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Investigation of photoelectrical properties and relaxation dynamics in photoexcited CdSe nanocrystals in thin film form

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Abstract

Electrical and photoelectrical properties of cubic CdSe nanocrystals in thin film form (including the relaxation dynamics of photocarriers) are investigated. Photoelectrical properties of the obtained films are controlled by chemical (varying the reagent concentration in the reaction system) and physical means (controlling the crystal dimensions). In the case of thin films with optimal photoelectrical properties, the calculated band gap energy and ionization energies of impurity levels (on the basis of experimentally obtained temperature dependence of dark electrical resistance) at 0 K are 1.85, 0.74 and 0.43 eV, correspondingly. The calculated optical band gap energy (on the basis of spectral dependence of photoconductivity) at room temperature of 1.75 eV is in excellent agreement with the value of 1.77 eV which is obtained on the basis of electronic absorption spectrum in the framework of parabolic approximation for dispersion relation. Upon thermal treatment of chemically deposited thin films of cubic CdSe quantum dots, as a result of processes of coalescence and crystal growth, the electronic contact between nanocrystals increases and the confinement effects irreversibly disappear. Relaxation of non-equilibrium charge carriers is practically carried out according to the linear mechanism. The calculated relaxation time of photoexcited charge carriers is 0.4 ms.

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1. Introduction

Semiconducting cadmium selenide crystals, in thin film form, with dimensions in the nanometer range have attracted considerable scientific interest [1]. Their properties deviate from the corresponding bulk material in a size-dependent manner as a result of confinement effects. The localization of charge carriers in a confined space (nanocrystal) is followed with quantization of electronic energy levels. The confinement effects in the case of cadmium selenide thin films are strongly manifested when the radius of crystals is lower or comparable to the Bohr's radius of bulk CdSe (i.e., 5.6 nm [2]).

The chemical deposition methods offer the possibility to tune specific properties (such as band gap energy) of

nanocrystalline semiconducting thin films depending on specific problems for which they are to be applied. Continuing our research in the field of semiconducting metal selenide thin films [3–7], we have chemically deposited nanocrystalline cubic CdSe thin films which strongly manifest quantum size effects, i.e., cadmium selenide nanocrystals behave as quantum dots. The band gap energy of as-deposited films is blue shifted by 0.34 eV with respect to the bulk value (1.74 eV [8]). As a result of electronic isolation of nanocrystalline particles, as-deposited CdSe thin films are characterized with high dark electrical resistance. Having in mind that CdSe thin films have a potential application in solar cells engineering [9–11], in this study we focus on the optimization of photoelectrical performances of nanocrystalline cadmium selenide thin films and investigation of their electrical properties, spectral dependence of photoconductivity and relaxation dynamics of photoexcited charge carriers.

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2. Experimental

Photoconducting cadmium selenide nanocrystals were chemically deposited in thin film form at about 60°C using sodium selenosulfate as a selenide ion precursor. We have previously reported the details of experimental procedure [7]. According to our investigations the control of low ionic concentrations and especially the alkalinity of the reaction system are of prime importance for deposition of photoconductive cadmium selenide thin films. Briefly, the low concentration of metal ions in the reaction system is controlled indirectly using appropriate ligands, which form relatively stable complex particles with metal cations. The low concentration of selenide ions is determined by slow dissociation of hydrogenselenide ions, which are obtained upon hydrolysis of selenosulfate ions. The novelty of the proposed method is in the usage of ammonia buffer solution (with pH=9) with double role—as a pH value and cadmium(II) ions concentration controller. Regarding the crystal structure, the prepared cadmium selenide in thin film form is cubic with a very high purity (with respect to the presence of hexagonal modification). On the other side, in most previously presented methods [12,13], the chemically deposited CdSe is a mixture of cubic and hexagonal modifications. The developed method allows designing of electrical and photoelectrical properties of cadmium selenide thin films by physical mean (controlling the crystal size) and by chemical one (varying in narrow range the chemical composition of the reaction system). The heterogeneous nucleation process of cadmium selenide crystal growth was initiated by stochastically distributed small crystals of tin(II) oxide onto the substrate surfaces which were formed upon pre-deposition treatment of used substrates (glass and polyester).

3. Thin film characterization

3.1. Ohmic contacts with CdSe thin films

To achieve an ohmic contact with CdSe thin films, silver paste was used. The silver electrodes with length of 1 cm were applied onto substrate's surface, 1 cm apart. The non-rectifying character of the metal–semiconductor contacts was proved on the basis of the measured current–voltage characteristics.

