Formation and transformation of II-VI semiconductor nanoparticles by laser radiation

A. I. SAVCHUK[a*], V. I. FEDIV[a], S. A. IVANCHAK[a], V. V. MAKOVIY[a], M. M. SMOLINSKY[a], O. A. SAVCHUK[a], A. PERRONE[b], L. CULTRERA[c]

[a]Department of Physics of Semiconductors and Nanostructures, Chernivtsi National University, 58012 Chernivtsi, Ukraine
[b]University of Salento, Physics Department and National Institute of Nuclear Physics, 73100 Lecce, Italy
[c]National Institute of Nuclear Physics, National Laboratory of Frascati, Frascati, Italy

Pulsed laser deposition has been applied for fabrication of $Cd_{1-x}Mn_xTe$ nanocrystals embedded in SiO_2 matrix. By further thermal annealing an increase of average size of nanoparticles and narrowing of their size distribution was reached. Colloidal chemistry methods were used for preparing of $Cd_{1-x}Mn_xS$ nanoparticles. After UV irradiation of the colloidal solution with $Cd_{1-x}Mn_xS$ nanoparticles the average size and size distribution was changed owing size-selective photoetching mechanism. Results of optical and magneto-optical characterizations of the as-grown and the treated nanoparticle samples are described.

1. Introduction

In recent years extensively studied magnetic impurity doped semiconductors have formed new branch in physics of semiconductors and new class of materials called diluted magnetic semiconductors (DMS) or semimagnetic semiconductors. Great interest to these materials is due to opening of the possibility to combine two important kinds of their properties, i.e. semiconducting and magnetic properties. A typical example of DMS is II-VI compounds doped with Mn [1]. The presence of paramagnetic Mn ions in the crystal lattice results in a strong enhancement of spin-related effects such as the Zeeman splitting of the band states and magneto-optical Faraday effect [1-4]. They are attributed to a large sp-d exchange interaction between the spins of the band carriers and localized Mn magnetic moments. In zero-dimensional structures type of DMS quantum dots, nanoparticles or nanocrystals there appear new functionality because the mentioned spin-related phenomena could be strongly modified due to the suppression of the electronic continuum. The DMS nanoparticles or nanocrystals have already been grown for different systems on the base of II-VI compounds: CdMnS [5-7], CdMnSe [8-10], CdMnTe [11-14], ZnMnS [15, 16] and ZnMnSe [17-19]. In many of these cases molecular beam epitaxy (MBE) technique has been applied [9-13, 18]. Among the other growth techniques to fabricate DMS nanoparticles the colloidal chemistry methods are widely applied [5-7, 15-17, 19]. In addition, application of magnetron sputtering technique [8, 14] and ion-implantation method [20, 21] has been reported. The laser assisted techniques can also be applied for the fabrication of 2D or 0D structures type of quantum wells, superlattices and nanocrystals as well for the modification of 0D nanostructures [22-25]. In this paper, we report on synthesis of $Cd_{1-x}Mn_xTe$ nanoparticles embedded in SiO_2 matrix by pulsed laser deposition technique and using of laser irradiation for transformation of colloidal $Cd_{1-x}Mn_xS$ nanoparticles. The grown DMS nanostructures are characterized by optical and magneto-optical spectroscopy.

2. Experimental

Pulsed laser deposition is widely applied technique for the preparing of high quality thin films and multilayer structures [26,27]. We have modified this technique for the fabrication of $Cd_{1-x}Mn_xTe$ semiconductor nanocrystals embedded in SiO_2 matrix [28]. Radiation from a xenon-chloride (XeCl) excimer laser (λ = 308 nm, τ = 30 ns, repetition rate of 10 Hz and energy density of 5×10^4 J/m^2) was focused onto 2×2 mm^2 rectangular spot at the surface of the single crystalline $Cd_{1-x}Mn_xTe$ or SiO_2 part of the target. The circle-like target is consisted of two segments which are filled by $Cd_{1-x}Mn_xTe$ and SiO_2. By rotating this target for 180° we can alternately change kind of ablated material. In case of deposition of separate thin layer of $Cd_{1-x}Mn_xTe$ we can obtain island-like structure which then is covered by SiO_2 material. In such a manner we have obtained array of islands embedded in SiO_2 matrix. Further post-annealing allows us to form nanoparticles of $Cd_{1-x}Mn_xTe$ which have shape close to spherical. To synthesize $Cd_{1-x}Mn_xS$ nanoparticles, colloidal chemistry technique was applied [29]. The final volume of solution that resulted from the synthesis was kept constant at 50 mL. Polyvinylalcohol (PVA) and mercaptoethanol (C_2H_5OSH) were used as a capping agents. The synthesis employed co-precipitation reaction of inorganic precursors of Cd^{2+} and S^{2+} with dopant ions Mn^{2+} in an aqueous

