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Photoluminescence quenching in disordered semiconductors from point of view of the barrier-cluster-heating model

I.BANIK[a], M. POPESCU[b]
[a]*Slovak University of Technology, 813 68 Bratislava, Radlinského 11, Slovak Republic*
[b]*National Institute R&D of Materials Physics, Bucharest-Magurele, P. O. Box MG.7, Romania*

The aim of this article is in the first place to familiarize the readers with barrier-cluster-heating model of the non-crystalline semiconductors, then briefly and digestedly present some results achieved by physical phenomena explanation in non-crystalline semiconductors within the frame of this model. The barrier-cluster-heating model of disordered semiconductor gives new view on photoluminescence in disordered semiconductors, too. This model enables to explain Stokes shift, Street´s empirical law, fatigue effect, PLE-characteristic, electric field influence on photoluminescence, and some other physical phenomena in disordered semiconductors, including the photoinduced structural changes.

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1. Introduction

Physical properties of disordered semiconductors are subjecst of intensive investigatios because of their broad scale of applications in electronics, optoelectronics, photovoltaics, etc. The attention of physicists is focusd mainly on the chalcogenide glasses and amorphous hydrogenated silicon (a-Si:H).

Vitreous chalcogenide alloys are promising luminescence materials for optoelectronics. These materials possess unique optical properties, including photostructural transformations. They are widely used in various devices of integrated and fiber optics [1-6,15]. Considerable interest in chalcogenide glasses is associated with the absence of high-energy phonons in their vibrational spectra, unlike the most known laser materials. Another important property of chalcogenide glasses is their high refractive index (>2,1), which leads to an increase in the cross section of absorption and emission of rare-earth ions. Chalcogenide glasses exhibit a band gap close to the energy of laser transitions in lanthanides. This makes possible optical pumping through interband absorption of a semiconductor matrix followed by the transfer of the excitation energy to lanthanide ions.

The amorphous semiconductors are metastable. They can undergo various transformations between different states. The most well-known examples are reversible photodarkening [1-3] in amorphous chalcogenides and Staebler-Wronski effect in a-Si:H.

Specifically, it is known, that upon illumination of sub-bandgap light, a covalent chalcogenide glass undergoes marked changes in optical, photoconductive, electrical, structural, thermal, mechanical and chemical properties [1-2]. Band gap illumination also gives some modifications in microscopic structures, which have been detected in X-ray diffraction, etc. However, real atomic changes remain speculative. In particular, substantial interests have been paid to the relationship between photodarkening and photoexpansion in As_2S_3 (Se) glasses [1].

Since Kolomiets first study of chalcogenide glasses [3-6], thousands of works have been published in the field of glassy semiconductors [7-14]. Majority of those works were of experimental character and brought experimental results. A variety of photoinduced phenomena have been discovered in chalcogenide glasses, after a comprehensive study by Ovshinsky´s group [1, 6].

In spite of the long history of experimental and theoretical studies, there are still no well-accepted models for electrical, optical phenomena and photoinduced changes in disordered semiconductors, too. No model has been suggested yet that would explain sufficiently the wide range of observed phenomena. Many models assume the existence of various centers in a matter, to which energy levels in the forbidden gap correspond. Among them, one most frequently used for covalent chalcogenide glasses such as As_2S_3 are the charged-defect and valence-alternation pairs models proposed by Street and Mott and Kastner et al. Existence of such centers wasn't proved in experiments up to now.

The great attention of physicists is devouted to hydrogenated amorphous silicon (a-Si:H). Research into amorphous silicon began, in England, nearly thirty years ago, but the major development, the demonstration of doping and the subsequent implementation of devices, was made in Scotland by Spear and LeComber, The intrinsic disorder in the amorphous silicon creates broken bonds which negatively impact the electronic properties of a-Si materials. Passivation of the broken bonds by hydrogen in hydrogenated amorphous silicon (a-Si-H) reduces their electrical density from ~10^{19} cm^{-3} present in unhydrogenated a-Si to as low as 10^{15} cm^{-3} in a-Si:H. The discovery of the importance of hydrogen in a-Si materials, led to a wide range of deposition techniques and conditions which attempted to improve the properties of a-Si:H.

The first report of amorphous silicon solar cells in 1976 [4, 5] sparked worldwide interest as an promising economically viable source of renewable energy. The materials used in the a-Si:H based solar cells are in fact silicon hydrogen alloys which typically contain about 5 to 20 at.% of hydrogen. The incorporation of hydrogen and disorder also have a profound effect on the band gap and optical absorption. a-Si:H does not behave like an indirect band gap semiconductor so that even though its band gap increases to ~1.7 eV it has the very high optical absorption typically associated with direct band gap semiconductors. Because of the low densities of defects in intrinsic materials the incorporation of dopants during deposition allows the formation of *n* and *p*-type materials making a-Si:H unique amongst amorphous materials. However, the hydrogen is unfortunately associated with light induced degradation of the material, termed the Staebler-Wronski effect [5].

