Effect of vanadium on the room temperature ferromagnetism of V-doped 6H–SiC powder*

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This study focuses on the effect of V-doping on the ferromagnetism (FM) of 6H–SiC powder. The X-ray diffraction results indicate that V is inserted into the 6H–SiC lattice. The Raman spectra reveal that with a V concentration of 25 ppm, the crystalline quality and carrier concentration of 6H–SiC are hardly varied. It is found that after the V-doping process, the saturation magnetization (M_s) and the vacancy concentration of 6H–SiC are both increased. From these results, it is deduced that the effect of V might contribute mainly to the increase of vacancy concentration, thus resulting in the increase of M_s of V-doped 6H–SiC.

Keywords: 6H–SiC, V-doping, ferromagnetism, vacancy concentration

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1. Introduction

As a wide band gap semiconductor, SiC possesses many excellent physical properties, which shows promise in applications of high-power, high-frequency, high-temperature electronic and optoelectronic devices.[1] In the past few years, some studies have shown that SiC can also be a good candidate for a dilute magnetic semiconductor (DMS) which has attracted wide interest in the application prospect of spintronic devices.[2–6] Up to now, the ferromagnetism (FM) has been found or calculated in 3C,[7,8] 4H,[9–11] and 6H–SiC[12–14] polytypes, including undoped, transition-metal doped, non-transition-metal doped and codoped SiC systems.

As a new research area which is just in the beginning stage, there are a lot of things that are unclear. Presently, there are several different points of view on the FM origin. For Mn-doped 3C–SiC, in Ref. [17] it was deduced that the FM was related to the co-effect of Mn doping and defects. For Al-doped 4H–SiC, in Ref. [9] it was assumed that the FM was from the sp^3/sp^2 hybridization. For undoped 6H–SiC, in Ref. [12] the FM was attributed to the divacancies ($V_{Si}V_C$). These results show that the FM may be related to intrinsic defects, doping ions, and other factors, though more evidence is still necessary.

Among the studies of 6H–SiC, a few research studies mentioned the FM of the V-doped 6H–SiC wafer.[13,15] Yet, the origin of the FM is still not clear. Furthermore, we found that VC owns FM, revealing that the introduction of VC is not a non-ferromagnetic-ion doping process. Besides, there are plenty of bulk structural defects in SiC crystal, such as micropipe,[16] stacking faults,[17] dislocations,[18] and misoriented domain,[19] which may be a huge disturbance to the FM. Therefore, we focus on the FM of 6H–SiC powder including undoped and V-doped samples. It is found that the undoped 6H–SiC shows a weak FM behavior. The introduction of V can lead to the increase of M_s as well as the increase of the vacancy concentration. These results imply that the effect of the V may be tuning the FM by varying the vacancy concentration rather than introducing the FM origin. It is also calculated that the increase of M_s is not from VC. All the results show the possibility of tuning the magnetization of 6H–SiC.

2. Experiment

V-doped 6H–SiC powder was prepared through the physical vapour transport (PVT) growth of V-doped 6H–SiC crystal. The growth temperature and Ar pressure were $\sim$ 2500 K and 4×10^3 Pa, respectively. 6H–SiC source (99.99%) and VC powder ($VC_{0.88}$, 99%, from Alfa Aesar) were used as the starting materials, the ratio of VC was 0.5%. After the crystal growth process, the material in the graphite crucible was taken out and made into powder.

The concentration of V was measured by the Glow–Discharge Mass Spectrometry (GDMS, VG-9000, from Thermo Elemental). The structure of the sample was obtained by X-ray diffraction (XRD, D8 ADVANCE, from BRUKER AXS GMBH) and Raman spectroscopy (from Renishaw inVia Raman Microscope) with 514-nm laser. The samples were wrapped by a capsule for magnetic measurement which was performed by a superconducting quantum interference device (SQUID, MPMS-5, from Quantum Design). The state of the

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spinning electron was analyzed by electron paramagnetic resonance spectrometer (EPR, JEOL-FA200) at 300 K and 123 K.

3. Results and discussion

Figure 1 shows the XRD patterns of undoped and V-doped SiC sample, which is corresponding to 6H–SiC (ICDD-PDF: 49-1428). No signal of VC (actually V_8C_7, ICDD-PDF: 35-0786) appears. Compared with the undoped one, peak positions of the V-doped 6H–SiC are all right shifted, suggesting that the lattice constant of 6H–SiC diminishes. This means that V has already inserted into the 6H–SiC lattice.

