

On photoluminescence in chalcogenide glasses based on barrier-cluster model

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Abstract

In the paper a discussion of the temperature dependence of luminescence in chalcogenide glasses at low temperatures on the base of a barrier-cluster model is presented. The empirically found Street's formula for luminescence and the gradual consolidation of photoluminescence is explained. The role of free electrons in luminescence processes is emphasized.

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1 INTRODUCTION

Many devices were developed with chalcogenide glasses, which can change their electro-physical and optical parameters under applied electrical field, exposure to light, electron beam, X-ray irradiation, etc. Chalcogenide glasses could be obtained using very simple technologies and in many cases they do not need very high purity. They allow fabrication of electrical switches, xerographic and thermoplastic media, photoresistant and holographic media, optical filters, optical sensors, thin films waveguides, nonlinear elements, etc. [1-4]. The rare-earth dopants are very important in modern optoelectronic technology because of their excellent luminescent properties that have permitted production of optical amplifiers and lasers for optical fiber telecommunication.

Although the chalcogenide glasses, a particular class of non-crystalline semiconductors, are widely used in modern technology, many physical processes in these materials are not fully understood. There is no generally accepted theory of non-crystalline semiconductors, that could explain all observed phenomena. The first fundamental knowledge on non-crystalline semiconductors can be found in [5-6]. Other relevant publications on these materials are [7-12].

2. OPTICAL PHENOMENA IN NON-CRYSTALLINE SEMICONDUCTORS

From the point of view of understanding the physical processes in non-crystalline semiconductors, it is very important to study optical properties of these materials, especially the optical absorption and luminescence (especially photoluminescence).

The optical phenomena in non-crystalline semiconductors are of high interest. In most crystalline solids, optical absorption is characterized by a sharp edge of the absorption band. Its position corresponds to the optical width of the forbidden band. However, the situation is different in the case of non-crystalline semiconductors. The absorption band near its border is smeared out and manifest itself as a tail that extends deeply into the forbidden band [5-9, 13-22]. Its profile is exponential as a rule. The exponential tails at higher temperatures tend to fit Urbach's formula. The slope of the tails changes with the temperature decrease. At low enough temperatures, the slope of the tail rises when the temperature decreases. However, a certain parallel shift of the curves towards lower absorption edge is observed.

The nature of the absorption edge in non-crystalline (amorphous) semiconductors has been longly discussed in the literature. The attempts of many authors to explain the absorption edge did not gave, up to day, satisfactory results [23-25].

In the papers [26-33], the explanation of some optical phenomena in chalcogenide glasses on the base of a barrier-cluster model was presented.

Street et al (1974) [34] discovered that the temperature dependence of the luminescence intensity in quenched a-As₂Se₃ has the form:

$$I \sim \exp(-T/T_0) \quad (1)$$

over four orders of magnitude of the intensity, where T_0 is a constant. This dependence $I(T)$ was observed for instance in [35-40].

There is a serious problem how to understand the photoluminescence and especially how to explain its temperature dependence. The luminescence is an important optical phenomenon useful for the theory of non-crystalline semiconductors.

The photoluminescence intensity in amorphous semiconductors decreases in time after the beginning the illumination at low temperatures. The experiments show [5, 6, 40-42] that the originally high luminescence level decreases gradually and stabilizes at a considerably lower level after a certain time. This fatigue effect is strongest in chalcogenide glasses (Cernogora et al. 1973) [43] but a comparatively weak fatiguing effect has been found recently in amorphous silicon (Morigaki et al 1980) [44]. Biegelsen and Street (1980) [45], using ESR data and Shah and DiGiovanni (1981) [46, 47] using luminescence decay data concluded that fatigue in a-As₂S₃ is due to the creation of non-radiative centers by the illumination. Kirby and Davis reported the luminescence fatigue in amorphous phosphorus as early as (1980) [48]. The experimental results presented in the papers [49-51].