The light induced degradation of a-Si:H materials' electronic properties was first observed as the large changes due to sunlight in the carrier transport of thin films which were found to be completely reversible after annealing the materials for several hours at temperatures 150 °C. These changes result from the introduction of meta-stable defects whose rate of creation and density depend on both the illumination intensity and the temperature. The degradation arises from the creation of additional dangling bonds, which are metastable and can be removed by annealing at elevated temperatures (>170 ^{o}C). The reversible changes that occur between an “annealed” state and a “light soaked” state have become one of the most investigated phenomena in a-Si:H-based materials and solar cells. There is still no general agreement on the exact nature of the light induced defects or the mechanism responsible for their creation. Continuous progress has been made over the years not only in improving the initial properties of a-Si based materials but also in reducing their light induced degradation. This has been achieved by optimizing the growth conditions of the materials that improved the incorporation.

We suppose that BCH model that was taken into account in this contribution, can be a basis for the understanding of wide spectrum of phenomena observed in disordered semiconductors.

2. Barrier-cluster-heating model of disordered semiconductors

The barrier-cluster-heating model is based on the notion that disordered semiconductors at nano-meter scales are inhomogeneous, consisting of nanoregions-clusters. Between clusters there are potential barriers affecting not only the electrical properties, but optical phenomena as well [2, 15-19].

The barriers restrict the transition of low energy conduction electrons from one region to the other. Such electrons behave between barriers in particular regions 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 (Fig.1).

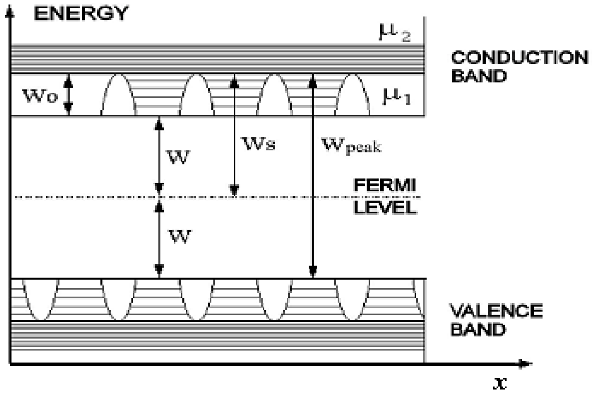

Fig. 1 The electron spectrum of an amorphous Semiconductor

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. (Quite a similar situation occurs at the edge of the valence band).

The states with energy above the peaks of barriers are delocalized. They create a sub-band with a high average mobility (μ_2). Thus, it is clear that the activation energy of an amorphous material as a whole becomes a highly questionable quantity.

The structural clusters as nanoobjects can have different form: they can be opened or closed. There is every indication that in the case of chalcogenide glasses they are mainly closed clusters [3]. The closed clusters that enable the best explanation of *ESR* results and X-ray structural experiments on these glasses. The non-existence of *ESR* signal in chalcogenide glasses can be only explained by the fact that these glasses consist of closed clusters, which represent systems without unoccupied bonds. If X-ray structural analyses are considered, then the results of these measurements correspond with actually observed data. In semiconductors as e.g. silicon, the clusters are obviously opened. It is revealed above all by the detected ESR signal.

The typical sign of the noncrystaline semiconductors is the existence of exponential tails of optical absorption. The creation of these tails is often attributed to the existence of exponential tails of the density of states in forbidden band of semiconductor. We assume, that the states in the forbidden band are not a priority cause of exponential tails. To support this idea, we can mention the fact that exponential tails of optical absorption also arise in those non-crystalline substances, in which the existence of states within the forbidden band could not be proved even by the most sophisticated experimental techniques.

Barrier-cluster-heating (BCH) model is capable to explain the formation of the exponential tails by some another means.

3. Barrier-cluster- heating model and optical phenomena

The potential barriers also significantly influence the optical absorption at the optical absorption edge. It is caused in the first line by their inducing a 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 and thus, on such a transition, the total of energy taken by an electron equals the sum of the photon and phonon energies (Fig. 2). This enables to explain existence of exponential tails of an optical absorption, which reach deeply inside of a forbidden band of a semiconductor [15-19]. 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, the absorption process is influenced by barriers. These facts enable us to explain successfully not only the creation of exponential tails at the optical absorption edge, but also their temperature dependence at high as well as low temperatures [15-19].

