UDC 538.956

RESEARCH OF RELAXATION CURVES OF PHOTOCONDUCTIVITY OF $ZnS_{0,5}Se_{0,5}$ THIN FILMS

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This paper presents research of photoconductivity relaxation curves of $ZnS_{0,5}Se_{0,5}$ polycrystalline thin films. The value of stationary photoconductivity, $\Delta\sigma_{st}$, is reduced if the sample temperature in the moment of illumination increases from 81 K to 300 K. From the slope dependency type $\ln(\Delta\sigma/\Delta\sigma_{st})=f(t)$ the lifetime (τ) of non-equilibrium charge carriers was calculated. The lifetime decreases with increasing sample temperature.

Keywords: thin films, photoconductivity, relaxation curves, lifetime.

Această lucrare prezintă cercetarea curbelor de relaxare a fotoconductivităţii straturilor subţiri policristaline de $ZnS_{0,5}Se_{0,5}$. Valoarea fotoconductivităţii staţionare, $\Delta\sigma_{st}$, se micşorează, dacă temperatura probei în momentul iluminării creşte de la 81 K până la 300 K. Din panta dependenţelor tip $\ln(\Delta\sigma/\Delta\sigma_{st})=f(t)$ a fost calculat timpul de viaţă (τ) a purtătorilor de sarcină de neechilibru. Valoarea timpului de relaxare se micşorează, odată cu creşterea temperaturii probei.

Cuvinte-cheie: straturi subţiri, fotoconductivitate, curbele de relaxare, timpul de relaxare.

INTRODUCTION

Photoconduction is the phenomenon of variation of electrical conductivity of a material as a result of absorption of the electromagnetic radiation in the respective material. The absorption of the electromagnetic radiation is associated with electronic transitions, leading to changes in electrical conductivity.

Depending on the produced electronic transitions we distinguish three main types of photoconduction:

Intrinsic photoconduction occurs when the action of illumination only band–band transitions, generating electron–hole pairs occurs. Such a photoconduction occurs if the energy of the quantum of radiation is greater than the width of the gap band, $h\nu > E_g$, so that the threshold of the intrinsic photoconduction corresponds to the width of gap band of the semiconductor. In this case, the concentration of free electrons increases, as well as that of the holes.

Extrinsic photoconduction appears in an extrinsic semiconductor, where as a result of excitation by light occur transitions between the levels of impurities and allowed bands (excitation of electrons from donor levels in the conduction band or excitation of the holes from the acceptor level in the valence band). Generally, this phenomenon includes processes related to photoionization of any energy levels from the gap band (centers of impurities, structural defects of different types, etc.). Consequently, free carriers are generated only by one type that varies the electrical conductivity of the semiconductor.

The photoconduction of free carriers occurs mainly at low temperatures, where the radiation is absorbed by free electrons of the semiconductor. In this case the energy exchange between electrons and the network is weak, the electrons acquire from the incident radiation an energy that is greater than the one that can be ceded through collision of the network. They can thus be characterized through an electronic temperature $T_e > T_o$, where T_o is the temperature of the network. This leads to changes in electron mobility and hence of the electrical conductivity.

In the semiconductor light as a result of the absorption of electromagnetic radiation, appear additional charge carriers, of the non-equilibrium and this leads to total electrical conductivity variation of the semiconductor can be written:

$$\sigma = \sigma_0 + \Delta\sigma, \quad (1)$$

where

$$\sigma_0 = e(n_0\mu_n + p_0\mu_p) = \sigma_I \quad (2)$$

is the electrical conductivity of the semiconductor in the dark (in the absence of illumination) and

$$\Delta\sigma = e(\mu_n \Delta n + \mu_p \Delta p) = \sigma_L \quad (3)$$

is photoconductivity, i.e. electrical conductivity caused by non-equilibrium charge carriers, which are generated a result of illumination.

This paper aims to investigate the relaxation curves of the $ZnS_{0,5}Se_{0,5}$ thin photoconductivity and to determine some parameters resulting from these dependencies.