Theoretical explanations of Street's empirical law have been given by Street (1976) [52], Philips (1980) [53], Gee and Kastner (1979) [54], Highasi and Kastner (1979) [55-56].

In crystals, the temperature dependence of luminescence is usually well described by a thermally activated escape process of the trapped carrier from the luminescence center to a non-radiative center. If such a model was used for a chalcogenide glass, temperature-dependent activation energies ranging from 1 meV at low temperatures to 100 meV at high temperatures should be assumed.

Gee and Kastner (1979) [54] and Higashi and Kastner (1979) [55] have suggested that the Street's formula (1) is the result of a distribution of non-radiative rates which arises, in turn, from a distribution of activation energies for the non-radiative process. It will be immediately noticed that the assumption of a single radiative rate is certainly incorrect. Indeed Highasi and Kastner (1979) showed that in the time dependence (fatigue) of the photoluminescence the total light decay is determined by the very broad spectrum of radiative rates.

In present no model exists, which is able to explain a sufficiently wide spectrum of physical phenomena in non-crystalline semiconductors. The existing models of luminescence in non-crystalline semiconductors were derived from the VAPs concept for these materials.

The present state of knowledge is full of many contradictions.

Recently, Tanaka has questioned the presence of the charged defects [57]. The new knowledge's above possible cluster structure of chalcogenide glasses (especially closed clusters) questioned the model based on VAPs [58-60]. In [58] we can read: "Recently, a novel model for photodarkening in a-As₂Se(S)₃ has been proposed. Unlike the previous theories, the new model takes into account the layered cluster structure of semiconductors."

The problems of the structure of non-crystalline semiconductors was studied in [61-63]. The explanation of the laws of luminescence on the base of a barrier model is presented in the papers [64-67]. This model explains the present problems with ESR experimental results. However, many questions are still open.

3. STRUCTURE

In spite of tremendous efforts dedicated to chalcogenide glasses, the structure of these materials is not completely understood [68-76]. Some models have been developed with the aim to explain the first sharp diffraction peak in the diffraction pattern of various non-crystalline materials.

Many years ago it was pointed out that no ESR signal was detected in amorphous chalcogenides (a-Se, a-As₂S₃). This observation, i.e. the absence of spins in chalcogenide glasses, led Anderson [68] and Street and Mott [69] to formulate their negative effective correlation energy (negative-U) models, in terms of charged defects. The model assumes the presence of dangling bonds, but with the combination of positively and negatively charged dangling bonds, D⁺ and D⁻ having respectively no and two spin-paired electrons, being energetically favored over the neutral dangling bond D⁰ with one unpaired electron. The defect-based version of the negative-U model was subsequently developed by Kastner, Adler and Fritzsche [70] for the case of a-Se with singly coordinated, negatively charged

selenium (C_1^-) and a three-fold coordinated, positively charged site (C_3^+) emerged as the most likely equilibrium defect configurations. Thus, the valence alternation pair concept appeared. Up to day no direct experimental evidence was found for the valence alternation pair in chalcogenide glasses. Recently, Tanaka [57] has questioned the presence of the charged defects, on the basis of optical absorption measurements on highly purified As_2S_3 samples.

The discoveries of the fullerenes led to the suggestion that other low-dimensional covalent systems, as e.g. chalcogenides, could present special configurations similar to fullerenes or nanotubes. Fullerene-like objects and nanotubes with or without closed ends have been simulated in order to demonstrate that such special "objects" are possible at least in arsenic chalcogenides [58-60, 62, 63]. The self-organization in arsenic chalcogenides is (basically) vital for the formation of the low dimensional objects in chalcogenides.

Several types of closed nanoclusters of As_2S_3 were built (proposed). The fairly good agreement of several characteristics, calculated from the model, with the experimental ones, allows the conclusion that a model with closed ends is very attractive.

