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RESEARCH ARTICLE

STRUCTURE, OPTICAL AND LUMINESCENT PROPERTIES OF GaSe AND InSe NANOPARTICLES

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ABSTRACT

Experimental resultson preparation of nanoparticles on the basis of GaSe crystals, analysis of structure and investigation of their electric, optical and photoluminescent characteristics are presented. Nanoparticles and thin GaSeand InSe films on a glass substrate were grown by hydro-chemical sedimentation method from a solution, containing sodium selenosulphide, gallium chloride and indium chloride. As substrates we choose a glass and GaSe crystals grown by a Bridgman method. By means of X-ray diffraction analysis (XRD), atomic force microscope (AFM), energy dispersive analysis of X-rays (EDAX), and a scanning electronic microscope (SEM) researches of the internal constitution and structure of the received samples have been conducted. Absorption spectra have been measured using JOBIN-YVON monochromator with diffraction lattice with subsequent detecting by FEU-100. Photoluminescence spectra were investigated by means of Cary Eclipse spectrophotometer. Using X-ray analysis it is established that nanoparticles belong to β-modification of GaSe (a=3,75Å, c=15,94 Å) with hexagonal structure. Dependence of electrical conductivity on temperature for GaSe and InSe on GaSe substrate and current-voltage characteristics for GaSe and InSe on a glass substrate and GaSe substrate have been investigated. On the basis of spectral dependence the band-gap energy for nano-particles and activation energy for impurity the levels located in the band-gap have been defined.

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INTRODUCTION

Researches of the dimensional quantum phenomena in poorly studied but that time perspective layered A^3B^6 type semiconductors open big prospects for designing on their basis new devices with a wide spectrum of functionality. Ionic-covalent bond between atoms in layers and weak Van der Waals interaction between them are responsible for strong anisotropy of their physical properties and are principal reason of observation some effects unusual for other anisotropic semiconductors. On the other hand, due to presence of low density of dangling bonds on the cleavage surface (less than 10^{10} cm^{-2}) layered semiconductors can be used as solid-state substrates (De Blasi *et al.,* 1989) for formation quantum points, growing fullerenes, polymers, as well as for reception Van der Waals epitaxy (Michel Cote*et al.,* 1998; Tu *et al.,* 2004; Xiang-Bai Chen *et al.,* 2006; Muradov *et al.,* 2006; Bahtinov *et al.,* 2007; Drapak and Kovaljuk, 2007; Kh. Mirzade *et al.,* 2008) in manufacturing solar elements (Lee *et al.,* 1976; Di Giulio *et al.,* 1987). Detectors of X-ray radiation (Joint Committee on Powder Diffraction Standards, 1987), optical converters (Gillan and Barron, 1997), photo-trigger devices (Le Comber *et al.,* 1972) and photo-detectors for ultra-violet, visible and near-IR ranges of the electromagnetic radiation spectrum based on layered crystals favorably differ from others by high radiation resistance, increased photosensitivity and high-speed response (Pankove, 1971; Kyazymzade *et al.,* 2007). Due to high nonlinear susceptibility, these compounds possess non-linear optical properties, and in them were observed such effects, as two-photon absorption, parametrical generation of light, generation of the second harmonic, optical bistability, generation of laser radiation, etc. (Abdullayev *et al.,* 1973; Abdullayev *et al.,* 1970; Kyazymzade *et al.,* 2007; Guseynov *et al.,* 1999; Bidadi *et al.,* 1996). Carried out theoretical analysis as an example GaSe has shown that from thermodynamic reasons it is probably existence of nanotubes 40-48Åin radius (Tu, Yang, *et al.,* 2004). Later they have been received for GaSe by laser and thermally induced exfoliation. It is known also about reception of GaSe nanotubes by evaporation and exfoliation by organic or through steam-liquid-solid phase growth mechanism during thermal evaporation of GaSe using gold nanoparticles as catalyst.

