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ON THE RELATION OF OPTICAL ABSORPTION, LUMINESCENCE AND PHOTOCONDUCTIVITY IN NON-CRYSTALLINE SEMICONDUCTORS FROM THE POINT OF VIEW OF THE BARRIER-CLUSTER MODEL

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Arguments are presented to support the barrier-cluster model of non-crystalline semiconductors. It turns out that several experimental facts and from the field of optical phenomena can be explained successfully using this model complemented by the idea that free electrons in a non-crystalline semiconductor stimulate non-radiant recombinations. The article presents new, as well as earlier published facts in favour of this model.

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1. Introduction

Optical processes in non-crystalline semiconductors represent a complex set of phenomena, whose mysteries resist stubbornly for a long time in spite of the intense effort of scientiststo explain them [1-14]. Up to day, there is no generally accepted model which could explain a wide range of optical phenomena. The state of art is the same as Overhof put it years ago in his lecture on the occassion of the N. Mott´s 90th birthday anniversary [15]. He said: *„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."*

In this paper we introduce arguments in favour of the barrier-cluster model as well as in favour of a supplementary hypothesis according to which free electrons in a non-crystalline solid are capable of stimulating non-radiant recombinations of bound electron-hole pairs. It is shown that based on such concept, absorption, luminescence and photoconductivity processes as well as their mutual interdependence can be easily understood.

1.1 Barrier-cluster model

The elementary features of the barrier-cluster model of a non-crystalline semiconductor were described in [16-26]. The model assumes that the non-crystalline material is composed of clusters having potential barriers between them. The barriers influence not only the electric transport of current carriers but also the optical characteristics of the material. Firstly, the barriers between clusters contribute to a strong electron-phonon interaction, which is an important factor in optical processes in these solids. Apart from it, it is significant, too, that optical absorption at low temperatures is connected with tunnelling of electrons through the potential barriers.

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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. And it is 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 the case of such non-crystalline semiconductors as e. g. silicon, the clusters are obviously opened. This is clearly revealed by the detected ESR signal.

A strong electron-phonon interaction in chalcogenide glasses allows to make optical transitions with the participation of phonon energy. In other words, in such transitions, an electron absorbs simultaneously the photon as well as the phonon energy. Thus, the total energy accepted by an electron is a sum of photon and phonon energy. This absorption mechanism allows to understand the existence of exponential tails of optical absorption, which encroach deep into the forbidden band of a non-crystalline semiconductor. In this way, the characteristic features of newly emerged exponential tails at higher temperatures can be explained without a need to assume the existence of density-of-state tails within the forbidden band. However, such an absorption mechanism does not *a priori* exclude the existence of states within the forbidden band of some non-crystalline semiconductors. Nevertheless, the states in the forbidden band are not the main cause of the exponential tails. To support this idea, we can mention the fact that the exponential tails of optical absorption also appear in those non-crystalline substances, in which the existence of states within the forbidden band could not be demonstrated even by the most sophisticated experimental techniques.

The concept of a barrier model was for the first time presented and discussed by the author in previous studies (1972-1983). At the beginning, the model was designated as a crystallite model, later as barrier model. (Naturally, nothing was known before on the existence of fullerene- or nanotube types of clusters). The designation *"barrier-cluster model"* was for the first time used by the autor as earlier as 2006 in the works [17-18]. In the studies [16-22], the appearance of the exponential tails of optical absorption in the regions situated at higher and lower temperatures was explained and the temperature dependence of exponential tails at lower temperatures was discussed. The influence of the electric field on the optical absorption, i. e. electroabsorption, was studied in [16, 18] from the point of view of the barrier-cluster model. The influence of temperature on optical absorption and electroabsorption was analyzed in [19]. The study carried out in [16, 20, 21] designed a model of photoluminescence in chalcogenide glasses or generally, in non-crystalline semiconductors.

1.2 Free electrons as stimulators of non-radiant recombinations

In [20], the Street´s formula was derived for the dependence of photoluminescence on temperature, based on the concept that the photoluminescence process in a non-crystalline matter is strongly influenced by free electrons.The role of catalytic agents of non-radiant transitions (recombinations) has been ascribed to free electrons. Thus, due to free electrons, the number of radiant optical luminescence transitions decreases and luminescence is suppressed. Moreover, photoluminescent radiation arises from a spontaneous radiant recombination of the *e-h* couples bound by coulomb interaction.