3.2. Measurements of dark electrical resistance of the thin films, temperature dependence of dark electrical resistance and spectral dependence of stationary photoconductivity

The dark electrical resistance of thin films of cadmium selenide was measured using the two-point and four-

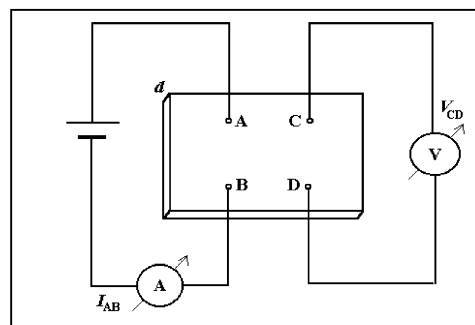


Fig. 1. Experimental setup for dark electrical resistance measurements using the four-point probe method (van der Pauw method).

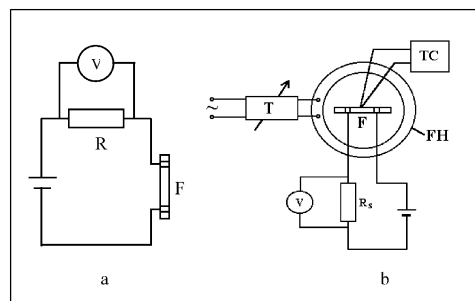


Fig. 2. Experimental setup for measurements of dark electrical resistance of the thin films by the constant field method (a), the temperature dependence of the thin film dark electrical resistance (b) as well as of the spectral dependence of stationary photoconductivity.

point probe methods, as well as the constant field method. In the case of *two-point probe method*, the silver electrodes were applied 1 cm in length and 1 cm apart (i.e., the length and width of thin films were 1 cm) and the values of thin film resistance were reported in “ohms per square” units.

In the case of *four-point probe method* (van der Pauw method) four-point silver probe (with spacing between point contacts much larger compared to the film thickness (d)) was applied on the film's surface as shown in Fig. 1. Two sets of current–voltage measurements were performed. First, the point probes A and B were connected to the d.c. source and the voltage drop was detected between points C and D (V_{CD}). Subsequently, the contacts B and C were connected to the d.c. source and the A and D points detect the voltage drop (V_{DA}).

The *constant field method* for measurement of film resistance is based on usage of electrical circuit (presented in Fig. 2a) which contains serially connected d.c. source to a standard resistor R (with resistance R_s) and to the investigated thin film sample F (with dark electrical resistance R_f).

The dependence of thin film dark resistance on temperature was measured in inert (argon) atmosphere at $P = 80$ kPa using a setup (presented in Fig. 2b) which contains a special furnace (FH), a thermocouple with

voltmeter (TC), variable transformer (T), a d.c. source and a standard resistor (R_s). The investigated thin film sample, 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 investigated sample (with dark electrical resistance R_f) was serially connected to a d.c. source and to a standard resistor with resistance R_s . The dark electrical resistance of the investigated sample (at every measured temperature) is calculated using the constant field method.

The spectral dependence of stationary photoconductivity of cadmium selenide thin films was measured on the basis of the constant field method. The used setup (Fig. 2a) contains d.c. source serially connected to a standard resistor (R_s) and investigated CdSe thin film sample (F). A monochromator from spectrophotometer Beckman DU-2 was used as a source of radiation within wavelength range from 400 to 1200 nm.

The thin films samples, which were used in photoelectrical investigations, were previously appropriately prepared. They are characterized with length of 4 mm and width of 3 mm. The silver electrodes were applied 4 mm apart. The applied voltage and electrical resistance of standard resistor were 30 V and $1 \text{ k}\Omega$, correspondingly.

3.3. Type of electrical conductivity of CdSe thin films

The type of electrical conductivity of cadmium selenide thin films was determined using the routine method which is based on the thermoelectrical (Seebeck) effect.

3.4. Relaxation dynamics of non-equilibrium charge carriers in CdSe photoconductive nanocrystals in thin film form

The relaxation dynamics of non-equilibrium charge carriers, from the kinetic aspect, is investigated using the oscillographic method. On the basis of experimentally obtained relaxation curves, the mechanism of relaxation and relaxation time of non-equilibrium charge carriers are determined.

The used setup contains serially connected d.c. source, standard resistor (R_s) and investigated sample (F) (Fig. 3). The sample of CdSe thin film, prepared in an equal manner as in the case of measurement of spectral dependence of stationary photoconductivity, was placed in a dark chamber. The generation of non-equilibrium charge carriers was achieved upon interaction with white light impulse from a flash lamp (FL). In principle, the measurement of time dependence of non-equilibrium charge carriers concentration, after illumination with

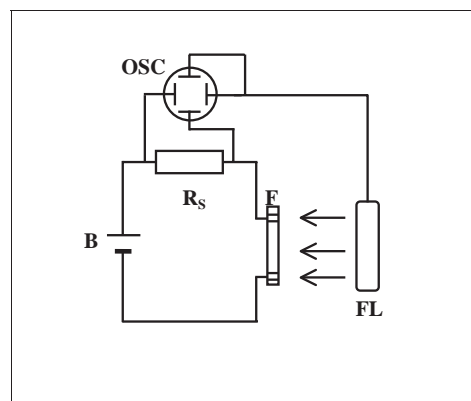


Fig. 3. Experimental setup used for investigation of the relaxation dynamics of non-equilibrium charge carriers in CdSe thin films by the oscillographic method.

white light from flash lamp, is based on registration of voltage drop at the ends of standard resistor using oscilloscope with previously calibrated time and voltage axes. The electrical resistance of investigated sample is calculated according to the constant field method.