medium containing the capping molecules. PVA in solution played role of the stabilizer of colloidal nanoparticles. Salt solutions were mixed with the aqueous solution of PVA in various proportions in the presence of the mercaptoethanol, stirred and allowed to react for a time period extending from 15 min to 5 days. One of the ways for controlling the size of colloidal nanoparticles is using intense light from laser source or power lamp. For these purposes we have used a pulsed Nd:YAG laser with a pulse duration of 1 ms and wavelength of 532 nm (second harmonic of fundamental frequency) and a 1 kW Xe lamp combined with cut-off filters or a monochromator. The solution with $Cd_{1-x}Mn_xS$ nanoparticles in quartz container was stirred continuously during irradiation. Optical and magneto-optical characterizations were done using grating monochromator for wavelength in range of 200-2200 nm and a water-cooled electromagnet with maximum magnetic field of 5 T. Transmission electron microscopy (TEM) with maximum resolution of 0.7 nm was used to determine the average size of $Cd_{1-x}Mn_xS$ nanoparticles.

3. Results and discussion

Fig. 1 shows the spectral dependence of the optical density measured for the sample of $Cd_{0.64}Mn_{0.36}Te$ nanocrystals into SiO_2 matrix grown by PLD. It is presented the spectrum for as-grown sample and for the annealed ones at 620^oC for 2 and 5 hours. In the first case one can see the broadened absorption edge due to wide distribution of nanoparticle size in this technological method. Thermal annealing of the studied samples leads to the decrease of the size of the $Cd_{0.64}Mn_{0.36}Te$ nanoparticles and improving of their size distribution. The estimated average diameter on the base of photon energy position of the absorption edge for the annealed samples is 12 nm. These are the smallest nanoparticles which are formed at annealing duration of 5 hours.
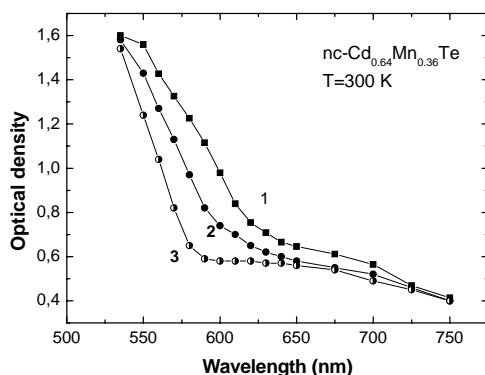
Magneto-optical Faraday effect was applied to confirm the presence of magnetic component into nanoparticles. Faraday rotation spectrum for $Cd_{0.64}Mn_{0.36}Te$ nanocrystals is shown in Figure 2. Main results of this experiment is negative sign of the angle of rotation Θ_F like to bulk DMD crystals and large absolute value of the Verdet constant ($V = \Theta_F/B$ d, where B is magnetic induction and d is thickness). For example, at $\lambda = 570$ nm $V = -3$ deg/mT×cm which is an order of magnitude higher than that in bulk $Cd_{0.64}Mn_{0.36}Te$ crystal [2].
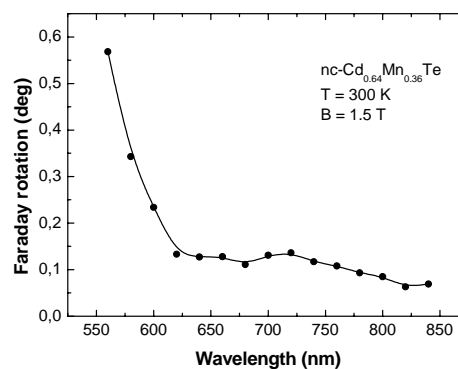

Fig. 2. Spectral dependence of the Faraday rotation of $Cd_{0.64}Mn_{0.36}Te$ nanocrystal grown by PLD (for as-grown sample). Sign of the Faraday rotation angle is negative.

