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Laser formation of semiconductor coatings using droplet technology

Antipov[a] A.A., Arakelian[a] S.M., Zimin[b] S.P., Kutrovskaya[a] S.V., Kucherik, A.O[a,*]., Osipov[a] A.V., Prokoshev[a] V.G.

[a]*Vladimir State University named after Alexander Grigorievich and Nikolai Grigorievich Stoletovs", Vladimir, Gorkii st. 87, 600000, Russia*

[b]*Yaroslavl State University named after P.G.Demidov, Soveskaya st.14 , 150000, Russia*

Abstract

The results on laser production of semiconductor nanoparticles under continuous laser action of near-by infrared range (up to 106W/cm2) on a massive PbX sample in a liquid are presented. The method of drop deposition for setting PbX quantum dots on a substrate has been considered. With the use of a simulation model there have been described the features of forming a deposited layer in the process of drop evaporation.

Keywords: colloidal solution; semiconductor particles; laser action; Monte-Carlo method

1. Motivation / State of the Art

Semiconductor nanoparticles are being increasingly used in various fields of technology. The properties of nano-dimensional particles with the size of 2-50nm consisting of 10^3 - 10^5 atoms are changing greatly as compared to massive material. Dependence of optical properties of nanoparticles on their size gives an opportunity to create new generations of solar batteries, lasers, light-emitting diodes, etc. on their basis [1].

* Corresponding author. Tel.: +74-922-479621 ; fax: +74-922-333369 .
E-mail address: kucherik@vlsu.ru .

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2. Experimental Results

The method of producing semiconductor nanoparticles of lead chalcogenides with an average size of 5 -50nm by means of continuous laser radiation of a moderate intensity near-by infrared range (up to 10^6W/cm^2) has been proposed in this paper. As it is shown in our papers [2,3] the application of continuous laser radiation enables to initiate the nanostructuring of PbTe, PbS semiconductors without specific demands to the environmental conditions. Radiation with 1.06 micrometers wavelength corresponds to a quantum of photon energy which considerably exceeds the width of a prohibited zone of semiconductors being used. The method of laser ablation in liquids [4,5] has been used for obtaining colloid systems; ethanol (C2H5OH) and glycerin (C3H5(OH)3) having been used as solvents.

The sizes of the particles obtained were determined by means of the particle size analyzer Horiba LB-550; the principle of its operation relying on the phenomenon of dynamic light scattering. The analyzer is designed for measuring particles in the range from 3nm to 6 micrometers. Table 1 gives average values of a middle-size semiconductor particle calculated on the basis of six successive measurements with the time difference of one minute. There was no shift of the histogram of the particle size distribution which is the evidence of the colloid solution stability and of a spherical shape of nanoparticles being formed.

The results of Table 1 indicate that in all cases the size of nanoparticles obtained in glycerin is less than of those obtained in ethanol. Thus, solvent viscosity has a great effect on the kinetic processes of nanocrystal formation.

Table 1. Average size of colloidal particles obtained from the targets in solutions

Solution	Target	Intensity W/cm^2	Average size of colloidal particles, R_0, nm
C3H5(OH)3	PbS	10^4-10^6	6-26
C2H5OH	PbS	10^4-10^6	5-18
C3H5(OH)3	PbTe	10^4-10^6	6-30
C2H5OH	PbTe	10^4-10^6	4-13

For the lead chalcogenides having large values of a high frequency dielectric constant and small values of effective masses of electrons and holes [6], Bohr radius of exciton a_B calculated for the isotropic case has large values being equal to 50nm for PbTe and to 18nm for PbS.

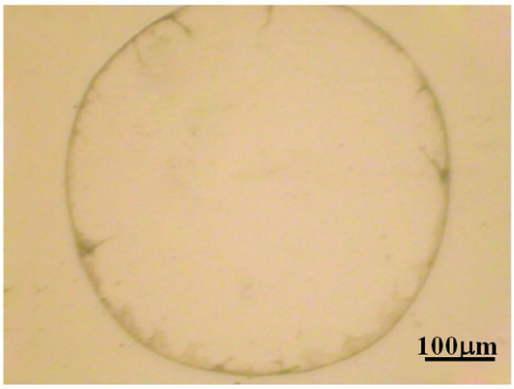

Fig. 1. Optical image of the deposited drop

Comparison of sizes of the particles being obtained (Table1) with the value of exciton Bohr radius shows that the strict condition $R_0 \leq a_B$ is met for telluride nanocrystals. As for the lead sulfide nanoparticles it sometimes fails to create crystals being less than exciton Bohr radius and $R_0 \leq a_B$. The above comparison enables to say that the conditions of dimensional quantization are satisfied for PbTe nanoparticles and PbSe nanocrystals with small sizes. As a result electronic spectra of lead chalcogenides quantum dots have energy gaps which can considerably exceed the width value of volumetric material prohibited zone [7]. Thus, the proposed method enables to get quantum dots of lead chalcogenides under laser evaporation of massive crystal targets in the liquid.