4. Results and discussion

4.1. Electrical measurements

4.1.1. Ohmic contact with cadmium selenide thin films

The ohmic contact with cadmium selenide thin films is of prime importance for investigation of their electrical and photoelectrical properties. Namely, the metal–semiconductor contacts are very important for construction of electronic devices because across such contacts charge carriers are transported from semiconductor to metal or conversely.

The current–voltage characteristics of silver–cadmium selenide contact are presented in Fig. 4. As can be seen, I – V dependence is linear and this proves that the contact is ohmic. Namely, the derivative $(\partial I/\partial V)^{-1}$ is constant and practically equal to dark electrical resistance of investigated cadmium selenide thin film.

4.1.2. Measurements of dark electrical resistance of cadmium selenide thin films

The measured dark electrical resistances of thin film samples using the two-point, four-point probe methods, as well as the constant field method are in excellent agreement.

In the case of four-point probe method, the dark electrical resistivity of investigated samples was calculated numerically solving the equation [14]

$$\exp\left(-\pi \frac{d V_{CD}}{\rho I_{AB}}\right) + \exp\left(-\pi \frac{d V_{DA}}{\rho I_{BC}}\right) = 1, \quad (1)$$

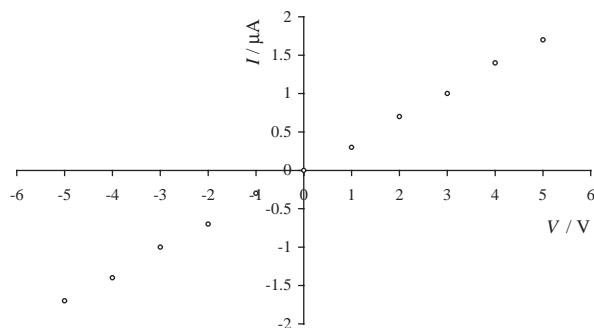


Fig. 4. Current–voltage characteristics of silver–cadmium selenide contact.

where d is film's thickness, ρ is the density of semiconducting material, V_{CD} and V_{DA} are the voltage drops between points (C and D) and (D and A) correspondingly, while I_{AB} and I_{BC} are the corresponding electric currents passed between points (A and B) and (B and C), respectively.

By mathematical analysis of electrical circuit (presented in Fig. 2a), which was applied in film resistance measurements using the constant field method, the following equation was obtained:

$$R_f = \frac{V_b R_s}{V_s} - R_s, \quad (2)$$

where V_b is the applied voltage and V_s is the voltage drop at the ends of the resistor (R_s). If $R_s \ll R_f$ the dark electrical resistance of thin film sample is determined by Eq. (3), which is the basis of constant field method,

$$R_f = \frac{V_b R_s}{V_s}. \quad (3)$$

The dark electrical resistance of thin films depends on experimental conditions of the deposition process, initial concentrations of reactants and post-deposition treatment. As-deposited cadmium selenide thin films, are characterized with high dark electrical resistance of the order of GΩs, regardless on chemical composition of reaction system. The high dark electrical resistance of as-deposited thin films is due to the electrical isolation between CdSe nanocrystals (i.e., localization of charge carriers in the nanocrystal). The electrical isolation between CdSe nanocrystals implies a potential barrier between them [15]. According to our investigations the quantum size effects are strongly manifested in the case of chemically deposited CdSe thin films [7]. As we have previously reported, the estimated average radius (on the basis of XRD patterns and within spherical approximation) of CdSe quantum dots, chemically deposited in thin film form, is 2.6 nm and the experimentally obtained blue shift of band gap energy is 0.34 eV.

