

Growth and Characterization of Cd₃As₂ + MnAs Composite

A.V. Kochura¹, S.F. Marenkin^{2,3}, A.I. Ril'², A.L. Zheludkevich⁴, P.V. Abakumov¹, A.F. Knjazev¹,
M.B. Dobromyslov⁵

¹ South-West State University, Regional Centre of Nanotechnology,
94, 50 let Otyabrya St., 305040 Kursk, Russia

² Institute of General and Inorganic Chemistry of Russian Academy of Sciences,
31, Leninskii Pr., 119991 Moscow, Russia

³ Moscow Institute of Steel and Alloys (National University of Science and Technology),
4, Leninskii Pr., 119049 Moscow, Russia

⁴ Scientific-Practical Materials Research Centre of the National Academy of Sciences of Belarus,
Minsk, Belarus

⁵ Pacific National University, 136, Tikhookeanskaya St., 680035 Khabarovsk, Russia

(Received 02 October 2015; published online 24 December 2015)

Bulk samples of cadmium arsenide and manganese arsenide alloys were synthesized by crystallization from double-component melt. According to data of differential-thermal and X-ray phase analysis, the nature of the interaction between Cd₃As₂ and MnAs is eutectic; the melting temperature of eutectic is 855 K. The samples were ferromagnetic with Curie temperature of 320 K. By vacuum-thermal evaporation from the alloy of the composite, films Cd₃As₂ + MnAs have been obtained. The distribution of the elements in them was uniform and the composition corresponded to the initial composition. The films consisted from nanocrystallites with a size of 20 to 50 nm.

Keywords: Magnetic composite, Cadmium arsenide, Spintronic materials, Thin solid films, Magnetic clusters.

PACS numbers: 81.15.Dj, 68.55.Nq,
75.70.Ak, 78.30.Hv

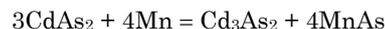
1. INTRODUCTION

Cadmium arsenide (Cd₃As₂) – narrow-band semiconductor material of group II-V with the tetragonal crystal structure and an inverse arrangement of bands [1]. It features the biggest value of mobility (up to 900 m²/(V·s) at 5 K [2] of the main charge carriers observed in tetragonal semiconductor materials. Earlier, it was proposed to use Cd₃As₂ as material for thermoelements [3], Hall sensors [4] and highly effective sources of infrared radiation [5]. However, recent theoretical [6] and experimental [7] investigations showed that cadmium arsenide is Dirac semimetal. That is, it belongs to materials for which the law of quasiparticle dispersion is linear in all three directions of momentum space, which causes such effects as Hall quantum spin effect, huge diamagnetism, insensibility of Dirac fermions to spin – orbital interaction. Besides, cadmium arsenide can serve as a basic matrix for research of such exotic phases as Weyl semimetals, axion dielectrics and topological superconductors [8]. That makes it extremely promising for use in spintronics – the rapidly developing field of nanoelectronics, in which storage, information transfer and processing is carried out by means of the electron spin. At doping of semiconductors with 3D metals (most often Mn), it is possible to obtain ferromagnetic semiconductors in which control of a spin subsystem can be exercised by electric field [9]. Earlier it was shown that in semiconductor compounds of group II-V doped with manganese at low temperatures, the state of spin glass was observed [10, 11]. When the Mn content in these compounds is greater than a certain threshold, the high-temperature ferromagnetism occurs, which is due to nano- and microinclusions of the

phase Mn-V (MnAs, MnP) [12-14]. It means that such materials synthesized in the form of volume crystals represent the composites consisting from a semiconductor (magnetic or nonmagnetic) matrix and ferromagnetic clusters. It was revealed for films II-V : Mn that they also are composite and have the granulated structure [15, 16]. Such films are promising as materials of spintronics devices since in them it is possible to implement the effect of the huge magnetoresistance [17, 18]. All of this stimulates interest in producing and research of properties of both volume crystals and films of Cd₃As₂, doped with manganese.

2. EXPERIMENTAL DETAILS

Polycrystalline samples of Cd₃As₂-MnAs were prepared by direct alloying of preliminary synthesized powders CdAs₂ and MnAs. Their mass ratio was chosen according to the reaction:



Films Cd₃As₂-MnAs were deposited from powder by vacuum thermal evaporation technique on substrates from silicon (001) and leucosapphire L-Al₂O₃ [0001] with the VUP-5 installation according to the methodology described in [16].

Needle monocrystals of solid solution (Cd_{1-x}Zn_x)₃As₂ were grown (x = 0.1) from a steam phase and used as a test sample at the research of Raman light scattering (RLS) spectra of the produced films.

Identification of samples by the X-ray phase analysis (XRFA) was made by means of X-ray scanning of composite powder on the Bruker D8 ADVANCE diffrac-

tometer (CuK α -radiation, the graphite monochromator); phases were identified by using powder diffractometer data of ICDD PDF 2.