For evaporating a solvent and placing nanoparticles on a substrate there were used the methods of drop deposition which enable to form a deposited layer with various morphology under the change of drop sizes and the temperature difference of a colloid solution and a substrate. The peculiarity of this method of depositing nano coatings is connected with the fact that the morphology of a deposited layer [8,9] to a great extent depends on the liquid solvent properties, colloid particles sizes, the temperature of a drop and a substrate and so on.

A drop of a colloid solution consist of semiconductor particles being at the room temperature was deposited on the substrate surface heated from 20^0C to 100^0C. Fig. 1 gives an optical picture of the evaporated drop at the temperature of 20^0C deposited on the surface of quartz glass.

In all cases the deposition had a clear-cut boundary tending to a regular geometrical shape. Fig. 2 shows that the increase of the substrate temperature results in great changes of a deposited layer morphology.

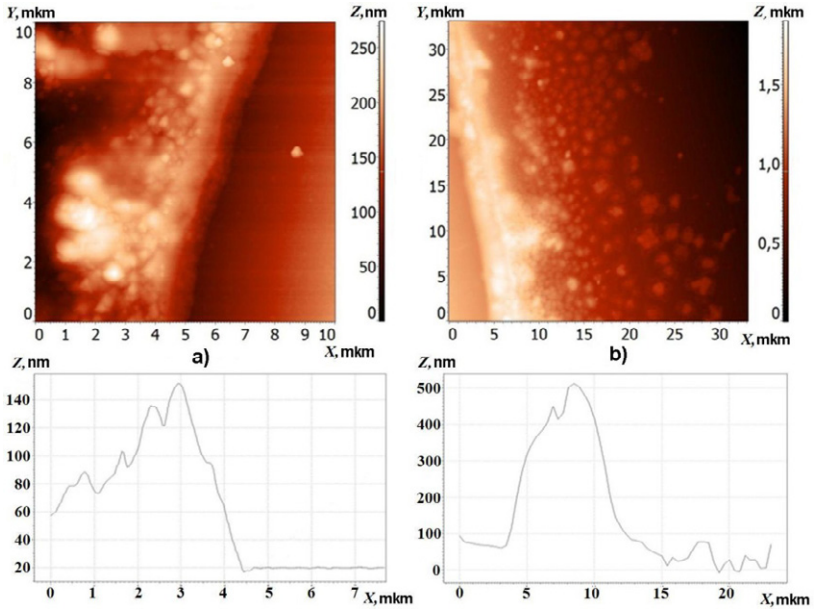

Fig. 2. AFM-images of the drop borders for the different temperatures of the quartz substrate: a) 20^0C; b) 100^0C

Actually, when the temperatures of a substrate and a colloid drop are the same (20^0C) there occurs an active migration of particles to the drop edges. But a comparatively slow speed of evaporation enables to shape a deposition boundary with the height of 150nm and the characteristic width of 3micrometers.

Deposition occurs mainly at the drop boundary; the particles having a tendency to shape extensive filamentary structures on the surface with the characteristic grain of the order 100nm. With the temperature increase the height of the boundary layer starts to raise and at the temperature of 100^0C accounts to 500nm, the width being ~ 5micrometers. In this case a more homogeneous deposition is achieved; the particles deposit not only at the boundary but also within the evaporating drop and form the second deposition ring. A deposited layer is denser but separate islands sized 1.5 micrometers and composed of the particles, having the size of 50nm.

Spectra of the deposited films combinational scattering are given in fig. 3. These data have been obtained at the room temperature on the serial combined atomic power microscope and on the confocal combinational scattering microscope Integra-Spectra under the action of the primary beam of the argon laser at the wavelength of 800nm. A detailed analysis of the measured spectra features under varying the conditions of depositing will be given in the next paper. Now it is very important to note that the peaks being observed close to 180cm^{-1} for PbTe and 150cm^{-1} for PbS correspond to the theoretically calculated and experimentally observed values [10] for telluride and lead sulfide in crystal and nanocrystal states for 2LO(X) and LA(L)PbS. This confirms that when a laser acts, PbTe and PbS nanoparticles are formed in a liquid and then they are put on the substrate.