According to our investigations, thermal treatment of cadmium selenide thin films, leads to processes of

coalescence of CdSe nanocrystals, i.e., to increase of connectivity between nanocrystals and to crystal growth. The result of these processes is electrical connection between nanoparticles and irreversible loss of confinement effects. Thus, as we have reported previously, annealed CdSe thin films are characterized with an average crystal radius of 12 nm and the blue shift of optical band gap energy of 0.03 eV with respect to the bulk band gap energy value. With a prolonged treatment at 300°C or even higher temperature the optical band gap energy shift will vanish. According to our measurements, upon thermal treatments of thin films, the dark electrical resistance of thin films decreases (with respect to the unannealed thin films) and it is of the order from several GΩs to several MΩs depending on the chemical composition of growth solution. The decrease of dark electrical resistance of CdSe thin films, upon annealing processes, is due to electrical contact between nanocrystals. On the other hand, the chemical composition of reaction system influences the stoichiometry of obtained cadmium selenide. The small changes in the stoichiometry, which are under detection limit of XRD analysis, act as impurities with chemical character. Their presence in band structure is manifested through discrete impurity levels, in the forbidden band, which are almost completely ionized at room temperature (300 K). As a result of ionization of impurity levels, the equilibrium concentrations of charge carriers increase and dark electrical resistance decreases. On the other hand, cadmium selenide, in thin film form which manifests maximal photoconductivity, is stoichiometrical and acts as intrinsic semiconductor, i.e., it is characterized with high dark electrical resistance.

4.1.3. Determination of type of electrical conductivity of cadmium selenide in thin film form

On the basis of the obtained sign of the thermoelectric force of CdSe–metal thermocouple, the dominant charge carriers are electrons. This is in agreement with the theoretical predictions, since the effective electron mass is smaller than effective hole mass ($m_e^* < m_h^*$) [8] for this semiconductor.

4.1.4. Measurements of thermal band gap energy and activation energies of impurity levels of photoconductive CdSe nanocrystals in thin film form

The thermal band gap energy of photoconductive CdSe nanocrystals in thin film form and ionization energies of impurity levels were obtained on the basis of experimentally obtained temperature dependence of the dark electrical resistance.

The experimentally obtained temperature dependence of dark electrical resistance of cadmium selenide thin films is an exponential function, according to the

theoretical prediction

$$R = R_0 e^{E_g/2kT}, \quad (4)$$

where R is dark electrical resistance, T is temperature, E_g is thermal band gap energy, k is Boltzmann constant, while R_0 is constant.

For calculation of band gap energy of photoconducting CdSe nanoparticles (in thin film form) and ionization energies of impurity levels the experimentally obtained temperature dependence of dark electrical resistance is mathematically transformed. On the basis of this dependence, the plot of $\ln R$ vs. $1/T$ was constructed. In Fig. 5 the dependence of $\ln R$ vs. $1/T$ in the temperature region from 373 to 543 K is presented. The three linear trends indicate presence of two impurity donor levels having in mind the type of CdSe conductivity. In the lower temperature region (373–478 K) the electrical conductivity is due to the electronic transitions from donor levels to the conduction band. The conductivity of CdSe thin films in this temperature region is known as impurity or extrinsic conductivity. The decrease of thin film dark resistance in the region of extrinsic conductivity is according to the following equation:

$$R = R_0' e^{\Delta E/kT}, \quad (5)$$

where ΔE is ionization energy of donor level.

Using linear correlation analysis, the data from the dependence of $\ln R$ vs. $1/T$ in temperature region from 373 to 403 K and from 403 to 478 K were fitted according to the equation

$$\ln R = \frac{\Delta E}{k} \frac{1}{T} + \ln R_0'. \quad (6)$$

The calculated ionization energies of impurity levels (at 0 K) are 0.43 and 0.74 eV.

The temperature region from 478 to 543 K corresponds to the intrinsic conduction. The decrease of dark

electrical resistance in this region is due to the band to band electronic transitions. Using linear correlation analysis, the data from this dependence were fitted according to the equation

$$\ln R = \frac{E_g}{2k} \frac{1}{T} + \ln R_0. \quad (7)$$

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 [8]), and also with the optical band gap value calculated on the basis of optical spectra and on the spectral dependence of photoconductivity.

The measurements of temperature dependence of dark electrical resistance are reproducible. In Fig. 6 the dependence of $\ln R$ vs. $1/T$ during a single heating-cooling cycle is presented.

4.2. Photoelectrical measurements

4.2.1. Measurements of spectral dependence of photoconductivity

The interaction of semiconducting materials with electromagnetic radiation from the intrinsic region is followed by generation and recombination of non-equilibrium charge carriers. Under stationary conditions the rates of these two processes are equal and the photoconductivity (or non-equilibrium conductivity) is constant [16].

