Thin-film ferromagnetic semiconductors based on $Sb_{2-x}V_xTe_3$ with T_C of 177 K

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Thin-film ferromagnetic semiconductors $Sb_{2-x}V_xTe_3$ with the Curie temperature as high as 177 K were prepared on sapphire (0001) substrates by molecular-beam epitaxy. Films of $Sb_{2-x}V_xTe_3$ with x up to 0.35 display robust, out-of-plane ferromagnetic ordering that depends on the concentration of vanadium in the structure. The Curie temperature was determined from magnetization measurements and Arrott plots. Ferromagnetic order is manifested by hysteresis loops observed in magnetization, magnetoresistivity, and the anomalous Hall effect. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2045561]

By combining charge and spin degrees of freedom, dilute magnetic semiconductors (DMSs) have attracted considerable interest both for their intrinsic scientific value as well as for their potential spintronics applications. A wide variety of semiconductors has been screened for their ability to support a long-range magnetic order. These include II-VI,[1,2] IV-VI,[3,4] and III-V compounds doped with transition metals such as Mn and Cr.[5,6] Among these, by far the greatest attention has focused on the low-temperature molecular-beam-epitaxy (MBE)-grown GaAs films doped with Mn wherein, after nearly a decade-long intensive effort, the Curie temperature has reached about 170 K.[7,8] Achieving magnetic ordering above the ambient temperature, the necessary prerequisite for practical applications of DMSs, has been reported for certain transition metal-doped III-V nitrides,[9,10] $Zn_{1-x}Cr_xTe$,[2] and transition metal-doped oxides.[11–13] However, these results are critically sensitive on the details of the synthesis process and often it is not clear whether the magnetic state is intrinsic or the result of some secondary phase formation that happens to be magnetic.

Over the past three years, we and others have reported on the ferromagnetic state developing in certain bulk tetradymite-type $A_2^{V}B_3^{VI}$ $(A=\mathrm{Bi},\mathrm{Sb};B=\mathrm{Te})$ semiconductors when doped with Cr, Fe, and V.[14–16] Specifically, we have shown that bulk single crystals of $Sb_{2-x}V_xTe_3$ $(x\leqslant 0.03)$ and $Sb_{2-x}Cr_xTe_3$ $(x\leqslant 0.06)$ are ferromagnetic at temperatures up to 22 K, while $Sb_{2-x}Mn_xTe_3$ crystals remained merely paramagnetic in spite of the Sb_2Te_3 matrix accommodating in excess of $x=0.04$ of Mn.[17] Taking a hint from the work on $Ga_{1-x}Mn_xAs$, where a robust ferromagnetic state sets in only when the structure is prepared as a thin film (via a low-temperature MBE growth) and the solubility of Mn is greatly enhanced in comparison to its content in the bulk doped gallium arsenide, we have decided to prepare thin films of $Sb_{2-x}V_xTe_3$ with the hope of significantly enhancing the solubility of vanadium and thus extending the ferromagnetic ordering to much higher temperatures.

$Sb_{2-x}V_xTe_3$ thin films were grown by MBE on sapphire (0001) substrates. Growth rate of 1.7–1.8 Å/s was used for all samples with a fixed flux ratio $(\mathrm{Sb},\mathrm{V}):\mathrm{Te}=1:2$ at a substrate temperature of 310 °C. A miniature e-beam evaporator was used for the deposition of vanadium and the Knudsen cells for antimony and tellurium. The reflection high-energy electron diffraction patterns indicate that the films grow with their c axis perpendicular to the plane of the substrate and streak-like diffraction attests to a near two-dimensional mode of film growth. Films were subsequently analyzed by x rays and microprobe to confirm their tetradymite-type crystal structure, stoichiometry, and the content and homogeneity of vanadium. Only $(000.n)$ peaks in the hexagonal unit cell are present in the x-ray diffraction patterns, confirming that the films grow parallel to the c-axis direction. No trace of any secondary phase formation was detected in the x-ray diffraction scans. The preparation details can be found elsewhere.[18]

