PHOTOCONDUCTIVITY IN CHALCOGENIDE GLASSES IN NON-STATIONARY REGIME AND THE BARRIER-CLUSTER MODEL

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ABSTRACT

The aim of this article is in the first place to familiarize the readers with the barrier-cluster model of non-crystalline semiconductors, then briefly and succinctly to present some results concerning chalcogenide glasses. The barrier-cluster model is based on the assumption that in non-crystalline semiconductors, there exist micro-regions (clusters) separated from each other by potential barriers. It is shown that such a concept allows to understand optical absorption, electroabsorption, photoluminescence and photoconductivity processes, as well as their mutual interdependence. In this article, we attempt to explain on the base of the barrier-cluster model non-stationary photoconductivity processes and the influence of the some physical factors on them. Electrical and optical properties of non-crystalline semiconductors are a hot subject of interest of investigators for the wide applicability of these materials.

Keywords: *Chalcogenide glass, Photoconductivity, Cluster, Barrier-cluster model, Amorphous, Semiconductor*

1. INTRODUCTION

In physics of non crystalline materials, there are many unsolved problems yet [1-8]. Since Kolomiets began first to study chalcogenide glasses, thousands works have been published in the field of glassy semiconductors. Majority of those works were of experimental character and brought experimental results. The theory in this field lagged behind the experiment. No model has been suggested yet that could explain sufficiently the wide range of observed phenomena. The status of the theory of non-crystalline solids still stays like that one as it was expressed by H. Overhof in „Fundamental concepts in the physics of amorphous semiconductors" [9]: „It seems to me, as far as the theory of non-crystalline semiconductors is concerned, that one of the fundamental pillars of the pedestal, on which such a theory should rest, is still unknown to us." We present in this article some remarks on current open problems of the physics of non-crystalline semiconductors and suggest potential possibilities of barrier-cluster model to explain the problems.

Optical properties of non-crystalline semiconductors are a hot subject of interest of investigators for the wide applicability of these materials, as well as for the hope to obtain important information about processes in such materials.

Non-crystalline semiconductors are now applied as optical light-guides, as elements of optoelectronics (optical switches and so on), xero-materials, memory elements and others [1-9]. The situation still seems to be unsatisfactory if one wants to understand physical processes running in these materials. Up to now there is no generally accepted model which would be capable to describe the wide spectrum of optical and other phenomena in these matterials.

In Refs. [10-22] the so-called barrier-cluster model of a non-crystalline semiconductor was presented. On the base of the barrier-cluster model, some phenomena were explained (mainly optical ones) in non-crystalline semiconductors. Especially, it is the explanation of exponential tails in the optical absorption and explanation of thermal influence both at low and high temperatures. On the base of the barrier-cluster model also the mechanisms of electroabsorption and photoluminescence have been described quantitatively.

In this article, some basic ideas of the barrier-cluster model will be introduced, and then an explanation of optical phenomena. based on it. Therefore, processes connected with photoconductivity will be described in more detail. We deal especialy with transient photoconductivity processes.

The photoelectric conductivity σ of chalcogenide glasses exhibits usually an activation dependence in a relatively wide range of temperatures [1,3]. A relation of the following type can thus express it

$$\ln \sigma \approx -W_{photo}/\,\mathrm{k}T \tag{1}$$

where W_{photo} is a relevant activation energy. In this case we have in mind the stationary regime [19]. Now we will be interested in the photoconductivity right after the exposition by a stimulating radiation and also relaxation after finishing the radiation.

2. BARRIER-CLUSTER MODEL AND OPTICAL PHENOMENA

2.1. Barrier-cluster model - basic ideas

The discoveries of fullerens led to the suggestion that other low-dimensional covalent systems, as e.g. chalcogenides could present special configurations similar to fullerenes or nanotubes - clusters. The barrier-cluster model assumes that an amorphous semiconductor consists of microscopic regions – perhaps closed clusters - separated from each other by potential barriers [10-22]. The barriers hamper the transfer of low energy conduction electrons from one region to the other. Such electrons behave between barriers in particular regions of the material in a similar way as electrons do in a crystal. The potential barriers can be depicted inside both the conduction and valence band of an amorphous material,

separating individual localized energy states at the edges of the bands (Fig. 1). The electron levels between the barriers, due to the small dimensions of the microscopic regions, exhibit a distinct discrete character. At the lower margin of the conduction band, a sub-band with carriers of low average mobility is created. The states with energy above the peaks of barriers are delocalized. They create a sub-band with a high average mobility. Quite a similar situation occurs at the edge of the valence band.