This enhancement is due to combining of both sp-d exchange interaction in DMS with quantum confinement effect in related nanoparticles. The other kind of II-VI based DMS nanoparticles under investigation were $Cd_{1-x}Mn_xS$ nanocrystals grown by colloidal chemistry methods. TEM image of the chemically synthesized $Cd_{0.97}Mn_{0.03}S$ nanoparticles is shown in Fig. 3.
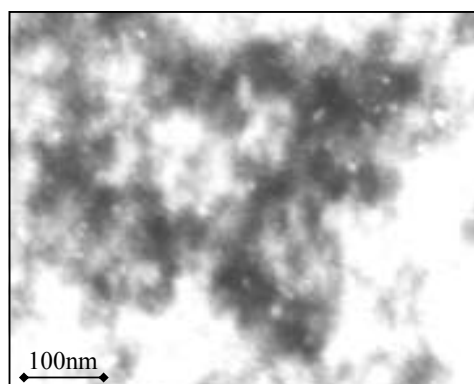

Fig. 1. Spectral dependence of optical density of $Cd_{0.64}Mn_{0.36}Te$ nanocrystals grown by PLD (curve 1 corresponds to as-grown sample, curve 2 to the annealed sample at $620\,^oC$ for 2 h, curve 3 to the annealed sample at 620^oC for 5 h).

Fig. 3. TEM image of a typical sample of colloidal $Cd_{0.97}Mn_{0.03}S$ nanoparticles.

The nanoparticles have a spherical morphology with an average diameter of 18 nm. As in previous case of $Cd_{1-x}Mn_xTe$ nanocrystals as-grown $Cd_{0.97}Mn_{0.03}S$ nanoparticles are characterized by wide distribution of the particle size. It was made attempt to improve this distribution by light irradiation. We have used approach already described previously for case of undoped II-VI semiconductor nanoparticles [30-34]. In particular, according to work [32] monodisperse CdS and ZnS nanoparticles can be prepared by size-selective photoetching method. The main principle of the size-selective photoetching is based on the facts that metal chalcohenide semiconductor particles are photocorroded in aqueous solution under irradiation and that the energy gap of size-quantized semiconductor nanoparticles increases with a decrease in the particle size. If the irradiation is performed with use of the monochromatic light, which can induce photoexcitation of the large particles alone, these particles are selectively photoetched to smaller ones until the irradiated photons are not absorbed anymore in the nanoparticles, due to the size quantization effect. In fact, the performed experiments on $Cd_{1-x}Mn_xS$ nanoparticles confirm these principle of photoetching mechanisms that were previously demonstrated for undoped CdS nanoparticles [32]. Figure 4 shows absorption spectra of $Cd_{0.97}Mn_{0.03}S$ colloid solution with irradiation of monochromatic light. It was found that the absorption spectra of $Cd_{0.97}Mn_{0.03}S$ colloid solution were blue-shifted and more abrupt with a decrease in the wavelength of irradiation light. These findings are well correlated with the obtained data for undoped CdS nanoparticles [32-34]. In the Faraday rotation spectra, shown in Figure 5, it was observed change of sign of the rotation angle Θ_F from positive for CdS nanoparticles to negative for $Cd_{0.97}Mn_{0.03}S$ ones. In fact, the curve for CdS nanoparticles is located higher on the Faraday rotation scale than the curve for PVA solution. It means that these nanoparticles give additional positive contribution in the total Faraday effect. In contrast, the curve for $Cd_{0.97}Mn_{0.03}S$ nanoparticles is located lower, hence they give negative contribution in total Faraday rotation.
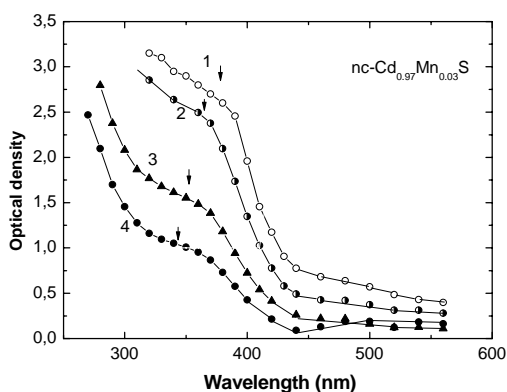
Fig. 4. Spectral dependence of optical density of colloidal $Cd_{0.97}Mn_{0.03}S$ nanoparticles for different

wavelengths of the irradiated light (curve 1 corresponds to as-grown sample, curve 2 to the sample irradiated at 380 nm, curve 3 to the sample irradiated at 360 nm, curve 4 to the sample irradiated at 330 nm).

