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Ferromagnetic transition in $Ge_{1-x}Mn_xTe$ semiconductor layers

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Magnetic properties of thin layers of p-$Ge_{1-x}Mn_xTe$ ($x < 0.2$) semimagnetic (diluted magnetic) semiconductor exhibiting carrier induced ferromagnetism were experimentally studied. The layers were grown on BaF_2 (111) substrates by molecular beam epitaxy technique. X-ray diffraction analysis performed at room temperature revealed monocrystalline (111)-oriented rhombohedral (exhibiting ferroelectric properties) crystal structure of $Ge_{1-x}Mn_xTe$ layers in the entire range of Mn content studied. The examination of the magnetic properties of the layers carried out by superconducting SQUID magnetometry and ferromagnetic resonance technique showed the ferromagnetic transition with the Curie temperature in the range 10–100 K depending on the Mn content and the hole concentration. Contrary to polycrystalline GeMnTe layers, it was experimentally found that in monocrystalline layers of GeMnTe an easy magnetization axis is directed along a normal to the layer plane. This effect is discussed in terms of strain present in these layers due to thermal expansion coefficients mismatch between the substrate and the GeMnTe layer.

Key words: *ferromagnetic transition; thin layer; semimagnetic semiconductor*

1. Introduction

$Ge_{1-x}Mn_xTe$ mixed crystals are substitutional solid solutions from the family of IV–VI semimagnetic (diluted magnetic) semiconductors [1, 2]. These materials exhibit ferromagnetic transition induced by a very high conducting hole concentration ($p = 10^{19}$–10^{21} cm^{-3}) [1–6]. Very high carrier concentration and the metallic type of electrical conductivity observed in GeMnTe crystals is related to non-stoichiometric crystal composition and high concentration of electrically active native defects (cation vacancies) [1, 2]. Ferromagnetism of GeMnTe is driven by the Ruderman–Kittel –Kasuya–Yosida (RKKY) indirect exchange interaction between well localized $S = 5/2$ magnetic moments of Mn^{2+} ions (electronic configuration $3d^5$) and conducting carriers with the p–d exchange constant $J_{pd} = 0.6$–0.8 eV [4, 5]. In this material,

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a ferroelectric structural transition from the rock salt (high temperature) to the rhombohedral (low temperature, ferroelectric) phase takes place [2, 4]. Upon increasing the Mn content in $Ge_{1-x}Mn_xTe$ crystals, the ferromagnetic transition temperature increases (up to 150 K for $x = 0.5$) while the ferroelectric transition temperature decreases (670 K for GeTe while 300 K for $x = 0.2$) [4]. It offers a unique possibility to realize various temperature scenarios for both transitions.

So far, $Ge_{1-x}Mn_xTe$ alloys have been mostly studied in the form of quenched bulk polycrystals [3, 4] and thin layers grown by either sputtering [5] or ionized cluster beam deposition method [6] of crystal quality not sufficient for the experimental investigations of the interplay of structural (ferroelectric) and ferromagnetic transitions. In this work, we experimentally study the magnetic properties of thin monocrystalline layers of $Ge_{1-x}Mn_xTe$ grown by molecular beam epitaxy (MBE) as well as analyze the relation between the structural and magnetic properties of the layers.

2. Growth, structural and electrical characterization of layers

$Ge_{1-x}Mn_xTe$ layers were grown by home-built MBE facility on freshly cleaved (111) surface of BaF_2 single crystals using effusion cells for GeTe (material purity 5N), Mn (5N), and Te (5N). The growth of $Ge_{1-x}Mn_xTe$ layers was performed under various technological conditions with substrate temperature of about 400-450 °C and pressure during deposition of about 10^{-8} mbar. The thickness of $Ge_{1-x}Mn_xTe$ layers was typically about 0.25 μm. The maximum content of Mn in $Ge_{1-x}Mn_xTe$ was 20 at. % as checked by energy dispersive X-ray fluorescence analysis, while the typical content of Mn in a set of about 30 samples grown for this study was approximately 5–10 at. %. The growth of the $Ge_{1-x}Mn_xTe$ layers was monitored *in situ* by the reflection high energy electron diffraction (RHEED) technique revealing well defined, streaky pattern characteristic of two-dimensional mode of growth. Oscillations of the intensity of specular spot of RHEED diffraction pattern were not observed.