As a consequence, the dangling bonds are naturally eliminated during the glass formation, and, therefore, no significant amount of charged coordination defects is necessary to explain the glass structure. On the contrary, the formation of high amount of VAPs is predicted during illumination, and in the light saturated state of the glass. A closed cluster model for the binary arsenic-chalcogen glasses seems to be attractive for the explanation of the structural and electronic properties of non-crystalline chalcogenides. In the same time the direct consequence of the model is the absence of the defects of coordination.

4. BARRIER-CLUSTER MODEL – BASIC INFORMATION

4.1 Electronic spectrum

The barrier-cluster model [26-33] assumes that there exist potential barriers in a non-crystalline semiconductor, which separate certain micro-regions – closed-clusters and in this way, they hinder the transport of the carriers at the margin of the conduction or valence bands. In the same time, however, the barriers have also an influence upon the optical absorption at the optical absorption edge. The influence is caused in the first line by strong electron-phonon interaction, which results in the fact that on optical transition, apart from the energy of a photon, an electron can also take the energy of a phonon. Thus, on such a transition, the total of energy taken by an electron equals the sum of the photon and phonon energies (Fig. 1). Another important factor - as far as influence of barriers is concerned - is that the absorption of light in the region of the optical absorption edge at low temperatures is usually connected with tunneling of carriers through the potential barrier. Due to this fact, the absorption process is influenced by barriers. These facts enable us to explain not only the creation of exponential tails at the optical absorption edge, but also their temperature dependence at high, as well as low, temperatures. The barrier model allows us to clarify also the luminescence and photoelectric phenomena in chalcogenide glasses. This concept gives a new look at the density of states within the forbidden band of a semiconductor and it explains why attempts to identify gap-states by various optical and other methods failed.

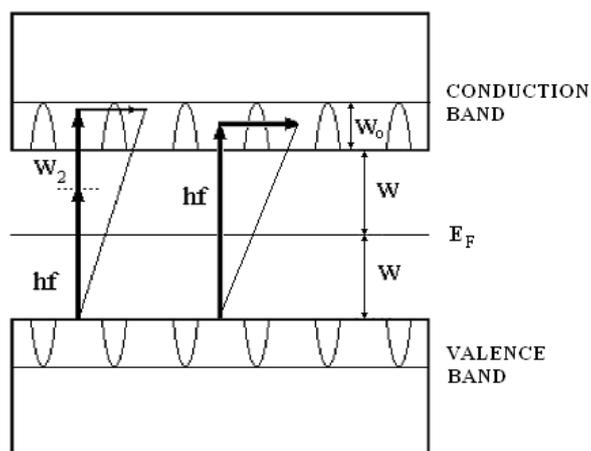


Fig. 1 *Electronic spectrum of non-crystalline semiconductor and optical transition at higher (left) and at lower (right) temperature*

The barrier-cluster model assumes that the electrons (at low energy) behave between barriers in particular regions (closed cluster) of material in a similar way as electrons in a crystal do. The potential barriers can be depicted inside the conduction and valence bands of an amorphous material, separating individual localized energy states at the edge of the band (Fig. 1). The electron levels between 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 (μ_1) is created. The states with energy above the peaks of barriers are delocalized. They create a sub-band with a high average mobility (μ_2).

4.2 Optical phenomena and barrier-cluster model

Optical transitions in non-crystalline semiconductors at the edge of optical absorption were studied in [26-33, 64-67] from the point of view of a barrier-cluster model. It was explained why the exponential tails of optical absorption can extend deeply in the forbidden band of a non-crystalline semiconductor. It is due to strong electron-phonon interaction.

The barrier-cluster model can explain the parallel shift of exponential tails, too.

