THE GROWTH PROCESS AND SOME OPTICAL PROPERTIES OF NANOPARTICLES GaSe, FORMED IN THE VOLUME OF GLASS MATRIX

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The nanoparticles of gallium selenide in the volume of glass matrix are obtained with the help of the crystallization method in the matrix. The X-ray diffraction investigations show, that the nanoparticles of gallium selenide with structure δ-GaSe form in the glass matrix. In the obtained structures, the photoluminescence radiation spectra (at the excitation wave length 510nm) have half-widths of lines ~0,23eV with the radiation maximum 710nm.

Introduction

Last years, the big attention has been paid for the technology working of the obtaining and studying of nanoparticle physical properties of layered gallium selenide semiconductor [1-5]. The limit of particle sizes leads to very interest physical phenomena. With the decrease of the particle sizes, the material physical properties change significantly. The decrease of the particle sizes increases the ratio of surface area (S) to the particle volume (V) and increases the contribution of the surface atoms to the physical and thermodynamical properties of nanoparticles. For example, the decrease of nanoparticle sizes CdSe from 10 nm to 1nm increases the past of surface atoms practically from 20% till 100% [6]. The increase of the ratio (S/V) at the decrease of the particle sizes increases the contribution of surface energy to the free energy. As result, the materials, which are unstable in the volume state, can be stable in the nanoparticle form [7]. The semiconductor nanoparticles are perspective materials in the computers, medicine and instrument making [6]. The one of the important problem of the computers is the increase of system speed, which can be solved with the help of nanomaterials, having the high nonlinear-optical properties [6]. Such materials can allow to create the computing systems, working in the terahertz regions. That's why the working of new technologies and materials for the high-speed computers present the big interest. The composite materials on the base of nanoparticles of layered semiconductor GaSe, which has the high nonlinear optical properties can become the one of such materials. As it is known with the decrease of nanoparticle sizes the forbidden band width of material increases because of quant-size effect [8-9]. However, the situations are possible at witch with the decrease of the particle sizes, the forbidden band width of nanomaterials decreases. Such situation described in the work [10] is realized for nanotubes of GaSe. It is shown, that such systems are stable. The possibilities of the change of forbidden band width of GaSe in the wide interval make this material one of the interest object of scientific researches.

The technology of obtaining and nanoparticle structure of GaSe

The meaning of the technology is that nanoparticle and matrix materials (or its components) are taken into quartz ampoule or corundum crucible. The matrix melting point should be lower, than nanoparticle material melting point.

The mixture is heated up to the homogeneous mass formation at the temperature higher than melting point of nanoparticle material. Moreover, components (anions and cations) of nanoparticle dissolve in the melt of matrix material and form the homogeneous mixture. Further the mixture is cooled by the definite program. At the mixture cooling, the supersaturation on semiconductor components forms in the system. At the same time, the creation of buds and nanoparticle formation begins. The process of nanoparticle formation in the matrix melt volume accompanies with the creation of buds of different sizes and carrying out of crystallization process. Moreover, the absorption of small particles by the big ones is benefit on energy expenditure.

As result, the nanoparticle crystallization centers form. The formation of these centers in the matrix melts volume decreases of supersaturation factor around the nanocrystal. In this connection, the probability of new bud creation around nanoparticles decreases. The sizes of the created microcrytals depend on the mixture duration time at such temperature. After that the mixture is cooled till the room temperature by the definite program.

The GaSe nanoparticles in the volume of glass matrix are formed by us by the following method. The glass and components of nanoparticle (Ga and Se) are taken in the quartz ampoule. Metallic Ga and Se in the stoichiometric weight ratio are mixed with the well ground glass and are taken in the quartz ampoule. The nanomaterial components are 5% in the weight ratio with matrix. The quartz ampoule is pumped, with the help of forvacuum pump and made unbrazing. After that the ampoule is taken in the muffle stove and is heated till the temperature 1200^0C. The heating time was near 90 minutes. Moreover, the homogeneous mixture creates. The Ga and Se components interreact in the volume and totally dissolve in the glass melt. After that the homogeneous melt is cooled by the special program. The melt is kept at the temperature 850^0C during 60 minutes, later the melt is cooled till the room temperature. The obtained composite material is porous one. The planes, prepared from this material, are treated by the thermal annealing at the temperature 570^0C during hours. In the result of this process, the nonhomogeneous of composite material removed.

The GaSe nanoparticle structure is defined with the help of X-ray diffraction analysis (DRON 2.0). The glass, in the volume of which the gallium selenide nanoparticles are formed, is ground in the mortar. After that the powder X-ray-grams are obtained (fig.1).

