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$Zn_{1-x}(Mn,Co)_xGeAs_2$ Ferromagnetic Semiconductor: Magnetic and Transport Properties

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We present the studies of magnetic and transport properties of the bulk $Zn_{1-x}(Mn,Co)_xGeAs_2$ mixed crystals with $0.052 \leq x \leq 0.182$ grown using direct fusion method. Magnetic investigations showed that for samples with $x \geq 0.078$ we observed a behavior typical of ferromagnets, with the Curie temperatures $T_C \geq 300$ K. The observed ferromagnetism was probably connected with the spinodal decomposition of the Mn ions in the alloy. The transport studies including resistivity and Hall effect (at $B = 1.4$ T) were performed. The samples showed p-type conductivity with semiconducting or metallic character, depending on the alloy composition. The Hall carrier concentration, $p \geq 10^{18}$ cm^{-3}, was composition dependent.

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1. Introduction

The semiconductors showing ferromagnetic ordering at room temperature turned on large interest in the last several years due to the possibility to utilize them in the future spintronic devices [1]. The most intensively studied diluted magnetic semiconductor (DMS) was $Ga_{1-x}Mn_xAs$ with the Curie temperatures

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much lower than $T = 300$ K (maximum $T_C \approx 173$ K [2]). However, there exists a class of semiconductors with the Curie temperatures exceeding 300 K. This class consists of a several chalcopyrite II–IV–V_2 DMS such as $Cd_{1-x}Mn_xGeP_2$ (T_C = 320 K [3]) and $Zn_{1-x}Mn_xSnAs_2$ (T_C = 329 K [4]) with the Curie temperatures exceeding room temperature.

In this paper we studied the magnetic and transport properties of the chalcopyrite $Zn_{1-x}(Mn,Co)_xGeAs_2$ alloy. The nonmagnetic equivalent of the studied system, namely $ZnGeAs_2$, has many interesting properties. The nondegenerate top of the valence band makes this compound a possible efficient source of the spin polarized photoelectrons [5]. Large nonlinear optical coefficients were found in this system [6] and a direct energy gap of $E_g = 1.15$ eV (at room temperature) at the Γ-point of the Brillouin zone [7] makes this material suitable for the applications in the nonlinear optics. The $ZnGeAs_2$ compound seems to be lattice matched with GaAs [8], which makes this material compatible with existing technology. In our earlier work [9] we reported preliminary results obtained for $Zn_{1-x}Mn_xGeAs_2$ alloy with $x \geq 0.078$. We reported there the highest obtained Curie temperature $T_C = 367$ K (sample with $x = 0.182$) for this class of compounds. In this work we extended our studies to a larger range of magnetic ion content in order to shed light on the origin of the magnetic and transport properties of the investigated alloy.

2. Experimental results and discussion

The studied $Zn_{1-x}(Mn,Co)_xGeAs_2$ samples were grown using a direct fusion method from the stoichiometric ratio of the high purity powders of $ZnAs_2$ and Ge [10]. As-grown ingots were cut into thin slices. The chemical composition of the slices was determined using the X-ray fluorescence technique. Typical uncertainty of this method is about 10%. The obtained results showed that the distribution of the elements along the ingots was uniform. The obtained Mn and Co amounts are shown in Table.

TABLE

The results of a basic $Zn_{1-x}(Mn,Co)_xGeAs_2$ sample characterization where TM is the type of the substitutional ion, x is the molar fraction of the alloying element, a and c are the lattice parameters, ρ_{xx} is the resistivity, p is the carrier concentration, and μ is the Hall mobility.

TM	x	a [Å]	c [Å]	ρ_{xx} (10^{-2}) [Ω cm]	p (10^{19}) [cm^{-3}]	μ [cm^2 V^{-1} s^{-1}]
Co	0.052	5.673	11.149	8.47	0.66	11.1
Mn	0.053	5.658	11.242	1.61	3.62	10.7
Mn	0.078	5.651	11.232	4.58	5.22	2.61
Mn	0.182	5.654	11.197	3.29	7.73	2.45

The inspection of Table showed that the studied $Zn_{1-x}Mn_xGeAs_2$ samples had Mn molar fraction x varying between $0.053 \leq x \leq 0.182$. One additional Co alloyed $Zn_{1-x}Co_xGeAs_2$ sample had chemical composition x equal to 0.052.

The crystallographic characterization was done using the X-ray diffraction (XRD) method. The measurements were performed at room temperature. The obtained results showed that the studied $Zn_{1-x}(Mn,Co)_xGeAs_2$ samples with $x \approx 0.052$ were monocrystalline, while the samples with $x \geq 0.078$ were polycrystalline. Additionally the XRD measurements showed that all the studied samples were a single phase and crystallized in the chalcopyrite structure. The lattice parameters of the tetragonal chalcopyrite crystal lattice of the studied samples are given in Table. The crystallographic parameters obtained for the studied samples have values close to the $ZnGeAs_2$ lattice constants $a = 5.672$Å and $c = 11.153$ Å [8]. The lattice parameters showed a deviation from the Vegard law.

