Advanced Materials for Spintronic Based on Zn(Si, Ge)As$_2$ Chalcoprytes

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A$^{\text{II}}$B$^{\text{IV}}$C$_2^\text{V}$ semiconductors doped with Mn are perspective materials for spintronic. Structural, chemical and magnetic properties of these materials have been analyzed. The combinations of these compounds with the traditional semiconductors are perspective to create “system on chip” devices. The coexistence of ferromagnetic and paramagnetic phases was observed. The ferromagnetic phase is likely due to the presence of MnAs nanoclusters (3-5 nm). Paramagnetic properties appear due to Mn complexes (dimmer and trimmer).

Index Terms—Chalcopryte, diluted magnetic semiconductor, ferromagnetic-semiconductor structure, spintronic.

I. INTRODUCTION

SPI TRONIC has several directions of development, only two of which have found practical application thus far, those effects are the giant magnetoresistance (GMR) and the magnetic tunnel junction (MTJ). Since 2004 the MTJ is used in magnetoresistive random access memory (MRAM) and has replaced the devices based on GMR in the hard drives. The combination of “silicon technology” and MTJ principle can accelerate the integration of “semiconductor spintronics” into life. One of the main problems here is the incompatibility of the conventionally used semiconductors and ferromagnetic materials. An obvious solution is fabrication of materials which are ferromagnetic and semiconductor at the same time.

Ternary chalcopryte semiconductors of the $\text{II} - \text{IV} - \text{V}_2$ system are considered as structural and electronic counterparts of III-V compounds [1], [2] and IVa semiconductors as a consequence. They have better solubility of $d$-elements and can readily accept a high concentration of Mn atoms. This is a natural property of chalcoprytes used as two-cation semiconductor [3]. Now there are nine known compounds with high temperature ferromagnetic ordering among Mn-doped $\text{II} - \text{IV} - \text{V}_2$ semiconductors (listed in Table I) [4], [5], [6]-[15]. For such materials the highest $T_C \approx 367^\circ\text{K}$ has been observed for ZnGeAs$_2$, doped with Mn [11]. The differences of GaAs and Ge lattice constants with ZnSiAs$_2$ one are about 0.3 and 4%, respectively. In this way ZnSiAs$_2$ is also promising compound, because of the difference of lattice constants between Si and ZnSiAs$_2$ is nearly 2%. It provides good conditions for an epitaxy of ternary ferromagnetic semiconductors on substrates which are used in modern electronics (Si, Ge, III-V and others). This work is devoted to magnetic properties investigation of typical representatives of the group of $\text{II} - \text{IV} - \text{V}_2$ Mn-doped semiconductors, including Cd$_{1-x}$Zn$_x$GeAs$_2$ : Mn, ZnSiAs$_2$ : Mn bulk crystals, ZnSiAs$_2$ : Mn/Si heterostructures, which are structural and electronic counterparts of III-V compounds.

II. SAMPLES PREPARATION

Analysis of phase equilibria of $\text{II} - \text{IV} - \text{V}_2$ ternary systems shows that, as a rule, one congruently melting ternary compound A$^{\text{II}}$B$^{\text{IV}}$C$_2^\text{V}$ forms in these systems.

The most probable quasi-binary sections in which these ternary compounds can form are the $\text{A}^{\text{II}} - \text{B}^{\text{IV}} \text{C}_2^\text{V}$ and $\text{B}^{\text{IV}} - \text{A}^{\text{II}} \text{C}_2^\text{V}$ sections (Fig. 1). The physicochemical properties of the binary compounds that form in the boundary binary systems indicate that the most optimal way to synthesize ternary compound is through the interaction of the components along the $\text{B}^{\text{IV}} - \text{A}^{\text{II}} \text{C}_2^\text{V}$ section. The preparation of the batch along this section considerably decreases the free volume in synthetic ampoules as compared with the batch consisting of individual components. This makes it possible to reduce the possibility of removal of a volatile component from the reaction zone and, thus, ensures the preparation of the stoichiometric composition of the synthesized ternary compound. The preparation of a batch along the $\text{A}^{\text{II}} - \text{B}^{\text{IV}} \text{C}_2^\text{V}$ section is less efficient since the $\text{B}^{\text{IV}} \text{C}_2^\text{V}$ compounds are more difficult to synthesize than the $\text{A}^{\text{II}} \text{C}_2^\text{V}$ compounds.