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As to nanoparticles (quantum points), for their reception a number of methods of high-temperature chemical synthesis has been used. Thus D.F. Kelley, V. Chikan have received GaSe nanoparticles having the form of a disk in diameter of 2-6 nm and thickness in four monoatomic layers (Se-Ga-Ga-Se) (Tu *et al.,* 2004).Among a wide spectrum of nanomaterials special place occupy nanostructured materials for nanoelectronics. Nanostructuring of the substances allows directionally change spectrum of its physical and chemical properties. Due to it in the literature a term a programmed matter was appeared which in narrow sense can be understood as creation materials with a set of characteristics by the nanostructuring method. Interest to synthesis of small particles, nanocrystals of various substances has essentially grown, when it was found out that reduction of the crystallite size below some threshold size can lead to considerable change on crystal structure and occurrence of quantum properties. Quantum effects are observed most distinctly when the size of particles are less than 10 nm. A spherical form of the nanocrystals thus is very important in order to ensure an optimum discrete energy levels spectrum of the quantum points. The method of chemical sedimentation from water solutions allows receive semiconductor nanocrystals much more the smaller size, than methods molecular-beam epitaxy or lithographic technology. Origin of germs and their growth in a solution at chemical sedimentation leads to the form nanocrystallites close to spherical, while filming by methods of molecular-beam epitaxy or electrochemical sedimentation gives non-spherical forms. In this work experimental results of reception nanoparticles on the basis of GaSe crystals, an analysis of structure and research of their electric, optical and photo-luminescent characteristics have been presented.

Experimental method of reception of nanoparticles

GaSe nanoparticles have been received by chemical sedimentation a method (M-CBD). Thus an important role is due to manufacturing of substrates, preparation of compositions and the very process of reception. As substrates we choose a glass and GaSe crystals. GaSe crystals were grown by a Bridgman method. The sizes of crystal substrates were 10x6x0,5 mm^3. Glass substrates were preliminary carefully cleared in a solution of potassium dichromate and sulfuric acid, then consistently washed out in hydrochloric acid, acetone and repeatedly in the distilled water, and after washing were dried up in vacuum drying box. Thin GaSe films on a glass substrate were grown by hydro-chemical sedimentation method from a solution, containing sodiumselenosulphide (Na_2SeSO_3) gallium chloride ($GaCl_3$) and indium chloride ($\dot{I}nCl_3$).As initial raw materials especially pure substances were used: $Se, Ga, \dot{I}n, Na_2SO_3$ and HCl. Initially Na_2SeSO_3, $GaCl_3$ and $\dot{I}nCl_3$ compounds on below-mentioned reactions were synthesized:

$$Na_2SO_3 + Se \rightarrow Na_2SeSO_3,$$

$$2Ga + 6HCl \leftrightarrow 2GaCl_3 + 3H_2,$$

$$2\dot{I}n + 6HCl \leftrightarrow 2\dot{I}nCl_3 + 3H_2, \quad (1)$$

then water solutions of sodiumselenosulphide and gallium chloride in the ratio, necessary for GaSe formation, with composition corresponding stoichiometric composition have been prepared. In this solution substrates were maintained during from one to ten minutes. Further, growing of GaSe nanoparticles was made on the following sequence: four reservoirs with liquids were used. In the first reservoir there was a solution of gallium chloride, in the second - the distilled water, in the third - solution of sodiumselenosulphide and in the fourth, also the distilled water. Substrates were consistently maintained in these reservoirs during 20 seconds, 10 seconds, 15 seconds and 10 seconds, accordingly. This process repeated 30 consecutive times. Using X-ray diffraction analysis (XRD), atomic force microscope (AFM), energy dispersive analysis of X-rays (EDAX), and a scanning electronic microscope (SEM), researches of the internal constitution and structure of the received samples have been conducted. Current-voltage characteristics were registered by means of digital measuring devices. For ohmic contacts silver paste were used. Absorption spectra have been measured using JOBIN-YVON monochromator with diffraction lattice with subsequent detecting by FEU-100. Output signals directed to transient digitizer system which included storage oscilloscope (Le Groy 9400) and computer system (board Master 800 ABI 8). Photoluminescence spectra were investigated by means of Cary Eclipse spectrophotometer. As a radiation source the xenon lamp was used.