Magnetization measurements were done in a Quantum Design superconducting quantum interference device-based magnetometer equipped with a 5.5 T magnet. Great care was taken when extracting the magnetization data of the film samples. The magnetizations of the sapphire substrate as well as the plastic straw holder were measured separately and their contributions were subtracted from the raw data. Figure 1 shows the temperature-dependent magnetization of $Sb_{2-x}V_xTe_3(x=0.15,0.32,0.35)$ thin films during field cooling from 300 to 2 K in the field of 500 Oe applied parallel to the c axis of the films (parallel to the growth direction). Sharp upturns on the curves indicate the development of spontaneous magnetization. The arrows in Fig. 1 mark the

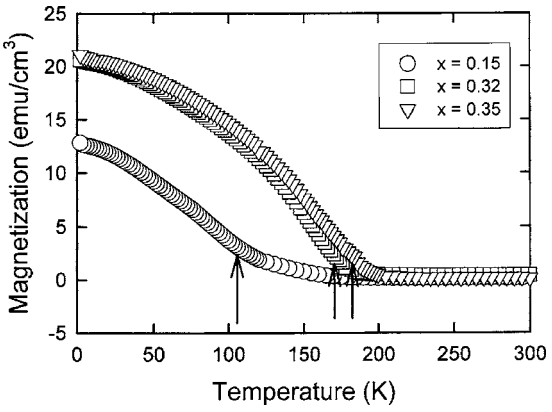

FIG. 1. Temperature-dependent magnetization of $Sb_{2-x}V_xTe_3$ thin films during field cooling in 500 Oe from 300 to 2 K. The magnetic field is applied parallel to the c axis of the films. The thicknesses are 170, 520, and 480 nm for films with $x=0.15$, 0.32, and 0.35, respectively.

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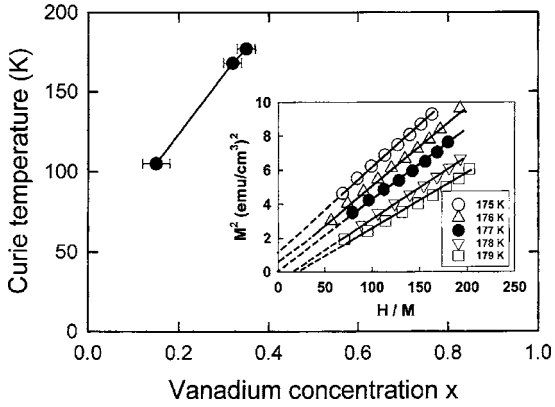

FIG. 2. Ordering temperature of $Sb_{2-x}V_xTe_3$ thin films as a function of the vanadium concentration x. The error bars indicate an uncertainty in the content of vanadium. The inset shows the Arrott plot for thin-film sample $Sb_{1.65}V_{0.35}Te_3$ that yields the ordering temperature of 177 K.

inflection points on the curves that are usually taken as temperatures where the structure orders magnetically. Fitting the high-temperature susceptibility data to the Curie-Weiss law, we obtained the (paramagnetic) Curie temperatures of 110, 171, and 182 K for $x=0.15$, 0.32, and 0.35, respectively. We use Arrott plots to pinpoint the value of the ordering temperature T_C since the effect of magnetic anisotropy and domain rotation can be minimized.[19] As an example, the inset in Fig. 2 shows the Arrott plot for sample $Sb_{1.65}V_{0.35}Te_3$ around T_C. It yields a transition temperature of 177 K, which is 5 K less than the value obtained from the high-temperature susceptibility results. Arrott plots yield T_C of 104, 168, and 177 K for $x=0.15$, 0.32, and 0.35, respectively. The dependence of the ordering temperature on the vanadium concentration is shown in Fig. 2 and indicates a linear trend. The data suggest that even higher values of the ordering temperature may be possible if one can further increase the concentration of vanadium.