3.1 Optical absorption and BCH model

In this article we concentrated on the photoluminiscence in disordered semiconductors. The condition for the origin of photoluminescence is however the absorption of the excitatory radiation. Therefore, in the first place, we will mention something about the absorption.

In most crystalline solids, optical absorption is characterized by a sharp edge at the margin 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 it creates a tail that extends deep in to the forbidden band. Its profile is exponential as a rule. The exponential tails at higher temperatures tends to fit Urbachs formula. The slope of the tails changes with further temperature decrease. At lower temperatures, the slope of the tails does not change with further temperature decrease. However, a certain parallel shift towards lower absorption is observed. Optical phenomena in non-crystalline semiconductors represent a number of complex phenomena. One of the great puzzles to be explained is the origin of exponential tails.

- **Higher temperature range**

The starting point of the following considerations on the base of barrier model is an assumption that the potential barriers in non-crystalline semiconductors proper conditions occur for a distinct absorption of light, with phonons participating in the energy exchange [15-19]. We assume that an electron in an optical transition accepts not only the energy *hf* of a photon but also the phonon energy $W_{\text{phon}} = W_2$ (Fig. 2). Thus, the whole energy accepted is

$$hf + W_{\text{phon}} \tag{1}$$

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

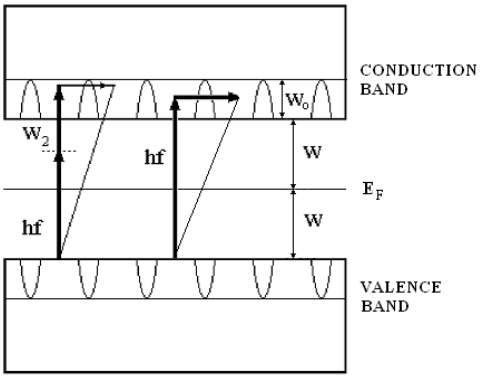

Fig. 2 Optical transition at higher (left) and at lower (right) temperature

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 rests in strong electron-phonon interaction caused by the barriers. The number of electrons that can acquire such energy from a phonon field depends on temperature. The number of electron transitions when irradiating 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 energy needed for transition.

The number of electrons, which can acquire such energy from a phonon field depends on temperature and is thus determined by the expression

$$\exp\left[-\ \frac{W_{peak}-hf}{2kT}\right] \qquad (2)$$

The number of electron transitions when irradiating material by "low energy" photons (and thus, also the coefficient of optical absorption α) is directly proportional to this expression. For the absorption coefficient, in accordance with (3), it can be written

$$\alpha \approx \exp\left[\frac{hf - W_{peak}}{2kT}\right] \qquad (3)$$

$$\ln\alpha = \frac{hf - W_{peak}}{2kT} + const \qquad (4)$$

or, for a particular (constant) temperature

$$\ln\alpha = \mathrm{hf} + \mathrm{const} \qquad (5)$$

which is a mathematical expression of an exponential tail of optical absorption [15-19]. However, the slope of tails is also temperature dependent. Formula (2) is of the same kind as the 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 can be absorbed by the material. There are not enough phonons with sufficiently high energies to realize the high-temperature mechanism of absorption. The optical transition of an electron can be virtually divided into two parts [15-19]: The first part (Fig. 2 - right) 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 tunneling of the electron through a potential barrier.
The absorption can be in this case expressed by means of exponential function [15-19]

$$\alpha = \alpha_0 \exp\left(hf + CT\right) \qquad (6)$$

$$\alpha = \alpha_0 \exp\left(hf + CT\right) \qquad (7)$$

The barrier model explains in this case the temperature parallel shift of the exponential tails. As regards on the photoluminescence (on which is our article pointed) is here important just the low temperatured mechanism of the absorption. By the higher temperatures is the photoluminescence very strongly supressed.

3.2 Photoluminescence

Luminescence generally offers important information on the electron structure of solids, as well as on processes running in the solids. Recombinations are really important for a proper explanation-elucidation of optical properties of non-crystalline solids. Generally, the recombinations can be radiant or non-radiant. The radiant transitions are responsible for luminescence. The non-radiant recombinations produce the phonons of optical origin.

- **Specific features**

With non-crystalline semiconductors, the photoluminescence is endowed with several specific features.

- **The Stokes' shift**

The Stokes shift is not rare even with other solids. However, it is rather very expressive namely in the chalcogenide glasses. Energy of emitted photons is essentially lower (roughly halflegth), than energy of photons of primary excitatory radiation. This is documented by Fig. 3. Typical is there a bell-shaped photoluminiscence curve PL. The profile and the position of this curve – both were until now not satisfactory elucidated.