The structural analysis of GaSe nanoparticles

On Fig. 1 and 2 are presented diffraction patterns (XRD) of GaSe nanoparticles on a glass substrate and on GaSe crystal, accordingly.

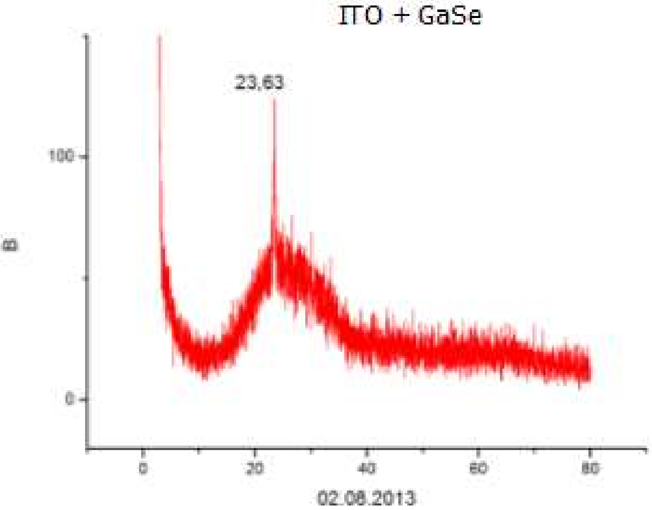

Fig. 1. Diffraction pattern (XRD) for GaSe nanoparticles on a glass substrate

Using X-ray analysis it is established that nano-particles belong to β-modification of GaSe (a=3,75Å, c=15,94 Å) with hexagonal structure (Bourdon, 1974).

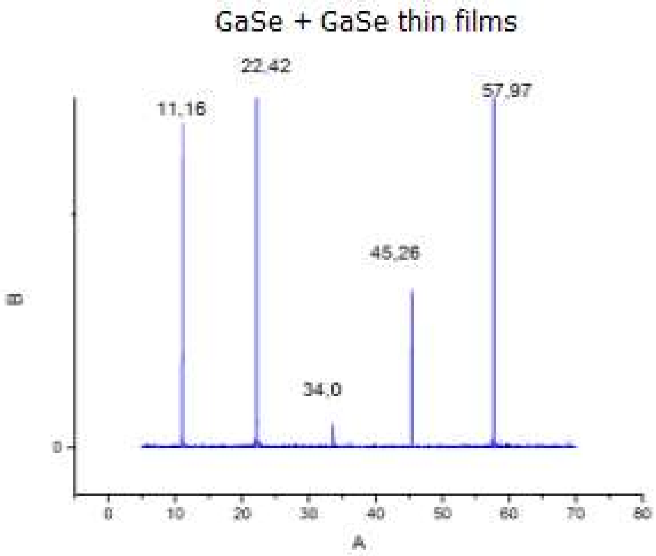

Fig. 2.Diffraction pattern (XRD) for GaSe nanoparticles on GaSe substrate

Space group of symmetry is D_{6h}^{4}. In the Table the calculated values of lattice parameters for GaSe are presented. On the basis of X-ray diffraction patterns by means of the Debay-Sherer formula sizes of received nanoparticles have been calculated (Weller, 1977). Estimations show that sizes of GaSe nanoparticles lie in an interval 7÷20 nm. On Fig. 3AFM images of GaSe nanoparticles on a glass substrate (a) and on GaSe substrate (b) are presented. As is seen from figures, in the presented figures homogeneous distribution of particles are not observed.

By means of energy dispersive analysis of X-rays (EDAX) (Fig. 4) and a scanning electronic microscope (SEM) (Fig. 5) researches of the internal constitution and structure of the GaSe nanoparticles have been conducted. The images received by means of SEM show that the received substances consist of spherical nanoparticles with the dimensions (7-20) nm which gather in polydispersive form. By EDAX method it is established that gallium to selenium ratio equals Ga: Se=1:1, showing that the substance structure is in stoichiometrical parity.

