Defects mediated ferromagnetism in a V-doped 6H–SiC single crystal*

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(Received 16 November 2011; revised manuscript received 1 December 2011)

Undoped and V-doped 6H–SiC single crystals have been grown by the physical vapor transport method. The V concentration is determined to be 3.76×10^{17} at/cm^3 and 6.14×10^{17} at/cm^3 by secondary ion mass spectrometry for low V-doped and high V-doped SiC samples, respectively. The undoped 6H–SiC shows diamagnetism, while the V-doped 6H–SiC exhibits weak ferromagnetism. The lower V-doped sample shows stronger ferromagnetism compared to that of the higher V-doped sample. However, the structural characterization indicates that the lower V-doped SiC has a relative poor crystalline quality. It is found that both V dopants and defects are essential for introducing ferromagnetic exchange in V-doped SiC single crystals.

Keywords: V-doping, 6H–SiC, defects, magnetic materials

PACS: 75.50.Pp, 75.30.–m, 71.70.Gm **DOI:** 10.1088/1674-1056/21/6/067503

1. Introduction

Diluted magnetic semiconductors (DMSs) such as InAs,[1] GaAs,[2] GaN,[3] and ZnO[4] doped with 3d transition metals have attracted a lot of attention in recent years due to their potential applications in spintronics. Although the Curie temperature, near or above room temperature, has been observed in a number of DMSs, there remain some issues that are still controversial: (i) the doped-transition metals and their compounds may precipitate and form a so-called "secondary phase", which will contribute to the observed ferromagnetism; (ii) room-temperature ferromagnetism is often observed in polycrystalline thin films and nano-particles, but not in single crystal materials. Such ferromagnetic materials are not regarded as the real DMSs because there are lots of defects in the surface or the interface between the polycrystalline thin films and nano-particles;[5] (iii) the ferromagnetism mechanism of DMS is still controversial. Typical theories such as the carrier mediated double exchange model,[6] the mean-field theory,[7] the Ruderman–Kittel–Kasuya–Yosida theory,[7] and bound magnetic polarons (BMPs)[8] have been proposed. It has been proposed that a single crystal semiconductor doped with non-magnetic elements is an ideal system to solve the above issues.

SiC is an important wide band gap semiconductor with a high breakdown field, high thermal conductivity, and excellent carrier transport properties. It is also a potential candidate for DMSs. Los[9] and Zhou *et al.*[10] theoretically predicted that 3d transition metals doped SiC could behave like ferromagnetism. Room-temperature ferromagnetism was observed in Cr-,[11] Mn-,[12] Fe-,[13] and Co-doped[14] SiC. V is regarded as a good dopant because metallic V[15] and VC[16] compounds are non-ferromagnetic materials. Up to now, few studies have focused on the V-doped 6H–SiC single crystals. In this paper, we perform an in-depth study on the magnetic properties of V-doped 6H–SiC single crystals and focus on the relationship between the crystalline properties and ferromagnetism.

*Project supported by the Young Scientists Fund of the National Natural Science Foundation of China (Grant No. 51002176) and the Innovation Programs of the Chinese Academy of Sciences (Grant No. KJCX2-EW-W10).