Microstructural investigations were done on the scanning electron microscope (SEM) of Carle Zeiss NVision40 equipped with the analyzer Oxford Instruments X-maximum. At a survey, detectors of secondary electrons (InLens, Everhart-Thornley) and the EsB detector of backscattered electrons were used.

Spectra of RLS were measured at room temperature by means of the combined system of the scanning probe microscopy (SPM) with a confocal fluorescent spectrometer and a spectrometer of RLS OmegaScopeTM (AIST-NT Inc.) with the wavelength of laser radiation $\lambda_0 = 473$ nm, 50 mW and the size of a spot of the focused light on the sample surface about 500 nm. The spectral resolution of the device was 2 cm^{-1} .

Magnetic properties were measured with the vibration magnetometer of the firm "Cryogenic Ltd." at temperatures in the range of 5-310 K and the magnetic field induction in the range of 0.01-14 T.

3. RESULTS AND DISCUSSION

According to data of the differential thermal analysis (DTA) and XRFA, the nature of the interaction between Cd $_3$ As $_2$ and MnAs was the eutectic. In Fig. 1 shown is a thermogram of alloy Cd $_3$ As $_2$ -MnAs. The main features presented on this thermogram: the melting temperature of eutectic (855 K); temperature of polymorphic transformation $\alpha \rightarrow \beta$ Cd $_3$ As $_2$ (863 K); liquidus point (960 K).

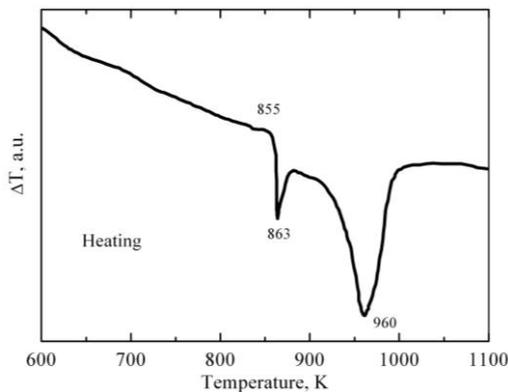


Fig. 1 – Results of DTA analysis for composition Cd $_3$ As $_2$ -MnAs

Using alloys of Cd $_3$ As $_2$ with MnAs as targets, films about $1 \mu\text{m}$ thick were produced.

As standard specimen for studying RLS spectra, the single-crystal needles of solid Cd $_{2.8}$ Zn $_{0.2}$ As $_2$ solution which are grown from a steam phase were used, whose type of the crystal lattice is identical to Cd $_3$ As $_2$ lattice type (tetragonal, spatial symmetry group I41cd).

Raman spectra of the film Cd $_3$ As $_2$ -MnAs/Si and single crystal Cd $_{2.8}$ Zn $_{0.2}$ As $_2$ are presented in Fig. 2. It is shown in [19] that the most part of the main Raman – active modes of cadmium arsenide:

$$\text{GR} = 26 A_1 + 27 B_1 + 27 B_2 + 65 E,$$

sits in the area $\lambda < 100 \text{ cm}^{-1}$. Unfortunately, because of features of the Raman scattering equipment that we

used Raman scattering spectra were measured only at $\lambda > 130 \text{ cm}^{-1}$. In this area, three wide peaks which are not a manifestation of the classical mechanism of inelastic scattering should be observed: about 140; 250 and 310 cm^{-1} . Their emergence is dictated by the features of Cd $_3$ As $_2$ band structure and explained by the three-band model with consideration for both interband and intraband transitions [19]. As a general view of spectra of single-crystal and film samples are similar, it is possible to conclude that the films obtained have high crystallinity degree with the tetragonal structure similar to volume crystals of Cd $_3$ As $_2$

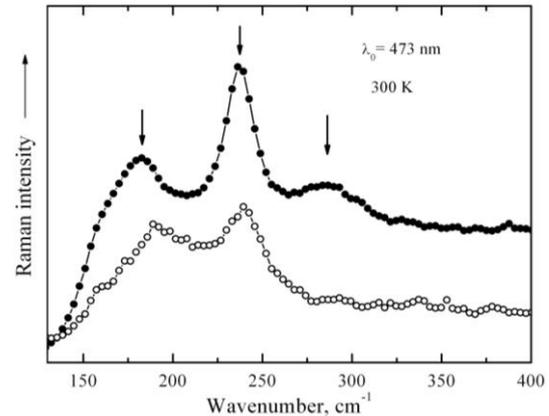


Fig. 2 – Raman spectra of Cd $_{2.8}$ Zn $_{0.2}$ As $_2$ single crystals (filled circles) and Cd $_3$ As $_2$ films – MnAs/Si (open circles) measured at room temperature. Arrows indicate maxima corresponding to ones observed in [19] that arise thanks to interband and intraband transitions of electrons and their interaction with holes

The use of SEM in the mode of secondary electrons showed that the films produced consisted of nanocrystallites 20-50 nm in size (Fig. 3a). Their structures were close, and an average percentage of atoms (see the Table 1) shows an increase in the content of As atoms in comparison with stoichiometric by about 12 %.

