ACADEMIC PRESS

Available online at www.sciencedirect.com

SCIENCE DIRECT

Journal of Solid State Chemistry 172 (2003) 381–388

JOURNAL OF SOLID STATE CHEMISTRY

http://elsevier.com/locate/jssc

Chemical deposition of semiconducting cadmium selenide quantum dots in thin film form and investigation of their optical and electrical properties

Biljana Pejova,[a,*] Atanas Tanuševski,[b] and Ivan Grozdanov[a]

[a] Faculty of Natural Sciences and Mathematics, Institute of Chemistry, Sts. Cyril and Methodius University, ROB 162, Skopje 1000, Macedonia
[b] Faculty of Natural Sciences and Mathematics, Institute of Physics, Sts. Cyril and Methodius University, ROB 162, Skopje 1000, Macedonia

Received 9 September 2002; received in revised form 15 November 2002; accepted 21 November 2002

Abstract

Cadmium selenide quantum dots with cubic crystal structure are chemically deposited in thin film form using selenosulfate as a precursor for selenide ions and ammonia buffer with double role: as a ligand and as a pH value controller. The optical band gap energies of as-deposited and thermally treated cadmium selenide thin films, calculated within the framework of parabolic approximation for the dispersion relation, on the basis of equations which arise from the Fermi's golden rule for electronic transitions from valence to conduction band, are 2.08 and 1.77 eV, correspondingly. The blue shift of band gap energy of 0.34 eV for as-deposited thin films with respect to the bulk value is due to the quantum size effects (i.e., nanocrystals behave as quantum dots) and this finding is in agreement with the theoretical predictions. During the thermal treatment the nanocrystals are sintered, the increase of crystal size being in correlation with the decrease of band gap energy. The annealed thin films are practically non-quantized. From the resistance–temperature measurements, on the basis of the dependence of $\ln(R/\Omega)$ vs $1/T$ in the region of intrinsic conduction, the thermal band gap energy (at 0 K) of 1.85 eV was calculated.

Keywords: Cadmium selenide; Thin films; Semiconductors; Chemical deposition; Nanocrystals; Band gap energy; Quantum size effects

1. Introduction

The development of contemporary, sophisticated technologies which increase the quality of human life is closely related to the semiconducting materials. The science and technology of semiconducting thin films have a crucial role in high-tech industry. Thin films of semiconducting materials are applicable in the field of microelectronics, optical electronics, in communication technologies, as well as in energy generation and conservation strategies, etc. [1].

In recent years, the field of nanocrystalline semiconducting thin films is rapidly expanding. The increasing interest for these materials is due to the fact that they are characterized by properties which are substantially different from the corresponding ones for bulk semiconductors [2]. These phenomena are known as confinement effects or quantum size effects and are of special interest in nanotechnology. The nanodimensions of semiconducting crystals influence the band structure which allows the nanotechnologists to design a semiconductor with suitable optical and electrical properties (i.e., suitable band gap energy) for various technical applications by controlling the crystal size [3].

Continuing our research in the field of semiconducting metal selenide thin films [4–7], especially those systems in which quantum size effects are exhibited, in this study we focus on the cadmium selenide quantum dots in thin film form.

The thin films of cadmium selenide, which belongs to the $A^{II}B^{VI}$ group of semiconductors, are of great technical interest. The characteristic combination of properties, determined from the band structure, makes cadmium selenide of prime importance in energy conservation problems [8–10]. Usually, the thin films

---

*Corresponding author. Fax: +389-2-226-865.
E-mail address: biljana@iunona.pmf.ukim.edu.mk (B. Pejova).

0022-4596/03/$ - see front matter © 2003 Elsevier Science (USA). All rights reserved.
doi:10.1016/S0022-4596(03)00014-8

of cadmium selenide are of interest for their application as thin film transistors [11], gas sensors [12,13], acousto-optical devices [14], vidicones [15], photographic photoreceptors [16], etc.

Cadmium selenide exists in two polymorph modifications: cubic and hexagonal [17]. The structure of cubic modification is of sphalerite type, whereas the hexagonal modification is of vurcite-type structure. The cubic cadmium selenide converts to hexagonal modification at 350–400°C [18]. Although the number of published papers treating cadmium selenide is rather large [19–25], especially the cubic modification of this semiconductor is one of the least studied $A^{II}B^{VI}$ systems. The structure of synthesized cadmium selenide thin films depends on the experimental conditions. Thus, the preparation of thin films of cubic cadmium selenide is a very difficult task. This is in correlation with the relatively small number of published methods [19,20] for this modification. According to Kainthla and co-workers [21,22], the prepared cadmium selenide in thin film form, using a method of chemical deposition, is mostly a mixture of cubic and hexagonal modifications. The films deposited from (strongly alkaline) reaction system which is supersaturated with $Cd(OH)_2$ have mixed cubic and hexagonal structure, while upon deposition from a clear solution at relatively lower pH value cadmium selenide crystallizes in cubic modification. The sophisticated technologies (such as molecular beam epitaxy, vacuum evaporation, electrodeposition [23–25]) have been mostly used for preparation of cubic CdSe thin films.