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2. Experimental details

Semi-insulating 6H–SiC ingots were grown by the physical vapour transport (PVT) method with Si-face (0001) seed crystals at ∼2500 K. High-purity (≥99.99%) SiC and VC powders were used as raw materials with a nominal weight ratio in order to introduce different V concentrations. The ingots were sliced into wafers of about 450-μm thick and then both sides were lapped and polished, and finally were washed using the standard RCA technique. Typical wafers were chosen and cut into small pieces for the next measurement. The 6H–SiC samples with nominal non-, low-, and high-V contents were labeled as S1, S2, and S3 in the following text and figures. The V concentration was measured by secondary ion mass spectrometry (SIMS, CAMECA IMS-4F). The sample was bombarded by 8-keV oxygen ions in an area of about 300 μm ×300 μm with a depth of about 3 μm. The magnetic properties were performed on a Quantum Design vibrating sample magnetometer (VSM) at room temperature. The electrical properties were measured by a Hall effect measurement system (Lakeshore 7704A) using four-point Van Der Pauw configuration. The Raman spectroscopy was used on a Renishaw Invia Raman microscope with a 514-nm laser. The crystalline qualities were characterized by high resolution X-ray diffraction (HRXRD, Bruker D8 Discover) operating at 40 kV and 40 mA. The carbon K edge X-ray absorption spectra (XAS) of SiC single crystals were measured at the National Synchrotron Radiation Laboratory (NSRL, U19 station) using the total electron yield (TEY) mode in a vacuum environment of 1.5×10^{-7} Pa.

3. Results and discussion

The magnetization as a function of applied field (M–H) curves of S1, S2, and S3 are shown in Fig. 1. The diamagnetic signals from the SiC matrix are subtracted from the raw curves for samples S2 and S3. A typical diamagnetic behaviour is seen for S1, while a hysteresis loop is observed for S2 and S3. Especially for S2, it shows a clear hysteresis loop with a coercive field (H_c) of ∼ 0.01 T. It can be seen that the saturation magnetization of S2 is much stronger than that of S3. We perform a curve of the magnetization as a function of temperature (M–T) with an applied field of 0.05 T for S2 as shown in the inset of Fig. 1. The magnetization remains 1.2×10^{-4} emu/g even when the temperature is increased to 300 K, which indicates that the Curie temperature of S2 is above room temperature. The magnetic properties imply room-temperature ferromagnetism in the V-doped SiC single crystal. The V concentrations in S1, S2, and S3 are $< 5.0 \times 10^{13}$, 3.76×10^{17}, and 6.14×10^{17} at/cm^3, respectively, which are determined by SIMS.

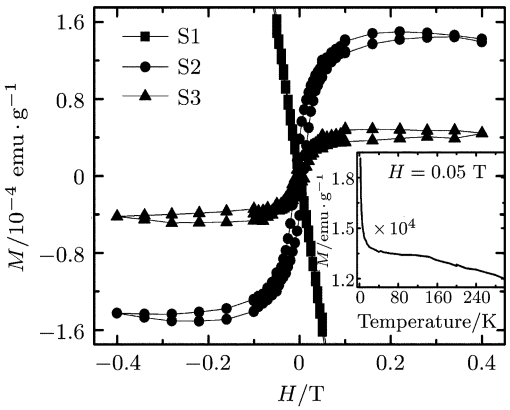


Fig. 1. Room-temperature M–H curves of S1, S2, and S3 with the inset showing M–T curve of S2 with an applied field of 0.05 T.

The crystalline properties of S1, S2, and S3 were measured by a Raman spectroscope with an excited laser of 514 nm at room temperature. The Raman shift spectra shown in Fig. 2, are divided into a low vibrating region of 150 cm^{-1}–530 cm^{-1} and a high vibrating region of 530 cm^{-1}–1030 cm^{-1}. The peaks located at 151.0, 266.4, 504.1, 515.0, 767.7, 789.2, and 965.9 cm^{-1} correspond to the folded transverse acoustic (FTA) modes, folded transverse optic (FTO) modes, folded longitudinal acoustic (FLA) modes, and folded longitudinal optic (FLO) modes,[17] respectively. All of these peaks are consistent with the standard Raman spectra of 6H–SiC. No peaks corresponding to impurities or other SiC polytypes are observed, which indicates that the as-grown SiC crystals are a monotype of 6H–SiC. The crystalline properties were also characterized by HRXRD rocking curves. Figure 3 shows the HRXRD rocking curves of S1, S2, and S3. The inset shows the survey scan curve of S3. There are only (006) and (0012) diffraction peaks at $2\theta = 35.60°$ and $2\theta = 75.90°$. No other peak corresponding to impurities is observed. The HRXRD results indicate that all the samples are hexagonal 6H–SiC single crystals, which is consistent with the Raman results. The (006) diffraction peaks of S1, S2, and S3 were scanned in rocking curve mode with a fixed diffraction angle at $\theta = 17.80°$. Multi-peaks are clearly seen in the rocking curves of S1 and S2, while there is no obvious