The revealed reversal of the direction of the Faraday rotation in its spectral dependence is associated with a positive and a negative part due to pure Zeeman and sp-d spin exchange interaction contribution, respectively. Nevertheless, the calculated value of the Verdet constant in case of $Cd_{0.97}Mn_{0.03}S$ nanoparticles ($V= - 0.16$ deg/mT×cm at $\lambda=475$ nm) has the same order as for bulk non-magnetic CdS crystals [2] because of their low magnetization at room temperature and small content of Mn in the nanocrystals.
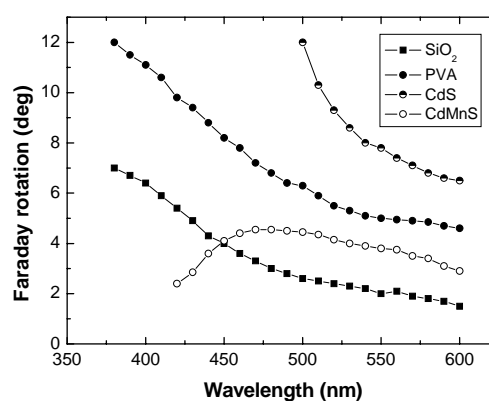
Fig. 5. Spectral dependence of the Faraday rotation for empty quartz container, PVA solution, colloidal nanoparticles of CdS and $Cd_{0.97}Mn_{0.03}S$ in solution. The inner thickness of the quartz container is 10 mm and the induction of magnetic field is 1 T.

The performed experiments with laser irradiation of nanocomposite $Cd_{0.97}Mn_{0.03}S$/PVA films suggest of possible mechanism of laser annealing of these nanostructures similarly to the mentioned thermal annealing of the $Cd_{0.64}Mn_{0.36}Te$ nanocrystals in SiO_2 matrix. However. the observed blue shift of the absorption edge is too small to be attributed to the photoetching effect.

4. Conclusions

The $Cd_{1-x}Mn_xTe$ nanocrystals embedded in SiO_2 matrix have been successfully grown by PLD technique. The average size of the nanoparticles decreases after thermal post annealing of the samples. For preparing of $Cd_{1-x}Mn_xS$ nanoparticles the methods of colloidal chemistry have been applied. Power laser radiation and monochromatic light of Xe lamp was used for irradiation of colloidal solution with $Cd_{1-x}Mn_xS$ nanoparticles and $Cd_{1-x}Mn_xS$/PVA nanocomposite films. It was revealed that

the average size of the $Cd_{1-x}Mn_xS$ nanoparticles decreases with a decrease in the wavelength of irradiation light due to photo-etching effect. In contrast, changes in absorption spectra of $Cd_{1-x}Mn_xS$/PVA nanocomposites after irradiation by laser source are not significant. The magneto-optical studies suggest of typical for DMS materials giant Faraday rotation and even additional enhancement in case of $Cd_{1-x}Mn_xTe$ nanocrystals and ordinary Faraday effect for $Cd_{1-x}Mn_xS$ nanoparticles. The observed findings are important for the controlled manufacturing of II-VI based DMS nanoparticles with the adjusted properties.

References

[1] J. K. Furdyna, J. Appl. Phys., **64,** R29 (1988).
[2] P. I. Nikitin, A. I. Savchuk, Sov. Phys. Usp., **33,** 974 (1990).
[3] K. Sato, H. Katayama-Yoshida, Semicond. Sci. Technol., **17,** 367 (2002).
[4] T. Fukumura, H. Toyosaki, Y. Yamada, Semicond. Sci. Technol., **20,** S103 (2005).
[5] L. Levy, N. Feltin, D. Ingert, M. P. Pileni, J. Phys. Chem., **B 101**, 9153 (1997).
[6] R. N. Bhargava, D. Gallagher, A. Nurmikko, Phys. Rev. Lett., **72**, 416 (1994).
[7] Q. Pang, B. C. Guo, C. L. Yang, S. H. Yang, M. L. Gong, W. K. Ge, J. N. Wang, J. Crystal Growth, **269**, 213 (2004).
[8] K. Yanata, K. Suzuki, Y. Oka, J. Appl. Phys. **73**, 4595 (1993).
[9] A. Hundt, J. Puls, F. Henneberger, Phys. Rev. **B 69**, 121309R (2004).
[10] P. R. Kratzert, J. Puls, M. Rabe, F. Henneberger, Appl. Phys. Lett., **79**, 2814 (2001).
[11] P. Wojnar, J. Suffczynski, K. Kowalik, A. Golnik, G. Karczewski, J. Kossut, Phys. Rev. **B 75**, 155301 (2007).
[12] L. Besombes, Y. Leger, L. Maingault, D. Ferrand, H. Mariette, J. Cibert, Phys. Rev. Lett. **93**, 207403 (2004).
[13] A. V. Scherbakov, A. V. Akimov, D. R. Yakovlev, W. Ossau, L. W. Molenkamp, Y. Terai, S. Kuroda, K. Takita, I. Souma, Y. Oka, Phys. Stat. Sol.(b), **241**, 361 (2004).
[14] H. Nasu, M. Hayashi, J. Matsuoka, K. Kamiya, K. Tanaka, K. Hirao, Jpn. J. Appl. Phys. **34**, L440 (1995).

