钒, 这与二次离子质谱分析结果相吻合. 通过对样品进行吸收光谱和低温光致发光测量, 发现钒受主能级在 6H-SiC 中位于导带下 0.62eV 处.

关键词: 6H-SiC; 半绝缘; 钒掺杂; 补偿; 钒受主能级

PACC: 6170W; 7155

中图分类号: TN304.2

文献标识码: A

文章编号: 0253-4177(2008)02-0206-04

* 国家自然科学基金(批准号:60376001), 教育部重点项目(批准号:106150)及西安应用材料基金(批准号:XA-AM-200607)资助项目

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2007-08-06 收到, 2007-08-29 定稿