The basic transport characterization of the investigated alloy was performed using the standard DC current six contact technique. We measured the resistivity and Hall effect. The measurements were performed at room temperature. The samples were polished and etched before depositing gold contacts with indium solder. The transport measurements were performed using the constant current up to $I = 10$ mA. The Hall constant $R_{\text{H}} = 1/ep$, where e is the elementary charge and p is the Hall carrier concentration, was measured as a function of the applied magnetic field $0 \leq B \leq 1.4$ T at $T = 300$ K. The obtained dependence of R_{H} on the magnetic field was linear, i.e. we did not see an appearance of the anomalous Hall effect (AHE). Thus we concluded that the Hall carrier concentration (measured in the constant magnetic field $B = 1.4$ T) was not influenced by the presence of the AHE. The obtained results of the transport characterization are gathered in Table. The inspection of Table leads to the following conclusions:

- The resistivity of the alloy increases with increasing amount of Mn in the sample reaching a maximum value for the sample with $x = 0.078$ and has a smaller value for $x = 0.182$. The difference between the samples with $x = 0.078$ and $x = 0.182$ was probably due to the increase in the Hall carrier concentration p. The samples with $x \geq 0.078$ were polycrystalline, which may be the source of the ρ_{xx} increase. The carrier transport in the polycrystalline media is dominated by the processes occurring at the grain boundaries (acting as the Schottky barriers for conducting carriers).
- Comparison of the monocrystalline samples shows that the sample with Co has a much higher resistivity than the samples containing Mn. This may originate from the fact that Co ions were poorly substituting for the Zn^{2+} sites in the $ZnGeAs_2$ host lattice creating more defects (acting as scattering centers for the conducting carriers).
- All the investigated samples showed p-type conductivity. The Hall carrier concentration is an increasing function of Mn content in the alloy. The rise in p with x in the polycrystalline samples is due to the fact that usually

the grain boundaries contain a large amount of defects (i.e. Zn^{2+} or Ge^{2+} vacancies) increasing the hole concentration.

- The Co alloyed sample is characterized by the smallest Hall carrier concentration.
- The Hall carrier mobility has the largest value for the monocrystalline samples which is a reasonable result indicating that the grain boundaries significantly influence the carrier transport in the polycrystalline samples. However all the studied samples were characterized by relatively low Hall mobilities $\mu \leq 12$ cm^2/(V s).

The magnetic investigations were performed using a SQUID magnetometer. The measurements were performed over a temperature range $T = 4.5{-}400$ K at magnetic fields up to 7 T. The experimentally determined $M(T)$ curves in a constant magnetic field $B = 10$ mT for the studied $Zn_{1-x}(Mn,Co)_xGeAs_2$ samples are presented in Fig. 1a.

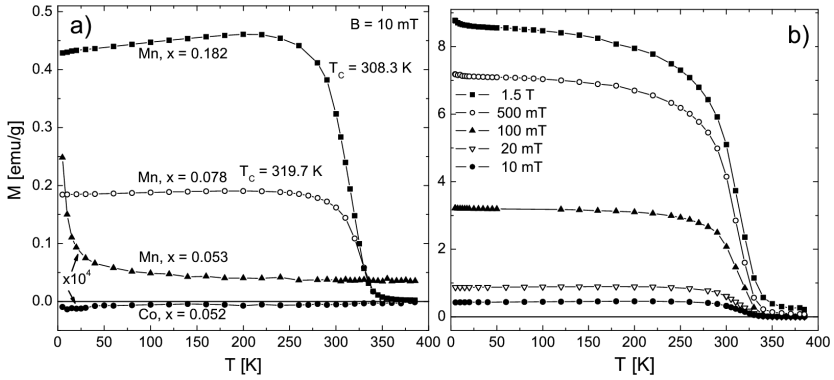

Fig. 1. The magnetization M as a function of temperature: (a) measured for the $Zn_{1-x}(Mn,Co)_xGeAs_2$ samples with different chemical compositions (labels), and (b) measured using different applied magnetic fields (legend) for the $Zn_{0.818}Mn_{0.182}GeAs_2$ sample.