For describing the features of shaping a deposited layer during the drop evaporation process a simulation model was realized.

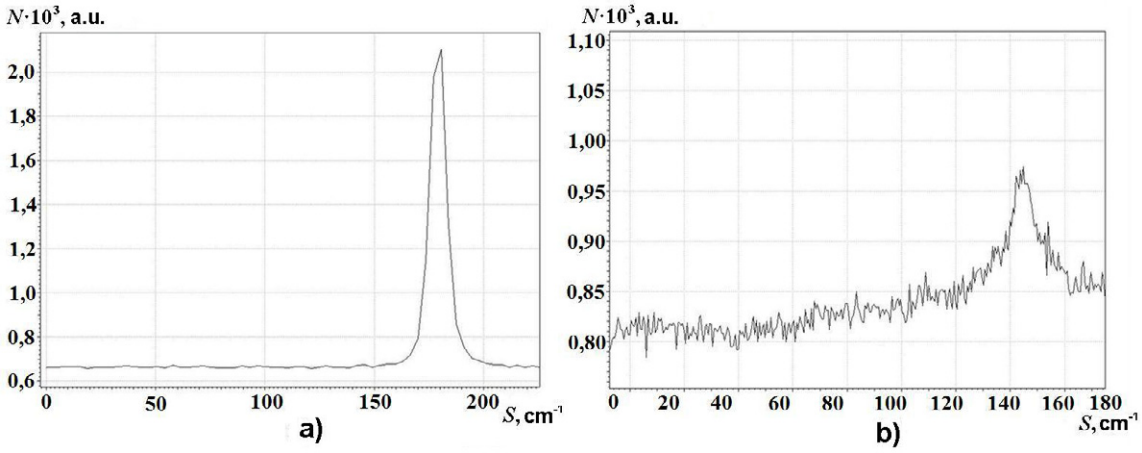

Fig. 3. Raman-spectra of obtained nanoparticles: a)PbTe; b)PbS

3. Results and Discussion

When there is a drop deposition of nanoparticles from a colloid solution, the process of a deposited layer formation can be symbolically divided into two phases: drop spreading and drop evaporation.

The dynamics of the drop spreading process is determined by the following factors: surface tension, wetting, viscosity, heat conduction, ionic bonds [11]. Thus, when the concentration of particles in the drop is rather small, a spreading process can be presented similarly to the case of isotropic medium.

While falling from the height h the drop stores potential energy

$$W = mgh, \tag{1}$$

where m - drop mass, g – free fall acceleration.

Drop mass can be determined from the equilibrium condition.

$$\sigma = mg/\pi d, \tag{2}$$

where σ - surface tension coefficient, d – capillary inner diameter.

The given energy will be spent on the increase of the drop surface energy ΔE and on the creation of molecular coupling with the surface Q [12].

Surface energy change can be described as:

$$\Delta E = \sigma\pi(R_k^2 - 2d^2), \tag{3}$$

where $R_к$ – drop base radius.

Formation of molecular bonds with the surface is determined as [11,12]:

$$Q = \frac{\Delta Q \pi R_к^2}{k\gamma a^2}, \tag{4}$$

where ΔQ - the energy of one bond activation, k – coefficient of the surface substrate roughness, γ – the extent of covering a base area with particles ($0 < \gamma \leq 1$),a – the area per one bond (~ m).

10^{-9}Then the drop radius can be defined as:

$$R_к = \sqrt{mgh + 2\sigma\pi d^2/\sigma\pi + \frac{\Delta Q}{k\gamma a^2}} \quad (5)$$

It is possible to determine the time of drop evaporation by means of Maxwell equation for small sized drops [13]:

$$dm/dt = 4\pi R_к DM(p_к - p_п)/RT, \quad (6)$$

where R – universal gas constant, D – diffusion coefficient, $p_ж$ – partial pressure over a drop, $p_п$ – partial pressure over a flat surface.