High temperature range: The starting point of the considerations in [26] on the base of barrier-cluster model is the assumption that due to the potential barriers in non-crystalline semiconductors proper conditions occur for a distinct absorption of light, with phonons participating in the energy exchange. An electron in an optical transition accepts not only the energy hf of a photon but also the phonon energy W_{phon} . Thus, the whole energy accepted is $hf + W_{\text{phon}}$ where W_{phon} is the energy acquired from a phonon "field". The quantity hf is positively determined by the wavelength of radiation, while $W_{\text{phon}} = W_2$ (Fig.1) has a statistical character. The average value of W_{phon} is dependent on the temperature. On the left part of Fig. 1 is shown the optical transition at high temperatures. The transition on the right part is typical for low temperatures.

In principle, a photon can be absorbed only when the whole energy of the electron

$$hf + W_{\text{phon}}$$

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 the barriers will dominate at high temperatures. In this case, the probability of transition within a single localized region is small. The levels in adjacent micro-regions offer more combinatory possibilities. 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 caused by the barriers. In the next we put $W_{\text{trans}} = 2W + W_0$.

The number of electrons that can acquire such deficit of energy ($W_{\text{trans}} - hf$) from a phonon field depends on temperature. The number of electron transitions during the irradiation of the material by "low energy" photons (and thus, also the coefficient of optical absorption α) and number of such sufficiently energetic phonons at temperature T are proportional. For the absorption coefficient it can be written [26,27] that

$$\alpha \approx \exp\left(\frac{hf - W_{\text{trans}}}{2kT}\right) \quad (2a)$$

$$\ln \alpha = \frac{hf - W_{\text{trans}}}{2kT} + \text{const.} \quad (2b)$$

or, for a particular (constant) temperature

$$\ln \alpha \sim hf + \text{const}$$

which is a mathematical expression of an exponential tail of optical absorption [26]. However, the slope of tails is also temperature dependent. Formulae (2a,b) are of the same kind as Urbach's formula. It explains the temperature dependence of the slope of exponential tails at higher temperature.

Low temperature range: At low temperatures, only photons with sufficient energy, exceeding $2W$ (the width of the forbidden band), can be absorbed in material (Fig. 1). The optical transition of the electron is connected with a tunneling process. The "skewed" optical transition can be virtually divided into two parts [26]: The first part is a vertical transition on a virtual energy level inside its own localized region (without tunneling); the next part represents a horizontal tunneling transition on a level in an adjacent localized region. Thus, the mechanism of the

absorption of a photon in a low-temperature range is connected with the tunneling of an electron through a potential barrier. Let us remark that at lower temperatures, absorption of light in the vicinity of the optical absorption edge could mainly run without any tunneling process, i.e. within a single localized region. However, the probability of such transitions is small due to a distinctly discrete character of the lowest levels as well as due to a small number of such levels in a single micro-region. Therefore, the absorption related to tunneling to adjacent regions is more probable.

4.3 Some remarks on the parallel shift of the exponential tails of the optical absorption at low temperatures

In this section we discuss the parallel shift of the exponential tails of optical absorption in non-crystalline semiconductors at low temperatures.

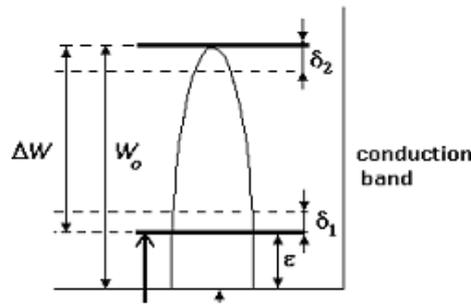


Fig. 3 The influence of temperature on the process of tunneling of electron through the potential barrier

The absorption of light at low temperatures and photon energy, hf , from the interval $2W < hf < 2W + W_0$ is, according to the barrier-cluster model connected with the tunneling of the electrons through the potential barrier (Fig. 1,2). The probability, p , of the tunneling depends on the energy level, on which the tunneling runs. In the case of a parabolic potential barrier (Fig. 2), the dependence of potential energy $W(x)$ of electron on its position can be denoted as