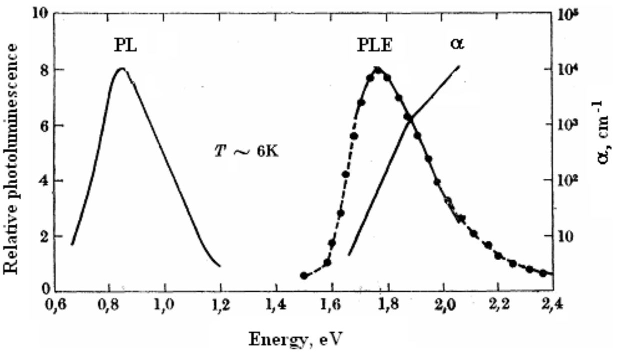

Fig. 3 Three dependances: α-dependance of optical absorption upon photons energy, PL-spectrum of photoluminiscence, PLE-photo- luminiscence - excitation characteristic.

- **Street's law**

The temperature dependence of the photoluminescence in chalcogenide glasses has also a specific character. The photoluminescence decreases expressively with the increase of the temperature, according to the (empirical) so called Street law

$$I \approx \exp\left(-\frac{T}{T_0}\right) \qquad (8)$$

This dependence is ilustrated in experimental graphs shown in Fig. 4.

The intensity of the photoluminescence is high at low temperatures, but it rapidly falls down if the temperature increases. It is almost totally suppressed at temperature around 200 K.

- **Fatigue effect**

With chalcogenide glasses, an interesting effect is observed: the so-called “fatigue of luminescence”. It can be interpreted as follows. After applying the excitative irradiation on the sample, the photoluminescence achieves more-or-less rapidly a relatively high pseudostationar level, but afterwards it becomes attenuated slowly: it undergoes a “fatigue”. Gradually, it becomes practically stable, but on a much lower level than its first maximum.

- **PLE-characteristic**

Further important thing, which is needed to explain in connectivity with photoluminiscence, is so called PLE-characteristic of chalcogenide glasses. (PLE-photo-luminescence excitation). It is especially surprising that the photoluminescent effectiveness of the primary excitative irradiation exhibits the maximum value in the region of the exponential tail of the optical absorption (the Urbach region). This efficiency express the photoluminescence excitation charakteristics (PLE-characteristics). This region corresponds actually to an interval in the forbidden band. Serious questions arise regarding how to clarify these phenomena. Here we have arrived at a *terra incognita* in fact.

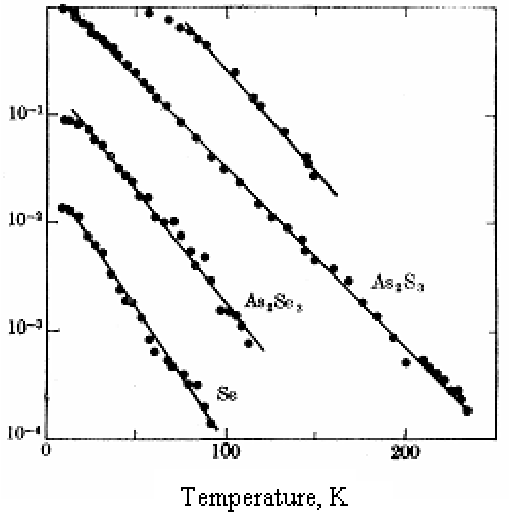

Fig. 4. Temperature dependence of the photo-luminescence for some CHG.

3.3 Electric-field dependence of photoluminescence

Strong electric field – as it is known from experimental observations – depresses the level of photoluminescence in non-crystalline semiconductors.

4. Explanation this phenomena on the base of the BCH model

How is our barrier-cluster-heating model capable to cope with these facts? The point of departure is what we see in Fig. 5. In this figure, there is a scheme of the photoluminescence according to our model.

We see the schematic suggestion of the absorption of photons without the phonon participation; this absorption is connected with the tunneling across one barrier, or possibly across a cascade of several barriers. The most of excited electrons cannot go too far from corresponding holes. An actual hole is (in our simplified case) localized. At least for the sake of simplicity, we will not consider its motion.

Owing to the Coulomb interaction (in fact the electron-hole interaction), the electron finds itself in an “exciton” state. We do not assume that it is the exciton in the sense as it is well known in crystalline semiconductors. I suppose that we may realize a pair – two localized quasiparticles – each being in a different nano-region. Their localization in a sense is secured (but not absolute) by potential-energy barriers. As a result of the electron-hole bond, the electron occupies an exciton level below the lower margin of the conduction band. The position of the exciton level depends on the distant of the electron and hole of *e-h* pair. As the distance between the electron and hole in the pair grows, their “exciton” level tends to the bottom of the conduction band. However, if the electron (in process of optical transition) finds itself after the (possibly multiple) tunneling too far from the hole partner, it becomes free.