In this paper, a relatively simple chemical deposition method for preparation of nanocrystalline photoconductive thin films of cubic cadmium selenide with a very high purity (with respect to the presence of hexagonal modification) is presented. The novelty of this method is in the usage of an ammonia buffer solution with a double role—as a both complexing agent (for Cd^{2+} ions) and as a pH-value-controller (within a rather narrow range) of the reaction system in the film deposition process. The involved deposition mechanism (ion-by-ion vs cluster one) is studied employing the coherent light scattering experiments.

The optical and electrical properties of the obtained thin films are thoroughly investigated. Special emphasis is put on the influence of experimental deposition conditions on these properties. Also, the post-deposition annealing influence on the optical and electrical characteristics of CdSe thin films is investigated. The manifestations of quantum size effects in the optical spectroscopic characteristics of the films are also studied, including the influence of the sintering process on these effects. The obtained experimental spectroscopic data regarding the manifestation of the quantum size effects are compared with the predictions based on the model of Brus [26,27] for the confined charge carrier motion in three spatial dimension (zero-dimensional nanostructures, i.e., quantum dots).

2. Experimental procedure

2.1. Preparation of the substrates

The thin films of cadmium selenide were deposited onto glass and polyester substrates with dimensions of a standard microscope glass. The adhesion with the substrate is of prime importance for the quality of the deposited thin films. To improve the film adhesion, the used substrates were immersed in a diluted solution of tin chloride prior to the deposition process and afterwards thermally treated at 200°C. As a result of this treatment, small crystals of tin(II) oxide with stochastic distribution are formed onto the substrate surface which, during the deposition process, initiate heterogeneous nucleation [6].

2.2. Chemical deposition of cadmium selenide thin films

Cadmium selenide thin films were prepared by the method of chemical deposition. As precursor of selenide ions, sodium selenosulfate was used. For control of cadmium(II) ion concentration and alkalinity of the reaction system an ammonia buffer solution (with pH = 9) was used. The experimental conditions of chemical deposition were optimized (in a classical way) regarding the thin film's photoelectrical performances. We found that the pH value of the reaction system is of prime importance for chemical deposition of cadmium selenide thin films which manifest photoconductivity. According to the experimental results, the photoelectrical properties can be modified by controlling the concentration of the used buffer solution, prepared from NH_3 and NH_4Cl, with $c_0(NH_3) = 1\,mol/dm^3$ and $c_0(NH_4Cl) = 1\,mol/dm^3$. The precursor of selenide ions, sodium selenosulfate, was used in the form of solution, which has been obtained by adding gray selenium to a hot solution of sodium sulfite, stirring this mixture for 1 h at 90°C and filtering the excess of gray selenium. The solution of sodium selenosulfate is relatively unstable and therefore it must be freshly prepared prior to the thin film deposition process. The sulfite ions (due to their reduction properties; $E^\circ(SO_4^{2-}/SO_3^{2-}) = -0.90\,V$ [28]) present in excess in the selenosulfate solution, are of prime importance for its stability. The optimal chemical composition of the reaction system for preparation of photoconductive cadmium selenide thin films was obtained by mixing the following solutions: $10\,cm^3$ $CdNO_3$ ($c(CdNO_3) = 0.1\,mol/dm^3$), $70\,cm^3$ ammonia buffer solution, $15\,cm^3$ Na_2SeSO_3 ($c(Na_2SeSO_3) = 1\,mol/dm^3$) and distillated water to a total volume of $100\,cm^3$. According to the obtained experimental results, the optimal temperature for chemical deposition of cadmium selenide thin films is 60°C.

2.3. Thin film characterization

The identification of the thin films of cadmium selenide was carried out by X-ray diffraction analysis with monochromatic Cu$K\alpha$ radiation, using the method of glazing incidence and in order to predict the grain size, the Debye–Scherrer formula was used. The diffractograms were recorded on a Philips PW 1710 diffractometer.

The optical (electronic) spectra of chemically deposited thin films of CdSe were recorded on a *Cary 50* spectrophotometer in the UV–VIS–NIR spectral range. The spectra processing was performed using the MS EXCEL software package [28].

The dark electrical resistance of the deposited thin films was measured using two- and four-point probes and constant electrical field methods. To achieve ohmic contact with the thin films a silver paste was used. The non-rectifying character of the metal–semiconductor contacts was proved on the basis of the measured current–voltage characteristics. A hot probe method was used to determine the type of major charge carriers in the obtained films.