The study assumes that the source of free electrons in a non-crystalline material at low temperatures during irradiation is a mechanism of multiple tunnelling of a small portion of electrons during the very act of the optical absorption. The essence of this mechanism is that some electrons at the optical transition connected with tunnelling through barriers do not undergo a simple tunnelling but an s-fold tunnelling through *s* barriers one after another. In this way, they end up in a considerable distance from the mother localization region (along with the respective partner hole). These newly emerged free electrons stimulate then - as we suppose - non-radiant transitions of bound *e-h* couples.

2. The existing success of the model with the explanation of some optical phenomena

Some serious arguments can be given in a support of the barrier-cluster model and the idea about the role of free electrons as catalyst agents of non-radiant transitions in a non-crystalline matter. The proposed concept (hypothesis) allows us to explain successfully several optical phenomena observed in non-crystalline semiconductors. In this part we introduce some facts that have been already published by the author. In the last part, we will describe hitherto unpublished arguments.

2.1 Temperature dependence of photoluminescence

The idea of the role of free electrons as catalyst agents of non-radiant transitions in a non-crystalline solid can be also supported by the fact that the Street´s photoluminescence law

$$I \sim \exp\left(-\frac{\mathrm{T}}{\mathrm{T}_{\mathrm{o}}}\right) \tag{1}$$

was derived in [20] on the base of this concept.

Symbol T_o stands for a constant. This relation expresses the dependence of luminescence intensity on temperature T. It is shown in the mentioned work that for luminescence intensity, I the following relation is valid

$$I = \frac{C_1}{C_2 + nC_4} \tag{2}$$

where also the concentration n of free electrons in solid appears, apart from the constants, C_i. The Street´s law was derived from (3) provided that $C_2 < nC_4$.

Apart from it, from (2) also follows the gradual time decrease of photoluminescence intensity, beginning from the start point of the exciting irradiation. The photoluminescence level in the first phase of irradiation is

$$I = \frac{C_1}{C_2} \tag{3}$$

because the initial value n is negligibly small at low temparatures (so that $n = 0$) and free electrons could not yet be produced in optical way. However, the steady state of photoluminescence level (luminescence after passing a longer time) is determined by (2). This level is already considerably lower than the previous one due to an increase of free electrons concentration n to a certain steady-state value.

2.2 Dependence of photoluminescence on energy of exciting photons

Another serious argument in favour of the presented concept on the role of free electrons is the fact that the photoluminescence level depends strongly on the energy of the exciting photons. This problem was studied in [20]. At lower energies of the exciting photons in the region of exponential absorption tail, the photoluminescence intensity increases with the increase of the photon energy, as the absorption does. Thus, photoluminescence in this region copies the course of absorption. 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 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, absorption will continue to increase exponentially but luminescence passes through a maximum and will decrease with further increase of photons energy.

This experimental finding (after our opinion) is due to the fact that at higher photon energies tunnelling of electrons through barriers runs on higher energy levels, which strongly increases the probability of *s*-fold tunnelling of some electrons to larger distances. In this way the production of free electrons increases considerably with the increase of energy of exciting photons and, consequently, also the amount of non-radiant recombinations. The number of radiant transitions, and thus also the photoluminescence level, decrease.

Based on this concept, a generalized Street´s law was derived in [21], in the form

$$I \sim \exp\left(-\frac{hf}{H_0}\right)\exp\left(-\frac{T}{T_o}\right) \tag{4}$$

which expresses the dependence of luminescence intensity on temperature and on photon energy of exciting radiation. The quantities H_0 a T_0 are constants. This relation applies in the region of low temperatures and in the region of energies hf corresponding to the upper part of the exponential tail (thus, if $C_2 < nC_4$ is met in the relation (2)).