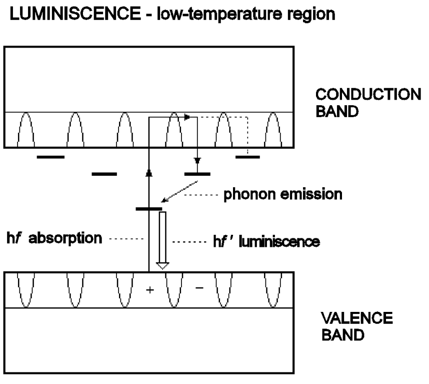

Fig. 5. Schematic delineation of the photoluminiscence.

The energy levels under consideration form a ”funnel”. Any electron inside the funnel is hardly capable to cut off from its partner hole. After some tunneling steps and undergoing a diffusion process, it will probably approach the position of the hole. The transitions of the electron in the funnel are non-radiant, being accompanied with a production of phonons. Finally the electron will occupy the lowest energy level in a nano-region, i.e. in a ”cluster”, where a radiant recombination will take place. The energy of the emitted photon is smaller (usually it is one half) than the energy of the exciting photons. In this way, we can comprehend the Stokes shift.

It should be emphasized that most of the electrons during the optical absorption under consideration will stay trapped in the funnel region, but few of them will tunnel through some sufficiently numerous array of barriers to become free. It should also be pointed out that after the onset of the primary exciting irradiation, the density of the freed electrons will only very slowly increase, tending to become stable after some relative long enough time. I must draw the attention to this fact, since it is important for the proper understanding of the fatigue effect in the luminescence.

Another assumption for the explanation (elucidation) of the luminescence is also vital. It is an assumption that might seem audacious, but its correctness has been de facto verified. It is that the free electrons are catalyzing the non-radiant recombination of electron-hole pairs. When a free electron comes to the vicinity of an electron-hole pair, this pair undergoes the non-radiant recombination. So, when accepting this assumption, we can easily clarify the fatigue process.

- **The mathematical description of processes connected with the photoluminiscence**

The theoretical description of processes conjoint with photoluminescence on the basis of BCH model come out of a conception, that intensity of photoluminescence is directly proportional to concentration of binded e-h pairs. This is influenced on one hand with the level of optical absorption, and on other hand with the concentration of free electrons.

Starting point for a theoretical description of actual processes are the equations describing the generation-recombination process of the bound electron-hole pairs and the generation-recombination process of the free electrons. This process is represented with two following differential equations

$$\frac{dN}{dt} = C_1 - C_2N - C_3N\exp\,(3/2.sAkT) - C_4Nn + C_5n^2 \qquad (9)$$

$$\frac{dn}{dt} = \mathrm{C}_3\mathrm{N}\exp\,(3/2.sAkT) - C_5n^2 \qquad (10)$$

where N is the concentration of the bound pairs, and n is the concentration of the free electrons. These equations involves even a formal description of the catalytic process of free electrons [7-11]. These equations describe a non-stationary kinetics, namely how the concentrations under consideration vary in time. The equations

$$0 = C_1 - C_2N - C_3N\exp\,(3/2.\mathrm{s}AkT) - C_4Nn + C_5n^2 \qquad (11)$$

$$0 = C_3N\exp\,(3/2.sAkT) - C_5n^2 \qquad (12)$$

corresponds to the final stationary state. After solving these equations, we can obtain the stationary concentrations N and n of the bound *e-h* pairs and of the free electrons, respectively. For our further consideration is here very important simple relation

$$N = \frac{C_1}{C_2 + C_4n} \qquad (13)$$

between concentrations n a N, which follows from relations (11,12) in stationary state.

- **Fatigue effect on the base BCH model**

The luminescence grows after the onset of the irradiation towards a high enough level, because there are no free electrons in the sample. Electron-hole pairs try to undergo radiant recombination. However, the gradually increase of the number of free electrons implies the increase of non-radiant recombinations, while the number of the radiant recombinations decreases. The intensity of the luminescence decreases. In other words, the fatigue process takes place.

Indeed, there was no such clarification of the fatigue effect until now. Some authors did publish about some unknown luminescence centers and on criteria that these centers should obey, but the problem remained to be open. We can here repeat only: the fatigue process is due to the catalytic action for which free electrons are responsible. There are more arguments supporting this view.