Post-growth, the layers were characterized by X-ray diffraction (XRD) analysis at room temperature revealing the monocrystaline (111)-oriented rhombohedral (ferroelectric) crystal structure of $Ge_{1-x}Mn_xTe$ in the entire range of Mn content studied. The relatively small width of the X-ray rocking curve (100–600 arcsec) observed in $Ge_{1-x}Mn_xTe$ layers proves their good crystalline quality. XRD measurements showed a linear decrease of GeMnTe lattice parameter with an increase of Mn content, in a good agreement with the Vegard law reported in literature for bulk polycrystals [4] and thin layers [5]. Chemical homogeneity of the alloy was examined by secondary ion mass spectroscopy (SIMS), while surface morphology analysis performed by AFM microscopy revealed RMS roughness parameter of 1–10 nm over 10×10 micron area. For electrical characterization of p-type $Ge_{1-x}Mn_xTe$, the standard four-probe dc Hall effect measurements were carried out at room temperature and liquid nitrogen temperature revealing, as expected, very high ($p = 10^{19}$–10^{21} cm^{-3}) hole concentration in $Ge_{1-x}Mn_xTe$ layers.

3. Magnetic properties

The examination of the magnetic properties of $Ge_{1-x}Mn_xTe$ layers was carried out in a broad temperature range of T = 1.9–200 K by superconducting SQUID magnetometry and ferromagnetic resonance (FMR) measurements. Figure 1 shows the temperature dependence of magnetization of $Ge_{1-x}Mn_xTe$ (x = 0.15) layer, exhibiting ferromagnetic transition with the Curie temperature of about 16 K. Magnetic hysteresis loops for the same layer are presented in Fig. 2 and are characterized by coercive field and saturation field (at T = 5 K) of about 100 Oe and 1 kOe, respectively. Both measurements clearly indicate that an easy magnetization axis in GeMnTe layers is directed along normal to the layer plane. This experimental finding is also confirmed by ferromagnetic resonance analysis of magnetic anisotropy in GeMnTe layers. The FMR spectra shown in Fig. 3 reveal that the resonance field is lower for external magnetic field applied along normal to the layer (as compared to the field in-plane case). For regular thin ferromagnetic layer with in-plane easy axis (determined by shape anisotropy), the opposite effect is typically observed (i.e., the FMR resonance field is higher for out-of-plane configuration of external magnetic field due to large demagnetization effects).

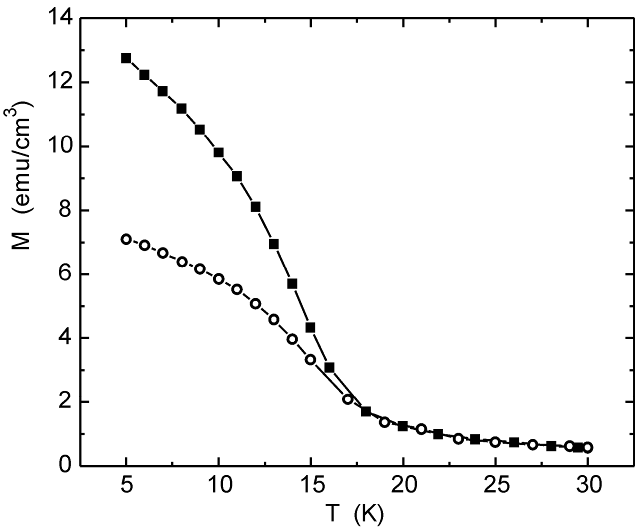

Fig. 1. Temperature dependence of magnetization of $Ge_{1-x}Mn_xTe$ (x = 0.15) layer. External magnetic field of 100 Oe applied perpendicular (full squares) and parallel (open circles) to the plane of the layer

In a set of about 30 $Ge_{1-x}Mn_xTe$ ($x<0.2$) layers studied so far, ferromagnetic transition was found in the temperature range of T = 10–100 K depending on Mn content and hole concentration. However, for the layers with the highest Curie temperatures a very broad transition region is observed with quasi-linear temperature dependence of magnetization below the transition point. This indicates an insufficient electrical or chemical homogeneity of these layers. This is also confirmed by a large (up tp 1 kOe) line width of the FMR in GeMnTe layers. To solve this problem, additional technological steps (annealing in MBE vacuum chamber or post-growth isothermal annealing in Te atmosphere) can be applied.