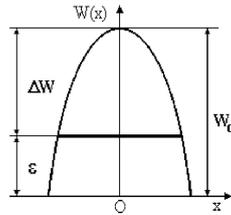


Fig. 2 The potential barrier

$$W(x) = -ax^2 + W_0$$

W_0 , means the height of the barrier from the bottom of the conduction band and the quantity a describes the width of the barrier. For the probability of the tunneling it can be written [26]

$$p \approx \exp \{-A \Delta W\} \quad (3)$$

where A is a constant depending on the dimensions of the barrier

$$A = \left\{ \frac{\pi}{\hbar} \sqrt{\frac{2m}{a}} \right\}$$

and ΔW is the energy difference between the energy level of peaks of potential barriers and the energy level on which the tunneling is running, m is the mass of the electron.

Should an electron take only the photon energy on absorption, we could write on the base of Fig. 2, 3

$$\Delta W = 2W + W_0 - hf \quad (4)$$

The probability of the tunneling is determined first of all by the energy of the absorbed photon. Phonons play a role in the low-temperature absorption.

4.4 The influence of temperature on the optical absorption

In papers [26, 28], the effect of temperature on electron tunneling across barriers was studied (Fig. 2,3). It was shown there, that for the quantity ΔW the relation (4) had to be replaced by the relation

$$\Delta W = 2W + W_0 - hf - CT \quad (5)$$

so that the relation (3) should take the form

$$p \approx \exp[-A(2W + W_0 - (hf + CT))] \quad (6)$$

It was assumed, that $\Delta W(T) = \Delta W(0) - \delta_1 - \delta_2$ (Fig. 3) and that the values δ_1, δ_2 were linearly dependent on the temperature.

The coefficient of optical absorption of light, α , is directly proportional to probability, p [3], so that

$$\alpha \approx p \quad (7)$$

Based on (3,6,7), the absorption coefficient would be

$$\alpha \approx p \approx \exp[-A(2W + W_0 - (hf + CT))] \quad (8)$$

or

$$\alpha \approx \exp[A(hf + CT)] \quad (9)$$

This relation gives a true picture not only for experimentally observed exponential tails of optical absorption at low temperatures, which were already clarified in [26], but also for the parallel shifting of these towards lower absorption, with decreasing temperature.

As far as the dependence $\alpha(hf)$ is concerned, it also follows from (9) that

$$\alpha \approx \exp(Ahf) \quad (10)$$

In this article we present a new view on the photoluminescence - we attempt to explain the temperature dependence of photoluminescence and its fatigue, i.e. its stabilization in the course of time.

We submit the explanation of Street's formula (1) representing the temperature dependence of photoluminescence and experimental observations concerning luminescence.

5. PHOTOLUMINESCENCE

5.1 Photoluminescence in chalcogenide glasses

One concept of the physical nature of photoluminescence in chalcogenide glasses at low temperatures, from the point of view of the barrier-cluster model, is presented in Fig. 4 [64-67]. An electron during the optical transition, connected with tunneling, arrives at an adjacent or a near region on an energy level, which is below the peak level of the potential barriers. At low 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 micro-region between the neighboring barriers.

5.2 Bound electron-hole ($e-h$) couples

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 lays.

This level will be below the bottom of the conduction band. Levels of this kind will arise not only in the neighboring micro-region (cluster), but also in the more distant regions. The position of these levels will depend on the distance from the "mother" micro-region (for the sake of simplification, we suppose that the hole did not move). With increasing distance between the electron and hole, these levels will approach the bottom of the conduction band.

In Fig. 4, some these levels are depicted on both sides of the hole (in a one-dimensional model). These levels create a kind of "funnel" of levels. A new energy level will appear not only in adjacent micro-regions but also in the original mother micro-region in which the hole lays. The electron level in the mother region is the lowest one from among all levels of the funnel.

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. These levels are not shown in the diagram.