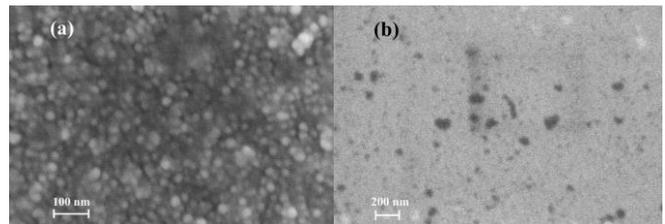


Fig. 3 – The microstructure of the film Cd $_3$ As $_2$ -MnAs obtained by the scanning electron microscopy: in the mode of secondary electrons (a) and in the mode of the backscattered electrons (b)

Table 1 – The average atomic composition of Cd $_3$ As $_2$ -MnAs films in percentage

Mn	As	Cd
14.17	50.51	35.32

According to XRPA, in films the inclusions of MnAs, which is ferromagnetic semimetal with Curie temperature $T_C^{\text{MnAs}} = 317 \text{ K}$ [20], were revealed. The microstructure patterns obtained in the mode of the backscattered electrons (Fig. 3b) contained darker inclusions which belonged to lighter phase and, apparently, were inclusions of MnAs.

The typical image of a site of the film $\text{Cd}_3\text{As}_2\text{-MnAs}$ surface obtained by means of SPM at room temperature are given in Fig. 4. As well as at SEM (Fig. 3), the granulated structure of the surface with an average size of granules about 30 nm (Fig. 4a) has been found. It is well noticeable that the profile of the magnetic interaction of the cantilever with the film (Fig. 4b) practically coincides with its relief defined in the mode of atomic force microscopy (Fig. 4a). So, in spite of the fact that ferromagnetic inclusions of MnAs occupy not all its surface, the film is ferromagnetic.

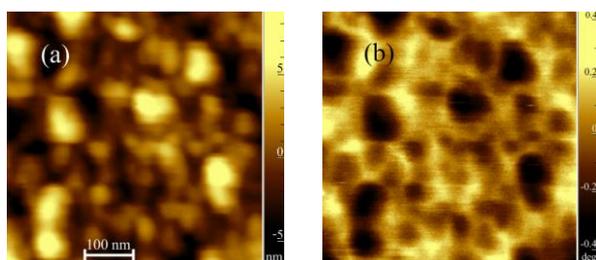


Fig. 4 – Images of a site of the surface for the film $\text{Cd}_3\text{As}_2\text{-MnAs}$ obtained by the SPM in the mode of atomic force (a) and magnetic force (b) microscopy

Investigations of the temperature dependence of magnetization $M(T)$ of the films $\text{Cd}_3\text{As}_2\text{-MnAs}$ (Fig. 5) also confirmed their ferromagnetism with Curie temperature about 320 K, which is close to the quantity T_C^{MnAs} . The fact that the branch FC (cooling of a sample in magnetic field after its heating in magnetic field) does not coincide with the branch ZFC (heating of a sample in magnetic field after its cooling in zero magnetic field) indicates that part of inclusions of MnAs are superparamagnetic and their magnetic moments at low temperatures are "frozen", that is their

direction cannot be changed by a weak external magnetic field. As temperature increases, the directions of the magnetic moments can deviate more and more with respect to the "frozen" direction, and magnetization poorly increases, until the blocking temperature of the magnetic moment T_b [21] is reached after which magnetization with growth of temperature decreases as it has to be in the case of ferromagnet. The similar picture was observed for nanoinclusions of MnAs in various semiconductor matrixes [12, 22-24] earlier. As the temperature determined by the maximum on ZFC branch is close to T_C^{MnAs} , the correct calculation of the size of superparamagnetic inclusions is not possible. By using the results of works [12, 22-24], it is only possible to estimate that this size has to be more than 10 nm, which indirectly is confirmed by SEM and SPM.