2.2. Optical absorption

The potential barriers also influence significantly the optical absorption at the optical absorption edge. It is caused first of all line by a strong electron-phonon interaction, which implies that an electron can also take the energy of a phonon at the optical transition and thus, the total energy taken by an electron equals the sum of the photon and phonon energies. This enables to explain existence of exponential tails at the optical absorption, which reach deeply inside the forbidden band of the semiconductor [10-22]. Another important factor - as far as the influence of barriers on optical phenomena is concerned - is that the absorption of light in the region of the absorption edge at low temperatures is usually connected with a tunneling of carriers through potential barriers. Thus, the absorption process is influenced by the barriers. These facts enable us to explain successfully not only the creation of exponential tails at the optical absorption edge, but also their temperature dependences both at high and at low temperatures [10-12].

The optical absorption in most crystalline solids is characterized by a sharp edge of the absorption band. The absorption band near its border in the case of non-crystalline semiconductors is smeared out and it creates a tail that extends deeply into the forbidden band. The profile of the tail is exponential as a rule. The exponential tails at higher temperatures tend to fit Urbach´s formula. The slope of the tails changes with a further temperature decrease. At lower temperatures, the slope of the tails does not vary with a further temperature decrease. However, a certain parallel shift towards lower absorption is observed.
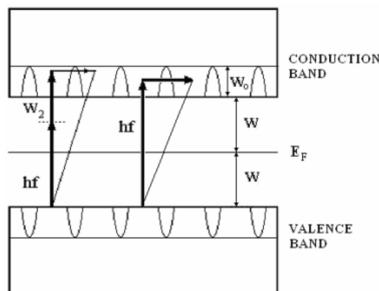
Fig. 1 Electronic spectrum of non-crystalline semiconductor and optical transition at higher (left) and at lower (right) temperature

The exponential tail

Higher temperature range: The starting point in the following discussion is an assumption that the potential barriers in non-crystalline semiconductors under proper conditions enables to explain a distinct absorption of light, with phonons participating in the energy exchange [10,14,15]. We assume that an electron in the optical transition accepts not only the energy hf of a photon but also the phonon energy $W_2 = W_{phon}$. Thus, the whole energy accepted is

$$hf + W_{phon} \tag{2}$$

where W_{phon} is the energy acquired from a phonon "field". The quantity hf is given by the wavelength of the radiation, while W_{phon} has a statistical character.

In principle, a photon can be absorbed only when the energy of the electron is sufficient to cause a transition of the electron into the conduction band. It should be taken into account, however, that optical transitions on the energy levels lying just below the tops of barriers will dominate at higher temperatures. In this case, the probability of transition within a single localized region is small. The levels in adjacent microregions offer more possibilities of combination. However, they are connected with tunneling through barriers. Under these assumptions, the transitions on levels just below the barrier peaks will be more probable for two reasons. The transitions on lower levels will be restricted considerably by a small tunneling probability. The second reason consists in the strong electron-phonon interaction in the presence of the barriers. The number of electrons that can acquire such energy from a phonon field depends on the temperature. The number of electron transitions when irradiating the material by „low energy" photons (and thus, also the coefficient of optical absorption α) is directly proportional to the phonon concentration corresponding to the minimal (least) energy needed for transition. For the absorption coefficient it can be written [10,19].

$$\alpha \approx \exp(hf/2k\text{T}) \tag{3}$$

or, for a particular (constant) temperature

$$\ln \alpha = hf + \text{const} \tag{4}$$

which is a mathematical expression of an exponential tail of optical absorption [1,2]. However, the slope of the tails is also temperature dependent. Formula is of the same kind as the Urbach's formula.