5.3 The luminescence

At low temperatures, an optically excited electron will, with a high probability, gradually come back to the mother region of the hole. Such an approach is connected with tunneling and diffusion. The approaching jumps "region-by-region", are connected to an interaction with phonons. Without phonons, such an approaching process would not be possible. These approaching processes are in principle not radiating. An electron loses gradually a considerable part of its energy. In the last phase a non-radiative transition occurs in to its own localization region. In this region, occurs radiative optical recombination of the $e-h$ pair, accompanied with emission of a luminescence photon, whose energy is considerably lower than that of photons of the exciting radiation. A distinct Stokes shift will occur.

If no other disturbing processes take place, a stationary state with a relatively high level of luminescence would be established quickly within the material. In fact, this corresponds rather well to a realistic situation in the first phase of irradiation. However, the state of high luminescence weakens rather quickly.

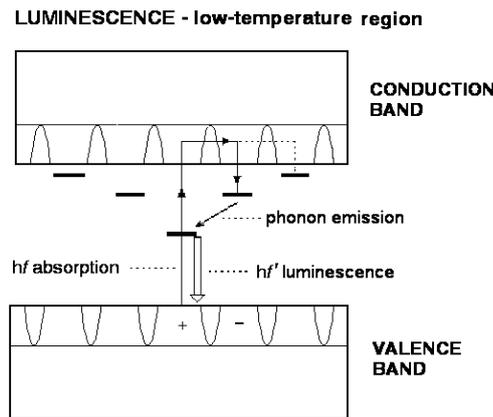


Fig. 4 The processes connected with photo-luminescence

5.4 The influence of free electrons

When irradiating a non-crystalline semiconductor by a flux of photons at low temperatures under conditions described above, free electrons are practically formed only by a multiple tunneling of a small amount of electrons, which perform the optical transition. The slow rise of concentration of free electrons is caused by the relatively low probability of the multiple-tunneling process. The concentration of free electrons in semiconductor stabilizes only after a long time, when some dynamical equilibrium of two mutually opposing effects establishes, i.e. the process of free electron appearance and the process of their annihilation by joining holes so that, new bound $e-h$ pairs are created.

When explaining the laws of luminescence on the basis of the barrier-cluster model, an extremely significant assumption is accepted 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.

After a long-time irradiation, the concentration, N , of bound $e-h$ pairs will be considerably lower than it was in the first phase of irradiation and this is the reason why, in the end, luminescence finally establishes at a lower value.

5.5 Creation of free electrons

The creation of free electrons occurs at low temperatures via the mechanism of multi-tunneling of a carrier through potential barriers (here, only tunneling of electrons is assumed). The probability of multi-tunneling depends on the energy level at which the tunneling is running. According to [26] the probability, p , of the single-tunneling can be expressed (3) as

$$p \sim \exp(-A \cdot \Delta W) \quad (11)$$

where A is a constant depending on dimensions of the barrier and ΔW is the energy difference between the energy level of peaks of potential barriers and the energy level on which the tunneling is running. In the case of tunneling an electron at temperature T , the value ΔW should be lowered by the value CT and the quantity ΔW has to be replaced by quantity $\Delta W - CT$.

The probability, p , of a single-event tunneling of such a particle will be proportional to the expression

$$\begin{aligned} p &\sim \exp(-A(\Delta W - CT)) = \\ &= \exp(-A \cdot \Delta W) \exp(ACT) \end{aligned} \quad (12)$$

The factor $\exp(ACT)$ represents a relative increase of the tunneling probability under the influence of temperature (at constant photon energy hf). Since probability P of the electron tunneling transition at temperature T is $P \sim p$, according to (12)

$$P \sim \exp(ACT)$$

For the probability of the multi-tunneling of the electron through s barriers, we can write

$$P^s \sim \exp(sACT) \quad (13)$$

The probability of the creation of a free electron will be proportional to the expression (13). Since the probability value is small, the number of free electrons will slowly increase after the beginning of the illumination of the glass. Therefore, the increase rate of non-radiant recombination of bound $e-h$ couples will be slow, too. This is why the process of stabilization of luminescence will be slow.