The experimental measurements of spectral dependence of stationary photoconductivity are based on registration of the voltage drop (v) at the ends of the resistor (R_s) during interaction between the investigated sample and monochromatic radiation. The voltage drop at the ends of the resistor (with resistance R) as a result of interaction with monochromatic radiation is

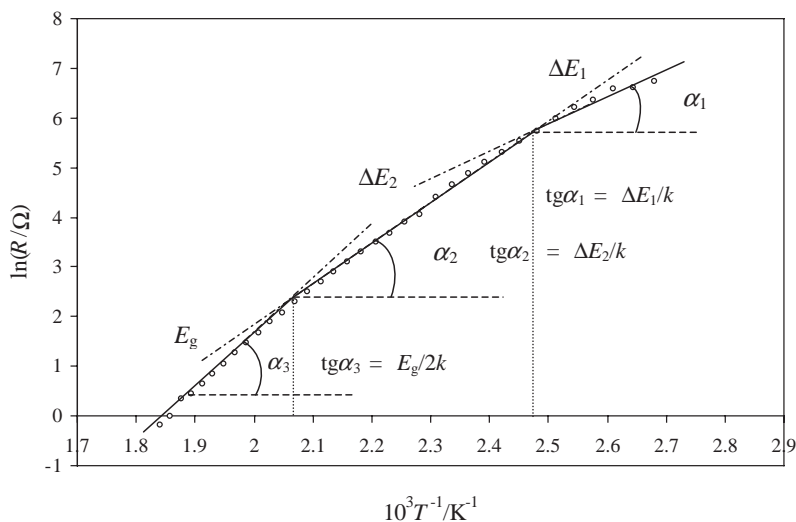


Fig. 5. Measured dependence of $\ln R$ vs. $1/T$ in temperature region from 373 to 543 K for a CdSe thin film.

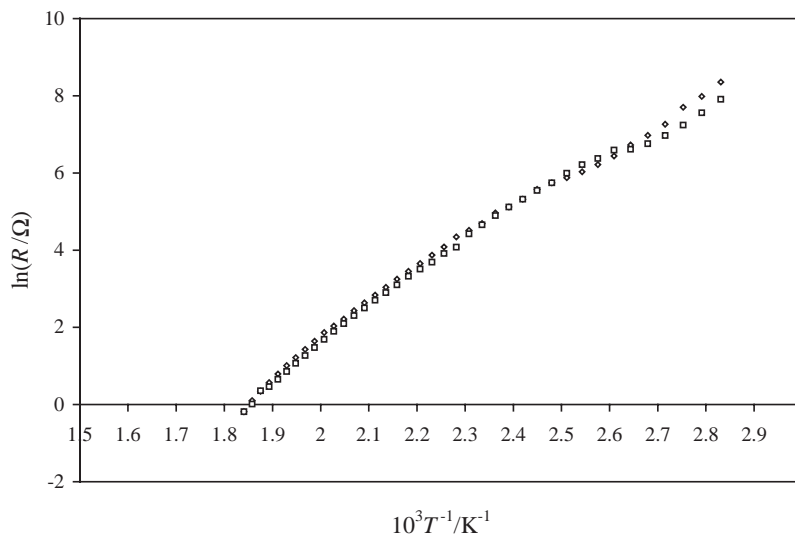


Fig. 6. Measured dependence of $\ln R$ vs. $1/T$ during a single heating–cooling cycle for a CdSe thin film.

determined with the following equation:

$$v = (I_l - I_d)R, \quad (8)$$

where I_d and I_l are dark current and current under light interaction correspondingly. On the other hand, I_d and I_l are determined in the following manner:

$$I_d = \frac{V}{R + r_0}, \quad (9)$$

$$I_l = \frac{V}{R + r_0 - \Delta r}, \quad (10)$$

where V is the applied voltage, r_0 is the dark electrical resistance and $r_0 - \Delta r$ is the electrical resistance during the interaction of the investigated sample with monochromatic radiation.

As can be shown, the stationary photoconductivity depends on dark electrical resistance of the investigated sample and resistance of the standard resistor according to the following equation:

$$\Delta\sigma_{st.} = \frac{v(R + r_0)^2}{r_0^2 VR - vr_0 R(r_0 + R)}. \quad (11)$$

In the case where $R \ll r_0$ (*constant field method*), the stationary photoconductivity is proportional to the voltage drop at the ends of the resistor:

$$\Delta\sigma_{st.} = \frac{v}{RV}. \quad (12)$$

As-deposited CdSe thin films, regardless on the chemical composition of the reaction system, are non-photoconductive. Namely, as was previously discussed, the very high dark electrical resistance and the absence of photoconductivity, regardless on the chemical composition of the reaction system, in the case of as-deposited cadmium selenide thin films are due to the localization of electrons and holes in a confined space (quantum

dot). Upon thermal treatment of the thin films, the nanocrystals are electrically connected and the confinement effects disappear irreversibly. The annealed thin films, which are characterized with dark electrical resistance of the order of several GΩs, manifest high photoconductivity upon interaction with white light. Changing the reactant concentrations (within a narrow range) in the growth solution, the thin films have dark electrical resistance of the order of MΩs and manifest small or negligible photoconductivity.