Electric, optical and luminescent propertiesof GaSe and InSenanoparticles

Fig. 6 shows dependence of electrical conductivity on temperature for GaSe and InSeon GaSe substrate. In the 200-300K temperature range dependence of electrical conductivity on temperature for GaSe on GaSe substrate has exponential character. From a slope of straight line of dependence log σ=f (1/T) activation energy for charge carriers was defined, which is equal E_a = 0.32 eV. In the 200-300K temperature range dependence logσ=f (1/T) activation energy for for GaSe + InSe was defined, which is equal E_a = 0.41 eV, E_a = 0.13 eV and E_a = 0.54 eV. On Fig. 7 current-voltage characteristics (CVC) for GaSe (a) and InSe (b) on a GaSe substrate at different temperatures are presented.

At small values of the applied external voltage CVC for GaSe on a glass substrate appear linear that is explained by the current of the equilibrium charge carriers, and at relatively high voltages is defined by laws of flow of space-charge limited currents.

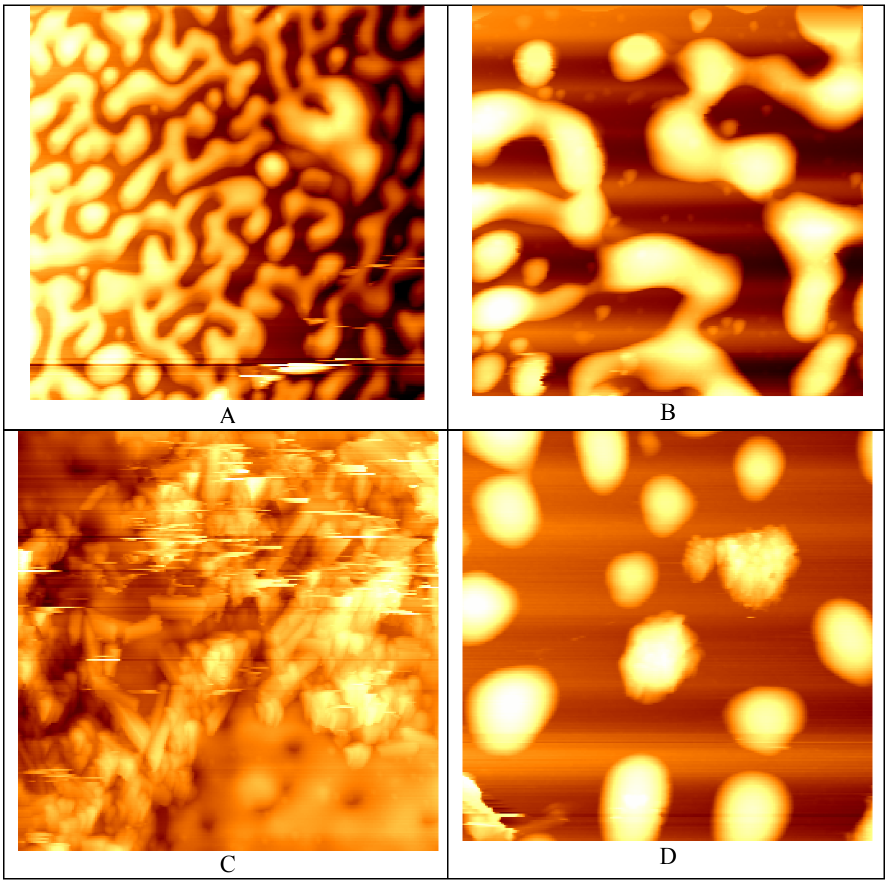

Fig. 3.AFM images of GaSe nano-particles on a glass substrate (a), (b) and on GaSe substrate (c), (d) before (a, c) and after (c, d) annealing, accordingly