EXPERIMENTAL DETAILS

$ZnS_{0,5}Se_{0,5}$ thin films were prepared onto glass substrates by physical vapour deposition under vacuum ($p<10^{-5}$ Torr). For preparation of sintered films the powders of ZnS (with purity 99.99%) and ZnSe (with purity 99.99%) were used.

The samples were prepared using the following deposition parameters: sourse (evaporator) – substrate distance was 8 cm; sourse temperature, T_{ev}, ranged between 1000 K and 1300 K; deposited rate, r_d, ranged from 1.2 nm to 1.7 nm; substrate temperature, T_s, was varied between 300 K and 600 K.

Film thickness was determined by an interferometric method and for studied samples ranged between 0.52 μm and 1.73 μm.

The installationused for determining the stationary photoconductivity is shown in fig. 1 [1, 2].

The electromagnetic radiation from the source S passes through the optical system OS (for focalization), is modulated with the help of the modulator MD (arotating disk provided with slots) and then falls on the entrance slot of monocromator M. The monocromator descomposes incident radiation in the monochromatic components, so that on the outlet slot and from here on sample (P) a beam of radiation with a known wavelength is sent. The sample is included in an electrical circuit (via electrodes deposited layer) which also contains a continuous voltage source (B) and a load resistance (R). Changing the sample resistance under the action of monochromatic radiation leads to changes in voltage across the load resistance, this change is amplified by selector amplifier A and then recorded by recorder I.

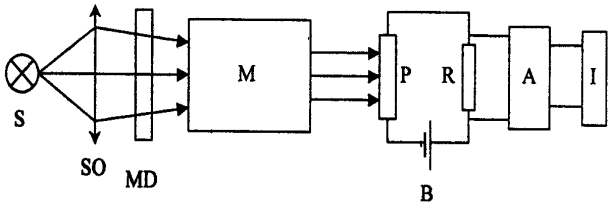

Fig. 1. The scheme of the installation for measuring stationary photoconductivity

The photoconductivity is defined as the difference between electrical conductivity of the illuminated sample (σ_L) and dark conductivity (σ_0) and is expressed by the equation [2]:

$$\Delta\sigma = \sigma_L - \sigma_0 = C\left(\frac{1}{R_L} - \frac{1}{R_0}\right) = \frac{C \cdot \Delta R}{R_0(R_0 - \Delta R)}, \quad (4)$$

where $C=\ell/d\cdot L$ is a constant that depends on the geometry of the sample, R_0 is the resistance of darkness, R_L is the resistance of the sample in conditions of illumination, ΔR is the variation of the electrical resistance of the sample due to illumination.

Voltage across the load resistor has a continuous component, caused by the darkness current I_0 and a variable component determined by the current light I_L whose frequency is determined by the frequency of the modulator. This frequency must be chosen in such a way that during the illumination, the photoconductivity would reachthe stationary value, $\Delta\sigma_{st}$ (maximum value for given lighting photoconductivity). The selective amplifier amplifies the variable component, v, whose size is [2]:

$$v = (I_L - I_0)R_s = \left[\frac{U}{R_s + R_0 - \Delta R} - \frac{U}{R_s + R_0}\right]R_s, \quad (5)$$

where U is the voltage supplied by the battery (B) (fig.1).

If from the relation (5) of the variation resistance to lighting ΔR is removed and it is replaced in the equation (4), then the photoconductivity is expressed by the formula [2]:

$$\Delta\sigma_{st} = \frac{C}{R_0 R_s} \frac{v(R_0 + R_s)^2}{UR_0 - v(R_0 + R_s)}. \quad (6)$$

If the load resistance is chosen so that we have $R_S << R_0$, from relation (6) is obtained [2]:

$$\Delta\sigma_{st} = \frac{Cv}{UR_s}, \quad (7)$$

and if it is chosen so that provides $R_S >> R_0$, we obtain [2]:

$$\Delta\sigma_{st} = \frac{CvR_s}{R_0(UR_0 - vR_s)}. \quad (8)$$

For a given sample we can obtain the maximum value of the signal through the choice of load resistence so that $dv/dR_s=0$ (maximum sensitivity regime). In this case we obtain [2]:

$$v_{\max} \approx \frac{U}{4}\frac{\Delta\sigma_{st}}{\sigma_0}. \quad (9)$$

Changing the wavelength of the incident radiation we can record spectral characteristics of stationary photoconductivity $\Delta\sigma = f(\lambda)$.