The spectral dependence of stationary photoconductivity of cadmium selenide thin film (which is characterized with dark electrical resistance of 2 GΩ) is presented in Fig. 7. Upon interaction with white light (from an overhead projector), the electrical resistance of the thin film decreases to 18 MΩ. After light switch-off the resistance momentarily increases to dark value. This finding indicates that cadmium selenide thin films exhibit fast photoconductivity.

The spectral dependence of photoconductivity of CdSe thin films is determined from their absorption spectra (presented in Ref. [7]). The manifested photoconductivity is a result of the internal photoelectric effect, i.e., it is due to the fundamental (band to band) electronic transitions and generation of non-equilibrium charge carriers. As can be seen from Fig. 7 the absorption edge, i.e., the red limit of internal photoelectric effect is about 1.60 eV. Upon interaction with photons with energy of 1.94 eV the stationary photoconductivity of cadmium selenide is maximal. On the side of larger photon energies, the stationary photoconductivity decreases as a result of *surface relaxation processes* [16]. The interaction of CdSe with photons with energies larger than the band gap energy (1.77 eV [7]) is followed by intensive surface absorption and increase of non-equilibrium charge carrier concentra-

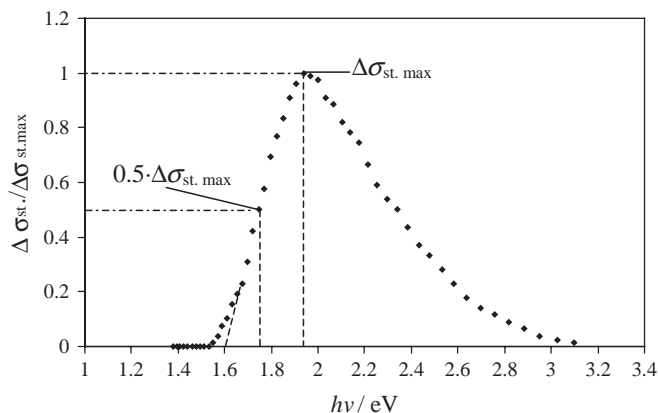


Fig. 7. Measured spectral dependence of photoconductivity for a CdSe thin film.

tions. On the other hand, the high concentration of photocarriers favors the annihilation processes and decrease of photocarrier's lifetime.

4.2.2. Determination of optical band gap energy of photoconductive CdSe thin films on the basis of spectral dependence of stationary photoconductivity

The spectral dependence of stationary photoconductivity of semiconducting materials is determined from their absorption spectra, i.e., from their band structure. Several methods for determination of optical band gap energy of semiconducting materials, on the basis of spectral dependence of stationary photoconductivity, have been proposed in the literature [17]. According to the presented methodologies, the band gap energy corresponds to the maximal stationary photoconductivity, to the red limit of internal photoelectric effect or to the photon energy which corresponds to $0.5 \Delta\sigma_{st,max}$. In our case, the determined optical band gap energy of photoconductive CdSe thin film, on the basis of photon energy which corresponds to $0.5 \Delta\sigma_{st,max}$, is 1.75 eV (Fig. 7). This is in excellent agreement with the value of 1.77 eV [7] calculated on the basis of absorption spectrum in the framework of parabolic approximation for dispersion relation using Fermi's golden rule for electronic transitions from valence to conduction band.

4.2.3. Relaxation dynamics of non-equilibrium charge carriers in photoconductive CdSe nanocrystals in thin film form

Recombination phenomena of non-equilibrium charge carriers can be classified as direct (band to band recombination) and indirect (via band gap recombination centers) processes. The released energy that results from the recombination process can be emitted as a photon or dissipated to the lattice in the form of heat. When a photon is emitted, the process is called radiative recombination, otherwise it is called non-radiative recombination. From kinetic aspect, the non-equilibrium

charge carriers are relaxed according to the mechanism of linear or quadratic relaxation [16].

In Figs. 8a and b the obtained oscillograms for CdSe thin film (with dark conductivity of $5 \times 10^{-10} \Omega^{-1}$) are shown. Using Eq. (12), on the basis of time dependence of voltage drop at the end of the resistor R_s , the relaxation curve (i.e., the time dependence of the stationary photoconductivity) was constructed.