5.6 Mathematical description of the development of a luminescence process

The level of luminescence of a non-crystalline semiconductor will depend on the concentration, N , of the bound pairs $e-h$. This value depends on the concentration, n , of free electrons in the material. The time dependence of the concentrations mentioned above can be described by the following system of two differential equations:

$$\frac{dN}{dt} = C_1 - C_2N - C_3C_1 \exp(sACT) - C_4Nn + C_5n^2 \quad (14a)$$

$$\frac{dn}{dt} = C_3C_1 \exp(sACT) - C_5n^2 \quad (14b)$$

where dN/dt is the change of the concentration of the bound $e-h$ pairs per time unit, the dn/dt is the change of the concentration of the free electrons per time unit. The first term, C_1 , at the right hand side of the equation (14) represents the number of pairs produced by incident photons per time unit. The term C_2N means the number of radiant recombination of bound $e-h$ couples per time unit. The term $C_3C_1 \exp(sACT)$ is, according to (13), the number of multi-tunneling electrons through s -barriers, and simultaneously the number of newly created free electrons. The term C_4Nn means the number a non-radiant recombination of bound pairs having passed through a non-radiant transition under the catalyst influence of free electrons. The term C_5n^2 is the number of free electrons captured by a free hole and creating a new bound $e-h$ couple with it.

5.7 The first phase of photoluminescence

During the first phase of semiconductor irradiation, the catalyst effect of free electrons does not take part yet as their concentration is negligibly small ($n = 0$). At this stage, the luminescence level is the result of two opposing processes – the process of arising of bound pairs produced by light and that of radiant recombination of bound pairs. The number of non-radiant recombination is small. A quasi-stationary state would arise for which, considering equation (14) and based on the conditions $n = 0$

$$C_3 C_1 \exp(sACT) \ll C_1 - C_2 N \quad (15)$$

$$\frac{dN}{dt} = 0 \quad (16)$$

we can write approximately

$$C_1 - C_2 N = 0 \quad (17)$$

from where ($N = N_1$)

$$N_1 = \frac{C_1}{C_2} \quad (18)$$

Under these circumstances, for the intensity of luminescence, $I = I_1$, we find that

$$I_1 = C_2 N_1 = C_1 \quad (19)$$

This is an idealized stationary state of maximum luminescence at which, the same amount of photons emitted during luminescence are absorbed. However, the energy of the luminescent photons is considerably lower than the energy of photons of the exciting radiation.

Note: In our simplified model, we do not consider non-radiant recombination of $e-h$ couples caused by other factors than free electrons. Influence of free electrons in this model is dominant. It does not mean, however, that other mechanisms of non-radiant recombination would not occur. There is rather a cooperative relationship of different mechanisms between each other than a competitive one.

5.8 Stabilized luminescence

After a sufficiently long exposure to light of a non-crystalline semiconductor, a real stationary state establishes when

$$\frac{dN}{dt} = 0, \quad \frac{dn}{dt} = 0 \quad (20)$$

For this state, we obtain from (14, 15)

$$0 = C_1 - C_2 N - C_3 C_1 \exp(sACT) - C_4 N n + C_5 n^2 \quad (21a)$$

$$0 = C_3 C_1 \exp(sACT) - C_5 n^2 \quad (21b)$$

The first equation will simplify with respect to validity of the second one. Hence, the system takes the form