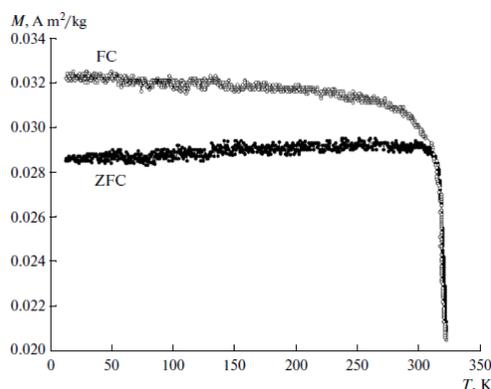


Fig. 5 – Temperature dependence of magnetization of the film $\text{Cd}_3\text{As}_2\text{-MnAs}$ measured in the ZFC and FC modes in a 0,01 T magnetic field

The reported study was funded in part by RFBR according to the research project № 13-03-00125

REFERENCES

- E.K. Arushanov, *Prog. Cryst. Growth Charact.* **25**, 131 (1992).
- T. Liang, G. Gibson, M.N. Ali, M. Liu, R.J. Cava, N.P. Ong, *Nat. Mater.* **14**, 280 (2015).
- A. Kierski, *Acta Phys. Pol. A* **73**, 311 (1988).
- S.F. Marenkin, V.M. Trukhan, *Fosfidi i arsenide cinka i kadmija* (Minsk: 2010) [in Russian].
- D.K. Harris, P.M. Allen, H.-S. Han, B.J. Walker, J. Lee, M.G. Bawendi, *J. Am. Chem. Soc.* **133**, 4676 (2011).
- Z. Wang, H. Weng, Q. Wu, X. Dai, Z. Fang, *Phys. Rev. B* **88**, 125427 (2013).
- S. Borisenko, Q. Gibson, D. Evtushinsky, V. Zabolotnyy, B. Buchner, R.J. Cava, *Phys. Rev. Lett.* **113**, 027603 (2014).
- Z.K. Liu, J. Jiang, B. Zhou, Z.J. Wang, Y. Zhang, H.M. Weng, D. Prabhakaran, S.-K. Mo, H. Peng, P. Dudin, T. Kim, M. Hoesch, Z. Fang, X. Dai, Z.X. Shen, D.L. Feng, Z. Hussain, Y.L. Chen, *Nat. Mater.* **13**, 677 (2014).
- T. Dietl, H. Ohno, *Rev. Mod. Phys.* **86**, 187 (2014).
- C.J.M. Denissen, H. Nishihara, J.C. van Gool, W.J.M. de Jonge, *Phys. Rev. B* **33**, 7637 (1986).
- A.V. Lashkul, E. Lahderanta, R. Laiho, V.S. Zakhvalinskiy, *Phys. Rev. B* **46**, 6251 (1992).
- R. Laiho, K.G. Lisunov, E. Lahderanta, V.S. Zakhvalinskii, *J. Phys.: Cond. Mat.* **11**, 8697 (1999).
- S.F. Marenkin, V.M. Trukhan, I.V. Fedorchenko, *Inorg. Mater.* **49**, 545 (2013).
- S.F. Marenkin, V.M. Trukhan, I.V. Fedorchenko, S.V. Trukhanov, T.V. Sholkava, *Russ. J. Inorg. Chem.* **59**, 355 (2014).
- A.V. Kochura, S.F. Marenkin, A.D. Izotov, P.N. Vasil'ev, P.V. Abakumov, A.P. Kuzmenko, *Inorg. Mater.* **51**, 754 (2015).
- A.V. Kochura, S.F. Marenkin, I.V. Fedorchenko, P.V. Abakumov, *J. Nano-Electron. Phys.* **6** No 4, 04008 (2014).
- Physico-Chemical Phenomena in Thin Films and at Solid Surfaces* (Ed. L.I. Trakhtenberg, Sh.H. Lin, O.J. Ilegbusi) (Amsterdam: Elsevier: 2007).
- S.F. Marenkin, A.D. Izotov, I.V. Fedorchenko, V.M. Novotortsev, *Russ. J. Inorg. Chem.* **60**, 295 (2015).
- J. Weszka, M. Renucci, A. Zwick, *phys. status solidi b* **133**, 57 (1986).
- L. Pytlik, A. Zieba, *J. Magn. Magn. Mater.* **51**, 199 (1985).
- C.P. Bean, J.D. Livingston, *J. Appl. Phys.* **30**, S120 (1959).
- A.V. Kochura, S.V. Ivanenko, A. Lashkul, E.P. Kochura, S.F. Marenkin, I.V. Fedorchenko, A.P. Kuzmenko, E. Lahderanta, *J. Nano-Electron. Phys.* **5** No 4, 04013 (2013).
- A.V. Kochura, R. Laiho, A. Lashkul, E. Lahderanta, M.S. Shakhov, I.S. Zakharov, S.F. Marenkin, A.V. Molchanov, S.G. Mikhailov, G.S. Jurev, *J. Phys. Condens. Matt.* **20**, 335220 (2008).
- V.M. Novotortsev, S.F. Marenkin, L.I. Koroleva, T.A. Kupriyanova, I.V. Fedorchenko, R. Szymczak, L. Kilanski, V. Domuchowski, A.V. Kochura, *Russ. J. Inorg. Chem.* **54**, 1350 (2009).