The experimental data from dependence $\Delta\sigma/\Delta\sigma_{max} = f(t)$ are fitted with functions, which determine the time dependence of photocarrier's concentration in the case of linear and quadratic recombination processes. On the basis of the obtained results it can be concluded that within the short starting time interval (<0.2 ms) the photocarriers are relaxed according to the quadratic relaxation mechanism. The dependence of non-equilibrium charge carrier's concentration (ΔN) on time, in the case of quadratic relaxation mechanism, is described with the equation

$$\Delta N = \sqrt{\frac{\alpha\beta I}{\gamma}} \frac{1}{t\sqrt{\alpha\beta\gamma I} + 1}, \quad (13)$$

where α , β , γ and I are absorption coefficient, quantum yield, recombination coefficient and intensity of incident radiation, correspondingly. On the basis of experimental results, within the short starting time interval (<0.2 ms), we have constructed the function $(1/\Delta\sigma) = f(t)$ and have obtained a linear dependence (Fig. 9), which is in agreement with our conclusions with reference to quadratic recombination mechanism in the beginning of relaxation process. In the first time interval the concentration of non-equilibrium charge carriers in photoexcited CdSe nanocrystals is very high and the electrons from conduction band are recombined with the holes from valence band. The rate of recombination, in this case, depends on the concentrations of both charge carriers [16]. After about 0.2 ms the photocarrier's concentrations decrease and the non-equilibrium

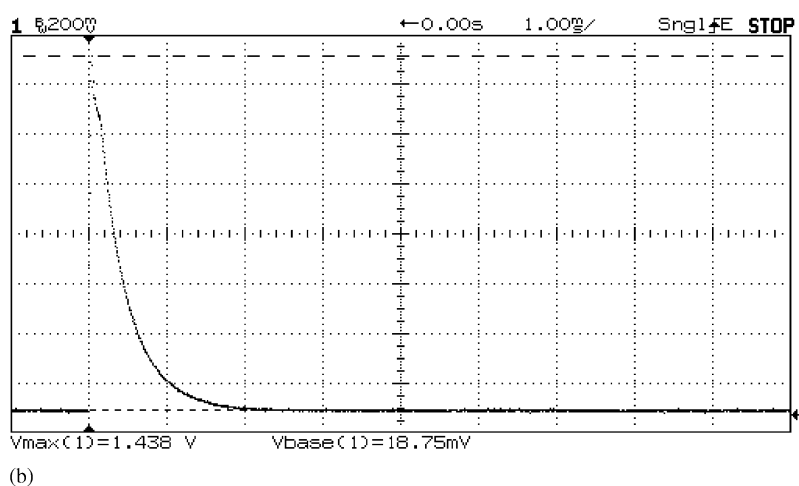
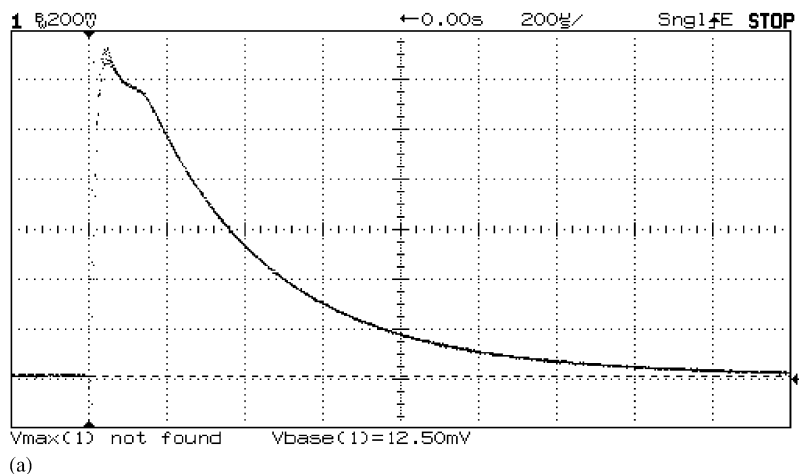


Fig. 8. Recorded oscillograms for a photoexcited CdSe thin film (a—normal t -axis, b—extended t -axis) after the interaction with electromagnetic radiation is switched off.

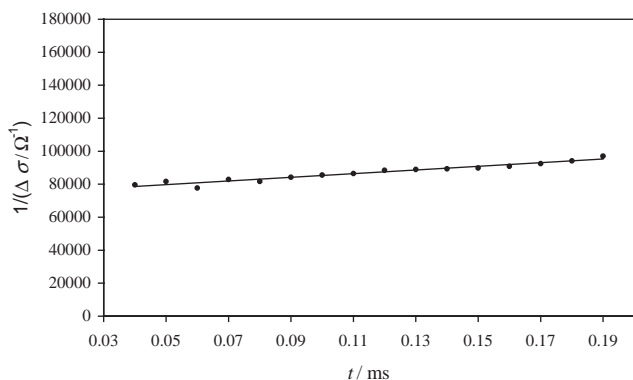


Fig. 9. Dependence of $1/\Delta\sigma$ vs. t in the starting time interval of relaxation process of non-equilibrium charge carriers in CdSe thin film.

charge carriers are relaxed via band gap recombination centers according to the linear relaxation mechanism. On the basis of experimental data that correspond to the

linear relaxation mechanism the lifetime of non-equilibrium charge carriers was calculated. In the case of linear relaxation process, the non-equilibrium conductivity decreases exponentially [16]:

$$\Delta\sigma = \Delta\sigma_{st} e^{-t/\tau} \tag{14}$$

The dependence of $\ln(\Delta\sigma)$ on t was constructed (Fig. 10) and the data from this dependence were fitted with a linear function. The average lifetime (i.e., relaxation time) of non-equilibrium charge carriers in photoexcited CdSe nanocrystals (in thin film form), calculated on the basis of slope of $\ln(\Delta\sigma)$ as a function of t is 0.4 ms. The obtained CdSe nanocrystals in thin film form have a potential application in fabrication of solar cells having in mind that the calculated photocarrier's lifetime, is relatively high on an absolute scale.