The dependence $R = f(T)$ was measured in inert (argon) atmosphere at $P = 80$ kPa using a setup which is presented in Fig. 1. The setup contains a special furnace from Frank–Hertz's experiments (FH), a thermocouple with voltmeter (TC), variable transformer (T), a d.c. source and a standard resistor (R_s). The investigated thin film, which is characterized with surface area of 1 cm^2, was placed in the furnace. The furnace was heated slowly by the variable transformer (T), while the film temperature was registered on the basis of temperature dependence of thermoelectromotive force of the used Fe–Constantane thermocouple. The electrical circuit (which contains a standard resistor with resistance R_s and the investigated thin film with dark electrical resistance R_f) is of prime importance for determination of temperature dependence of electrical resistance of the investigated thin film. By mathematical analysis of this electrical circuit (in case when $R_s \ll R_f$) the following equation is obtained:

$$R_f = \frac{U_b R_s}{U_s}, \tag{2.1}$$

where U_b is the applied voltage and U_s is the voltage drop at the ends of the resistor (R_s).

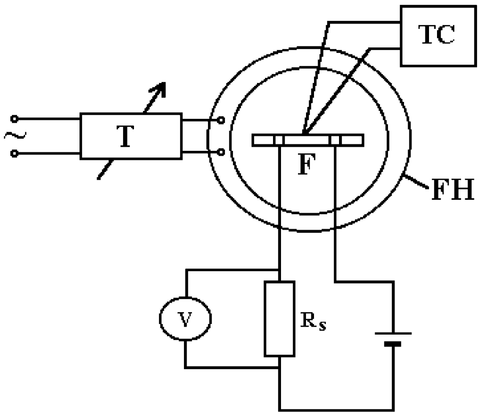

Fig. 1. The experimental setup for $R-T$ measurements.

Coherent light-scattering experiments were used to investigate the mechanism of thin film deposition.

3. Results and discussion

3.1. Considerations of the chemistry and the deposition mechanism of thin film synthesis

Thin films of cadmium selenide were chemically deposited using a sodium selenosulfate as a precursor of selenide ions. In principle, the method is based on hydrolysis of selenosulfate ions in alkaline solution of complexed cadmium(II) ions. Several equilibria exist in the reaction system which can be presented in the following way:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-, \tag{3.1}$$

$$Cd^{2+} + 4NH_3 \rightleftharpoons [Cd(NH_3)_4]^{2+}, \tag{3.2}$$

$$SeSO_3^{2-} + H_2O \rightleftharpoons H_2Se + SO_4^{2-}, \tag{3.3}$$

$$H_2Se + OH^- \rightleftharpoons H_2O + HSe^-, \tag{3.4}$$

$$HSe^- + OH^- \rightleftharpoons H_2O + Se^{2-}, \tag{3.5}$$

$$Cd^{2+} + Se^{2-} \rightleftharpoons CdSe. \tag{3.6}$$

The selenosulfate ions hydrolyze to hydrogenselenide acid which is characterized by acidity constant (K_a) with magnitude of 1.3×10^{-15} mol^{2}dm^{-6} at 25°C [29]. As a result of the low acidity constant value, the concentration of selenide anions in the reaction system is very small. The concentration of (hydrated) cadmium cations in the solution is determined by thermodynamic stability of tetraaminecadmium ions. The deposition of cadmium selenide starts when the product of cadmium and selenide ion equilibrium concentrations is at least equal to the solubility product (K_{sp}) of cadmium selenide:

$$Cd^{2+}_{(aq)} + Se^{2-}_{(aq)} \rightleftharpoons CdSe_{(aq)} \rightleftharpoons CdSe_{(s)}, \tag{3.7}$$

$$K_{sp(CdSe)} \leqslant c(Cd^{2+})c(Se^{2-}). \tag{3.8}$$

In the matter of photoelectrical performances of thin films of cadmium selenide, the control of pH of the reaction system is of prime importance. Namely, the presence of CdO and $Cd(OH)_2$ impurities in relatively large quantities reflects negatively on the photoelectrical properties of cadmium selenide. On the other side, in acidic medium selenide ions oxidize to red selenium. For these reasons, the chemical deposition of thin films of cadmium selenide was carried out in the presence of ammonia buffer solution with $pH = 9$. Namely, as mentioned before, the ammonia buffer has a double function. It controls the alkalinity of the reaction system and, on the other side, the ammonia forms tetraaminecadmium ions with stability constant of $1.32 \times 10^7\,mol^{-4}\,dm^{12}$ [29] and thus determines the concentration of cadmium ions.

In principle, the small concentrations of selenide and cadmium ions are of prime importance for cadmium selenide deposition, first of all, as thin film onto the substrate surface. Thus, the small concentration of Cd^{2+} ions is controlled indirectly using ammonia as a complexing reagent, whereas the small concentration of selenide ions is determined by slow dissociation of hydrogen selenide ions.

