Room-Temperature Ferromagnetism in Novel Mn-doped ZnSiAs$_2$ Chalcopyrite

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Abstract. Based on Mn-doped chalcopyrite ZnSiAs$_2$ the new dilute magnetic semiconductor with $p$-type conductivity was produced. The Curie temperature behaviour of the produced semiconductor is distinctly dependent on the Mn concentration: 325 K for 1 wt.% and 337 K for 2 wt.% of Mn, consequently. Magnetization, electrical resistance, magnetic resistance and Hall effect of mentioned compositions were studied. Temperature dependence of magnetization $M(T)$ have complicate behaviour. For $T \leq 15$ K the $M(T)$ dependence is characteristic for superparamagnetic and at $T > 15$ K, magnetization is sum of magnetizations of ensemble of superparamagnetic clusters and ferromagnetic phase contained frustration regions.

1. Introduction
At the present time the new way of solid state physic is growing rapidly. This way relate with possibility of transfer oriented electronic spin from ferromagnetic to paramagnetic semiconductor [1, 2]. These investigations will allow produce one electron logic structure and spin-information systems with using electron spin as a memory cell: one spin – one information bit [3]. In order to achieve high polarized spin and to find solution of electrical contact between ferromagnetic and semiconductor, it is interesting to get ferromagnetic semiconductor with Curie temperature more that 300 K by dope of conventional semiconductor by element with the not fully filled 3d-shell. The best results were achieved on Ga$_{1-x}$Mn$_x$As films with Curie temperature $T_C \sim 170$ K [4, 5]. However for spintronic application ferromagnetic semiconductors with $T_C > 300$ K are desirable. Recently high temperature ferromagnetism was observed in Mn-doped A$^{II}$B$^IV$C$^{V}_2$ chalcopyrite. Its were CdGeP$_2$:Mn [6], ZnGeP$_2$:Mn [7] and ZnSnAs$_2$:Mn [8] compounds with $T_C$ up to 350 K. In our papers [9, 10] new chalcopyrite CdGeAs$_2$:Mn with $T_C = 355$ K and ZnGeAs$_2$:Mn with $T_C = 367$ K were discussed. A$^{II}$B$^IV$C$^{V}_2$ ternary semiconductors are crystal-chemical and electronic twins of A$^{III}$B$^V$ semiconductors [11]. These compounds mostly have covalent type of chemical bond, small carrier effective mass, high

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carrier mobility and absolute minima and maxima of conduction and valence bands in the centre of Brillouin zone. New compounds of ZnSiAs$_2$:Mn with $T_\text{c} > 300$ K were produced and observed in this paper. The value of these compositions is in the fact that they are combined with «siliceous technology», i.e. it is possibility to make on them of epitaxy and other technological processes allowed to create the devices of the solid state electronics [12]. Mentioned compound ZnSiAs$_2$ have following characteristics: band-gap energy is 2.1 eV and maximum carrier mobility is $\sim$150 cm$^2$/V.s (for holes with $4\cdot10^{15}$ cm$^{-3}$ concentration).

2. Experimental methods

At the present paper magnetization intensity, electrical resistance $\rho$, magnetic resistance $\Delta\rho/\rho = (\rho_H - \rho_{H=0})/\rho_{H=0}$ and Hall effect of Mn 1 and 2 wt % doped ZnSiAs$_2$:Mn polycrystalline were studied. Magnetization was measured by SQUID-magnetometer in a $5 \leq T \leq 300$ K temperature range and by weight method with electromagnetic compensation in a $T \geq 290$ K. The last method normally used to measure paramagnetic susceptibility, but due to low Mn consumption and low magnetization amount it was possible to apply it for measure magnetization. To measure $\rho$ and $\Delta\rho/\rho$ a four-probe method was applied. Electrical contacts to samples were prepared on etched and polished surface using indium solder and gold wires.

3. Samples producing and analysis

Polycrystalline ZnSiAs$_2$:Mn samples have been prepared by direct fusion method from high purity powders of Si, ZnAs$_2$ and Mn with temperature 10 – 15$^\circ$C higher that ZnSiAs$_2$ melting point. Based on analysis of quasi-binary cut Si – ZnAs$_2$ this method looks more efficient [13, 14]. In order to increase Mn solubility in the alloy, crystals were cooled down with high speed 10$^\circ$/c. Samples identification were done by x-ray phase analysis, thermal differential analysis (DTA), micrographic analysis, x-ray fluorescence analysis as well as by electron microscope. X-ray phase analysis stated that samples consist of ZnSiAs$_2$ phase with following parameters: $a = 5.6084$ Å; $c = 10.8816$ Å. These parameters good enough comply with dates from International center of diffraction data, 2007. X-ray fluorescence analysis also endorses x-ray phase analysis results.

4. Magnetic and electrical properties of ZnSiAs$_2$

Figure 1 and 2 show temperature dependence versus magnetization for composite with 2 wt.% of Mn measured in applied magnetic field 10 and 50 kOe respectively (curve 1).