Using Tomson formula defining the pressure of saturated vapor:

$$\ln\left(\frac{p_к}{p_п}\right) = \frac{2\sigma M}{\rho RTR_к} \quad (7)$$

where ρ – liquid density, the time of drop evaporation $t_и$ can be defined by means of the expression [18]:

$$t_и = R_k^2 / \frac{2MDp_п}{RT\rho}\left[exp\left(\frac{2\sigma M}{\rho RTR_к}\right) - 1\right] \quad (8)$$

Spreading time is usually characterized within the range of 10-100 microseconds while the evaporation can take from tens of seconds to tens of minutes depending on the type of the solvent being used. Therefore it is possible to neglect the movement of particles at this stage and think that they are uniformly distributed in the drop volume.

Thus, the model of nanoparticles deposition process can be presented in the following way:

1) defining maximally possible sizes of a drop;
2) calculating the time of drop evaporation;
3) overlapping the grid defining the movement of particles in the rated area;
4) giving a linear speed of shifting drop boundaries;
5) determining a relative mobility of particles
6) movement and deposition of particles

As a method of simulating the process of the particle movement and deposition there was used a kinetic method of Monte-Carlo which is effectively used for the computer simulation of physical systems at the atomic level in the research of many technological processes of coating, such as molecular beam epitaxy, plasma deposition and etching, magnetron deposition and others [14].

In our problem the particles are considered to be uniformly distributed in a drop volume at the initial time (after drop spreading). The particles go through the sites of a computational lattice in Monte-Carlo method; arbitrary initial speed of the particles is determined by heat energy:

$$\frac{mv^2}{2} = \frac{3}{2}kT \quad (9)$$

and is normalized with the use of the coefficient of mobility:

$$u = \frac{1}{6}\pi\nu r', \tag{10}$$

where ν – liquid viscosity, r' – nanoparticle radius.

A particle is supposed to be fixed on the surface if moving across the lattice it reaches the boundary of a computational area; its kinetic energy being less than the energy of bond activation. Fig. 5 shows the images of deposited particles obtained by the given procedure at different temperatures of a substrate and a colloid drop.

Thus, the simulation results (fig. 4) match correspondingly match the data obtained during the experiment (fig. 2).

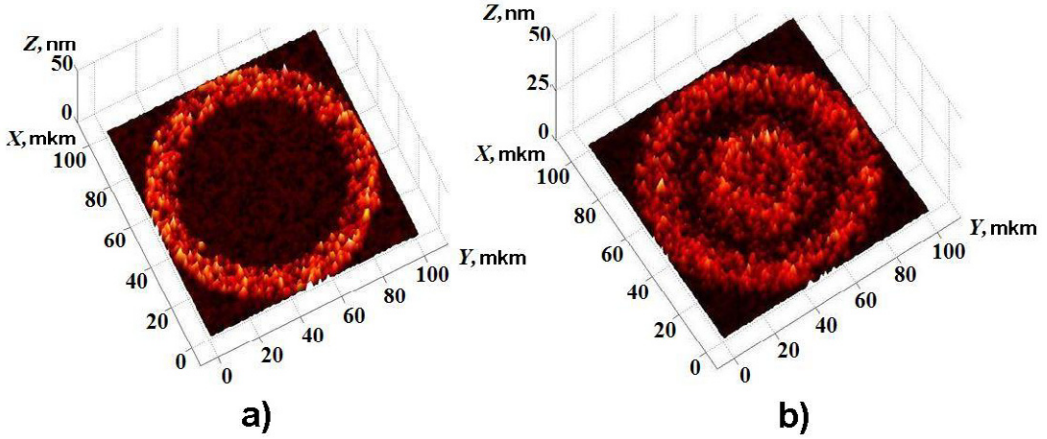

Fig. 4. Modeling images of deposited drop for different temperatures of the quartz substrate: a) 20^0C; b) 100^0C

Conclusion

The paper represents the results of laser synthesis of semiconductor nanoparticles of lead chalcogenides. The method of laser evaporation in liquid was used for obtaining nanoparticles. The way proposed for obtaining nanoparticles under the action of continuous laser radiation has shown that nanoparticles can be quantum dots by their geometric properties. The method of drop deposition used for shaping a deposited layer consisting of quantum dots has been considered. It has been demonstrated that the given method enables to obtain structures with various morphology which depends on the substrate temperature. Later, optical and electro-physical properties of the obtained structures will be studied which is very important for their use in the devices of optoelectronics and photonics. The present work is partly supported by the grants within the framework of Federal Program " The development of a higher school scientific potential" # 2.3313.2011, Federal Program "Research and development in priority areas of scientific and technical complex of Russia for 2007-2013" contract #14.518.11.7030 as well as by the grant RFBR 12-02-90419 – Ukr_a.

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