The thin film deposition involves two processes: process of nucleation and process of crystal growth. The ratio of rates of these two processes is of fundamental importance for the crystal size of the deposited cadmium selenide thin films. The rate of nucleation depends on the relative supersaturation of solution. Namely, low relative supersaturation of the reaction solution favors heterogeneous nucleation. By increasing the solution supersaturation, on the other hand, the rate of nucleation increases exponentially and the homogeneous nucleation dominates. In principle, the crystal growth process can be based on two types of mechanisms: *ion-by-ion* mechanism and *cluster* or *colloidal* mechanism [30]. According to the ion-by-ion mechanism, the crystal growth is a result of the reaction between cadmium(II) and selenide ions which are present in low concentration in the growth solution:

$$(CdSe)_n + Cd^{2+} + Se^{2-} \rightleftharpoons (CdSe)_{n+1}, \qquad (3.9)$$

$$(CdSe)_{n+1} + Cd^{2+} + Se^{2-} \rightleftharpoons (CdSe)_{n+2}, \qquad (3.10)$$

where n is the number of formula units which form a stable nucleus. On the other side, the low equilibrium ionic concentrations lead to practically only heterogeneous nucleation and absence of precipitation in the growth solution.

Cluster mechanism of crystal growth is based on adsorption and coagulation (which involves coalescention and aggregation) of colloidal particles:

$$(CdSe)_l + (CdSe)_k \rightleftharpoons (CdSe)_{l+k}, \qquad (3.11)$$

where $l, k > n$.

According to the cluster mechanism, besides heterogeneous nucleation, the homogeneous nucleation also precedes to the crystal growth process. The colloidal particles, formed in the solution, migrate to the substrate surface. Regarding the chemical composition of colloidal particles, they can be cadmium selenide, cadmium hydroxide and hydrated cadmium oxide, which spontaneously convert to cadmium selenide as a result of the lower solubility product of CdSe in comparison to cadmium hydroxide and cadmium oxide.

The mechanism of cadmium selenide crystal growth (in thin film form) was investigated using a light scattering experiment. Thus, if the crystal growth process is based on the cluster mechanism, the colloidal particles, which are present in the solution, scatter the used monochromatic light. In the opposite case, the crystal growth is based on ion-by-ion mechanism. According to the experimental results, the deposition of cadmium selenide thin films is dominated by the cluster mechanism.

3.2. Identification of thin films of cadmium selenide

The X-ray powder diffraction method was used for identification of the chemically deposited thin film materials. Also, the recorded XRD patterns were employed for estimation of the average crystal size (in spherical approximation), according to the Debye–Scherrer's approximation which is based on the following equation:

$$d = \frac{4}{3}\frac{0.9\lambda}{\beta\cos\theta}, \qquad (3.12)$$

where d is the average diameter of the crystals (in spherical approximation), λ is the wavelength of used X-ray radiation, β is the full-width at half-maximum intensity of the peak and θ is the angle which corresponds to diffraction maximum [31].

According to the results of X-ray diffraction analysis (Figs. 2 and 3) the thin films and corresponding precipitates of CdSe, obtained under identical

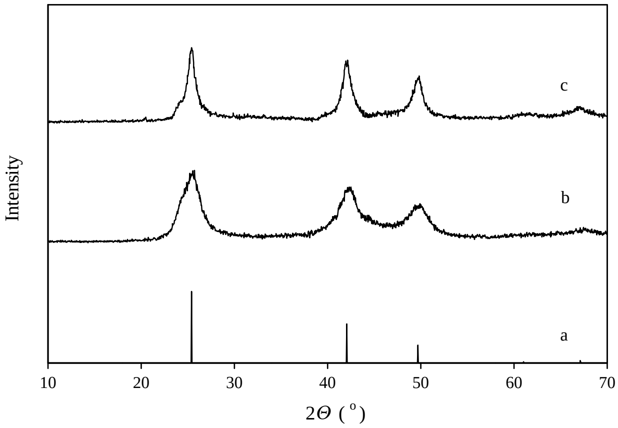

Fig. 2. The XRD patterns of: (a) standard, (b) precipitate of CdSe and (c) annealed precipitate of CdSe (at 300°C).

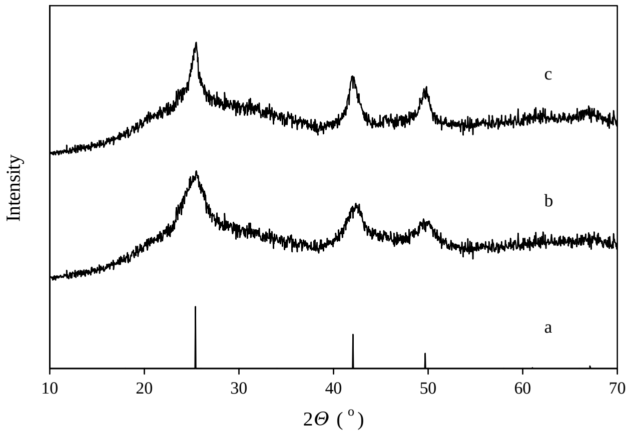

Fig. 3. The XRD patterns of: (a) standard, (b) as-deposited thin film of CdSe (onto glass substrate) and (c) annealed thin film of CdSe (onto glass substrate at 300°C).

experimental conditions, are polycrystalline. The prepared CdSe thin films belong to cubic crystal system (with unit-cell parameter of 6.077 Å [32]) and are characterized with sphalerite type of structure. The results about the crystal structure of the obtained thin films of cadmium selenide are in correlation with the conclusions of Kainthla and co-workers [21,22].