Low temperature range: At low temperatures, only photons with sufficient energy can be absorbed by the material. There are not enough phonons with sufficiently high energies to realize the high-temperature mechanism of the absorption. The optical transition of an electron can be virtually divided into two parts [10,13-15]. The first part (Fig. 1) is a vertical transition onto an energy level inside its own localized region; the second part represents a horizontal tunneling transition onto a real level in an adjacent localized region. Thus, absorption of a photon in a low-temperature mechanism is connected with the tunneling of the electron through a potential barrier. The barrier model explains in this case the temperature dependence parallel shift of the exponential tails [13].

2.3. Electroabsorption

The electroabsorption means the influence an external electric field on optical absorption [1]. Kolomiec with co-workers observed electro-absorption in the amorphous

semiconductor As_2S_3 and in several other chalcogenide materials. As experiments show, an increase of optical absorption in non-crystalline semiconductors is observed if the electric field is strong. The influence of the field is relatively small and is proportional to the square of the intensity of the field. The change of absorption coefficient $\Delta\alpha$, influenced by the field, depends also on the energy of the absorbed photon. In article [11-12], the phenomena of the electroabsorption in chalcogenide glasses are explained on the base of the barrier model. For the relative change of the absorption coefficient under influence of an electric field E, the relations

$$\frac{\Delta\alpha}{\alpha} = -C_1 hf + C_2 \tag{5a}$$

$$\frac{\Delta\alpha}{\alpha} = const.E^2 \tag{5b}$$

are derived. This is in agreement with experiment. In paper [12] the problem of the influence of temperature on the optical absorption and electroabsorption in chalcogenide glasses in region of exponential tails is analyzed. The relation

$$\frac{\Delta\alpha}{\alpha} = -C_1(hf+CT)+C_2 \tag{6}$$

has been derived, which is in agreement with experiments.

2.4. Photoluminescence

A possible concept of the physical nature of the photoluminescence in chalcogenide glasses at low temperatures, from the point of view of the barrier-cluster model, has been is analyzed in Refs [16, 17, 21, 22]. An electron during the optical transition connected with the tunneling, gets to an adjacent or a nearly region on an energy level, which is below the peak level of the potential barriers. At lower temperatures, the excited electron after an optical transition, will pass on the lowest energy levels of a given localization region. It will be free only within its own localization region. Its wave function would be localized practically in its own microregion between the neighboring barriers. Due to the Coulomb interaction a bound state of an e-h couple arises. As a consequence, a new energy level is formed in the forbidden band. Let us assign this level formally to that localization region where the electron finds itself. This level will be below the bottom of the conduction band. Levels of this kind will arise not only in the neighboring microregion (cluster), but also in the more distant regions. The height of these levels will depend on the distance from the "mother" microregion (for the sake of simplification, we suppose that the hole did not move). With increasing distance, these levels will approach the bottom of the conduction band.

However, discrete levels of excited states in a given region also belong to each level of the funnel, as the lowest energy level of the given localization region. At low temperatures, an optically excited electron will, with a high probability, gradually get back to the mother region of the hole. Such an approach is connected to gradual tunneling and diffusion. The approaching jumps "region-by-region", are connected to an interaction with phonons. Without phonons, such a process would not be possible. These approaching processes are in principle not radiant. An electron loses gradually a considerable part of its energy in them. In the last phase of approach, a non-radiant transition occurs to its own localization region. In this region, radiant optical recombination of the e-h pair occurs, connected with emission of a luminescence photon, whose energy is considerably lower than that of photons of the exciting radiation. A distinct Stokesian shift will occur. If there were no other disturbing processes, a stationary state with a relatively high level of luminescence would establish quickly within the material. In fact, this corresponds rather well to a real situation in the first phase of irradiation. However, the state of a high luminescence begins to impair and weaken rather quickly.