EXPERIMENTAL RESULTS. ANALYSIS

In semiconductors with aligned band, as is the case of ZnSe and ZnS crystals, electronic band-band transitions are vertical and thus for the appearance of the intrinsic photoconductivity it is necessary that the energy $h\nu$ of the photonincidence is at least equal to the width of the gap band.

If, as a result of illumination electron-hole pairs are generated, the concentration of non-equilibrium electrons, Δn, will be equal to the non-equilibrium holes, Δp, i.e. $\Delta n = \Delta p$.

If n_0 and p_0 are the concentrations of equilibrium electrons, respectively for the equilibrium holes, then the total concentration of free charge carriers n and p will be:

$$n = n_0 + \Delta n, \quad (10)$$

$$p = p_0 + \Delta p. \quad (11)$$

In parallel with the generation process, recombination takes place (process of annihilation of electron-hole pairs as a result of electron transition from conduction band to valence band).

Return to steady state due to the recombination processes (after cessation of illumination) occurs after a certain appointed *time for life*. Lifetime characterizes the decreasing process of the concentration of non-equilibrium carriers and is an important parameter to describe photoconductive phenomenon.

Generation and recombination processes are characterized by the *generation rate G* (number of non-equilibrium carriers generated in a unit of time in a unit of volume) and *recombination rate R* (number of carriers that recombine in a unit time, in a unit volume). Obviously, $G = g + G_0$, where g is the rate of generation of non-equilibrium carriers, e.g. at lighting, and G_0 is the rate of heat generation. Thus, in the absence of diffusion and drift, the rate of decrease of the number of carriers for any type of recombination can be determined by the difference between the rate of generation and recombination rate, i.e. [2-7]:

$$\frac{\mathrm{dn}}{\mathrm{dt}} = \mathrm{G} - \mathrm{R} = (\mathrm{g} + \mathrm{G}_0) - \mathrm{R}. \quad (12)$$

In the case of bipolar generation, when the electrons in the conduction band recombine with holes from the valence band, the recombination rate should be proportional to the total concentration of free carriers, i.e. $R = \gamma np$, where γ is the recombination coefficient defined as the probability of transition of the conduction band electrons in to the valence band, averaged over all energy states of the two bands. At thermal equilibrium (in the absence of illumination, $g=0$), electron concentration is constant, $\frac{dn}{dt} = 0$, so the combination rate is equal to the rate of heat generation:

$$G_0 = R_0 = \gamma_0 n_0 p_0 = \gamma n_0 p_0. \quad (13)$$

It can be considered $\gamma_0 = \gamma$, i.e. the coefficient of recombination of carriers is equal to the balance of non-equilibrium carriers, because of the relaxation time $\tau_{rel} >> \tau$, the energy of the two types of carriers is almost the same.

Variation in time of the concentration of non-equilibrium charge carriers is described by the relation [2-7]:

$$\frac{dn}{dt} = \frac{d(\Delta n)}{dt} = G - \gamma(n_0 + \Delta n)(p_0 + \Delta p) \quad (14)$$

or according to relation (12), we obtain:

$$\frac{d(\Delta n)}{\Delta t} = g - \gamma(n_0\Delta p + p_0\Delta n + \Delta n\Delta p). \quad (15)$$

Taking into consideration that $\Delta n = \Delta p$, we obtain:

$$\frac{d(\Delta n)}{dt} = g - \frac{\Delta n}{\tau}, \qquad (16)$$

where it is noted:

$$\tau = \frac{1}{\gamma(n_0 + p_0 + \Delta n)}. \qquad (17)$$

The new introduced value τ has dimensions of time and represents the *lifetime* of non-equilibrium charge carriers.