As it shown on figures, $M(T)$ curve under $T > 50$ K have shape characteristic for ferromagnetic. However, in case of $T < 15$ K magnetization rapid grow with $T$-decreasing and $M(T)$-dependence obeys by Langevin function

$$M/M_0 = \frac{c}{\mu} H/kT - kT/\mu H,$$

(1)

where $M_0$ is equal to $M$ at $T \rightarrow 0$ K and $\mu$ is magnetic moment of superparamagnetic cluster. We determined the $M_0$-value by extrapolation of $M(T)$ at $T \rightarrow 0$ K and $\mu$-value by selection to experimental curve. These values are next: $M_0 = 0.321$ emu/g and $\mu = 55 \mu_B$ in $H = 11$ kOe and $11 \mu_B$ in $H = 50$ kOe for compound with 2 wt %. Contrary to the conventional superparamagnets in this compound magnetic moments of clusters depend from the magnetic field value $H$: they diminish with grow $H$. Similar picture was observed for compound with 1 wt % of Mn. Here $\mu = 52 \mu_B$ in $H = 11$ kOe and $8.6 \mu_B$ in $H = 50$ kOe. Difference between FC and ZFC magnetization and shift of the hysteresis loop of FC sample observed at $T = 5$ K confirms the superparamagnetic clusters presence (figure 3). We proposed that at $T > 15$ K magnetization $M$ is sum of magnetization of ensemble of superparamagnetic clusters and magnetization from phase with long-range magnetic order. We separate $M(T)$-curve (curve 1 on figure 1 and 2) on curve of the superparamagnetic clusters magnetization (curve 2) and curve of $T$-dependence of magnetization from phase with long-range magnetic order $M_3(T)$ (curve 3) using a computer subtraction of curve 2 from curve 1. At $T > 15$ K
appears a spontaneous magnetization as figure 1 and 2 shows. $M_S$-value does not almost depend from $T$ at $100 \leq T \leq 250$ K. From highest value of $M_S$ in this $T$-region was determined a magnetic moment on f.u. It is found this magnetic moment on f.u. very understand comparison with the one at total ferromagnetic ordering of spins of Mn$^{2+}$ ions or antiferromagnetic ordering of spins Mn$^{2+}$ and Mn$^{3+}$, that is these compounds are frustrated magnetic at $T > 15$ K.

Figure 1. Temperature dependence of magnetization for composite with 2 wt.% of Mn measured in applied magnetic field 10 kOe (curve 1). Curve 1 is separated on $T$-dependence of magnetization of superparamagnetic clusters ensemble (curve 2) and the one of ferromagnetic phase contained frustration regions (3).

Figure 2. Temperature dependence of magnetization for composite with 2 wt.% of Mn measured in applied magnetic field 50 kOe (curve 1). Curve 1 is separated on $T$-dependence of magnetization of superparamagnetic clusters ensemble (curve 2) and the one of ferromagnetic phase contained frustration regions (3).

Figure 3. 2 wt.% Mn-doped ZnSiAs$_2$. Hysteresis loop measured with $T = 5$ K and in applied magnetic field from -0.1 kOe to 0.1 kOe after sample cooling from $T = 370$ K to $T = 5$ K under this field (circles, FC sample) and without field (squares, ZFC sample). Shift of the loop can be observed on the axis $H$ for FC sample, but for ZFC sample the loop is symmetrical.

Therefore their Curie points were determined by extrapolating the steepest part of $M_S(T)$ curve to intersection with $T$-axis. They are 325 and 337 K for samples with 1 and 2 wt % correspondingly.

The $p(T)$-dependence is semiconductive character with an activation energy $0.12 - 0.38$ eV at $124 \leq T \leq 263$ K (both compounds). Mobility and concentration of the charge carriers (holes) are 1.33, 2.13
cm$^2$/Vs and $2.2 \times 10^{16}$, $8 \times 10^{16}$ cm$^{-3}$ at $T = 293$ K compounds with 1 and 2 wt % correspondingly. Magnetoresistance of both compounds does not exceed of 0.4 % in $H = 10$ kOe.

5. Conclusion

Up to highest magnetic field (50 kOe), magnetization have complicated behaviour. At $T \leq 15$ K sample magnetization is a result of existence of superparamagnetic clusters. Its magnetic moment is decreasing while magnetic field is growing. This dependence might be due to split big magnetic clusters to small one under magnetic field. Existence of superparamagnetic clusters is confirmed by difference of magnetizations of FC- and ZFC-samples and by shift in hysteresis loop for FC-sample. At $T > 50$ K ferromagnetic phase become play the key role. At $100 \leq T \leq 250$ K there is not big change of this magnetization. At $T > 300$ K $M(T)$ curve drop down what is an evidence of Curie temperature. Obviously, Curie temperature idea for such system is tentatively: this is Curie temperature of frustrated ferromagnetic phase. Due to magnetic heterogeneity of the system it’s not possible to measure Curie temperature by using the thermodynamic coefficients method of Belov-Arrott. Also not true to measure $T_c$ from $M(T)$ in low magnetic fields, because this magnetization is a result of demagnetizing factor. Demagnetizing factor of frustrated ferromagnetic phase depend of phase configuration, which can be changed with temperature. Therefore Curie temperatures were determined by extrapolating the steepest part of $M_s(T)$ curve measured under 50 kOe to intersect with $T$-axis. They are 325 and 337 K for samples with 1 and 2 wt % correspondingly.

In work [15] was shown that modified RKKI interaction of Mn atoms positioned in the neighbour sites of Ga-sublattice in Ga$_{1-x}$Mn$_x$As leads to their attraction and promotes their clustering. One would expect a conclusion of [15] can be justly for chalcopyrite structure since it is crystallochemical analog of A$^{III}$B$^V$. In this case the cluster formation occurs in the same manner as in Ga$_{1-x}$Mn$_x$ As, as well as zinc to Mn replacement lead to cluster formation in ZnSiAs$_2$:Mn.

6. References

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