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Divacancies induced ferromagnetism in 3C-SiC thin films

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ABSTRACT

3C-SiC thin films were prepared by atmospheric pressure chemical vapor deposition. We performed a study on the effect of C/Si ratio on ferromagnetic properties and microstructures of 3C-SiC thin films. The 3C-SiC thin films show ferromagnetic behavior within the scope of C/Si ratio in our study. An initial increase in C/Si ratio leads to the enhancement of magnetization, while further increasing C/Si ratio reduces the magnetization. The ferromagnetism is associated with divacancy concentration in 3C-SiC thin films. Our study reveals that the ferromagnetism of 3C-SiC thin films is stable at room temperature, and this may be helpful for clarifying the current controversy of the ferromagnetism origin in diluted magnetism semiconductor.

1. Introduction

In recent years, following the report by Ohno [1,2], researches on magnetic semiconductors have mainly focused on the diluted magnetic semiconductors, especially on the wide-band-gap semiconductors due to their potential applications in spintronic devices [3–6]. One general approach to realize ferromagnetism in semiconductor is lightly doping magnetic ions into the non-magnetic semiconductors [7–9]. The other approach is defect engineering through intentionally creating vacancy, which may give rise to magnetic moments [10,11]. Theoretically, Zunger et al. [10] suggested that vacancy could transform the nonmagnetic insulating wide-band-gap materials into ferromagnetic half-metals. Dev et al. [5] claimed that vacancy could induce intrinsic ferromagnetism in wide-band-gap III-Nitrides by employing density-functional theory. Silicon carbide is a wide-band-gap semiconductor which possesses excellent properties. However, the study on its ferromagnetic properties remains controversial [12,13]. Wang et al. [8] assumed that the ferromagnetism of 3C-SiC originated from the vacancy defects and could be tuned by vanadium carbide (VC) doping. Song et al. [7] attributed the ferromagnetism of Al-doped 4H-SiC to the sp^3/sp^2 hybridization. Moreover, local magnetic moments of V_{Si}–V_C divacancies were regarded as the origin of ferromagnetism in neutron bombarded 6H-SiC [13] Therefore, it is necessary to further investigate the ferromagnetism in SiC materials. In this study, we demonstrate pronounced ferromagnetism in undoped 3C-SiC thin films. The ferromagnetism origin is defect-related and it can be adjusted by changing divacancy concentration through altering the C/Si ratio.

2. Experimental

The 3C-SiC thin films were grown by a horizontal cold-wall atmospheric pressure chemical vapor deposition (CVD) system. The system includes an 86 mm diameter quartz reactor and a SiC-coated graphite susceptor heated by a radio frequency induction power supply. The on-axis p-type Si(1 0 0) with a size of 4 cm × 2 cm was used as substrate. Propane (C_3H_8, 1% diluted in H_2) and silane (SiH_4, 2% diluted in H_2) were used as the precursors and high purity hydrogen (H_2, > 99.99999%) was used as carrier gas. Before the growth of 3C-SiC thin film, Si substrate was in-situ etched by a mixture gas of H_2/HCl and deposited an ultra thin carbon buffer layer. All of the samples were grown at 1350 °C using 0.8 sccm SiH_4 in order to keep the same thickness of 3C-SiC thin film. The propane/silane ratio is denoted by C/Si which means the ratio of C atom to Si atom in C_3H_8 and SiH_4. The C/Si ratio is changed from 1.6 to 3.2 by varying the C_3H_8 flow rate with a constant SiH_4 flow rate.

The film thickness was characterized by cross-sectional scanning electron microscope (SEM, S-4800, Hitachi). The impurity concentration was detected by proton induced X-ray emission (PIXE, 2 MV tandem accelerator, Beijing Normal University) using a 2.5 MeV proton beam. The structure and crystallization quality

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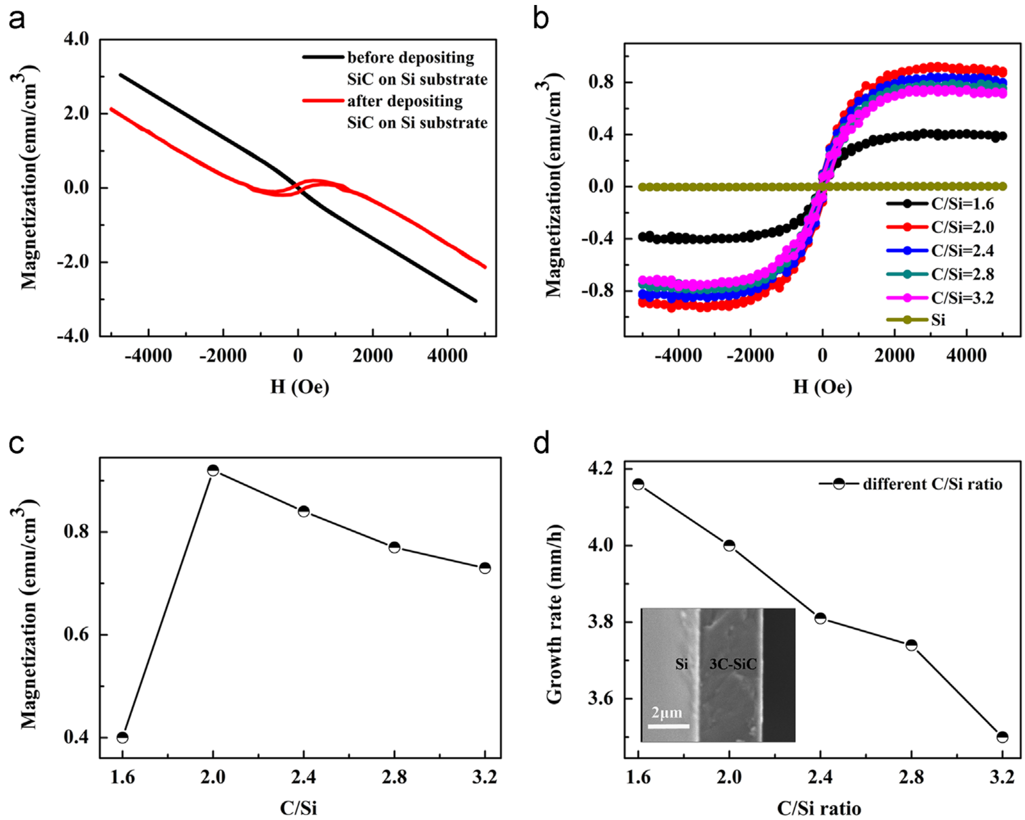