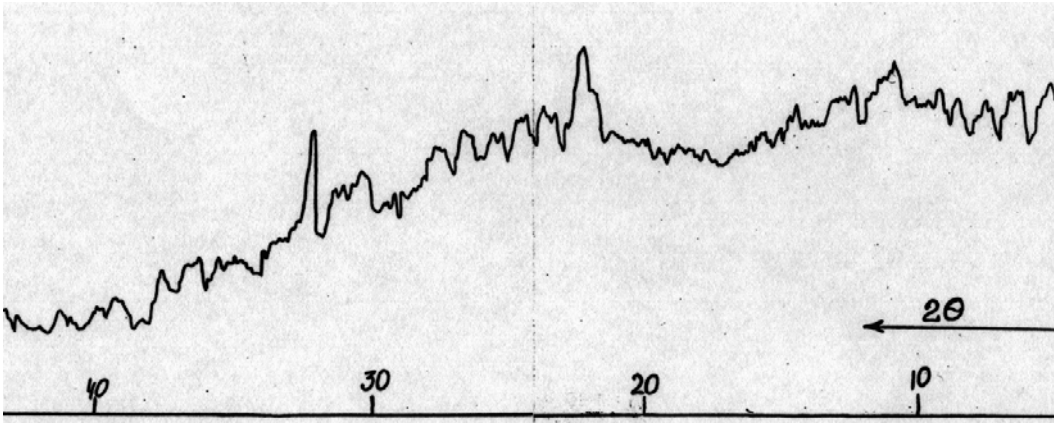

Fig1. X-ray diffraction from powder GaSe:glass

The analysis results are shown in the table 1. As it is seen from the table, the observable values of spacing of lattice planes significantly don't differ from standard values.

Table 1.

№	Observable value d in A^0	Standard value d in A^0	I	hkl
1	7,993	7,988	40	004
2	3,998	3,994	100	008
3	3,234	3,232	36	101
4	2,899	2,90	42	105
5	2,776	2,779	94	106
6	2,5226	2,527	12	108
7	2,3989	2,392	30	109
8	1,874	1,8697	15	1014

The value of interplanar distances corresponds to phase δ-GaSe. The nanoparticle sizes δ -GaSe are founded from the ratio [11].

$$d = \frac{0.9\lambda}{\beta \cos\theta} \quad , \qquad (1)$$

where β- is intensity half-width of diffraction line, measured in radians, λ=1,5406A^0 is wavelength CuKα, θ- is diffraction angle. The average value of particle sizes GaSe, calculated from the equation (1), is equal 15,6nm. Such small value for nanoparticle sizes of gallium selenide is explained by the fact, that duration time for crystallization process is chosen very small. In the result of this, the process of nanoparticle enlargement (coalescence) was difficulties. Besides, probably, the high temperature (850^0C) harms to the increase of the particles in the direction Van der Wasl forces evidently.

The photoluminescence in nanoparticles of GaSe

The optical properties of gallium selenide nanoparticles, formed in the metanol volume are investigated in detail in the ref.[1]. The particle sizes in these experiments change from 2nm till 6nm. The average particle size is 4,0nm. The half-width of radiation line depended on wavelength and changed in interval (0,16-0,7)eV. After chromatographic particle division on sizes the average size is equal ~ 2,5 nm. In this case the half-width of radiation line decreases in 1,5 times in the comparison with the previous samples.

The radiation spectra (fig.2a) and excitation spectra (fig.2b) in the GaSe nanoparticles: glass at the temperature 90K, are investigated by us. At the excitation by photos with the energy λ=510 nm, the not wide band with half-width, which is equal to 0,23 eV and radiation maximum at 710nm (1,75eV) are observed. The nanoparticle excitation spectra have very wide band with half-width E=0,42eV, and maximum is in the region 2,42 eV.

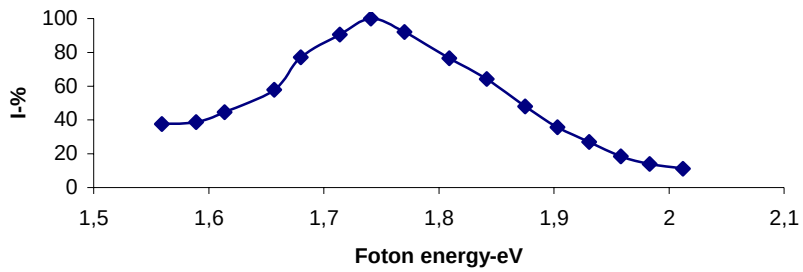

Fig. 2a. Radiation spectra of GaSe nanoparticles.

