Synthesis and Investigation of Nanoscale Structured Magnetic A II(3)BV(2):Mg Films

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Semiconductor Zn_3As_2 and Cd_3As_2 films doped with manganese were grown by vacuum thermal deposition on sapphire and silicon substrates. Structural and magnetic investigations showed the presence of ferromagnetic semimetal nanoprecipitate MnAs with Curie temperature about 308 К.

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1. INTRODUCTION

Now semiconductors which can be transformed to ferromagnetic by accepting of 3d-metal impurities are investigated actively. Incorporating of local magnetic moments into semiconductor matrix is one of suitable ways for realization of manipulating by both electron and spin subsystems and can be used for fabricate spintronic devices. [1] One of the most perspective spintronic materials is diluted magnetic semiconductor (DMS) $Ga_{1-x}Mn_xAs$ with Curie temperature $T_C \sim 200$ К [2]. To rich room temperature ferromagnetism it is possible to use hybrid structures. Here ferromagnetic material is inserted to nonmagnetic or diluted magnetic semiconductor. Incorporating Mn into III-As compounds layers can substantially alter the observed ferromagnetic characteristics [3, 4]. With relatively high Mn concentration the main contribution to magnetization of samples is by MnAs inclusions. The presence of ferromagnetic micro- and, especially, nanoprecipitates of MnAs (with $T_C = 317$ K in bulk samples [5]) embedded in the semiconductor matrix improves certain device properties of these materials [6-8]. These microsize clusters are responsible for high temperature behavior of magnetization and relatively high Curie temperature up to 367 K for Mn-doped II-IV-As_2 DMS [9]. The low-field magnetic properties of Mn-doped II-IV-As_2 semiconductors and $ZnSiAs_2$: Mn / Si heterostructures are connected to the nanosize MnAs particles, having size distribution like Gaussian or several overlapped Gaussians with most probable cluster radius from 3 nm up to 6 nm [10-12]. The contribution of paramagnetic phase to magnetization of DMS with magnetic precipitations rises at low temperatures. The source of this contribution is not only isolated Mn ions, but also small complexes, mainly dimmers and trimmers formed by Mn ions, substituting cation positions in crystal lattice [13-15].

Zero-gap semiconductor cadmium arsenide (Cd_3As_2) and open-gap ($E_g \sim 1$ eV), p-type semiconductor zinc arsenide (Zn_3As_2) doped with Mn have drawn attention as DMS materials with spin glasses magnetic behavior [16, 17]. Crystals of Cd_3As_2-Zn_3As_2 system are infrared photosensitivity [18, 19]. Together with demonstrating the high temperature magnetism it let to consider that Cd_3As_2 and Zn_3As_2 doped wit Mn are perspective materials for spintronic applications. Its provokes a further interest in the growing process as well as researching structural and magnetic properties.

2. EXPERIMANTAL DETAILS

To produce Cd_3As_2 and Zn_3As_2 films doped with Mn we have chosen vapor condensation in vacuum as the one that is broadly applied to obtain films and epitaxials layer of semiconductors. Congruent dissociation of $A_3^{II}B_2^{V}$ compounds allows to use vacuum thermal evaporation as a method of producing films.

Congruent dissociation of cadmium and zinc arsenides follows the reactions

$$Cd_3As_2 \longleftrightarrow 3Cd + 0.5As_4,$$
$$Zn_3As_2 \longleftrightarrow 3Zn + 0.5As_4, \qquad (1)$$
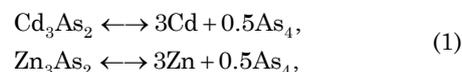
The As_4 molecules are dissociated when ntvperature (T) reach 1100 K, therefore for correct growth regime temperature of evaporation was less then 1100 K.

Vapor pressure (P) vs. (T) dependencies of cadmium and zinc arsenides were described as

$$Zn_3As_2 \text{ [20]}$$

$$\lg P = -(8160 \pm 50) \cdot \frac{1}{T} + 11.127 \pm 0.045 \qquad (2);$$

$$Cd_3As_2 \text{ [21]}$$

$$\lg P = 10.880 - 6700 \cdot \frac{1}{T} \pm \frac{\tau \cdot \sigma}{3.5} \qquad (3),$$

were $\tau = 0.9985$, $\sigma = \sqrt{0.13 - \dfrac{212.2}{T} + \dfrac{8.9 \cdot 10^4}{T^2}}$ and $\dfrac{\tau \cdot \sigma}{3.5} \approx 10^{-2} - 10^{-3}$ at $T \sim 800\text{-}900$ K.