As can be seen from the oscillogram presented in Fig. 8b, registered at extended t -axis of the oscilloscope (1 ms/cm), the obtained CdSe thin films do not manifest residual photoconductivity.

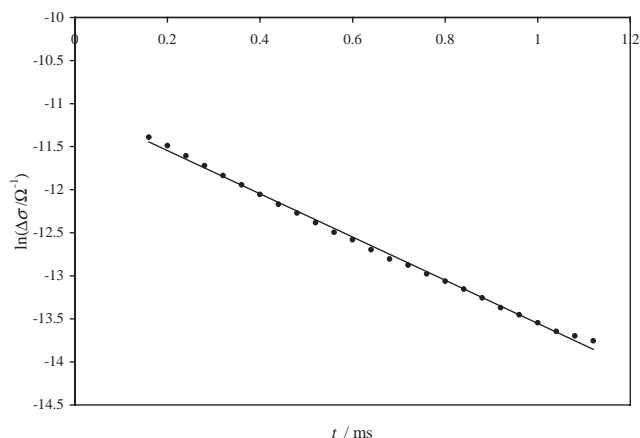


Fig. 10. Dependence of $\ln(\Delta\sigma/\Omega^{-1})$ vs. t within time interval which corresponds to the linear relaxation process of photocarriers in CdSe thin film.

4.2.4. Dependence of non-equilibrium conductivity on light intensity in the case of photoconductive CdSe thin films

Having in mind that photoconductive CdSe thin films are characterized with maximal photoconductivity upon interaction with light with wavelength of 640 nm, the dependence of non-equilibrium conductivity on light intensity is investigated using monochromatic radiation with wavelength of 640 nm.

It is well known that the stationary photoconductivity ($\Delta\sigma$) can be expressed as a power function of the light intensity (I):

$$\Delta\sigma \sim I^k, \quad (15)$$

where k is 1 or 1/2, depending on the type of relaxation mechanism (linear or quadratic, correspondingly). On the basis of dependence of $\ln(\Delta\sigma)$ on $\ln \Phi$ (presented in Fig. 11) the calculated value of k is approximately 1. According to these findings, in cumulative relaxation processes the linear mechanism has a dominant role.

5. Conclusions

Photoconductive performances of cubic cadmium selenide thin films are optimized by physical and chemical mean. Thermal treatment of as-deposited CdSe quantum dots in thin film form leads to electrical connection between nanoparticles and irreversible loss of confinement effects. The dark electrical resistance of thin films was measured using two- and four-point probe methods, as well as the constant field method. To achieve ohmic contact with the thin films silver paste was used. The non-rectifying character of the metal–semiconductor contacts was proved on the basis of the measured current–voltage characteristics. Hot probe method was used to determine the type of major charge carriers in the obtained films. On the basis of the

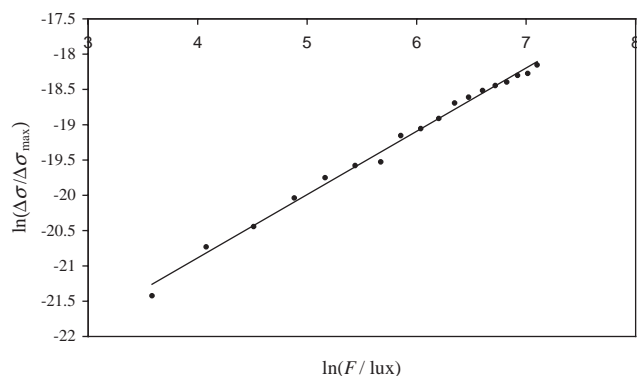


Fig. 11. Dependence of $\ln(\Delta\sigma)$ on $\ln \Phi$ in the case of CdSe thin film.

experimentally measured temperature dependence of the electrical resistance of the films, thermal band gap energy and activation energies of impurity levels were calculated.

The spectral dependence of photoconductivity was measured using the constant field method. The relaxation dynamics of non-equilibrium charge carriers in photoexcited nanocrystals was studied using the oscillographic method. On the basis of the obtained relaxation curves conclusions about the mechanism of relaxation (from the kinetic aspect) were derived and the phenomenological parameter τ (relaxation time) was calculated.

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