The inspection of Fig. 1a showed that the magnetic properties of the studied alloy are highly composition dependent. The obtained $M(T)$ curves for the samples with $x \geq 0.078$ showed features characteristic of the appearance of the paramagnet–ferromagnet phase transition. The Curie temperatures T_C for the samples with $x \geq 0.078$ were determined as the temperature of the inflection point in the $M(T)$ curve. The obtained T_C values were equal to 319.7 K and 308.3 K for the samples with $x = 0.078$ and 0.182, respectively. The obtained paramagnet-ferromagnet phase transition temperatures are close to the values reported in the literature for the $Ga_{1-x}Mn_xAs$ semimagnetic semiconductor containing MnAs precipitates ($T_C \approx 320$ K) [11]. However in the case of the studied $Zn_{1-x}Mn_xGeAs_2$

samples the X-ray characterization did not showed the appearance of crystallographic phases other than $ZnGeAs_2$ and we observed the changes of the Curie temperatures with varying the chemical composition of the alloy. These two facts led us to the conclusion that probably the nanometric fluctuations of the Mn content in the $Zn_{1-x}Mn_xGeAs_2$ samples with $x \geq 0.078$ (retaining the chalcopyrite crystal structure of the $ZnGeAs_2$ host) are responsible for the observed room temperature ferromagnetism. Such nanometric fluctuations of the chemical composition (called spinodal decomposition) were the source of the high T_C in many semimagnetic semiconductors [12].

In order to study the nature of the room temperature ferromagnetism observed in the $Zn_{1-x}Mn_xGeAs_2$ samples with $x \geq 0.078$ we performed the magnetization measurements applying different magnetic fields $10 \leq B \leq 1500$ mT. The results obtained during these measurements were similar for both ferromagnetic samples. The exemplary results obtained for the $Zn_{0.818}Mn_{0.182}GeAs_2$ sample are presented in Fig. 1b. The obtained results showed features typical of a ferromagnetic material. We can clearly see that the magnetization of the sample is an increasing function of the applied magnetic field. In ferromagnets this feature is characteristic of the observation of domain enlargement with increasing applied magnetic field. However at low temperatures we did observed the small increase in M when measuring using the highest magnetic fields. Such behavior is usually connected with the presence of frustrated nanoscale regions in the sample in which the short range dipole magnetic interactions play a major role. These effects were stronger for the sample with $x = 0.182$ indicating that the addition of Mn to the alloy in high amounts may result in aggregation of Mn ions.

The magnetization $M(H)$ curves were also studied at the isothermal conditions for the $Zn_{1-x}Mn_xGeAs_2$ samples with $x \geq 0.078$. The results obtained at 25 K are shown in Fig. 2.

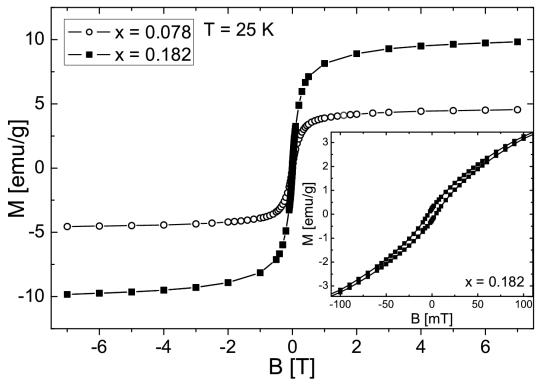

Fig. 2. The magnetization M as a function of the applied magnetic field B measured at isothermal conditions ($T = 25$ K) for the $Zn_{1-x}Mn_xGeAs_2$ samples (chemical composition x shown in legend).

The inspection of Fig. 2 shows features characteristic of ferromagnetic compounds. The obtained magnetization curves (see inset in Fig. 2) are characterized by low coercive field and remanent magnetization. This may indicate that the studied compound belongs to the class of soft magnetic materials. The magnetization of the sample with $x = 0.078$ saturates at magnetic fields $B \geq 3$ T. However for the sample with $x = 0.182$ we did not observe the saturation of the magnetization even at magnetic field $B = 7$ T. We observed the increase in the saturation magnetization M_{S} for the sample with a higher amount of Mn. The value of M_{S} can be used to calculate the amount of transition metal ions in the sample. The calculated molar fractions of the alloying elements were roughly twice lower than the values obtained using the X-ray fluorescence technique. These results support our earlier conclusion that Mn aggregation is present in the studied system.

3. Summary

We reported the preliminary results of the magnetic and transport properties of the $Zn_{1-x}(Mn,Co)_xGeAs_2$ alloy.

The transport properties depend strongly on the chemical composition of the alloy. We observed in the investigated samples a p-type conductivity with both semimetallic and semiconducting $\rho_{xx}(T)$ characteristics and the carrier concentrations $p \geq 6.6 \times 10^{18}$ cm^{-3}.

The magnetic measurements showed the presence of the ferromagnetic phase at $T < 320$ K for the samples with $x \geq 0.078$ with T_{C} varying with the chemical composition of the alloy. The high Curie temperatures observed in the studied system were probably due to the spinodal decomposition of the Mn ions.

In conclusion, we showed that via alloying we were able to tune the magnetic and transport properties of the $Zn_{1-x}(Mn,Co)_xGeAs_2$ alloy in a remarkable way.

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