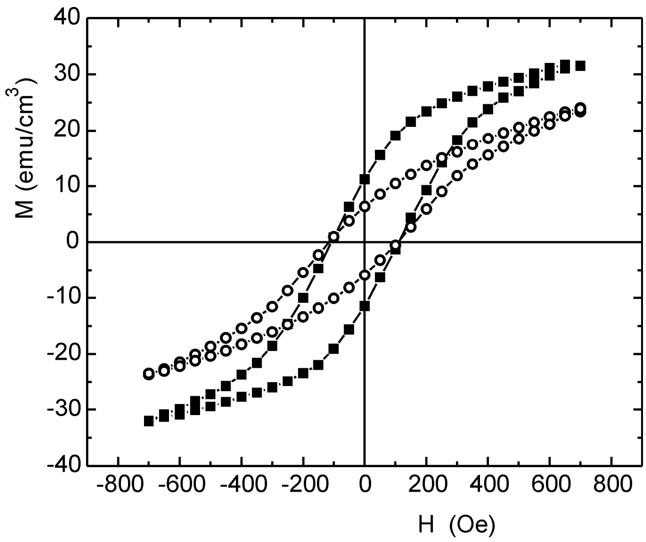

Fig. 2. Magnetic hysteresis loops of $Ge_{1-x}Mn_xTe$ ($x = 0.15$) layer at 5 K. External magnetic field applied perpendicular (full squares) and parallel (open circles) to the plane of the layer

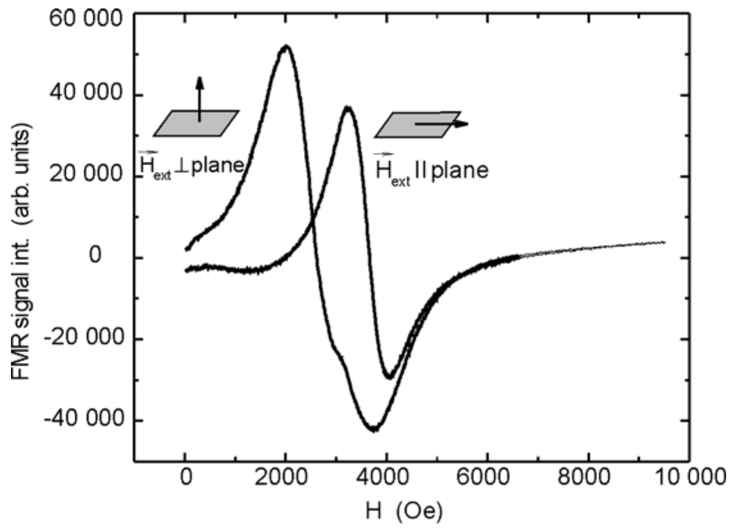

Fig. 3. X-band ferromagnetic resonance spectrum of $Ge_{1-x}Mn_xTe$ ($x = 0.1$) layer for two configurations of the external magnetic field with respect to the layer plane (shown in the figure)

4. Discussion and conclusions

The experimentally observed larger magnetization for the out-of-plane configuration of external magnetic field (as compared to the in-plane case), as well as the results of the FMR anisotropy study, provide evidence that in GeMnTe epitaxial layers grown on BaF_2 substrates the shape (dipolar) contribution to magnetic anisotropy is dominated by other mechanism minimizing the total magnetic energy of the layer for the magnetization vector directed normally to the plane of the layer (i.e., along [111] crystal growth direction). Although in GeMnTe crystal lattice all four [111] crystal directions are equivalent, the effect of thermal strain is expected to remove this degeneracy in epitaxial layers grown on BaF_2 (111) and preferentially select [111] direction normal to the layer. The effect of thermal strain is well known in the studies of optical, magnetic and transport properties of IV–VI semiconductors grown on BaF_2 (111) substrate [1, 2]. It originates from the difference of thermal expansion coefficients of the substrate and the layer (the expansion in the layer is larger than that in the substrate) and is expected to generate tensile strain in the plane of the layer (accompanied by compressive strain normal to the layer as given by Poisson coefficient) [1, 2]. One may also expect that the rhombohedral ferroelectric distortion along [111] directions taking place in these layers above room temperature will result in a single [111] ferroelectric domain structure. The experimental identification of the actual mechanism of this effect as well as the development of the microscopic model of the coupling between local distortion of the crystal lattice and magnetic moment of Mn ions will be the subject of further research in this field.

In conclusion, the magnetic properties of monocrystalline layers of semimagnetic (diluted magnetic) $Ge_{1-x}Mn_xTe$ ($x < 0.2$) semiconductors grown by molecular beam epitaxy on BaF_2 (111) substrates were studied by SQUID magnetometry and ferromagnetic resonance technique revealing ferromagnetic transition related to very high concentration of conducting holes. Magnetic hysteresis loops and ferromagnetic resonance analysis showed in these layers an easy magnetization axis directed along normal to the layer plane. This experimental finding was analyzed in relation to lattice distortions brought about in GeMnTe epitaxial layers by the strain induced by thermal expansion coefficients mismatch between the GeMnTe layer and the BaF_2 (111) substrate as well structural (ferroelectric) rhombohedral distortion of the rock salt lattice.

Acknowledgements

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