The broad diffraction peak in the diffractograms of CdSe thin films (which corresponds to 2θ values of 20–40°) is due to the amorphous structure of the glass substrates.

Using the equation of Debye and Scherrer, on the basis of the full-width at half-maximum of more intensive diffraction peaks, the average crystal sizes of unannealed and annealed (at 300°C in air atmosphere) cadmium selenide (in form of thin film and corresponding precipitate) were estimated. The average crystal diameter of unannealed cadmium selenide (thin film and precipitate) is 5.3 nm. In the case of annealed cadmium selenide at 300°C, as thin film and precipitate as well, the average crystal diameter of 24 nm was estimated. The identical values of crystal sizes of CdSe thin films and of the corresponding precipitates give a further support for the process of crystal growth according to the cluster mechanism [33].

3.3. Investigation of the optical properties of cadmium selenide thin films and the exhibited quantum size effects

The optical spectra of the thin films of cadmium selenide were recorded in the spectral range from 190 to 1100 nm. On the basis of the experimental data, the absorption coefficient (for each wavelength) was calculated using the following equation:

$$\alpha = \frac{1}{d}\ln\frac{I_0}{I}, \qquad (3.13)$$

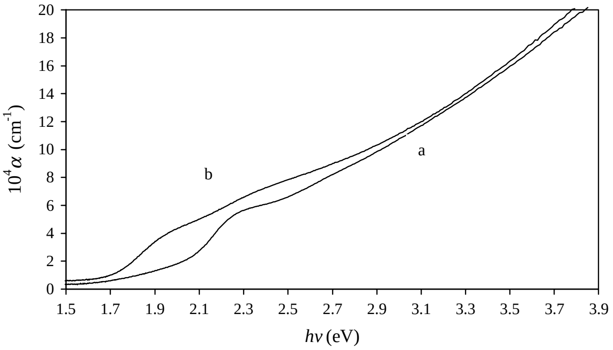

Fig. 4. (a,b) The dependence of absorption coefficient of as-deposited and annealed CdSe thin films on incident photon energy, correspondingly.

where d is the thickness of the investigated thin film, while I_0 and I are the intensity of incident and transmitted light, correspondingly.

On the basis of the magnitude of absorption coefficient in the investigated spectral range and its dependence on the incident photon energy, several conclusions about band structure of CdSe can be deduced.

The dependence of absorption coefficient on the incident photon energy for as-deposited and annealed (in air atmosphere at 300°C) cadmium selenide thin film is presented in Fig. 4a and b. The magnitude of absorption coefficient, in the investigated optical range, is of the order of $10^4\,\mathrm{cm}^{-1}$ or even higher. This fact indicates that the explored spectral region is the region of intrinsic absorption of cadmium selenide and the corresponding electronic transitions are of direct allowed type (i.e., band to band transitions). On the other side, the direct type of electronic transitions implies that identical electronic wave vector corresponds to the absolute minimum of the conduction band and the absolute maximum of valence band in the k-space and the electronic transitions do not involve phonons. The values of absorption coefficient larger than $10^4\,\mathrm{cm}^{-1}$ correspond to electronic transitions from valence band to higher energy levels of the conduction band. According to the literature data, the excited electrons in this way are thermalyzed to the lower edge of conduction band within 10^{-12} to 10^{-13} s [34]. The optical properties of cadmium selenide thin films changed irreversibly upon thermal treatment (which is accompanied by an irreversible change of color from yellowish-orange to brown). As can be seen from Fig. 4, upon thermal treatment the absorption edge is shifted towards lower photon energies (red shift).

The optical band gap energy of cadmium selenide thin films was calculated within the framework of parabolic approximation for dispersion relation, on the basis of equations, which arise from the Fermi's golden rule for electronic transitions from the valence to conduction band. Namely, the semiconductor's band structure determines the functional dependence of the absorption coefficient (α) on the photon energy. The Fermi's golden rule for fundamental "band to band" electronic transitions is defined in the following manner:

$$\alpha h\nu = C \sum_{\vec{k}} |P_{\mathrm{vc}}|^2 g(E) \delta(E_{\mathrm{c}} - E_{\mathrm{v}} - h\nu), \tag{3.14}$$

where $|P_{\mathrm{vc}}|^2$ is the transition dipole moment, $g(E)$ is the density of energy levels, $h\nu$ is the photon energy, while E_{c} and E_{v} correspond to the minimum of conduction band and the maximum of valence band correspondingly [35]. From further mathematical derivations based on (3.14) the following equation which is the basis of optical band gap energy calculations arises:

$$(\alpha h\nu)^n = A(h\nu - E_{\mathrm{g}}), \tag{3.15}$$

where the index n depends on the type of electronic transitions. In the case of direct-allowed and forbidden transitions the values of n are 2 and $\frac{2}{3}$ correspondingly, whereas for indirect type of transitions (allowed and forbidden) n has a value of $\frac{1}{2}$ and $\frac{1}{3}$ correspondingly.