The concentration N at the initial time interval, when the irradiation begins to be applied (that is when free electrons are absent, $n = 0$), will be kept for some time at a quasi-stationary level

$$N_1 = \frac{C_1}{C_2} \qquad (14)$$

As the concentration n of the free electrons grows, the concentration N of the bound electron-hole pairs will fall down, because

$$N = \frac{C_1}{C_2 + C_4n} \leq \frac{C_1}{C_2} = N_1 \qquad (15)$$

tending towards a value $N \rightarrow N_{stac}$

$$\mathrm{N}_{stac} = \frac{C_1}{C_2 + C_4n_{stac}} \qquad (16)$$

This value can be much lower than the value given by expression (12). The photoluminescence intensity I is proportional to concentration N (I~N). This corresponds mathematically to the fatigue effect.

- **Streets´ formula na the base BCH model**

(10)

We do not want to present here a mathematical derivation of the Street formula on the base of BCH model. Nevertheless, let allow us to suggest at least verbally how we can solve the problem.

If in (16) $C_4n >> C_2$ we obtain

$$\mathrm{N}_{stac} = \frac{C_1}{C_4n_{stac}} \qquad (17)$$

From this formula, taking into consideration equations (11,12), was in work [15-19] derived relationship

$$I_2 \sim N_2 \sim \exp\left(-\frac{T}{T_o}\right) \tag{18}$$

which is in agreement with empirical Street's law. In this way, we have explained the exponential dependences shown in the Fig. 4 [15-19].

- **PLE- characteristics on the basis of BCH model**

Let we ask a question: Why is efficacity of photoluminiscence excitation the highest just in Urbach´s region of energy (Fig. 3)? Said in other words, why has this curve PLE in Fig. 3 its maximum just in region of exponential tail. According of our BCH model, it is caused by this reality, that by these energies of photons take place an effective filling of funnels and along with to relative lower creation of free electrons (as catalysers of non-radiant recombinations). Just in this energy region, at the maximum extends, made itself felt the influence of potential barriers. At lower energies is a lower probability of manyfold tunnelling and creation of free electrons.

When energies of irradiating photons are enhanced, electrons are excited on higher energy levels in the barrier region. The tunneling probability rises with higher electron energies. Therefore, more electrons can undergo a multiple tunneling and then achieve larger distances from their partner holes. This means that their chance of becoming free is better. The growing concentration of the free electrons leads, owing to the catalytic effect of the free electrons, to the suppression of the luminescence. This is, we believe, the proper cause of why the effectiveness of the luminescence ceases to grow when the photon energies rise. On the contrary, the luminescence effectiveness begins remarkably to lose strength, as the PLE characteristics show in Fig. 3. Actually, this is a significant fact confirming the idea of the vital role of the free electrons as catalytic actors. Is this all accidental?

Remark

The equations (9,10) that we have commented above enable us to seek answers on non-stationary dynamic processes accompanying the photoluminescence. Attention should be paid on a good description of the steepness of the photoluminescence, of a starting point when the fatigue phenomenon becomes apparent, but also of the decay of the photoluminescence.

5. Influence of a strong electric field on photoluminescence – theoretical analysis

In this part we will be devoted to the elucidation of the dependence of photoluminescence on electric intensity on the basis of BCH model.

The strong electric field decreases the level of photoluminescent radiation. This experimental fact is sometimes interpreted in such a way that strong electric field contributes to the decay of bound exciton pairs and thus prevents the photoluminescent radiant recombination. In our opinion the suppression of photoluminiscence is caused by different mechanism. The most important determinant of electric field influence is - as we suppose - the fact that strong electric field increases the probability of the *s*-fold tunnelling of electrons through potential barriers during absorption, which results in the increase of production of free electrons and thus, suppression of photoluminescence.

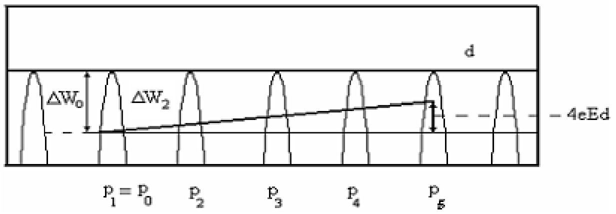

Fig. 6. Multiple tunneling of an electron in the direction of acting electric force.

- **Influence of an electric field on a process of multiple tunneling of electrons**

Effect of the field in a process of multiple tunneling rests on the fact that in the strong electric field affecting the energy of an electron is changing also during tunneling through the potential barriers. This state is depicted in Fig. 6. The energy of a moving electron in the direction of acting electric force increases, consequently tunneling of the electron is in progress gradually still on higher energy level. This way the probability of a tunnel transition through the next barrier gradually increases.