shoulder-peak in the diffraction curve of S3. In addition, the full widths at half maximum (FWHM) of S1 and S2 are both much larger than that of S3. This implies that S1 and S2 each have a relatively poor quality crystalline structure compared with S3. Some defects such as micro-pipe, V_{Si}–V_C, dislocation, etc., may exist.[18,19]

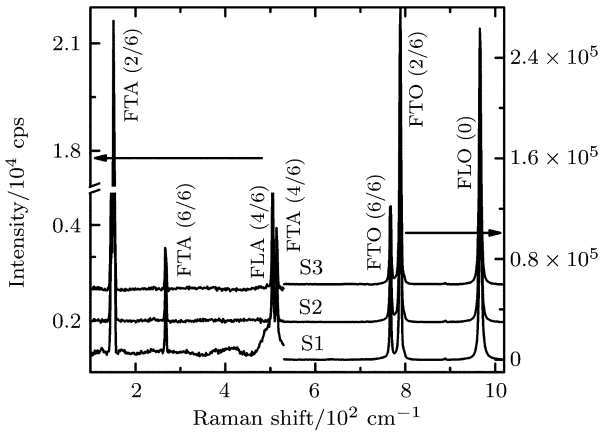


Fig. 2. Raman spectra of S1, S2, and S3.

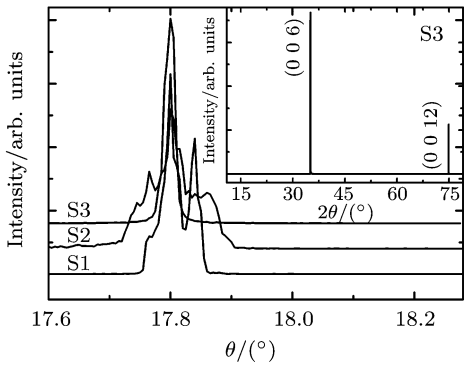


Fig. 3. HRXRD rocking curves of S1, S2, and S3, with the inset showing the survey curve of S3.

Figure 4 shows the normalized XAS spectra of S1, S2, and S3 in a photon energy range from 280 eV to 320 eV. For the carbon K edge absorption region, the excited photoelectrons show a transition from the core states (C 1s) to unoccupied final states (p-like final states above the Fermi level) according to the dipole-transition selection rule. Two regions can be divided into two subregions based on the XAS spectra: i) one is 280 eV to 285 eV, which contains peak A; ii) the other is 285 eV to 320 eV, which contains peaks B, C, D, E, and F. It can be seen that peak A is located at 284.8 eV. This is a typical π^* exciting resonance peak of a C=C chemical bond generally observed in graphite,[20] which is attributed to electron transition from 1s to anti-bonding states (sp^2 hybridization states). Peaks B, C, D, E, and F are located at 288.2 eV, 292.0 eV, 294.6 eV, 298.6 eV, and 302.8 eV, respectively. They are σ^* exciting resonance peaks and are attributed to electron transition from 1s to the anti-bonding states (sp^3 hybridization states) of a C–Si or C–V chemical bond.[21,22] Especially, there are 1s to σ^* transitions in C=C bounds contributing to the peak B and C in the latter region.[23] Compared with the XAS spectrum of S1, the XAS spectra of S2 and S3 show the peaks D, E, and F. This indicates that the number of σ^* empty orbitals is increased when the V dopants are introduced. In addition, the intensity of S2 is much stronger than that of S3, which means that the sp^3 hydration is reduced with the increase in V concentration.