Free electrons as stimulators of non-radiant recombination

After irradiating a non-crystalline semiconductor by a flux of photons at low temperatures under conditions described above, free electrons are practically formed in materials only by a multi-tunneling of a little part of electrons, which took part in the optical transition. The slow rise of concentration of free electrons is caused by the relatively low probability of multi-tunneling processes. The concentration of free electrons in the semiconductor becomes stable only after a long time, when a dynamical equilibrium of two mutually opposing effects establishes. This means the process of arising free electrons and the process of their annihilation by joining with holes, so that new bound e-h pairs are created. When explaining the laws of photoluminescence on the basis of the barrier-cluster model, an assumption is extremely important in our considerations, namely that free electrons, by their effect, stimulate the non-radiant recombination of bound e-h pairs (as a kind of a catalyst), and thus, they reduce the number of radiant transitions. So, ultimately, free electrons markedly influence the luminescence process. The free electron remains free after such individual catalyst process and continues triggering non-optical transitions, acting as a catalyst.

Influence of temperature

It was already said that a source of free electrons in a non-crystalline matter during photo-irradiation at low temperatures is a manifold tunneling of a small electron fraction during the optical absorption connected with tunneling. For this mechanism it is essential that the majority of electrons execute a tunneling through one potential barrier at the optical transition. Some electrons exibit the tunneling s-times (i.e. across s-barriers) consecutively at the optical transition. In this manner electrons travel a long distance from their original region (together with corresponding holes) and become free. The electron no longer will be bounded with a hole by the Coulomb force. In our model it is assumed that free electrons then activate non-radiate transitions of bounded pairs e-h. These pairs will not contribute to the luminescence. This is why the process of stabilization of

luminescence will be relative slow. In [17], the Street's formula

$$I \approx \exp\left(-T / T_0\right) \qquad (7)$$

was derived to give the dependence of photoluminescence on the temperature. It is based on the concept that the photoluminescence process in a non-crystalline matter is strongly influenced by free electrons.

Influence of the absorbed energy quanta

In [18] the first attempt was done to describe quantitatively the dependence of efficiency of an excitation radiation on the energy of stimulated photons in the region of the exponential tail.

At lower energies of the exciting photons in the region of the exponential absorption tail, the photoluminescence intensity increases with the increase of the photon energy hf, together with the absorption α. The, photoluminescence I in this region copies the course of the absorption α. We can speak of a good correlation). Strictly speaking, in this range of photon energies practically all generated e-h couples recombine radiantly. There is a negligibly small number of free electrons in the solid and therefore the non-radiant recombinations practically do not occur. At higher energies of the exciting photons in the region of the exponential tail, the absorption will continue to increase exponentially but photoluminescence passes through the maximum and will decrease with a further increase of photons energy.

This experimental fact is due - as we believe – standing on the basis of the barrier-cluster model - to the fact that at higher photon energies, the tunneling of electrons through barriers runs on higher energy levels. This circumstance strongly increases the probability of the s-fold tunneling of some electrons to larger distances. In this way the production of free electrons increases considerably with the increase of energy of the exciting photons and consequently, also with the amount of the non-radiant recombination. The number of radiant transitions decrease, and thus also of the photoluminescence level.

At higher photon energies, a tunneling of electrons trough barriers will run on higher energy levels. This increases the probability of the tunneling. The probability of the s-multiple tunneling of electrons reaching long distances will rise much faster. Therefore, with an energy increase of the activating photons a free electron production will increase essentially and thus also the number of the non-radiate e-h pair recombination. The number of radiating transitions as well as the luminescence "niveau", will no longer be proportional to the number of absorbed photons and consequently to the number of generated e-h pairs. With increasing the photon energy, the luminescence increase first slows down, and then stops and finally the luminescence decreases.

Based on this concept, a law was derived, determining the luminescence intensity dependence on the temperature (in a region of low temperatures) as well as on the photon energy in an energy region of the upper part of the exponential tail. The attempt to express the dependence of the photoluminescence effectivity on the photon energy of

the primary radiation from the whole region of the exponential tail will be presented in [21, 22].

2.5. Photoconductivity in a steady state

The basic ideas on photoconductivity in chalcogenidede glasses from the viewpoint of the barrier cluster model were published in [19] where we examined the stationary photoconductivity in more detail. A mathematical expression for the steady photoconductivity dependence on the temperature in a broad temperature interval was obtained there. The course of the corresponding theoretical curve well agrees with that experimental one. The experimental curves are characterized by one maximum and two exponential dependences on sides of this maximum. Non-stationary photoconductivity processes will be studied in the next section of this article. In its first subsection we shortly summarize ideas concerning the mechanism of photoconductivity already published in [19].