The recorded optical spectra of (as-deposited and annealed) CdSe thin films were mathematically transformed according to Fermi's golden role. The experimental data from the dependence of $\alpha h\nu = f(h\nu)$ were fitted according to Eq. (3.15). The linear dependence of $(\alpha h\nu)^n$ vs $h\nu$ was obtained for $n = 2$. This is in correlation with the previous conclusion that near to absorption edge the electronic transitions are direct (allowed) and do not involve phonons. The dependence of $(\alpha h\nu)^2$ vs $h\nu$ in the case of as-deposited and annealed thin films of CdSe is presented in Fig. 5a and b. The deviation from the linear dependence of $(\alpha h\nu)^2$ vs $h\nu$ is a result of deviations from parabolic approximation. By linear correlation analysis of experimental data within the region of linear dependence of $(\alpha h\nu)^2$ vs $h\nu$ the optical band gap energy was calculated. According to this analysis the optical band gap energy of as-deposited cadmium selenide (in thin film form) at room temperature is 2.08 eV.

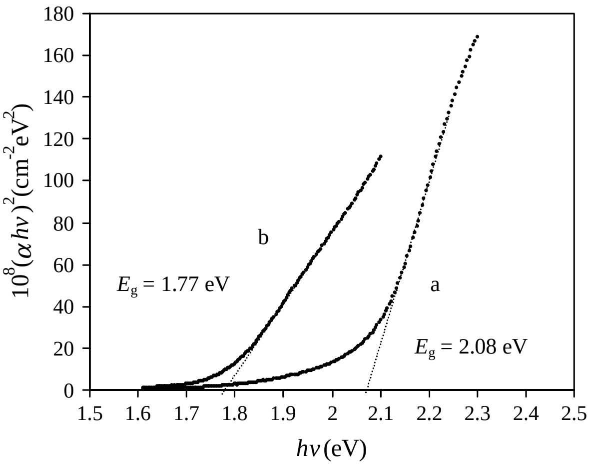

Fig. 5. (a,b) The dependence of $(\alpha h\nu)^2$ on $h\nu$ in the case of as-deposited and annealed CdSe thin films, correspondingly.

On the basis of linear plot of $(\alpha h\nu)^2$ vs $h\nu$ and using linear correlation analysis, the calculated optical band gap energy value in the case of annealed cadmium selenide (in thin film form) is 1.77 eV at room temperature.

The calculated optical band gap energy of annealed thin film of CdSe agrees with the literature value for this quantity (1.74 eV) corresponding to bulk CdSe [36]. In the case of as-deposited cadmium selenide thin films the optical band gap energy is higher by 0.34 eV in comparison with the bulk value. The shift of the band gap energy in the case of as-deposited cadmum selenide thin films results from the quantum size effects. This conclusion is in correlation with the results of X-ray diffraction analysis.

Namely, charge carries in semiconductors can be confined in one, two or three spatial dimensions. These regimes are termed quantum films, quantum wires and quantum dots (or zero-dimensional nanocrystals) correspondingly. Some fundamental differences exist for the three types of quantization. The confinement effects in three spatial dimensions can be explained in the framework of Brus's approach which is based on the particle in a box model [26,27]. According to this model, upon decrease of the crystal size the band structure of the semiconductor transforms to discrete energy structure. The confinement effects are strongly manifested in the case of small crystals with a radius which is lower or comparable with Bohr's radius (i.e., radius of an "exciton" in bulk semiconductors). According to the model of Brus, the energy spectrum of an exciton (treated as one particle with a reduced mass $m^* = [(m_{\mathrm{e}}^*)^{-1} + (m_{\mathrm{h}}^*)^{-1}]^{-1}$) in nanocrystal with a radius which is comparable to Bohr's radius is given by the following equation (within spherical particle approximation):

$$E(R) = E_{\mathrm{g}} + \frac{h^2}{8R^2}\left(\frac{1}{m_{\mathrm{e}}^*} + \frac{1}{m_{\mathrm{h}}^*}\right) - \frac{C_1 e^2}{\varepsilon R} - C_2 E_{\mathrm{Ry}}^*, \tag{3.16}$$

where R is the radius of the exciton, C_1 and C_2 are constants, ε is the dielectric constant of the semiconductor and E_{Ry}^* is the effective Rydberg constant.

According to the XRD analysis, as-deposited thin films are polycrystalline with average crystal radius (in spherical approximation) of 2.6 nm. The literature value for excitonic Bohr's radius in the case of bulk CdSe is 5.6 nm [34]. The comparison of the average crystal size with literature value of the Bohr's radius in bulk CdSe indicates that the as-deposited thin films are strongly quantized and the crystals with nanodimensions should be treated as quantum dots.