For the case of small deviations from equilibrium ($\Delta n=\Delta p<<n_0+p_0$), the relationship (17) becomes:

$$\tau = \frac{1}{\gamma(n_0 + p_0)}, \qquad (18)$$

so τ does not depend on Δn and assuming that the excitation starts abruptly at $t=0$, i.e. $\Delta n(0)=0$, the solution of the equation (16) for $g=const.$ gives the *growth law in time of non-equilibrium charge carriers.*

$$\Delta n = \Delta n_{st}\left(1 - e^{-\frac{t}{\tau}}\right) \qquad (19)$$

where $\Delta n_{st}=g\tau$ is the maximum value, stationary (for $t\to\infty$) of the concentration of non-equilibrium carriers.

If, after reaching the steady regime lighting ($g=0$) stops suddenly, the equation (16) becomes:

$$\frac{d(\Delta n)}{dt} = -\frac{\Delta n}{\tau} \qquad (20)$$

and considering $\Delta n(0)=\Delta n_{st}$, we obtain the *law of decrease in time of non-equilibrium charge carriers:*

$$\Delta n = \Delta n_{st} e^{-\frac{t}{\tau}}. \qquad (21)$$

For an n-type semiconductor, electrical conductivity caused by non-equilibrium carriers (photoconductivity) is written as:

$$\Delta\sigma = e\mu_n \Delta n. \qquad (22)$$

Substituting in this relation the expression of Δn relationship data relations (19) and (21) we obtain the time dependence of photoconductivity for the case as the linear recombination:

$$\Delta\sigma = \Delta\sigma_{st}\left(1 - e^{-\frac{t}{\tau}}\right) \qquad (23)$$

at illumination and:

$$\Delta\sigma = \Delta\sigma_{st} e^{-\frac{t}{\tau}} \qquad (24)$$

at interruption of illumination, where $\Delta\sigma_{st}$ is stationary photoconductivity.

These relationships are at the base of the study of photoconductivity relaxation curves of *ZnSe* thin films studied by us. From equation (24) through logarithms, we obtain:

$$\ln\left(\frac{\Delta\sigma}{\Delta\sigma_{st}}\right) = -\frac{t}{\tau}. \qquad (25)$$

If $\Delta\sigma_1$ represents the photoconductivity of the sample at time t_1 and $\Delta\sigma_2$ is photoconductivity of the sample at time t_2, then in accordance with the equation (25), we can write:

$$\ln\left(\frac{\Delta\sigma_1}{\Delta\sigma_{st}}\right) - \ln\left(\frac{\Delta\sigma_2}{\Delta\sigma_{st}}\right) = -\frac{1}{\tau}(t_1 - t_2) = \frac{1}{\tau}(t_2 - t_1) \qquad (26)$$

where:

$$\tau = \frac{t_2 - t_1}{\left(\ln\frac{\Delta\sigma_1}{\Delta\sigma_{st}}\right) - \left(\ln\frac{\Delta\sigma_2}{\Delta\sigma_{st}}\right)}. \qquad (27)$$

In fig. 2 a, b, c, d and e the relaxation curves of photoconductivity of a thin layer of *ZnSe* to its different temperature are represented. It is noted that stationary photoconductivity $\Delta\sigma_{st}$ decreases with the increase of sample temperature.

This is explained by the fact that at higher temperatures, the concentration of equilibrium charge carriers is higher and that is why it increases the probability of recombination ($R\sim\alpha$).

In fig. 3 are represented the dependences $ln(\Delta\sigma/\Delta\sigma_{st})=f(t)$, calculated from the relaxation curves for different temperatures of ZnS_xSe_{1-x} sample. It is not able that these dependencies are linear.

From the slope of these dependencies, using the relation (27), lifetime (τ) of non-equilibrium charge carriers was calculated. With the increase of temperature of the sample the value of τ decreases.