3. NON-STATIONARY PHOTOCONDUCTIVITY

3.1. Mechanism the origin of free electrons – basic ideas

If we want to treat a problem of photoconductivity in chalcogenide glasses we have at first to answer the question in which way in a chalcogenide glass free electrons can be created opticaly in a range of the exponential tail of the optical absorption. The free electrons are carriers of the photoelectric current. The photoabsorption in a range of the exponential tail is connected – as it was already said – with electron tunneling through potential barriers. Majority of electrons in this transition pass through one barrier but a certain (comparatively small) part of electrons can pass through many barriers.

The source of free electrons in a non-crystalline matter during photo-irradiation at low temperatures is a multiple tunneling of a small electron fraction in the process of the optical absorption connected with tunneling. For this mechanism, it is important that the majority of electrons execute a tunneling through one potential barrier at the optical transition. Some electrons tunnel s - times across s barriers. In this manner, electrons otravel a long distance from their original region (together with a corresponding hole) and become free. An electron will no longer be bound with a hole by the Coulomb force.

According to [12, 17,18], the probability, p, of a single tunneling is proportional to the expression

$$p \approx \exp\left[-A\left(2W + W_0 - (hf + CT)\right)\right] \qquad (9)$$

$$p \sim \exp\left(A\left(hf + CT\right)\right) \qquad (10)$$

For the probability p^s of the multiple-tunneling of the electron through s barriers, we can write

$$P^s \sim p^s \sim \exp\left[sA\left(hf + CT\right)\right] \qquad (11)$$

The probability of the creation of a free electron is proportional to expression (8). Since the probability is small, the number of free electrons will increase slowly after the beginning of the illumination of the glass.

The probability of a free electron appearance at the mechanism of the multiple tunneling during the absorption at the temperature T and energy of activating photon hf is given as follows

$$P^s = \exp(As.(hf + CT - \beta_o)) \tag{12}$$

where $\exp(-\beta_o)$ represents in fact the pre-factor in this relation.

3.2. Processes affecting free electron concentration

In our consideration we assume that free electrons are responsible for photoconductivity created in a process of optical absorption by the mechanism of the multiple electron tunneling through potential barriers occurring at the bottom of the conduction band. Generation of these free electrons can be described, in accord with the relation (12), by the formula

$$G = \left\{ \frac{dn}{dt} \right\}_{gen} = \exp\left[sA\left(hf + CT - \beta\right) \right] \tag{13}$$

The generation factor G determines the number of free electrons created in a unit time.

This number is of course proportional to the probability P^s of the multiple tunneling of an electron at optical absorption, where $\exp(-\beta)$ represents a new pre-factor.

The reverse process to the electron generation is the recombination which can be in general described by the relation

$$R = \left\{ \frac{dn}{dt} \right\}_{RECOMB} = K.\, n^2 \tag{14}$$

where R is the recombination factor. It represents the number of annihilated free electrons per unit time. K is a constant. In our next consideration, we will neglect the concentration n_t of thermal electrons. We suppose that this concentration is much smaller than the free electron concentration n of some optical origin, so that $n_t \ll n$.

The change of the free photoelectron concentration n with time is given by the relation

$$\left\{ \frac{dn}{dt} \right\} = \left\{ \frac{dn}{dt} \right\}_{GENER} - \left\{ \frac{dn}{dt} \right\}_{RECOMB} \tag{15}$$

$$\left\{ \frac{dn}{dt} \right\} = G - R \tag{16}$$

According to (13-16) it holds

$$\frac{dn}{dt} = \exp\left[sA\left(hf + CT - \beta\right) \right] - K.\, n^2 \tag{17}$$

This differential equation determines the time dependence of the free electron concentration at non-stationary processes, concerning the beginning of an optical exposition at constant intensity, or its interruption. In a non-stationary regime, when the intensity of an incident radiation would vary, the quantity G in the relation (16) would be time-dependent $G = G(t)$ and things could be

more complex. Such processes in this article will be not treated.