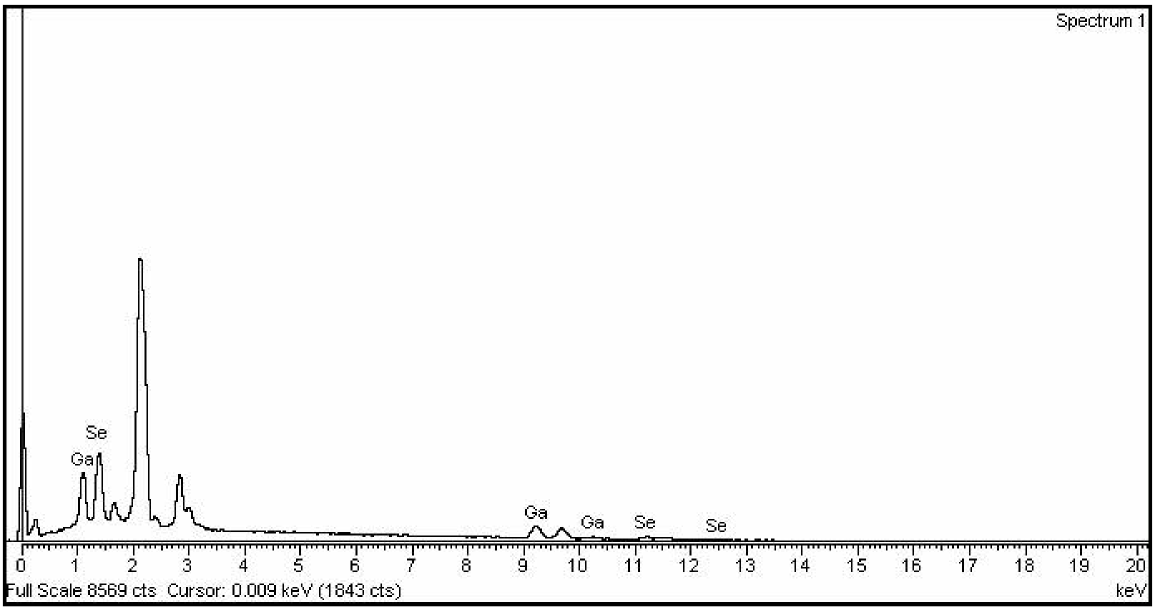

Fig. 4. EDAX images for GaSe nano-particles

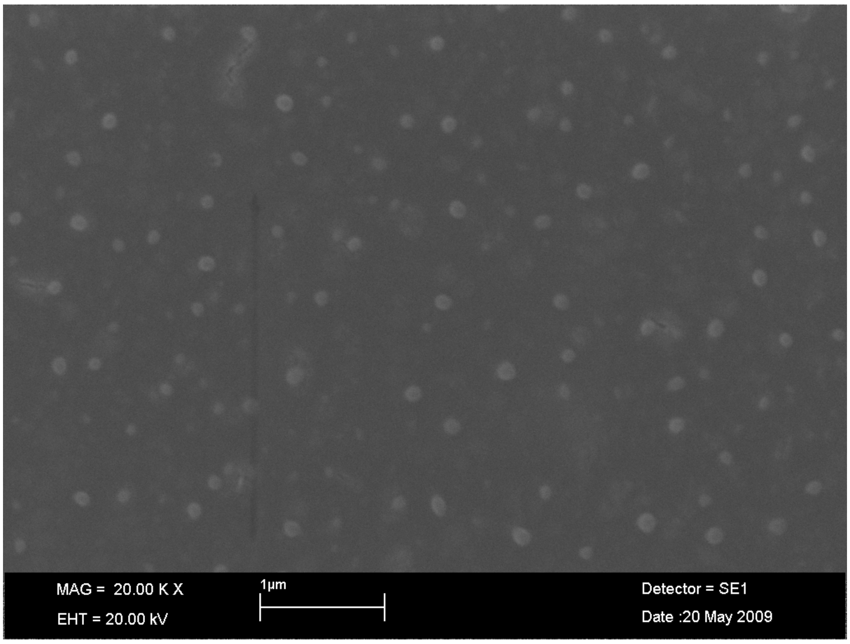

Fig. 5. SEM image for GaSe on a glass

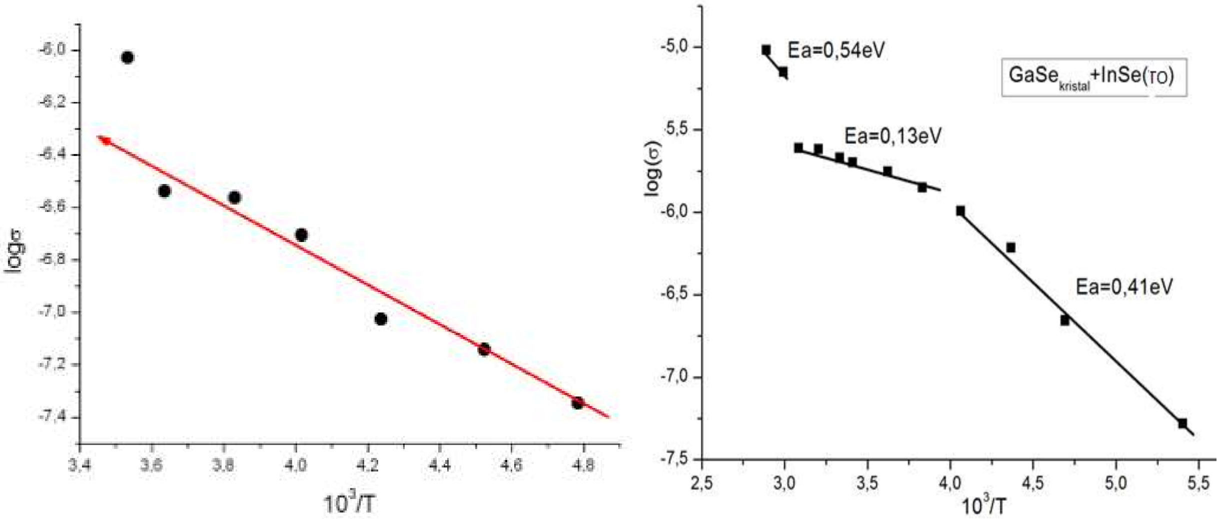

Fig. 6. log σ =f (1/T) for GaSe + GaSe (a) and for GaSe + InSe (b)

It is necessary to notice that at research of injection currents, it is necessary to consider properly an extremity of contact injection level and its parity with level of usual generation of free charge carriers. Defining role thus, certainly, plays also degree of initial filling of energy levels and value of their concentration which in the conditions considered by us are controlled by technological conditions of films sedimentation. On Fig. 8, an absorption spectrum for GaSe nanoparticles on a glass substrate is presented. On the basis of spectral dependence the band-gap energy for nanoparticles and activation energy for impurity the levels located in the band-gap have been defined. As is seen from figure, absorption in the short waves region corresponds to energy 3.69 eV. We believe that this value is equal to band-gap energy for studied GaSe nanoparticles. In this case band-gap energy for nanoparticles appears much more than E_g for GaSe crystals.

It is necessary to notice that the increase in band-gap of nanoparticles in comparison to a massive crystal is prominent feature of semiconductor nanoparticles. It is known that a band-gap of nanoparticles depends on the band-gap of the crystal (E_g), the reduced mass of the investigated crystal (m_r) and on dimensions of nano-particles (a) (Samuel, 2004).

$$E_g\,(\text{nano.}) = E_g\,(\text{cryst.}) + \frac{\hbar^2\pi^2}{2m_r a^2} \quad (4)$$

The estimations carried out by us taking into account GaSe parameters shows that the calculated values of the band-gap for nanoparticles agree satisfactorily with the found value on the basis of an absorption spectrum.

