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The influence of alloying GeTe with Sn and Mn on magnetic interactions and magnetotransport effects

ABSTRACT

Over the past several decades, rapid development based on metal-spintronics (utilizing both charge and spin of the carriers) has seen massive efforts which are associated with the detection of giant magnetoresistance phenomenon in thin metallic films [1,2]. Among a number of applications, several apparent uses are magnetic hard drives, random-access magnetic memories [3,4], race-track memories [5], spin-transfer nanooscillators [6], and many others. The pursuit to develop materials based on ferromagnetic semiconductors which could realize highly desirable semiconductor spintronic applications at room temperature has witnessed extensive research efforts. In addition to its metallic counterparts, semiconductor spintronics research is very promising due to several reasons e.g. spin-coherence times at room temperature are remarkably long and about three times longer in semiconductor spintronics than in metallic spintronics devices [7], motion of the spin-density packets in semiconductors is faster comparative to metals [8], electrical control of the ferromagnetic order is possible in semiconductors [9], among several others. The family of diluted magnetic semiconductors in which paramagnetic magnetic ions such as Mn are incorporated into semiconducting lattice was first coined in the mid twentieth century to integrate the electrical and magnetic characteristics of distinct materials into a common $A^{II}MnB^{VI}$ solid solution [10–12]. This was an important step towards inducing magnetic ordering in the semiconductor lattice via randomly placed Mn ions which would eventually lay foundation of semiconductor spintronics. This new materials design pioneered a vast research playground which rapidly expanded to state of the art compositions such as (II-VI) $Cd_{1-y}Mn_yTe$ [13], (III-V) $Ga_{1-y}Mn_yAs$ and $In_{1-y}Mn_yAs$ films [14,15], and others. In addition, the wide-gap (II-VI) and (III-V) oxides/nitrides incorporated with transition metals, e.g. $Zn_{1-y}Mn_yO$ [16] and $Ga_{1-y}Mn_yN$ [17], respectively, were developed. Apart from the above mentioned materials, the discovery of ferromagnetism in Mn doped narrow bandgap IV-VI semiconductors such as $Pb_{1-x-y}Sn_xMn_yTe$ [18], $Ge_{1-y}Mn_yTe$ [19] and $Sn_{1-y}Mn_yTe$ [20] provided more possibilities in regard to semiconductor spintronics research. One of the major milestones in regard to room temperature semiconductor spintronics has been the development of epitaxial growth of thin films such as $Ga_{1-y}Mn_yAs$ with ferromagnetic Curie temperature, $T_C \approx 200$ K obtained for these samples processed with the use of nanostructure patterning [21]. In addition, $Ge_{1-y}Mn_yTe$ epitaxial thin films have achieved ferromagnetic

Curie temperature, T_C = 200 K for y = 0.5 which makes this IV-VI material very promising candidate for room temperature semiconductor spintronics [22].

In addition to ferromagnetic order, certain representatives of IV-VI materials with narrow bandgap, E_g such as GeTe ($E_g \approx 0.6 - 0.7$ eV) [23,24] and SnTe ($E_g \approx 0.18$ eV) [25] hold superior characteristics such as spontaneous ferroelectricity for GeTe occurring below $T \approx 720$ K that arises from low symmetry rhombohedral phase [24], whereas for layered SnTe, ferroelectric critical temperature was enhanced from $T \approx 98$ K to room temperature [26], topological edge states were observed in SnTe [27], high temperature thermoelectric features of SnTe [28] and GeTe [29] are important from applications point of view, and control of spin-texture via ferroelectric polarization was achieved [30]. Owing to the above exciting features, IV-VI semiconductors alloyed with magnetic ions offer a wide range of possibilities to realize energy efficient semiconductor candidates for spintronics. Furthermore, the combination of ferromagnetic and ferroelectric orders can lead to Zeeman splitting and Rashba type splitting effects, respectively in a single system [31]. Therefore, diluted magnetic semiconductors such as $Ge_{1-x-y}Sn_xMn_yTe$ studied in this thesis offer exciting possibilities towards spectacular discoveries related to the interplay between electronic states, spin/orbital degrees of freedom, and coupling between ferroelectric and ferromagnetic orders [31].