At the motion of the electron in opposite direction (against the acting electric force) the state will be opposite. The electron energy will decrease; consequently the decrease of probability of each next tunneling will appear. Let us analyze the situation shown in Fig. 6. The probability p_0 of a tunnel transition through the first one of the potential barriers can be expressed by [15, 16]

$$p_o \approx \exp(-A\Delta W_o) \tag{19}$$

where *A* represents a parameter of the barrier and $\Delta W_o = \Delta W_1$ - the energy depth (measured from the level of barrier's peak) at which the tunneling takes place. The next tunnel transitions through barriers in a given field will be under way in successive steps on levels $\Delta W_o - eEd$ $(=\Delta W_2)$, $\Delta W_o - 2eEd$, $\Delta W_o - 3eEd$,…. $\Delta W_o - seEd$. Here *s* are actual number of barriers. It holds for corresponding probabilities of tunnel transition

$$p_1 = p_o \sim \exp(-A\Delta W_o) \tag{20}$$

$$p_2 \sim \exp(-A(\Delta W_o - eEd)) = p_o \exp(AeEd) \tag{21}$$

$$p_3 \sim \exp(-A(\Delta W_o - 2eEd)) = p_o \exp(2AeEd) \tag{22}$$

$$p_s \sim \exp(-A(\Delta W_o - (s-1)eEd)) = p_o \exp((s-1)AeEd) \tag{23}$$

- **Probability of multiple tunneling**

The probability of the multiple tunnel transition P_s through all s barriers will be

$$P_s = p_1 p_2 p_3 ... p_s \tag{24}$$

or, in accordance with relations (4-7)

$$P_s \sim p_o^{\,s} \exp(0{,}5.AeEd\,(s-1)s) \tag{25}$$

Then probability of the multiple tunneling can be written as

$$P_s \sim B_1 \exp(B_2 E) \tag{26}$$

where, taking into account relations (20, 25)

$$B_1 = p_o^{\,s} = B_1 = \exp(-As\Delta W_o) \tag{27}$$

$$B_2 = \frac{As(s-1)ed}{2} \tag{28}$$

Analogical relations could be obtained for electron tunneling in opposite direction to acting electric force. Such relations differ in sign of electric field intensity. Instead of the relation (26) the following one would be obtained

$$P_s' \sim B_1 \exp(-B_2 E) \tag{29}$$

Remark

In three dimensional case (3D) the state is more complex. Here we consider 1D case.

- **Effect of a field on free electron concentration**

An electron at an optical transition connected with multi tunneling can pass a long distance from a hole in two ways (in 1D case) – at the tunneling: in the direction of an acting electric force or in the opposite direction. In the first case the field evokes an increase of probability of that tunneling, in the second one the probability decreases (in comparison to the situation when field is not present). Further, we show that both changes do not compensate each other. From analysis it follows that a strong electric field increases the probability of multi-tunneling as a result. For mean probability of multi-tunneling trough the s -barriers provided the strong electric field is present can be taken the arithmetical average of probabilities (26) and (29)

$$\frac{P_s(+) + P_s(-)}{2} = \frac{B_1 \exp(B_2 E) + B_1 \exp(-B_2 E)}{2} \tag{30}$$

where $P(+) = P_s$ denotes the probability of multi-tunneling in the direction of an acting electric force and $P(-) = P'_s$ denotes the probability of multi-tunneling in the opposite direction. If electric field is not present (E = 0) from relation (14) one obtains

$$\frac{P_s(0) + P_s(0)}{2} = P_s(0) = B_1 \tag{31}$$

This relation determines the mean value of multi-tunneling probability in the absence of the field.

Let us suppose that the condition for the creation of free electron by optical absorption is tunneling of an electron l through some specific number of "s" barriers. The number of optically produced number of free electrons per unit time (the generation factor) in the absence of the field we denote by the symbol G (0), in the presence of the field $G(E)$. For $G(0)$ according to [7-11] equation (27) is valid, so that, taking (29, 30) into account we can write

$$G(0) = \left(\frac{dn}{dt}\right)_{E=0} = C\exp[-A(hf + CT)] \tag{32}$$

$$G(E) = \left(\frac{dn}{dt}\right)_{E\neq 0} = G(0).\frac{1}{2}[\exp(B_2 E) + \exp(-B_2 E)] \tag{33}$$

Assuming that for recombination is valid

$$R = \left(\frac{dn}{dt}\right)_{rec} = C.n^2 \tag{34}$$

For the equilibrium concentration of free electrons in the presence, respectively absence of the field can be written

$$G(E) = R, \qquad G(0) = R \tag{35}$$

From above written equations the concentrations $n(0)$, n(E)) of free electrons for both.cases can be calculated. We get:

$$n(0) = \sqrt{C}\ [\exp[-0{,}5.A(hf + CT)]] \tag{36}$$

$$n(E) = n(0)\left[\frac{1}{2}[\exp(B_2 E) + \exp(-B_2 E)]\right]^{\frac{1}{2}} \tag{37}$$