$$0 = C_1 - C_2 N - C_4 N n \quad (22)$$

$$0 = C_3 C_1 \exp(sACT) - C_5 n^2 \quad (23)$$

From equation (22) it follows for a stationary value $N = N_2$ that

$$N_2 = \frac{C_1}{C_2 + C_4 n} \quad (24)$$

where n is the stationary value of concentration of free electrons. Since

$$N_2 = \frac{C_1}{C_2 + C_4 n} \leq \frac{C_1}{C_2} = N_1 \quad (25)$$

the value N_2 is lower than the value N_1 determined by equation (18). Thus, with increasing number of free electrons, the concentration of bound pairs decreases from the value N_1 to the value N_2 . This decrease can be multiple – as it corresponds to experimental results. In a particular case, if concentration, n , of free electrons reaches a certain value, the condition

$$C_2 \ll C_4 n \quad (26)$$

can be satisfied. Then the equation (24) takes the approximate form

$$N_2 = \frac{C_1}{C_4 n} \quad (27)$$

If we express concentration n from (23) and insert it in (27), we obtain for $N = N_2$

$$N_2 = const \cdot \exp(-0.5.sACT) \quad (28)$$

where

$$const = \left[\frac{1}{C_4} \sqrt{\frac{C_1 C_5}{C_3}} \right]$$

We can write for stabilized luminescence $I = I_2$

$$I_2 \sim N_2 \sim \exp\left(-\frac{T}{T_o}\right) \quad (29)$$

where

$$T_o = \frac{2}{sAC} \quad (30)$$

The expression (29) corresponds to the dependence

$$I \sim \exp\left(-\frac{T}{T_o}\right) \quad (31)$$

observed empirically. Luminescence intensity decreases with increasing temperature. Let us mention that it is known from experiments that luminescence is suppressed almost completely at the temperature of 200 K.

For a non-crystalline semiconductor, as e.g. As_2S_3 , it follows from measurements [5,6] that $T_o = 26$ K. From the calculation using (30), for $A = 19 \text{ eV}^{-1}$ and $C = 7 \times 10^{-4} \text{ eV} \cdot \text{K}^{-1}$ we obtain $s = 5.78$ for the given material. In such a case, it would correspond to a multi-tunneling of an electron through 5-6 barriers.

5.9 Influence of strong electric field on luminescence

An intense electric field (as known from experiments [5-8]) lowers the level of photo-luminescence. This problem will be analyzed in another paper.

5.10 Fading away of the luminescence after interruption of illumination (photo-exposure)

Fading away of luminescence after interruption of irradiation of a non-crystalline semiconductor is determined by elimination of bound $e-h$ pairs by free electrons, by recombination of bound $e-h$ pairs via luminescence and by a process joining free electrons with free holes, which represents a supplementary source of bound pairs.

Note: Let us remark that the barrier-cluster model of the non-crystalline semiconductors in the actual state of its development (as barrier model) was used for the explanations of electric transport phenomena in weak and high electrical fields and at high pressure [77-82].

A further literature about the optical phenomena can be found in [83-94].

6 CONCLUSIONS

In this work, a new view at some optical phenomena, such as the effect of temperature upon optical absorption and photoluminescence in non-crystalline semiconductors at low temperatures, is presented. Temperature dependence of the photo-luminescence and time stabilizing of the level of luminescence after the beginning of

illumination of a sample can be explained on the base of barrier model. The high initial level of luminescence decreases in the course of time and it stabilizes subsequently at a considerably lower level. In our barrier-cluster model the role of free electrons (free carriers) upon the luminescence level in a semiconductor has been emphasized. In the framework of this model, the free (not bound) electrons behave as catalysts increasing the number of non-radiant recombination of bound electron-hole pairs. In this way, they significantly suppress the level of luminescence.

The barrier-cluster model allows the explanation not only of important optical and electrical features of chalcogenide glasses, but also of results of X-ray structure and ESR measurements which, at present, are in the attention of the physicists dealing with chalcogenide glasses. The presented explanation of the luminescence on the base of barrier-cluster model is an alternative to other models based on VAPs structural model of the chalcogenide glasses.

The barrier-cluster model is the structural ground for the development of a new interpretation of the physical phenomena in non-crystalline semiconductors.

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