3.3. Two mobility sub-bands of free electrons

Next we want to point out one important feature: a level of photoconductivity is not only determined by concentration n given by (17). The distribution of the total number n of electrons into two mobility sub-bandswil also be important. This distribution is caused by the temperature. One fraction of the concentration, n_1, in a steady state will be in sub-band of high mobility μ_1 therefore, at energy levels above the peaks of potential barriers. The second fraction of concentration, n_2, will be distributed in a sub-band of low mobility μ_2 at energy levels below the peaks of potential barriers. The number n_1 of free photo-electrons in the sub-band of high mobility can be expressed as

$$n_1 = n(t) \exp(-\frac{W_O}{2kT}) \tag{18}$$

The number of free electrons in the sub-band of low mobility (with energy width W_o) is determined by the difference $n - n_1 = n_2$, where

$$n_2 = n(t)\left[1 - \exp(-\frac{W_O}{2kT}) \right] \tag{19}$$

3.4. Photoelectric conductivity in non-stationare regime

The total photoconductivity is determined as

$$\sigma(t) \approx \mu_1 n_1(t) + \mu_2 n_2(t) \tag{20}$$

At some time it holds $\mu_1 > \mu_2$.

3.5. Photoelectric conductivity after switch on an exposition

Free electron concentration changes after activation of an optical exposition

We are interested in the time dependence of the transitive conductivity $\sigma(t)$ for $t \geq 0$, if the optical exposition of a glass startet at the time $t = 0$ when the free electron concentration was equal to $n = n_o = 0$.

The solution of the differential equation

$$\frac{dn}{dt} = \exp\left[sA\left(hf + CT - \beta\right) \right] - K.\, n^2 \tag{21}$$

obeying initial condition $n_o = 0$ is the function

$$n(t) = \sqrt{\frac{G}{K}} \tanh\left(\sqrt{KG}\, t \right) \tag{22}$$

which can be written, if we respect relations (13), as

$$n(t) = \sqrt{\frac{\exp\left[sA(hf + CT - \beta) \right]}{K}} \tanh\left(\sqrt{K \exp\left[sA(hf + CT + \beta) \right]}\, t \right) \tag{23}$$

This relation for free electron concentration will be used later in determining photoconductivity dependence on the time.

The time dependence of photoconductivity

With respect to the relations (18-20, 22, 23) one can write down

$$\sigma(t) \approx \sqrt{\frac{G}{K}} \ \tanh\left[\sqrt{KG}\ t\right]\left\{\mu_1 \exp\left(-\frac{W_o}{kT}\right) + \mu_2\left[1 - \exp\left(-\frac{W_o}{kT}\right)\right]\right\}$$

(24)

After a sufficiently long period of time $(t \to \infty)$ the photoconductivity aquires the stationary value

$$\sigma(t \to \infty) \approx \sqrt{\frac{G}{K}}\ \left\{\mu_1 \exp\left(-\frac{W_o}{kT}\right) + \mu_2\left[1 - \exp\left(-\frac{W_o}{kT}\right)\right]\right\}$$

(25)

or

$$\sigma_{stac} = \sigma(t \to \infty) \approx \sqrt{\frac{\exp\left[sA\left(hf + CT - \beta\right)\right]}{K}}$$
$$\left\{\mu_1 \exp\left(-\frac{W_o}{kT}\right) + \mu_2\left[1 - \exp\left(-\frac{W_o}{kT}\right)\right]\right\}$$

(26)

3.6. Photoconductivity after break of exposition

An initial state after the break of an optical exposition of a sample will be a steady state in which the initial free electron concentration is n_o. The steady state results from the fact, that for $t < 0$, $G =$ const. $\neq 0$. (On the contrary, for $t \geq 0$ the relation $G = 0$ will be valid.)