In this thesis, comprehensive structural characterizations followed by state of the art magnetic and magnetotransport investigations of $Ge_{1-x-y}Sn_xMn_yTe$ crystals were executed. The foremost purpose of this thesis was centered on studying and tuning the magnetic order induced by paramagnetic "Mn" and diamagnetic "Sn" ions, low temperature charge scattering and localization phenomena. The increase of Sn content in $Ge_{1-x-y}Sn_xMn_yTe$ crystals caused transition from polar rhombohedral (R3m) symmetry distorted along $\langle 111 \rangle$ direction to coexistence of rhombohedral + rock salt (Fm-3m) phases and eventually to pure (Fm-3m) phase for high contents of Sn and Mn ions. In the low concentration limits of $y \leq 0.04$, the crystals behave like paramagnet down to liquid helium temperature. In the Sn-rich regime, $Ge_{1-x-y}Sn_xMn_yTe$ crystals demonstrated large variation in the nature of magnetic ordering. A magnetically disordered state depicting properties close to a canonical spin-glass was observed in the intermediate level of $y \approx 0.05$, cluster-glass state for $0.052 \leq y \leq 0.07$, and ferromagnetic order for higher Mn contents was observed. The appearance of a cluster-glass state can be justified by phenomenological laws using both static and dynamic magnetometric results. The spin-dynamics and potential barrier analysis demonstrate that the cluster-glass state constitute small size frozen ferromagnetic-like clusters with spin relaxation time just above the spin-glass limit. Double maxima in dynamic magnetic susceptibility observed for the crystal with $x \approx 0.2$, $y = 0.06$ manifested frequency dependent maximum at $T \approx 21.5$ K which shifts to higher values as frequency increases. The second maximum at $T \approx 8$ K is independent of variation in the frequency of the applied magnetic field. The frequency independent maximum might be attributed to ferromagnetic-like clusters. This variation in the behavior of susceptibility maxima over a few Kelvins reflects that the magnetic clusters might be of different sizes. The magnetic clusters switch from small (frequency dependent maximum) to comparatively large size which opposes any change in the susceptibility maximum on the temperature scale with frequency variation. Apart from that, the sublinear dependence of effective magnetic moment, μ_{eff} on the Mn concentration suggests that the tuning of magnetic interactions is influenced by both Mn and Sn contents. The appearance of ferromagnetic-like Mn clusters is responsible for the slow spin dynamics in the Sn rich crystals when a large fraction of Ge is replaced by Sn.

In the second part of the thesis, the magnetotransport studies of $Ge_{1-x-y}Sn_xMn_yTe$ crystals are presented in the temperature range, $T \approx 1.6 - 300$ K, as a function magnetic field up to $|H| = 130$ kOe. The scattering mechanisms responsible for temperature dependence of resistivity, $\rho_{xx}(T)$, and hole mobility, $\mu_h(T)$, are analyzed. For $Ge_{1-x-y}Sn_xMn_yTe$ crystals, the $\rho_{xx}(T)$ results take contributions from mixed scattering mechanisms such as phonons and polarons. Also, the $\mu_h(T)$ curves reveal phonon scattering of carriers with polar lattice optical modes with possible polaron-induced scattering at high temperatures. From high field magnetotransport data, the anomalous Hall resistivity is discussed with a modified scaling law to separate the residual and temperature dependent scattering mechanisms. Such analysis allows distinguishing between the parameters resulting from residual and phononic scattering processes related to skew scattering, and quadratic term emanating from side jump/intrinsic mechanism which cannot be obtained using conventional scaling.