- **Effect of a field on photoluminescence**

Intensity I of photoluminescence in steady state is dependent on the free electron concentration n. According to [8, 10] it holds

$$I \sim \frac{C_x}{C_y + C_z n} \tag{38}$$

where C_y a C_z are constants. If $C_y << C_z n$ (at steady state) then (23)

$$I \sim \frac{C_x}{C_z n} \sim \frac{1}{n} \tag{39}$$

Under that condition for photoluminescence intensity can according to (39, 46,47) be writen

$$\frac{I}{I_o} = \frac{n(0)}{n(E)} \tag{40}$$

where $I = I(E)$ is the photoluminescence intensity at the presence of the field and I_o = I(0) without the field. One obtains from (36,37,40)

$$I = I_o \frac{2}{\left[\exp(B_2E) + \exp(-B_2E)\right]^{\frac{1}{2}}} \qquad (41)$$

This relation determines the dependence of PL intensity on the electric field in 1D-case.

- **Three-dimensional case**

In reality, a tunneling process in a non-crystalline semiconductor is 3D. The above obtained result holds for 1D-case. Then, there is a need for correction in 3D case. A detail analysis showed, that the quantity B_2 has to be changed in a 3D-case by the quantity twice less. It is due to the fact that after travelling a distance d in a random direction (from point O(0,0,0) to the point $B(x \geq 0, y, z)$) x-coordinate of an electron (assuming x is parallel to the field) changes at average only about $d/2$. Then d should be replaced simply by $d/2$. This implies that the average change in potential energy of an electron in the field E will be $eEd/2$. In 3D case

$$I = I_o \frac{2}{\left[\exp(B_2E) + \exp(-B_2E)\right]^{\frac{1}{2}}} \qquad (42)$$

Where

$$B_2 = \frac{As(s-1)ed}{4} \qquad (43)$$

- **Weak electric fields**

In the case of weak electric fields the exponential functions in (42) can expand into (rapid convergent) Taylor series. If we cut the series after quadratic terms in E, we obtain

$$I = I_o \frac{1}{\sqrt{1 + 0{,}5\, B_2{}^2 E^2}}$$

or approximately

$$I = I_o\left(1 - 0{,}25\, B_2{}^2 E^2\right) \qquad (44)$$

where the relation (43) holds for B_2. Under these conditions the intensity of photoluminescence decreases quadratically` with electric field intensity E. But the relation (42) is more general.

- **Strong electric fields**

In the case of strong electric fields $\exp(B_2E) >> \exp(-B_2E)$. Relation (42) takes the form

$$I = I_o \frac{1}{\sqrt{\exp(B_2E\ )}}$$

$$I = I_o \exp(-0{,}5.B_2E) \qquad (45)$$

In this area of the fields photoluminiscence declines exponentially with the field strength E.

6. Discussion - a brief confrontation with the experiment

Quadratic decrease in the PL level (equation (44b)) in the case of chalcogenide glasses was already published [5, 6]. This type of dependence in the low fields occurs also in the case of a-Si: H. In the strong fields (up to $3.10^7.\mathrm{Vm}^{-1}$) was in hydrogenated amorphous silicon [20] recorded an exponential decline, which can be expressed by an empirical relationship

$$I = I_o \exp(-\gamma E) \qquad (46)$$

with the value of the constant $\gamma = 3{,}1.10^{-6}\ \mathrm{V}^{-1}.\mathrm{cm}$ ($3{,}1.10^{-8}\ \mathrm{V}^{-1}.\mathrm{m}$). More detailed confrontation of the presented model with experiments will be published in [13]. It will also be shown there, that the value of the constant γ in equation (46) corresponds quite well with the value provided by our model. Numerical evaluations based on the relations (43, 45) offered a relative good agreement with experimental data published e.g. in [20]. Another dependencies, regarding the effect of the field on photoluminescence, which are in reasonably good agreement with the experiment based on BCH model will be given in [21].

7. Conclusion

The paper shows that the barrier-cluster-heating model is able in an acceptable way to explain the essence of photoluminescence in non-crystalline semiconductors and others phenomena connected with photoluminescence, including electric field action on photoluminescence level (field quenching of the photoluminescence). Described mechanism of photoluminescence and heating of the nanoregions at nonradiative recombination allows also explaining of the weak absorption tail formation and also why photoinduced changes (photoexpansion) correlated with photoconductivity and anti-correlated with photoluminescence.

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*Corresponding author: ivan.banik@stuba.sk
mihaip58@yahoo.com