The behavior of the electron concentration $n(t)$ for $t \geq 0$ under these conditions also determines the differential eq. (13,21), accounting that now $G = 0$. When solving the differential equation we obtain in this way

$$\frac{dn}{dt} = - K \cdot n^2$$

(27)

one can not refer to the solution of the more general eq. (13,21), which includes also our special case in which $G = 0$. The solution of eq. (27) obeying initial condition $n(t = 0) = n_o \neq 0$ is

$$n(t) = \frac{1}{\dfrac{1}{n_0} + Kt}$$

(28)

One can obtain the same result using the relation (22), if one puts $G = 0$ in it (which is not visible at the first glance). The value n_o corresponds to the stationary state created before the break of exposition. According to (23) (for $t \to \infty$) it is given as

$$n_0 = \sqrt{\frac{1}{K}} \exp\left[0.5\ sA\left(hf + CT - \beta\right)\right]$$

(29)

Since $\tanh(\infty) = 1$.

The behavior of photoconductivity after the break of exposition is given - in accord with relation (20) – as

$$\sigma \approx n(t)\left\{\mu_1 \exp\left(-\frac{W_o}{kT}\right) + \mu_2\left[1 - \exp\left(-\frac{W_o}{kT}\right)\right]\right\}$$

(30)

so that, with respect to (28) we have

$$\sigma(t) \approx \frac{1}{\dfrac{1}{n_0} + Kt}\left\{\mu_1 \exp\left(-\frac{W_o}{kT}\right) + \mu_2\left[1 - \exp\left(-\frac{W_o}{kT}\right)\right]\right\}$$

(31)

If $t \to \infty$, then $\sigma \to 0$. As is seen, here the decrease of photoconductivity with time is not exponential. The dependence, that we have obtained does not contain any relaxation constant, but is more complex. This result agrees with experiment.

Notice: At the time $t = 0$ the photoconductivity has the initial value – according to the relation (31) -

$$\sigma(0) \approx n_0\left\{\mu_1 \exp\left(-\frac{W_o}{kT}\right) + \mu_2\left[1 - \exp\left(-\frac{W_o}{kT}\right)\right]\right\}$$

(32)

Or, respecting (29), we have obtained;

$$\sigma(0) \approx \sqrt{\frac{1}{K}} \exp\left[0.5\ sA\left(hf + CT - \beta\right)\right]$$
$$\left\{\mu_1 \exp\left(-\frac{W_o}{kT}\right) + \mu_2\left[1 - \exp\left(-\frac{W_o}{kT}\right)\right]\right\}$$

(33)

4. DISCUSION

Theoretical dependences (24,31) have been derived in this paper. The derivation of them was based on the barrier-cluster model. Their comparison with experiment has proved to be in good agreement with known published dependences. The relations (24,31) describe also transient photoconductive phenomena in a chalcogenide glass under the assumption that free electrons dominate in it, created in an optical process, influencing electrons of thermal origin. This is the case when the concentration of thermal electrons n_t is much lower than the concentration n of photoconductive electrons.

Generalized ideas concerning influence of free thermal electrons on transient photoconductive phenomena, but also on phenomena of photoluminescence, will be published in [22]. The photoluminescence phenomena in accord with the barrier-cluster model are also closely connected with the concentration of free electrons. They are considered as stimulators of nonradiative recombination processes which cause a lowering of photoluminescence.

5. CONCLUSIONS

Important phenomena observed in non-crystalline semiconductors can be explained on the basis of the barrier-cluster model. This model allows explanation not only of a number of some optical and electrical features of chalcogenide glasses, but also the results of X-ray structure measurements. The closed-cluster structure can

explain the absence of an ESR signal in the case of chalcogenide glasses. This model provides a new explanation for the density of states within the forbidden band of a semiconductor and explains why the attempts to identify gap-states by various optical and other methods fail.

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REFERENCES

[1] MOTT, N. F. – DAVIS, E. A.: *Electronic processes in non-crystalline materials*, Clarendon Press, Oxford, UK, 1979.

[2] BRODSKY, M. H.: *Amorphous semiconductor*, Springer Verlag Berlin, Heidelberg, New York, 1979.

[3] ANDRIESH, A. M. – IOVU, M. S.: Optical properties of chalcogenide glasses, *Moldavian Journal of Physical Sciences*, 2 (3-4), pp. 246, 2003.