[15] M. Tanaka, J. Luminescence, **100**, 163 (2002).
[16] S. W. Lu, B. I. Lee, Z. L. Wang, W. Tong, B. K. Wagner, W. Park, C. J. Summers, J. Luminescence, **92**, 73 (2001).
[17] D. J. Norris, N. Yao, E. I. Charnock, T. A. Kennedy, Nano Lett., **1**, 3 (2001).
[18] S. Lee, M. Dobrowolska, J. K. Furdyna, Phys. Rev., **B 72**, 075320 (2005).
[19] R. Beaulac, P. I. Archer, D. R. Gamelin, J. Sol. State Chem., **181**, 1582 (2008).
[20] Y. Kanemitsu, H. Matsubara, C. W. White, Appl. Phys. Lett., **81**, 535 (2002).
[21] Y. Kanemitsu, A. Ishizumi, J. Luminescence, **119-120**, 161 (2006)
[22] A. A. Ruth, J. A. Young, Coll. Surf. A: Physchem. Eng. Aspects, **279,** 121 (2006).
[23] F. Antolini, A. Ghezelbash, C. Esposito, E. Trave, L. Tapfer, B. A. Korgel, Mater. Lett. **60,** 1095 (2006).
[24] M. Gajdardziska-Josifovska, V. Lazarov, J. Reynolds, V. V. Yakovlev, Appl. Phys. Lett., **78,** 3298 (2001).
[25] V. V. Yakovlev, V. Lazarov, J. Reynods, M. Gajdardziska-Josifovska, Appl. Phys. Lett. **76**, 2050 (2000).
[26] S. Acquaviva, M. L. De Giorgi, Appl. Surf. Sci. **208-209,** 620 (2003).
[27] A. P. Caricato, E. D'Anna, M. Fernandez, G. Leggieri, A. Luches, E. Mero, M. Martino, Thin Solid Films, **433,** 45 (2003).
[28] A. I. Savchuk, P. N. Gorley, V. V. Khomyak, A. G. Voloshchuk, V. I. Fediv, S .V. Bilichuk, I. D. Stolyarchuk, A. Perrone, Mater. Sci. Eng. **C 23,** 753 (2003).
[29] A. I. Savchuk, V. I. Fediv, A. G. Voloshchuk, T. A. Savchuk, Yu. Yu. Bacherikov, A. Perrone, Mater. Sci. Eng., **C 26,** 809 (2006).
[30] H. Matsumoto, T. Sakata, H. Mori, H. Yoneyama, J. Phys. Chem., **100,** 13781 (1996).
[31] Y. Ohko, M. Setani, T. Sakata, H. Mori, H. Yoneyama, Chem. Lett., **7,** 663 (1999).
[32] T. Torimoto, H. Kontani, Y. Shibutani, S. Kuwabata, T. Sakata, H. Mori, H. Yoneyama, J. Phys. Chem. B, **105,** 6838 (2001).
[33] M. Marandi, N. Taghavinia, A. Irajizad, S. M. Mahdavi, Nanotechnology, **16,** 334 (2005).
[34] K. Sato, S. Kojima, S. Hattori, T. Chiba, K. Ueda-Sarso T. Torimoto Y. Tachibana, S. Kuwabata, Nanotechnology, **18,** 465702 (2007).

_____
*Corresponding author: a.savchuk@chnu.edu.ua