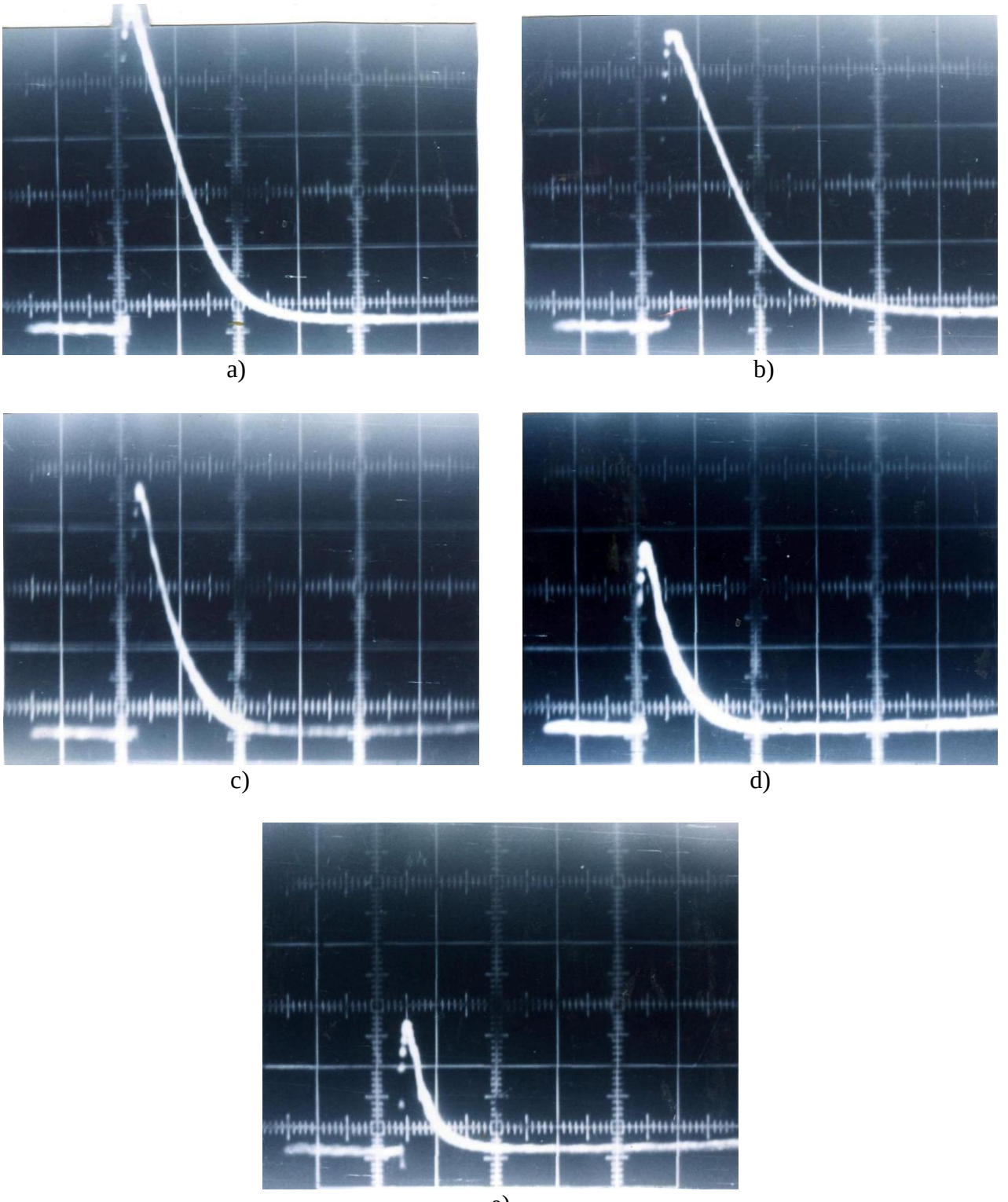

Fig. 2. Relaxation curves of photoconductivity of a thin film of ZnS_xSe_{1-x} at different temperatures of the sample A.090 (d=0.90 μm, T_{sup}=300 K, r_d=1.70 nm/s) (in ordinate is indicated $\Delta\sigma=\sigma_L-\sigma_0$ in relative units):
a) T=81 K (1cm=0.1 μs); b) T=175 K, (1 cm=0.2 μs); c) T=225 K, (1 cm=0.2 μs); d) T=262 K (1 cm=0.4 μs); e) T=300 K (1 cm=0.4 μs)