[4] POPESCU, M.: *Non-crystalline chalcogenides*, Solid state science and technology, Library, Vol. 8, Kluwer academic publishers, Dordrecht/Boston /London, 2000.

[5] BORISOVA, Z. U.: *Glassy semiconductors*, Plenum pres, New York, NY, USA, 1981.

[6] ZAKERY, A. – ELLIOTT, S. R.: Optical properties and aplications of chalcogenide glasses: a review, *Journal of Non-crystalline Solids*, Vol. 330, No. 1-3, pp. 1-12, 2003.

[7] STREET, R. A. – SEARLE, T. M. – AUSTIN, I. G.: Photoluminescence in amorphous As$_2$S$_3$, *Journal Physics C*, 6, pp. 1830-1840, 1973.

[8] STREET, R. A. – SEARLE, T. M. – AUSTIN, I. G.: *Amorphous and Liquid Semiconductors,* eds. J. Stuke, W. Brening, Taylor and Francis, London, 1974, 1974.

[9] OVERHOF, H.: Fundamental concept in the physics of amorphous semiconductors, *Journal of Non-Crystalline Solids*, Vol. 227-230, part I, pp. 15-22, 1998.

[10] BANIK, I.: The barrier-cluster model applied to chalcogenide glasses, *Journal of Non-Crystalline Solids* 353, pp. 1920-1924, 2007.

[11] BANÍK, I.: Electroabsorption in chalcogenide glasses and its expla-nation based on barrier-cluster model, *Journal of Optoelectronics and Advanced Materials*, Vol. 9, No. 10, pp. 3171-3176, 2007.

[12] BANÍK, I.: Temperature dependence of the optical absorption and electroabsorption in chalcogenide glasses based on barrier-cluster model, *Journal of Optoelectronics and Advanced Materials*, Vol. 10, No. 3, pp. 475-483, 2008.

[13] BANÍK, I.: On the physical processes in non-crystalline semiconductors, *Proc. 15. conf. of slovak and czech physicists*, September 2005, Košice, ed. by M. Reifers and J. Kováč. pp. 45-48, 2005.

[14] BANÍK, I.: On the relation of optical absorption, luminescence and photoconductivity in non-crystalline semiconductors from the point of view of the barrier-cluster model, *Journal of Ovonic Research,* Vol. 4, No. 2, pp. 35 – 41, 2008.

[15] BANÍK, I.: Optical transitions in chalcogenide glasses from point of view of a barrier-cluster model, Trans Tech Publications, Switzerland, *Advanced materials Research,* Vols. 39-40, pp. 253-256, 2008.

[16] BANÍK, I.: Electron processes connected with low energy optical absorption and with photolumi-nescence in non-crystalline semiconductors from point of view barrier-cluster model, *Chalcogenide Letters* Vol. 5, No. 5, pp. 87-93, 2008.

[17] BANÍK, I.: On photoluminescence in chalcogenide glasses based on barrier-cluster model, *Journal of Non-Oxide and Photonic Glasses*, Vol. 1, No. 1, pp. 6-18. (2009).

[18] BANÍK, I.: Relation between optical absorption and photoluminescence in non-crystalline semicon-ductors, *Journal of Optoelectronics and Advanced Materials*, Vol. 11, No. 2, pp. 91-103, (2009)

[19] BANÍK, I.: Photoconductivity in chalcogenide glasses on the base of barrier-cluster model, *Journal of Optoelectronics and Advanced Materials*, Vol. 11, No. 5, pp. 755-769, (2009).

[20] BANÍK, I.: An explanation of optical phenomena in non-crystalline semiconductors, *Central European Journal of Physics* 3(2), pp. 270-302, 2005.

[21] BANÍK, I.: The photoluminescence–excitation characteristic of a stimulative radiation in chalcogenide glasses, Proc. Conf. APCOM 2009, june 24-26. 2009, Liptovský Ján, Slovakia, pp. 131-135, (2009).

[22] BANÍK, I.: Barrier-cluster model – the base for understanding of the optical phenomena in non-crystalline semiconductors, *Journal of Optoelectronics and Advanced Materials*, Vol. 11, No. 12, pp. 1915-1930, (2009).

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