In the case of as-deposited cadmium selenide quantum dots (in thin film form), on the basis of the experimental data, the shift of optical band gap energy ($\Delta E = E(R) - E_g$) is 0.34 eV. According to the Brus model the predicted energy shift is 0.53 eV. The deviation of experimentally obtained ΔE value from the theoretically predicted one is due to the limited applicability of the *effective mass* model in the case of a crystal with a small radius of the order of several nanometers [36].

The thermal treatment of cadmium selenide thin films influences the average crystal size. Thus, according to XRD analysis the average crystal radius of annealed CdSe thin films at 300°C is 12 nm. The Brus model predicts a value of 0.03 eV for optical band gap energy shift, which excellently agrees with experimental result ($\Delta E_{\text{exp}} = 0.03$ eV). Annealed thin films of CdSe are practically non-quantized. With prolonged treatment at 300°C or even higher temperature the optical band gap energy shift will vanish. Namely, upon annealing of cadmium selenide thin films, the crystals are sintered, their dimensions increase and the confinement effects disappear irreversibly. In this way, by controlling the temperature and/or duration of annealing process, the properties of cadmium selenide thin films can be designed.

3.4. Electrical measurements

The as-deposited thin films of cadmium selenide are characterized with high dark electrical resistance. In the case of annealed thin films, this quantity is a function of the experimental conditions during the deposition process, i.e., the concentration of ammonia buffer solution used in preparation of the reaction system. The dark electrical resistance of the annealed thin films, prepared from the solution with the composition presented in Experimental details chapter, is of the order of several GΩ's, depending on film thickness. Thus, in the case of an annealed thin film with thickness of 200 nm the dark electrical resistance is 2 GΩ. With variation of chemical composition of the reaction system (i.e., concentration of ammonia buffer solution) the dark electrical resistance of the annealed thin films decreases.

According to the results of the hot probe method, based of Seebeck's effect, the majority of the charge carries are electrons and the cadmium selenide thin films are n-type semiconductors.

The thermal band gap energy of prepared thin films was obtained on the basis of experimentally obtained temperature dependence of the dark electrical resistance. The dependence $R = f(T)$ was measured in inert (argon) atmosphere at $P = 80$ kPa.

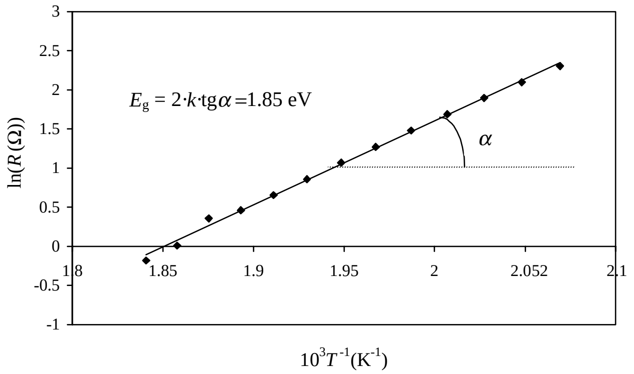

Fig. 6. The dependence of $\ln R$ on $1/T$ in the region of intrinsic conduction for CdSe thin film.

The experimentally obtained temperature dependence of dark electrical resistance of cadmium selenide thin films fits well with an exponential function, according to the theoretical prediction:

$$R = R_0 e^{E_g/2kT}, \tag{3.17}$$

where R is the dark electrical resistance, T is the temperature, E_g is the thermal band gap energy, k is the Boltzmann constant, while R_0 is constant. On the basis of temperature dependence of dark electrical resistance the plot of $\ln R$ vs $1/T$ was constructed. According to the experimental results the temperature region from 210°C to 270°C corresponds to the intrinsic conduction. The decrease of dark electrical resistance in this region is due to the band to band electronic transitions. The $\ln R$ vs $1/T$ dependence in the region of intrinsic conduction is presented in Fig. 6. Using linear correlation analysis, the data from this dependence were fitted according to the equation:

$$\ln R = \frac{E_g}{2k}\frac{1}{T} + \ln R_0. \tag{3.18}$$

The calculated thermal band gap energy at 0 K is 1.85 eV, which is in excellent agreement with the literature values (1.85 and 1.90 eV [36]), and also with the optical band gap value determined in this study.

The investigation of photoelectrical properties showed that the conductivity of the annealed thin films (deposited from reaction system with chemical composition presented before) increases for three orders of magnitude upon interaction with intensive white light from an overhead projector. By variation of experimental conditions of chemical deposition, the obtained annealed thin films manifest small photoconductivity or do not manifest photoconductivity at all. A detailed study of the photoelectrical properties of CdSe thin films deposited according to the route presented here (including the photoconductivity spectral dependence as well as photoconductivity relaxation phenomena) will be published elsewhere.

4. Conclusions

A chemical method for deposition of cadmium selenide quantum dots in thin film form with cubic structure onto glass and polyester substrates is presented. The presented method uses selenosulfate as precursor of selenide ions and ammonia buffer solution with double role: as a ligand and as a pH value controller. By controlling the chemical composition of reaction solution and post-deposition treatment, the presented method permits to design optoelectrical properties of CdSe thin films. According to the results from the coherent light-scattering experiments, the process of CdSe crystal growth is predominantly based on cluster mechanism.