To estimate the flux density of evaporate component, j_u we used Eqs. (2), (3) and Langmuir equation:

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$$j_u = 3{,}16 \cdot 10^{-3} \cdot \alpha_u \cdot \frac{P}{\sqrt{2 \cdot \pi \cdot R \cdot T \cdot M_B}} , \qquad (4)$$

were M_B – molecular weight of evaporate component; R – universal gas constant; α_u – evaporation coefficient (close to unity).

It can be used to calculate provisionally the pressure of the saturated steam for each elementary component if we apply the formulas of the dissociation reaction (1).

Consequently, the relationship of the saturated steam pressures of initial components when Cd_3As_2 or Zn_3As_2 is evaporating will be $P_{Cd}(P_{Zn}) : P_{0As_4} = 3 : 0.5$, and that is used to calculate the flux density. An aggregate flux of evaporation is the superposition of the fluxes of initial components (cadmium or zinc and arsenic) that are calculated by a well know equation of Lengmure. With the stable temperature of the evaporators cell, such preliminary evaluation enables us to find the time required to evaporate a film of a specified thickness.

Experimentally j_u can be found it one knows the rate of the growth of the film with know relative positions of the evaporator and the substrate.

The films have been grown from molybdenum evaporator cell. The pressure of residual vapours has never exceeded 10^{-4} Pa. Leucosapphire L-Al_2O_3, polished and oriented [0001] or silicon substrates, with the dimentions of 8×10 mm^2 have been used. Such materials have been chosen because the coefficients of thermal expansion of sapphire and $A_3^{II}B_2^{V}$ compounds are relatively close. Moreover, L-Al_2O_3 substrate, as it was shown in [21], has an orienting effect on the growth of the films of the above mentioned compounds.

Evaporations were made from powder doped by manganese (up to 10 % mass.),

During the period of growth the temperature of the substrates was about 300 K. A small tray with a set amount of $A_3^{II}B_2^{V}$ powder with 3-5 mkm grains size was placed inside the cylinder. The initial material was made from single crystals grown by the Bridgman method. The rate of evaporation was measured by the loss in weight of the initial powder. The rate of condensation was found by the changes in the thickness of the film considering the time of evaporating.

The thickness and surface structure of the films was measured by Linnic mikrointerferometr, atomic force (AFM) and scanning electronic (SEM) microscopy. The evaporator and the substrates had axially symmetric positioning.

Chemical composition of films was identify by X-ray electro-probe micro analyze. Preliminary calculations of the evaporation flux density and the condensation of Cd_3As_2 and Zn_3As_2 were made by the known equations for the pressures of zinc and cadmium arsenides saturated steam and sufficiently agree with experimentally obtained data.

Magnetization M of the samples was measured between 3-310 K in fields up to $B = 50$ kG using a superconducting quantum interference device (SQUID) magnetometer S600X from Cryogenic Ltd.