2.3 Dependence of photoluminescence on intensity of electric field

The third serious argument in favour of the described view of the role of free electrons during luminescence relates to the influence of strong electric field on the photoluminescence level. It is known from experiments that a strong electric field decreases the level of photoluminescent radiation. This 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. However, the center of the respective mechanism is - from our point of view - somewhere else. The most important determinant of electric field influence is - as we suppose - the fact that strong electric field increases the probability of the mentioned *s*-fold tunnelling during absorption, which results in the increase of production of free electrons and thus, suppression of photoluminescence. However, this view does not exclude the above mentioned possibility that a strong field contributes also to the decay of bound *e*-*h* couples.

3. New arguments confirming suitability (correctness) of the model

In the next part we present several facts in support of the concept of the role of free electrons, which were not published so far.

3.1 Stimulation of non-radiant recombinations by thermal electrons

Suppose that there are conditions in a non-crystalline solid when free electrons practically do not emerge via optical process (i. e. through the above described mechanism of *s*-fold tunnelling). It would happen, for example, if tunnelling through barriers ran on low energy levels. In such a case the probability of *s*-fold tunnelling would be minor. Free electrons of optical origin would have partically zero concentration. However, it does not mean that free electrons of other origin, e. g. electrons produced via temperature mechanism cannot exist in such a solid.

The analyses showed that the expression (2) for photoluminescence applies also in such a situation. In case the electrons are of thermal origin, then for their concentration is valid the relation:

$$n \approx \exp\left(-\frac{W}{kT}\right) \tag{5}$$

In a special case, if $nC_4 > C_2$, it follows from (2) and (5) for the luminescence intensity

$$I \approx \exp\left(\frac{W}{kT}\right) \tag{6}$$

However, this is quite different relationship than that, which is represented by the Street´s luminescence law. The dependence (5) expressed in the form

$$\ln I\left(\frac{1}{T}\right) \tag{7}$$

represents a straight line with a positive directive. Thus, photoluminescence rapidly decreases with increasing temperature owing to the growth of concentration n of free thermal electrons. The concentration of optically excited free electrons (via mechanism of s-fold tunnelling) is unimportant in this case.

3.2 Confrontation with the experiment

It is possible in this way also to explain e. g. the experimentally observed temperature dependence of photoluminescence for amorphous silicon *Si* as described in [2].

3.3 Confrontation of two dependencies

Let us stop for a while over the presented picture. Apart from a straight line dependence of photoluminescence on the argument ($1/T$), also a graph is depicted that displays the dependence of concentration of photoelectrons (photoconductivity) on the argument ($1/T$). It might seem at first sight that these two dependences contradict our described concept about the role of free electrons. It can be clearly seen from the graph that photoluminescence rapidly decreases with increasing temperature right in the place where the concentration of free electrons n is constant, i. e. stable. It is in direct contrast with our concept of the role of free electrons. We will demonstrate however, that this is only a seeming discrepancy. But a clarification of this dilemma needs a little more detailed consideration of photoconductivity.

It is well known from the photoconductivity in non-crystalline semiconductors that in the low temperature region it increases with increasing temperature. With further increase in temperature it reaches a maximum and then it falls down. Obviously, the same will apply to the concentration of photoelectrons in dependence on temperature, but in connection with the depicted graph - its last phase (i. e. decrease of photoconductivity with increasing the temperature in the high temperature region) is missing.

Let us observe here that in the high temperature region the photoconductivity curve begins to decrease because the mechanism of recombination is changing. This change is a consequence of thermal carriers, that begin to dominate over the photo carriers. Therefore, it is no surprising that photoconductivity electrons will not run any longer, but the predominating thermal electrons. So, suppression of photoluminescence with increasing temperature in the picture does not relate to the stabilized concentration of photoconductivity electrons, but to a rapid growth of concentration of free thermal electrons. Thus, these two graphs do not represent any dilemma as far as the role of free electrons in a photoluminescence process is concerned.

3.4 A theme for experiment

An experiment utilizing injection of free electrons from a suitable electrode into a photoluminescing sample (layer) of a non-crystalline semiconductor might perhaps tell more about the role of free electrons. A certain modulation effect might appear with such injection.

4. Conclusion

In this paper we introduce arguments in favour of the barrier-cluster model as well as in favour of a supplementary hypothesis according to which free electrons in a non-crystalline solid are capable of stimulating non-radiant recombinations of bound electron-hole pairs.

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