Fig. 1. (a) Magnetic hysteresis loop without subtracting the diamagnetic contribution for carbon coated Si substrate before and after depositing 3C-SiC thin films (C/Si=2.0). (b) Room-temperature hysteresis loops of 3C-SiC thin films deposited at different C/Si ratio. (c) Saturation magnetization as a function of C/Si ratio. (d) Growth rate as a function of C/Si ratio. The inset shows cross-sectional SEM image of 3C-SiC thin films for C/Si=3.2.

were characterized by high resolution X-ray diffraction (HRXRD, D8 DISCOVER, Bruker AXS) with Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å), transmission electron microscopy (TEM, Tecnai G2 F20) and micro-Raman spectroscopy (InVia Raman microscope, Renishaw) using a 514 nm excitation laser in back scattering configuration, respectively. The magnetic properties were measured by a superconducting quantum interference device (SQUID, MPMS-5, Quantum Design) which features a sensitivity of 10^{-8} emu. The state of electron spin was analyzed by electron paramagnetic resonance spectrometer (EPR, JEOL, JES-FA200). The defects in 3C-SiC were measured by photoluminescence (PL, LabRAM HR 800, Jobin Yvon) using a He-Cd laser with a line at 325 nm. The carriers concentration was characterized by using a Hall effect measurement system (Hall, LakeShore, 7704A).

3. Results and discussions

Fig. 1(a) shows the room temperature Magnetic hysteresis loop without subtracting the diamagnetic contribution for carbon coated Si substrate before and after depositing 3C-SiC thin films (C/Si=2.0). Only diamagnetic feature can be observed for carbon coated Si substrate before depositing SiC, while a clear hysteresis loop can be seen after depositing 3C-SiC thin film (C/Si=2.0). The diamagnetic feature is becoming weaker with increasing the applied field. Fig. 1(b) displays the magnetization curves of 3C-SiC thin films at different magnetic field, where the diamagnetic background has been subtracted from the raw data. It can be seen that all the 3C-SiC thin films show obvious ferromagnetic behavior. The saturation magnetization (M_s) does not monotonously increase with the increase in C/Si ratio. The M_s sharply rises with the C/Si ratio is increased from 1.6 to 2.0 and reaches a maximum value of 0.84 emu/cm^3, then it drops with further increase in C/Si ratio. The relationship between M_s and C/Si is quite clearly shown in Fig. 1(c). It should be noticed that the growth rate is reduced with increasing the C/Si ratio, as shown in Fig. 1(d). In order to reduce the effect of thickness on the crystalline quality, all the 3C-SiC thin films were deposited with a constant thickness of ~3 μm at different C/Si ratio by controlling the growth time, as shown in the inset of Fig. 1(d).

Table 1
Main impurities contained in the 3C-SiC thin film[a].

Cu (ppm)[b]	Cr (ppm)[b]	Mn (ppm)[b]	Fe (ppm)[b]	Co (ppm)[b]	Ni (ppm)[b]	Ti (ppm)[b]
~[c]	5	~[c]	2	~[c]	~[c]	2

[a] Same results for the other samples.
[b] Measured by PIXE.
[c] Below the detection limit.

PIXE is an effective non-destructive method to characterize impurities with a detection limit of ppm. The impurities that may induce ferromagnetism was excluded by PIXE, as shown in Table 1. It can be seen that the impurity of Cr, Fe, Ti is less than 5 ppm, while other magnetic impurities (i.e. Mn, Co, Ni, et al.) that can be responsible for extrinsic ferromagnetism is below the detection limit of PIXE. For the 3C-SiC sample with the Fe impurity of 2 ppm, the maximum ferromagnetic contribution from Fe impurity is about 3.6×10^{-5} emu/cm^3 (presume all the Fe atoms form one particle of Fe_3O_4 and M_s=92 emu/g for bulk Fe_3O_4), which is negligible for the bulk 3C-SiC thin films with the magnetic moment of ~emu/cm^3. Thus, it is confirmed that the ferromagnetic properties of 3C-SiC thin films is intrinsic property and cannot be caused by magnetic impurities.