Recent studies [6] revealed that photoconductivity from high relaxation time can be attributed to the presence in the sample of collective barriers of potential related to different types of heterogeneity.

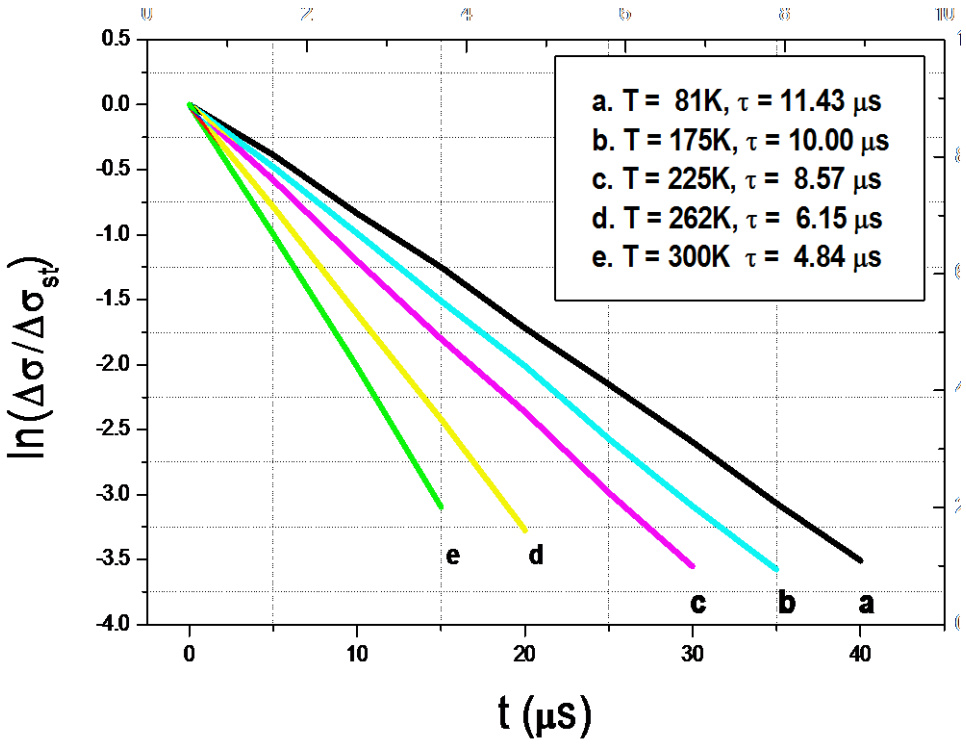

Fig. 3. Dependencies $ln(\Delta\sigma/\Delta\sigma_{st})=f(t)$ obtained at different temperatures of the $ZnS_{0,5}Se_{0,5}$ thin film (A.090 sample, d=0.90 μm, T_{sup}=300 K, r_d=1.70 nm/s)

The electric field of these barriers causes a separation of non-equilibrium charge carriers generated at illumination. In this case, the recombination rate is small because the probability that an electron will arrive into a region containing holes is very small. This phenomenon was highlighted in a series of semiconductors such as CdS, CdSe, CdTe, etc. [3, 6, 8].

CONCLUSIONS

Research results of photoconductivity relaxation curves of ZnS_xSe_{1-x} thin films are quite important because they provide information that would allow their use in radiation detectors, bolometers, solar batteries and other optoelectronic devices that are requested in industry and technology.

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Prezentat la redacţie la 8 decembrie 2014