3. RESULTS AND DISCUSSION

As it is described in Ref. 5, $A_3^{II}B_2^{V}$ films evaporated on a cold substrate ($T < 400$ K) are characterized by an excessive content of As and a low crystallinity, which predetermines their electrophysical parameters. Heating of the substrates during evaporating results in partial re-evaporating of the fugitive component thus enabling the regulation of the chemical composition of the growing films. For example the authors of Ref. 20 obtained the most closely paralleled with stoichiometrical composition of the evaporated $Cd_{1.2}Zn_{1.8}As_2$ films when $T_{subst} = 170 \pm 10$ °C.
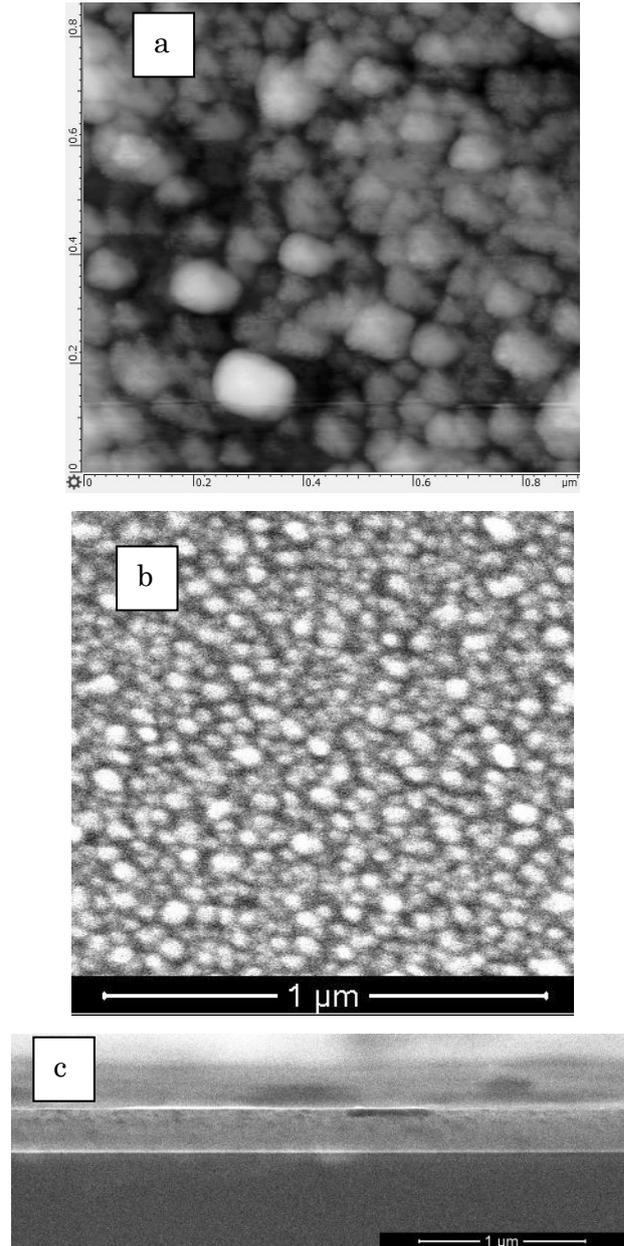
Fig. 1 – The microstructure of the $A_3^{II}B_2^{V}$:Mn films: the AFM image of the Zn_3As_2:Mn film surface (a); the SEM image of the Cd_3As_2 : Mn film surface (b) and edge (c)

SEM and AFM imaging show that unannealing films with stoichiometric composition consist of small grains with diameter 20-100 nm (Fig. 1). $Cd_3As_2:Mn$ films were more homogeneity at their surface then $Zn_3As_2:Mn$ films. The thickness of films was about 250 nm. Microphotographs of the surfaces of the grown films revealed that the crystallinity value changes depending upon the annealing time and temperature. When the temperature and the time period of annealing increase there appear a great number of crystal grains with the size of 0.25-1 mkm.

The temperature dependences of the magnetization measured after cooling the $Zn_3As_2:Mn$ film in zero field (ZFC) ($B < 0.1$ G) and while cooling in a field (FC) ($B = 100$ G) are shown in Fig. 2. The difference between the FC and ZFC clear visible on heating up to 270 K and disappeared at $B > 1$ kG. Value of T_C was estimated by extrapolation of the steepest part of the $M(T)$ curve to the intersect of T – axis. T_C determined in this way are 308 K and very close to T_C of MnAs. There is an increase in the magnetization which reaches a maximum around $T_b \approx 170$ K. M approaches zero with a further increase in temperature. It is manifestation of spin glass state of magnetic subsystem and indicate the presence of nanosize MnAs precipitations as it was observed early for Mn-doped II-IV-As_2 [8, 10, 12]. At $T > T_b$ or above the blocking temperature the thermal fluctuations lead to that assembly of such clusters exhibit superparamagnetic behavior. At $T < T_b$ the moments of the particles are blocked, with their directions distributed at random over the sample volume. In this case the source of

the blocking barrier is the anisotropy energy of individual particles. The moment of each particle is stabilized independently when anisotropy energy becomes enough to counteract the thermal excitations.
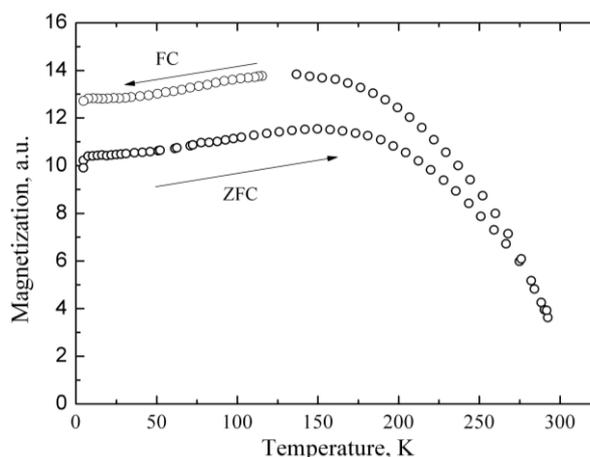

Fig. 2 – ZFC-FC temperature dependences of magnetization, measured in low magnetic field of $Zn_3As_2:Mn$ film

In conclusion we, elaborate growth method of $(Zn, Cd)_3As_2:Mn$ films, which can be used for synthesis of the semiconductor layers precipitated by ferromagnetic nanosize inclusions of MnAs with Curie temperature about room temperature.