The polycrystalline samples have been prepared as supersaturated solid solutions along the hypothetical section MnB$^{\text{IV}}$C$_2^\text{V} - \text{A}^{\text{II}}$B$^{\text{IV}}$C$_2^\text{V}$, using the high cooling speed of about $5 - 10^\circ\text{C}/\text{s}$.

The thin films ZnSiAs$_2$(Mn)/Si have been prepared according to the method described in [17]. The ZnAs$_2$ and Mn thin films were formed on a silicon substrate by vacuum thermal evaporation. The thickness ratio of ZnAs$_2$ to Mn was 50:1. Then the structures were placed in vacuum ampoules with pieces of arsenic and ZnAs$_2$ for compensating saturated vapor pressure and to save initial thickness of ZnAs$_2$. The temperature conditions were determined by the phase diagram.
Si – ZnAs2. The highest point of process was below the eutectic temperature from the silicon side. This temperature determined the richest ZnSiAs2:Mn composition of the solution melt. After 2 hours for homogenization of solution melt we decreased the rate of cooling was 1 °C/min. The composition of the solution melt was changing due to the liquidus curve. The thickness of ferromagnetic ZnSiAs2:Mn layer may be calculated by the lever rule. After reaching the lowest temperature of the process, the samples were cooling with high speed 5°C/s.

The identification of the samples was done by x-ray phase analysis, differential thermal analysis (DTA), metallographic, x-ray fluorescence analysis as well as by electronic microscope investigation.

### III. Magnetic Measurements and Its Discussion

Magnetization $M$ of the samples was measured between 5–310 K and 260–400 K in fields up to $H = 50$ kOe using a superconducting quantum interference device (SQUID) magnetometer.

Fig. 2. shows the temperature dependence of the magnetization of the ZnSiAs2:Mn/Si heterostructure (2) in a 50 kOe measuring field.

We can explain the behavior of the magnetization curve by the co-existence of two magnetic phases in the sample. The first is a ferromagnetic (FM) one with asymptotical Curie temperature $T_C \approx 340$ K. As observed in arsenic based semiconductors doped with Mn [18]–[20] their magnetic properties were substantially governed by the presence of MnAs clusters. MnAs is a ferromagnetic semimetal with $T_C \approx 335$ K at $H = 50$ kOe [21], which is close to $T_C$ obtained in our ZnSiAs2 : Mn/Si heterostructure. The second phase is a paramagnetic-like (PM) with magnetization described by the Langevin function

$$M_{PM} = M_0 \left[ \coth \left( \frac{\mu H}{k_B T} \right) - \frac{k_B T}{\mu H} \right]$$  \hspace{1cm} (1)

The total magnetization is $M = M_{PM} + M_{FM}$, where $M_{FM}$ is magnetization of the MnAs phase. At a high temperature $M \approx M_{FM}$ and in the fields above $H > 10$ kOe, the magnetization is saturated. Therefore, the temperature dependence of the saturation magnetization of MnAs phases, taking from [21], can be used for subtracting of ferromagnetic term from total magnetization to determine of $M_{PM}$. The PM part of magnetization can be accurately reproduced by (1) with two fitting parameters: $M_0 = 14.2 \pm 0.3$ amu, and $\mu = 7.6 \pm 0.2 \mu_B$ (Fig. 2, inset). $\mu$ exceeds the magnetic moment of Mn2+ ion ($5 \mu_B$) when substituting the Zn or Si site. The same situation was observed for the Mn-doped CdGeAs2 bulk crystal, where the mean magnetic
moment was \( \mu = 7.1-8.0 \mu_B \) [22] and depended on Mn content.

The value of \( m > 5 \mu_B \) can be observed in p-type magnetic semiconductors with \( \text{Mn}_2 \text{GeAs}_2 \) centers. In these materials the magnetic moments of the embedded Mn ions strongly interact with the magnetic moments of the charge—carrier holes. A high value of the pd-exchange constant \( J_{pd} (\sim 1 \text{ eV}) \) leads to a considerable increase in the magnetic moment of the Mn ion in an external magnetic field [23]:

\[
\mu = 5\mu_B \left( 1 + \frac{J_{pd}}{5\mu_B B B^2} \right) \approx 7\mu_B
\]

where \( s = 1/2 \) is hole spin, \( B = 0.4, 10^{21} \text{ cm}^3 \)—volume of the crystal lattice and \( p \approx 5.5, 10^{17} \text{ cm}^{-3} \)—the hole concentration of single crystal Mn-doped sample \( \text{CdlGeAs}_2 \) [23]. This explanation is not applicable for complex system with high concentrations of Mn ions, charge carriers (in our cases \( N_{\text{Mn}} > 10^{20} \text{ cm}^{-3} \), \( p \approx 10^{19} - 10^{20} \text{ cm}^{-3} \)) and ferromagnetic clusters.