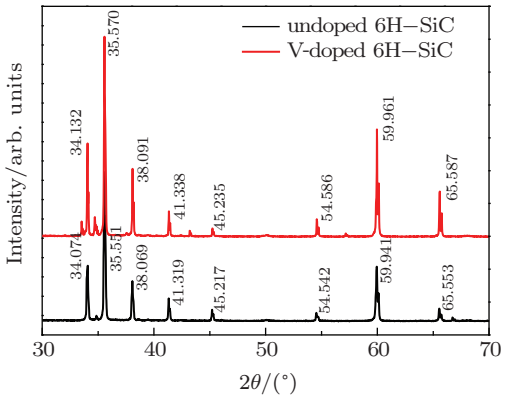


Fig. 1. (color online) XRD patterns of undoped and V-doped 6H–SiC.

Figure 2 shows the Raman spectra of undoped and V-doped 6H–SiC. It can be seen that the frequencies of the folded transverse optic (FTO) and folded longitudinal optic (FLO) modes of the two samples are almost located at the same position, and their values of full width at half maximum (FWHM) hardly vary. This means that the crystalline quality of 6H–SiC hardly varies after the V-doping process. Reference [20] pointed out that the band shifting toward the high-frequency side and broadening with the decrease of the peak intensity of FLO imply the increase of carrier density. So from Fig. 2 it can be deduced that there is probably no variation of carrier density after the introduction of V in this experiment. This is due to the fact that the doping concentration of V is only 25 ppm (measured by GDMS) and there are plenty of V^{4+} ions that replace the positions of Si^{4+} ions, which will not cause the variation of carrier concentration remarkably.

Figure 3(a) shows the magnetic hysteresis loops of undoped and V-doped 6H–SiC powder at 300 K, where the diamagnetic background has been subtracted from the raw data. Figure 3(b) shows the magnetic hysteresis loop of VC at 300 K, with no diamagnetic background subtracted. In Fig. 3(a), it can be seen that the undoped 6H–SiC shows very weak FM, implying that its FM of 6H–SiC is rooted in the intrinsic property. The M_s of V-doped 6H–SiC rises compared with that of the undoped one, suggesting that V is able to increase the M_s. In Fig. 3(b), it is found that VC owns FM, revealing that the introduction of VC is not a non-ferromagnetic-ion doping process. The GDMS results show that the V concentration is 25 ppm. Figure 3(b) shows that the M_s of VC is less than 5×10^{-1} emu/g, so the M_s of 25 ppm of VC is calculated to be less than 1.25×10^{-5} emu/g which is much smaller than the M_s of V-doped 6H–SiC ($\sim 2\times10^{-4}$ emu/g), implying that the increase of the M_s is not from VC.

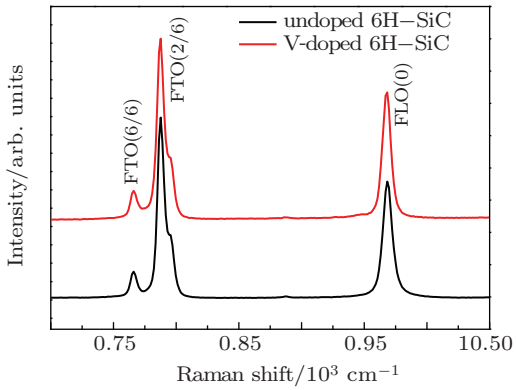


Fig. 2. (color online) Raman spectra of undoped and V-doped 6H–SiC.

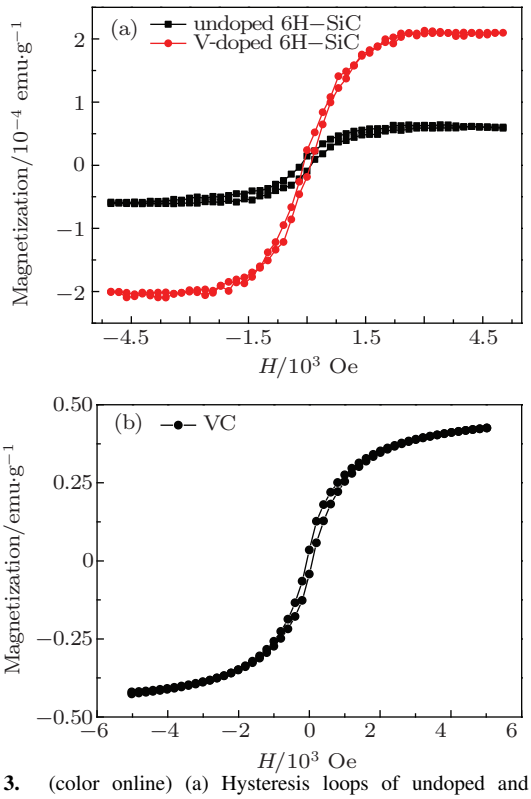


Fig. 3. (color online) (a) Hysteresis loops of undoped and V-doped 6H–SiC at 300 K; (b) Hysteresis loop of VC at 300 K,[21] 1 Oe=79.5775 A/m.