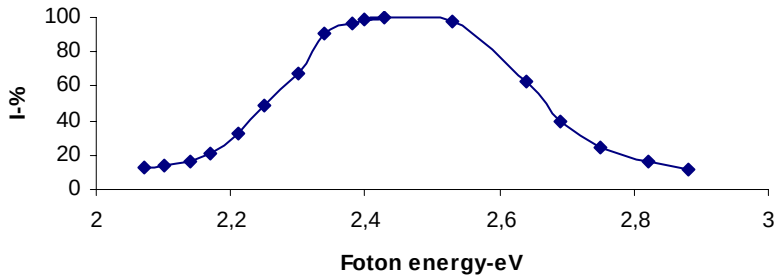

Fig. 2b. Excitation spectra of GaSe nanoparticles.

The observable by us wide excitation spectrum testifies about the wide interval of particle distribution on the sizes. In the result of which, the width of the prohibited band in the dependence on the sizes, changes in the wide range, according to the ref [8].

$$\Delta E = \frac{\pi^2 \hbar^2}{2 m^* d^2} \quad , \qquad (2)$$

where h is Plank's constant, d is particle size, m^* is effective reduced mass of electrons and holes, π=3,14 constant. In the result of which, the of fundamental absorption edge in the nanoparticles spreads.

The temperature dependence of photoluminescence of Ga Se nanoparticles, formed in the glass matrix is investigated also by us. The dependence of radiation intensity maximum (λ 710nm) on the sample heating temperature in the temperature interval 80-270K is investigated (fig.3).

As it is seen from the figure 3, in the temperature interval (80-120)K, the radiation intensity increases~15%, and in the temperature interval (120-200)K, the intensity change doesn't significant (less, than 2%). The temperature increase leads to the insignificant intensity increase of photoluminescence (~7%). Such form of temperature dependence is explained by the fact, that nonradiative transfers are near radiative transition. At the temperature increase, the carrier transition from the nonradiative transitions into the radiative one takes place, in the result of which the radiation intensity increases. The last heating leads to the radiation level saturation. In the temperature interval (200-270)K the decrease of the carrier concentration in the radiated level takes place and radiation intensity decreases.

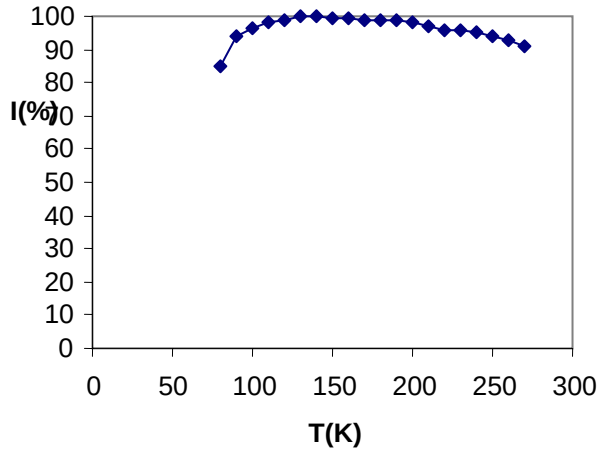

Fig.3. Temperature dependence of photoluminescence of GaSe nanoparticles.

Conclusion

Thus, for the first time the gallium selenide nanoparticles in the volume of glass matrix are formed by the crystallization method. By X-ray diffraction analysis, it is shown, that the nanoparticles with the structure б-GaSe form in the glass matrix. The wide value of excitation spectrum half-width is explained by the distribution of particle sizes in the big range. It is shown, that maximum radiation intensity of photoluminescence weakly depends on the temperature.

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ŞÜŞƏ MATRİSDƏ FORMALAŞDIRILMIŞ GASE NANOHİSSƏCİKLƏRİNİN BƏZİ FİZİKİ XASSƏLƏRİ

Matrisdə kristallaşma metodu ilə şüşə matrisdə GaSe nanohissəcikləri alınmışdır. Rentcen struktur analizi vasitəlsilə müəyyən edilmişdir ki, şüşə matrisdə δ-GaSe strukturlu nanohissəciklər formalaşır. Alınmış nümunələrdə fotolümenessensiya spektrinin yarım eni (510nm dalğa uzunluğu ilə həyəcanlandırıldıqda) ~0,23eV, şüalanma spektrinin maksimumu isə 710nm diapazonundadır.

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ПРОЦЕСС РОСТА И НЕКОТОРЫЕ ОПТИЧЕСКИЕ СВОЙСТВА НАНОЧАСТИЦ GaSe, СФОРМИРОВАННЫХ В ОБЪЕМЕ СТЕКЛЯННОЙ МАТРИЦЫ

С помощью метода кристаллизации в матрице были получены наночастицы селенида галлия в объме стеклянной матрицы. Рентгеноструктурными исследованиями было показано, что в стеклянной матрице формируются наночастицы селенида галлия со структурой δ-GaSe. В полученных структурах спектры излучения фотолюминесценции (при длине волны возбуждения 510нм) имеют полуширины линий ~0,23eV с максимумом излучения 710нм.