Theoretical calculations performed for (Ga,Mn)As system showed possibility of Mn clustering into stable and electronically active dimmers, trimmers or tetramers [9]. Such complexes was observed in InMnAs [10], (In,Mn)Sb epitaxial films [11] and can be source of ferromagnetic ordering. In these complexes Mn atoms placed on the positions in neighbor unit cells and interact antiferromagnetically. Therefore their effective magnetic moment is reduced. Mn atoms from complexes interact with other type atoms too, especially with As. So the most probably value of \( \mu \) for Mn atoms is close to \( \mu (\text{MnAs}) \) which is 3.4 \( \mu_B \) [24]. The value of magnetic moment 7–8 \( \mu_B \) is support of the assumption that most of Mn atoms in lattice formed complexes, especially dimmers and trimmers.

The temperature dependences of the magnetization measured after cooling of the ZnSiAsS_2 : Mn/Si heterostructure in zero field (ZFC) (\( B < 0.1 \) G) and while cooling in a low field (FC) are shown in the inset to Fig. 3. The difference between the FC and ZFC point out on existing superparamagnetic clusters with blocked magnetic moments.

Similar to \( \text{CdlGeAs}_2 \) [20] the blocking temperature of FM MnAs particles is [25]

\[
T_b = \frac{K V}{25 \lambda_k B}
\]

where \( K \) is the density of the anisotropy energy and \( V \) is the average volume of the particles. The distribution function of \( T_b \) can be calculated from [19]

\[
F(R_b) = \frac{1}{\sqrt{2\pi}} \int dT \left[ \frac{T \chi_{ZFC}(T)}{\sigma_S^2(T)} \right] - \lambda
\]

The distribution function \( F(R) \) of the radius of the sphere corresponding to the cluster volume, is calculated using (3) and the temperature dependences of \( K \) and saturation of magnetization \( \sigma_S \) [26]. The constants \( \lambda \) and \( \gamma \) are determined by normalizing \( F(R) \) to unity and using the condition \( F(R) = 0 \) at \( R = 0 \) (Fig. 4). Fitting \( F(R) \) with a Gaussian function, gives the most probable radius of the clusters \( R_1 = 5.1 \) nm with mean-square deviation \( \delta_1 = 1.4 \) nm (Fig. 4).

Magnetic investigations give evidence to existing in Mn-doped \( \text{II} - \text{IV} - \text{V}_2 \) semiconductors superparamagnetic MnAs particles with mean radius less than 5.1 nm. These clusters are responsible for the above room temperature ferromagnetism of \( \text{II} - \text{IV} - \text{V}_2 \) : Mn. Note that the higher \( T_C \) of \( \text{II} - \text{IV} - \text{V}_2 \) : Mn alloys can be rich by embedding of MnSb (\( T_C = 585 \) K) nanoclusters to the semiconductor matrix as it observed for GaSb:MnSb layers [16]. For example the promising candidate is \( \text{ZnSiSb}_2 \) : Mn.

**IV. CONCLUSION**

In summary, we have analyzed the structural and investigated the magnetic properties of \( \text{II} - \text{IV} - \text{V}_2 \) semiconductors doped with Mn, which are perspective materials for spintronic. These chalcopyrites are electronic and structural analog of III-V and IVa semiconductors and have Curie point above of room temperature and the magnetic properties of thin film and polycrystalline samples are similar. The paramagnetic and ferromagnetic phases were observed.
From the above presented results we can conclude that following inclusions contribute to magnetization in Mn-doped $\Pi - IV - V_2$:  
— MnAs nanoclusters (with mean radius $<$5nm) are responsible for high temperature behavior of magnetization;  
— Mn complexes, mainly dimmers formed from Mn ions are responsible for the paramagnetic background

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