The optical study shows that as-deposited CdSe thin films are size-quantized, i.e., nanocrystals behave as quantum dots with blue shifted band gap energy of 0.34 eV in comparison to the bulk value. Upon thermal treatment, the nanocrystals are sintered, their dimensions increase and the confinement effects disappear irreversibly.

On the basis of temperature dependence of dark electrical resistance of annealed cadmium selenide thin films the thermal band gap energy of 1.85 eV is calculated.

References

[1] M. Ohring, The Materials Science of Thin Films, Academic Press, New York, 1992.
[2] M.C. Troparesky, J.R. Chelikowsky, J. Chem. Phys. 144 (2001) 943.
[3] G. Hodes, I.D.J. Howel, L.M. Peter, J. Electrochem. Soc. 139 (1992) 3136.
[4] B. Pejova, M. Najdoski, I. Grozdanov, S.K. Dey, J. Mater. Chem. 9 (1999) 2889.
[5] B. Pejova, M. Najdoski, I. Grozdanov, S.K. Dey, Mater. Lett. 45 (2000) 2694.
[6] B. Pejova, I. Grozdanov, J. Solid State Chem. 158 (2001) 49.
[7] B. Pejova, I. Grozdanov, Thin Solid Films 408 (2002) 6.
[8] A.K. Pal, A. Mondal, S. Chaudhuri, Vacuum 41 (1990) 1460.
[9] T. Cruszecki, B. Holmstrom, Sol. Energy Mater. Sol. Cells 31 (1993) 227.
[10] S. Ericsson, T. Gruszecki, P. Carlsson, B. Holmström, Thin Solid Films 269 (1995) 14.
[11] A. Van Calster, F. Vanfleteren, I. DeRycke, J. De Baets, J. Appl. Phys. 64 (1988) 3282.
[12] N.G. Patel, C.J. Panchal, K.K. Makhijia, Cryst. Res. Technol. 29 (1994) 1013.
[13] V.A. Smyntyana, V. Gerasutenko, S. Kashulis, G. Mattogno, S. Reghini, Sensors Actuators 19 (1994) 464.
[14] B. Bonello, B. Fernandez, J. Phys. Chem. Solids 54 (1993) 209.
[15] J.C. Schottmiller, R.W. Francis, C. Wood, US patent 3884688, 1975.
[16] B.J. Curtis, H. Kiess, H.R. Brunner, K. Frick, Photogr. Sci. Eng. 24 (1980) 244.
[17] G.M. Fofanov, G.A. Kitaev, Russ. J. Inorg. Chem. 14 (1969) 322.
[18] O. Portillo-Moreno, R. Lozda-Morales, M. Rubín Falfán, J.A. Pérez-Álvarez, O. Zelaya-Angel, L. Baños-Lórez, J. Phys. Chem. Solids 61 (2000) 1751.
[19] R. Lozda-Morales, et al., J. Electrochem. Soc. 146 (1999) 2546.
[20] S. Gorrer, G. Hodes, Phys. Rev. 36 (1987) 4215.
[21] R.C. Kainthla, D.K. Pandya, K.L. Chopra, J. Electrochem. Soc. 127 (1980) 277.
[22] R.C. Kainthla, D.K. Pandya, K.L. Chopra, J. Electrochem. Soc. 129 (1980) 99.
[23] N. Samarth, H. Luo, J.K. Furdyone, S.B. Quadvi, Y.R. Lee, A.K. Ramdas, N. Otsuka, Appl. Phys. Lett. 54 (1989) 2162.
[24] L.P. Colletti, B.H. Flowers, J.L. Stickney, J. Electrochem. Soc. 145 (1998) 1442.
[25] T. Hayashi, R. Saeki, T. Suzuki, M. Fukaya, Y. Ema, J. Appl. Phys. 38 (1990) 5719.
[26] L.E. Brus, J. Chem. Phys. 79 (1983) 5566.
[27] L.E. Brus, J. Chem. Phys. 80 (1984) 4403.
[28] Microsoft® EXCEL 97 SR-1.
[29] Handbook of Chemistry and Physics, 64th Edition, Vol. 1983–1984, CRC Press, Boca Raton.
[30] M. Froment, D. Lincot, Electrochim. Acta 40 (1995) 1293.
[31] M.T. Weller, Inorganic Materials Chemistry, Oxford University Press, Oxford, 1997.
[32] JCPDS-International Center for Diffraction Data 75-1462.
[33] S. Gorer, G. Hodes, J. Phys. Chem. 98 (1994) 5338.
[34] R. Memming, Semiconductor Electrochemistry, Wiley, New York, 2001.
[35] M.P. Marder, Condensed Matter Physics, Wiley, New York, USA, 2000.
[36] A.B. Novoselova (Ed.), Physical and Chemical Properties of Semiconductors, Handbook, Moscow, 1978.