Figure 4 shows the EPR results of undoped and V-doped 6H–SiC powder; the weights of the two samples are identical. According to the EPR results, the g value is 2.0013, which corresponds to the central incorporating Si and C vacancies on adjacent lattice sites.[22] In Fig. 4(a), it can be seen that at 300 K, it seems to have no signal for undoped 6H–SiC, while there appears to be a signal for the V-doped one, implying that the status of the vacancies is varied after V-doping. In Fig. 4(b),

it is seen that at 123 K, there are signals for both, while the spin concentration increases after the introduction of V, suggesting that the V-doping can increase vacancy concentration in 6H–SiC. It is because when V is inserted into the lattice of 6H–SiC, the lattice constant of 6H–SiC diminishes, which is shown in Fig. 1. Such a variation may lower the formation energy of vacancy, thus increasing its concentration.

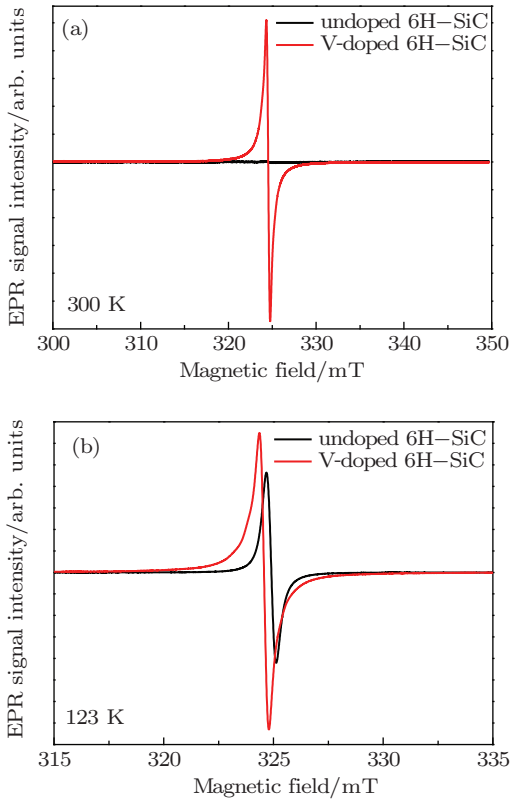


Fig. 4. (color online) EPR signals of undoped and V-doped 6H–SiC at (a) 300 K and (b) 123 K.

In Fig. 3(a), it has been demonstrated that the FM of 6H–SiC is rooted in the intrinsic property. It was demonstrated in Ref. [12] that divacancies ($V_{Si}V_C$) are responsible for the FM of undoped 6H–SiC, and this may also be the reason for the weak FM of undoped 6H–SiC. In Fig. 3(b), it is calculated that the FM signal of V-doped 6H–SiC is not from VC. In consideration of the results shown in Fig. 4, it can be deduced that the introduction of V contributes mainly to the increase of vacancy concentration, thus resulting in the increase of the M_s in V-doped 6H–SiC.

It was reported in Ref. [15] that the lower V-doped 6H–SiC crystal (3.76×10^{17} cm^{-3}, about 10 ppm) showed larger M_s than higher V-doped (6.14×10^{17} cm^{-3}, about 16 ppm) one, and their values of M_s were 1.2×10^{-4} emu/g and 4.0×10^{-5} emu/g, respectively. In Fig. 3(a) it can be seen that the M_s of our V-doped 6H–SiC sample is about 2×10^{-4} emu/g, which is larger than their results. Furthermore, the V concentration is 25 ppm for our V-doped 6H–SiC powder, which is also higher than theirs. That is to say, the M_s will not become smaller with higher doping of V. In Ref. [15] the larger M_s of lower V-doped 6H–SiC crystal is attributed to the poorer crystalline quality, on the assumption that structure defects may increase the M_s. It is indicated in Fig. 2 that the crystalline quality of undoped and V-doped 6H–SiC almost remain unchanged, while the M_s of V-doped 6H–SiC is larger than that of the undoped one. It means that the FM of 6H–SiC may be related to both vacancy defect and structure defect.

4. Conclusion

In this paper, V-doped 6H–SiC powder is prepared from the physical vapor transport (PVT) growth of V-doped 6H–SiC crystal. The effect of V-doping on the FM of 6H–SiC is studied. The magnetic tests show that the FM of 6H–SiC is rooted in the intrinsic property and can be enhanced by V-doping which leads to the increase of vacancy concentration. It is also confirmed that to some extent higher concentration of V-doping would not result in the decrease of M_s and the FM of 6H–SiC may be related to both vacancy defects and structure defects. All the results can help us to know more about the FM of 6H–SiC and show the possibility of tuning the magnetizations of SiC and other WBG semiconductors.

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