Figure 3 shows the field dependence of the magnetization of $Sb_{1.65}V_{0.35}Te_3$ measured at 2 and 160 K. The demagnetizing field with a demagnetizing factor of 1 in the films was subtracted from the applied magnetic field in the M-H plot. Well developed hysteresis loops are seen at both temperatures, although the coercive field has decreased from 1685 Oe to about 10 Oe as the temperature was raised from 2 to 160 K. Smooth hysteresis loops indicate a well-ordered ferromagnetic structure and coherent rotation of spins in the films. Equally robust and well developed hysteresis loops were observed on other vanadium-doped Sb_2Te_3 films except

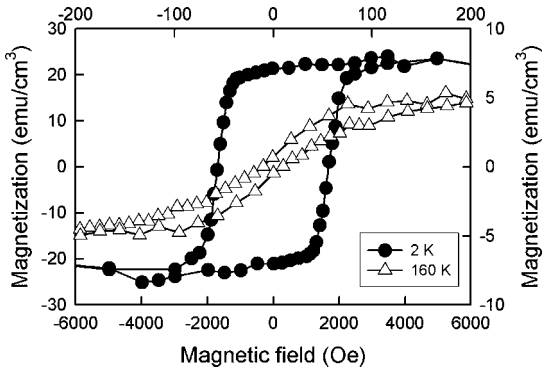

FIG. 3. Hysteresis loops obtained on the $Sb_{1.65}V_{0.35}Te_3$ film at 2 and 160 K.

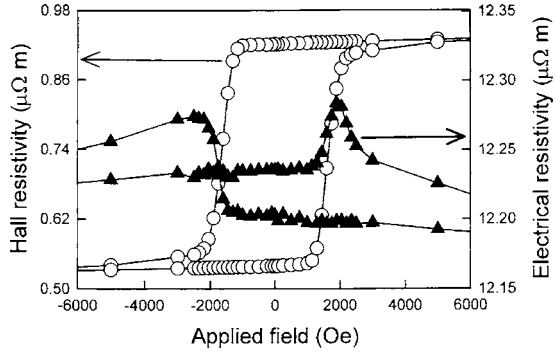

FIG. 4. Hysteresis loops in the Hall effect and magnetoresistance observed at 2 K on a film with the composition $Sb_{1.65}V_{0.35}Te_3$.

that their coercive fields and critical temperatures were different, corresponding to the different contents of vanadium.

The ferromagnetic state in $Sb_{2-x}V_xTe_3$ films was further confirmed by anomalous Hall effect and magnetoresistivity hysteresis measurements. Figure 4 shows the magnetic-field-dependent Hall resistivity and magnetoresistivity of $Sb_{1.65}V_{0.35}Te_3$ at 2 K. Both the electrical resistivity and Hall resistivity were measured with the field parallel to the c axis and the excitation current applied perpendicular to the c axis. Peaks in the magnetoresistance occur at magnetic fields that correspond to zero magnetization (coercive field) and therefore maximum spin disorder in the structure. The Hall resistivity in magnetic materials is expressed as[20]

$$\rho_H = R_0 B + R_M M, \tag{1}$$

where R_0 is the ordinary Hall coefficient, B is the magnetic field, R_S is the anomalous Hall coefficient, and M is the magnetization of the sample. While the ordinary Hall effect dominates at high fields, as seen by the linear dependence of ρ_H with B, the anomalous Hall effect dominates at low field due to the contribution from the magnetization. Hysteresis in both magnetoresistance and the Hall effect is detectable to within a couple of degrees of T_C.

In summary, we have prepared $Sb_{2-x}V_xTe_3$ films with x varying from 0 to 0.35 by MBE. Ferromagnetism that extends to temperatures of at least 177 K was found and confirmed by magnetization, magnetoresistance, and anomalous Hall effect measurements.

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