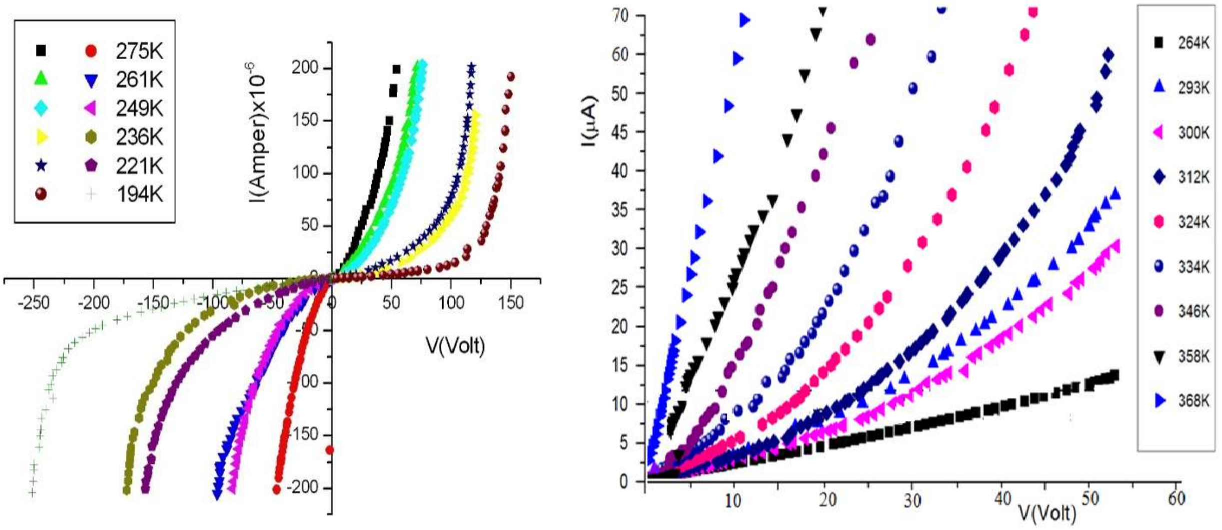

Fig. 7. Current-voltage characteristics of GaSe (a) and InSe(b) nanoparticles on GaSe substrate at different temperatures

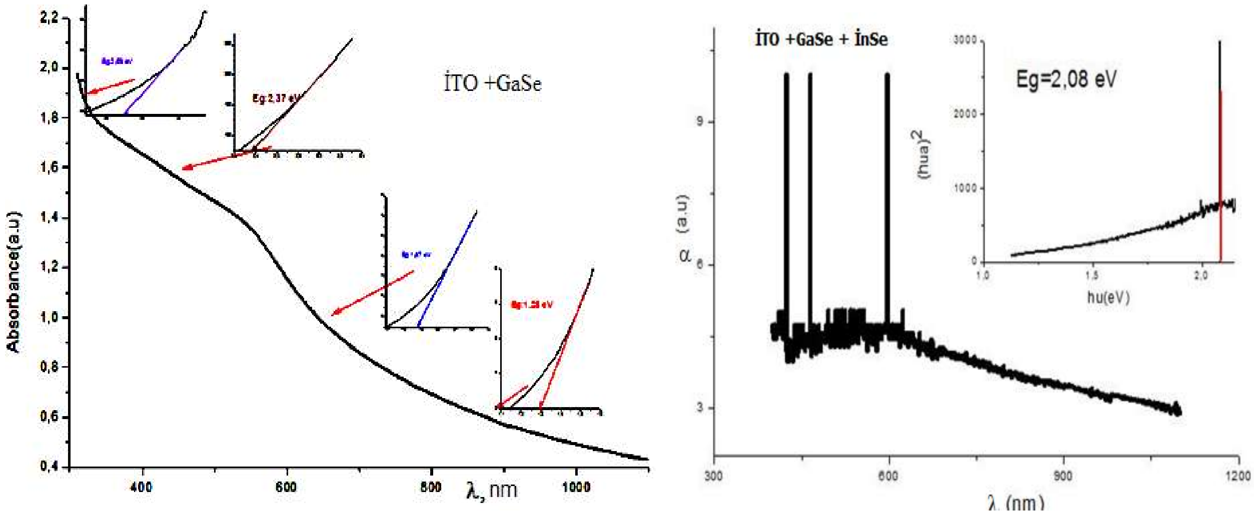

Fig. 8. a) Absorption spectrum of GaSe nanoparticles on a glass substrate, b) Absorption spectrum of ITO + GaSe +InSe

For comparison on Fig. 8, b, an absorption spectrum of GaSe crystals is presented. E_g values found by us for GaSe crystals has appeared equal E_g=1.98 eV.