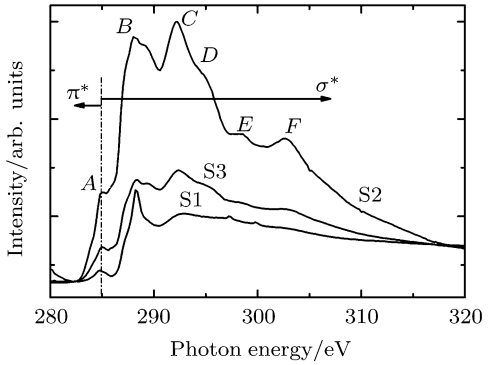


Fig. 4. XAS spectra of S1, S2, and S3.

The magnetic properties indicate that undoped SiC shows diamagnetism, while V-doped SiC exhibits ferromagnetic behaviour. The ferromagnetism coming from secondary phases such as metallic V, VC, and other compounds can be excluded from the V-doped SiC system. Thus we can conclude that the observed room-temperature ferromagnetism is the intrinsic property of the V-doped 6H–SiC. Carrier mediated double exchange and BMPs theories are often used to explain the ferromagnetism in ZnO- and III–V-based DMSs. The former is suitable for a high carrier concentration system, while the latter is often used for a low carrier density system. It is found that the resistivity and electron density of V-doped 6H–SiC single crystal is $> 1.0 \times 10^8$ Ω·cm and $< 1.0 \times 10^{15}$ cm^{-3}, respectively. Therefore, the V-doped SiC is a typical semi-insulating material and the ferromagnetic exchange cannot be mediated by free carriers. Maier *et al.*[24] and Bickermann *et al.*[25] reported that there exist three kinds of chemical valence states of V in a 6H–SiC single crystal: V^{3+}, V^{4+},

and V^{5+}. The outer cell electronic configurations of V^{3+}, V^{4+}, and V^{5+} are $3d^2$, $3d^1$, and $3d^0$, respectively. Hence, only V^{3+} and V^{4+} will make contributions to the ferromagnetic exchange. Although the V concentration of S2 is lower than that of S3, the saturation magnetization of S2 (lower V concentration) is larger than that of S3 (higher V concentration). This interesting result suggests that besides the V^{3+} and V^{4+} ions, other spin polarons may exist that contribute to the ferromagnetism in a V-doped SiC single crystal. Liu *et al.*[26] and Li *et al.*[27] reported that divacancies ($V_{Si}V_C$) will contribute to the ferromagnetism in the 6H–SiC single crystal. It is suggested that the defect state favours the formation of local moment and the extended tail of defect wave function makes the long-range spin coupling possible. In this paper, Raman and HRXRD studies indicate that the crystalline quality of S2 is worse than that of S3. It can be concluded that both the V dopants and defects are important for introducing ferromagnetic exchange into the V-doped SiC system.

4. Conclusion

Undoped and V-doped 6H–SiC single crystals were grown by the PVT method. Room-temperature ferromagnetism was observed in a V-doped SiC single crystal. The V-doped SiC shows semi-insulating behaviour with the resistivity $> 1.0 \times 10^8$ Ω·cm. The V concentrations are $< 5.0 \times 10^{13}$, 3.76×10^{17}, and 6.14×10^{17} at/cm^3 for undoped, low V-doped, and high V-doped SiC, respectively. Low V doping leads to stronger ferromagnetic behaviour, however, the crystalline quality characterizations measured by HRXRD and Raman spectroscopy indicate that low V doping has a relatively poor crystalline quality. It is found that both V dopants and defects are essential for introducing ferromagnetic exchange into the V-doped SiC single crystal, and the ferromagnetism may be mediated by defects. However, more efforts are necessary to clarify the relationship between ferromagnetism and defects in SiC-based DMS material.

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