REFERENCES

1. V.A. Ivanov, T.G. Aminov, V.M. Novotortsev, V.T. Kalinnikov, *Russ. Chem. Bull.* **53**, 2357 (2004).
2. L. Chen, X. Yang, F. Yang, J. Zhao, J. Misuraca, P. Xiong, S. von Molnar, *Nano Lett.* **11**, 2584 (2011).
3. R.K. Kawakami, E. Johnston-Halperin, L.F. Chen, M. Hanson, N. Guebels, J.S. Speck, A.C. Gossard, D.D. Awschalom, *Appl. Phys. Lett.* **77**, 3665 (2000).
4. Y. Tagaki, J. Lihnemann, B. Jenichen, J. Herfort, C. Hermann, U. Jahn, *Appl. Phys. Lett.* **108**, 123510 (2010).
5. L. Pultik, A. Zieba, *J. Magn. Magn. Mater.* **51**, 199 (1985).
6. K.Y. Wang, M. Sawicki, K.W. Edmonds, R.P. Campion, A.W. Rushforth, A.A. Freeman, C.T. Foxon, B.L. Gallagher, T. Dietl, *Appl. Phys. Lett.* **88**, 022510 (2006).
7. M.T. Elm, C. Michel, J. Stehr, D.M. Hofmann, P.J. Klar, S. Ito, S. Hara, H.-A. Krug von Nidda, *J. Appl. Phys.* **107**, 013701 (2010).
8. V.M. Novotortsev, A.V. Kochura, S.F. Marenkin, *Inorg. Mater.* **46**, 1421 (2010).
9. L.I. Koroleva, V.Yu. Pavlov, D.M. Zashchirinskiĭ, S.F. Marenkin, R. Szymczak, S.A. Varnavsky, W. Dobrowolski, L. Kilanski, *Phys. Solid State* **49**, 2121 (2007).
10. A.V. Kochura, R. Laiho, A. Lashkil, E. Lahderanta, M.S. Shakhov, I.S. Zakharov, S.F. Marenkin, A.V. Molchanov, S.G. Mikhailov, G.S. Jurev, *J. Phys.: Condens. Mater.* **20**, 335220 (2008).
11. A. Kochura, I. Fedorchenko, R. Laiho, A. Lashkul, E. Lahderanta, S. Marenkin, I. Zakharov, *phys. status solidi c* **6**, 1336 (2009).
12. 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).
13. H. Raebiger, A. Ayuela, J. von Boehm. *Phys. Rev. B* **72**, 014465 (2005).
14. A.V. Kochura, B.A. Aronzon, K.G. Lisunov, A.V. Lashkul, A.A. Sidorenko, R. De Renzi, S.F. Marenkin, M. Alam, A.P. Kuzmenko, E. Lahderanta, *J. Appl. Phys.* **113**, 083905 (2013).
15. A.V. Kochura, B.A. Aronzon, M. Alam, A. Lashkul, S.F. Marenkin, M.A. Shakhov, E.P. Kochura, E. Lahderanta, *J. Nano- Electron. Phys.* **5** No 4, 04015 (2013).
16. C.J.M. Denissen, H. Nishihara, J.C. van Gool, W.J.M. de Jonge, *Phys. Rev. B* **33**, 7637 (1986).
17. A.V. Lashkul, E. Lahderanta, R. Laiho, V.S. Zachvalinskiy, *Phys. Rev. B* **46**, 6251 (1992).
18. D.K. Harris, P.M. Allen, Hee-Sun Han, B.J. Walker, J. Lee, M.G. Bawendi, *J. Am. Chem. Soc.* **133**, 4676 (2011).
19. A.I. Belogorokhov, I.S. Zakharov, A.F. Knjazev, F.V. Kochura, *Inorg. Mater.* **36**, 653 (2000).
20. V. Gdanovich, *Structure and properties of $A^{II}B^V$. compounds. In books: Fiziko-khimiya tverdogo tela,* 72 (Moscow: 1972) [in Russian].
21. V.B. Lazarev, V.Ja. Shevchenko, Ja.H. Grinberg et. al., *Poluprovodnikovie soedinenija $A^{II}B^V$* (Moscow: 1978) (in Russian).