Observed on a absorption spectrum of GaSe nanoparticles peaks 2.37 eV, 1.87 eV and 1.28 eV, apparently are caused by electronic transitions from the capture centers D_1, D_2 and D_3, located in the band-gap, into conductivity band, accordingly.

On Fig. 9a photoluminescence spectrum of GaSe nanoparticles on a glass substrate is presented. As is seen from figure, photoluminescence spectra cover long-waves region, much more exceed edge luminescence and are in continuous absorption region. Band-gap energy for nanoparticles appears much more than E_g for GaSe crystals.

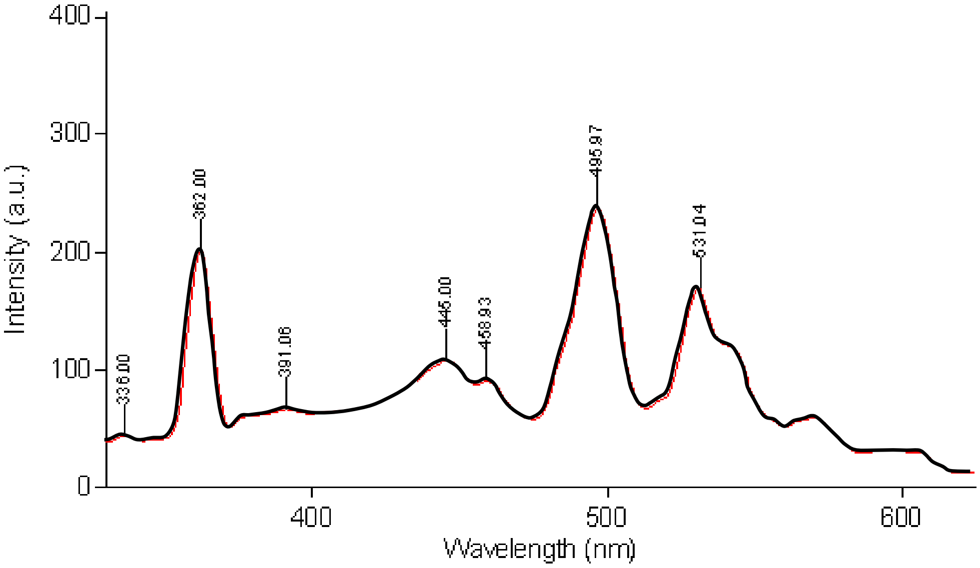

Fig. 9. Photoluminescence spectra of GaSe nanoparticles on a glass substrate

Conclusion

Experimental results of preparation nanoparticles on the basis of GaSe crystals, analysis of structure and research of their electric, optical and photoluminescent characteristics have been presented. GaSe nanoparticles were prepared by a method of chemical sedimentation. Thin GaSe films on a glass substrate were grown by hydrochemical sedimentation a method from a solution containing sodiumselenosulphide and gallium chloride. Using X-ray analysis it is established that nano-particles belong to β-modification of GaSe (a=3,75Å, c=15,94 Å) with hexagonal structure. The images received by means of SEM show that the received substances consist of spherical nanoparticles with sizes (7-20) nm which gather in polydispersive form. By EDAX method it is established that gallium to selenium ratio equals Ga: Se=1:1, showing that the substance structure is in stoichiometrical parity. In the 200-300K temperature range temperature dependence of electrical conductivity for GaSe on GaSe substrate has exponential character with activation energy $E_a = 0.32$ eV.

At small values of the applied external voltage current-voltage characteristics for GaSe on a glass substrate appear linear that is explained by the current of the equilibrium charge carriers, and at relatively high voltages is defined by laws of flow of space-charge limited currents. Current-voltage characteristics for GaSe on GaSe substrate are described well enough by exponential dependence, and at low temperatures in the backward direction at relatively low voltages CVC of studied structures obeys the linear law, at the high backward voltage a soft breakdown occurs. On the basis of spectral dependence the band-gap energy for nanoparticles and activation energy for impurity the levels located in the band-gap have been defined.

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