

## **ELECTRON PROCESSES CONNECTED WITH LOW ENERGY OPTICAL ABSORPTION AND WITH PHOTOLUMINESCENCE IN NON-CRYSTALLINE SEMICONDUCTORS FROM POINT OF VIEW OF BARRIER-CLUSTER MODEL**

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Physical mechanism of origin of photoluminescence band in chalcogenide glasses is explained in the submitted paper. A typical feature of this band is its bell-shaped frequency profile and a relatively large width. Apart from it, the mechanism of arising of second exponential tails of optical absorption as well as the mechanism of intensifying (stimulating) effect of an additional low-energy radiation on the luminescence level is presented. The explanation comes out from the barrier-cluster model of a non-crystalline semiconductor.

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### **1. Introduction**

The physical principle of optical phenomena in non-crystalline semiconductors have not been fully understood yet. There is hitherto not a model, which would be able to clarify a wider range of optical phenomena in these solids. And at that, technical applications of these solids constantly grow. An enormous quantity of papers are published. However, the theory seriously remains behind [1-9].

It appears that a barrier-cluster model of a non-crystalline semiconductor is able to explain several significant phenomena in non-crystalline semiconductors, especially in chalcogenide glasses [10-19]. Up to now, the model was used in explanation of origin and features of exponential tails in optical absorption, in physics of electroabsorption and photoluminescence and in some other optical connections.

In this letter some optical phenomena of non-crystalline solids, misunderstood up to now, are explained in the frame of the barrier-cluster model. A mechanism of photoluminescence band origin is described in chalcogenide glasses, its frequency bell bottomed profile as well as the band width. An electron scheme of exponential tails origin of the optical absorption is introduced. A scheme facilitates to understand stimulated luminescence effect of a supplementary low energy radiation in the resulting luminescence level.

### **2. Barrier-cluster model and optical phenomena in chalcogenide glasses**

The barrier-cluster model comes out from the assumption that there exist potential barriers in a non-crystalline semiconductor, which separate certain microregions – clusters and in this way, they

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hinder the transport of the carriers at the margin of the conduction or valence bands [10-16]. The barriers also influence significantly the optical absorption at the optical absorption edge. It is caused firstly by the induction of a strong electron-phonon interaction, which leads to the fact that during 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. 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 not only the creation of exponential tails at the optical absorption edge, but also their temperature dependence at high as well as the low temperatures behaviour.

### 3. Physical nature of photoluminescence

A possible explanation of the physical nature of photoluminescence in chalcogenide glasses at low temperatures, from point of view of a barrier-cluster model, is shown in Fig. 1. During optical transition, an electron connected with tunneling, goes to an adjacent or a nearby region on an energy level, which is below the peak level of potential barriers. At lower temperatures, the excited electron after an optical transition, will pass on the lowest energy levels of a given localization region. It will be free only within its own localization region. Its wave function would be localized practically in its own micro-region between the neighboring barriers.

Due to Coulomb interaction and the poorly penetrable potential barrier between them, a bound state of such 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 rests. 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 height of these levels will depend on the distance from the "mother" micro-region (for the sake of simplification, we suppose that the hole do not move). With increasing distance, these levels will approach the bottom of the conduction band.

In Fig. 1, several such levels are depicted on both sides of the hole (in 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 rests. 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.

At low temperatures, an optically excited electron will, with a high probability, gradually get back to the mother region of the hole. Such an approach is connected to gradual tunneling and diffusion. At that, 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 radiant. An electron loses gradually a considerable part of its energy in them. In the last phase of approach, a non-radiant transition occurs in its own localization region. In this region, radiant optical recombinations of the  $e-h$  pairs occur, connected with emission of luminescence photons, whose energy is considerably lower than that of photons of the exciting radiation. A distinct Stokes shift will occur.

If there are no other disturbing processes, 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 real situation in the first phase of irradiation. However, the state of a high luminescence begins to impair and weaken rather quickly.

When explaining the laws of luminescence on the basis of the barrier-cluster model, an extremely significant assumption is important in our considerations, namely that free electrons, by their effect, stimulate the non-radiant recombination of bound  $e-h$  pairs (as a kind of a catalyst), and thus, they reduce the number of radiant transitions. So, ultimately, free electrons markedly

influence the luminescence process. The 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) [14-16].

#### 4. Arising of luminescence band in chalcogenide glasses

Photoluminescence in non-crystalline semiconductors is, from the barrier-cluster model point of view, caused by radiant recombination of bound electron-hole ( $e-h$ ) couples. A radiant transition occurs when an electron enters the localization region, in which the respective hole,  $h$  is localized. A picture of this final process can be followed in Fig. 2. A transition of an electron from the level A to the level B is depicted there.

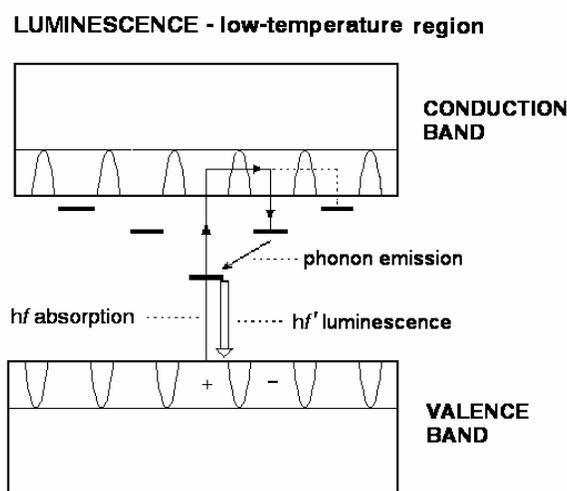


Fig. 1. The processes connected with photoluminescence.

We would expect at the first sight that the transition  $A \rightarrow B$  (Fig. 2) occurs in such a way that the entire superfluous energy  $E_A - E_B$  is radiated in a form of phonon. In the next phase, a luminescent transition of electron occurs from the  $B$  level onto the "hole" level  $C$  within the valence band. However, we encounter a problem using this explanation. At low temperatures, the hole is obviously localized between barriers, on the uppermost levels  $C$  of the valence band. The luminescent transitions from the discrete level  $B$  to the level  $C$ , bound to the upper level of the valence band should exhibit a narrow frequency spectrum, which does not correspond to reality. A luminescence spectrum in chalcogenide glasses is, in fact, relatively wide and it has a bell-shaped profile as a rule. This indicates that the luminescence mechanism will somewhat differ from that described above.

We assume that a real final process, leading to luminescence, runs differently. We suppose that on  $A \rightarrow B$  transition, a part of energy  $E_A - E_B$  is, no doubt, given to a phonon (without participation of which, the transition of electron to the neighboring localization region would not be possible at all), but the rest of this energy is consumed by excitation of the hole (Fig. 2b). On such an excitation, the hole gets to a certain excited level  $D$  of the valence band in the barriers region. The factual luminescence transition occurs at last by a transition of an electron from the  $B$  level to the  $D$  level (Fig. 2c). At that, the  $D$  levels will be spread statistically as energy of radiated phonons is statistically determined too.

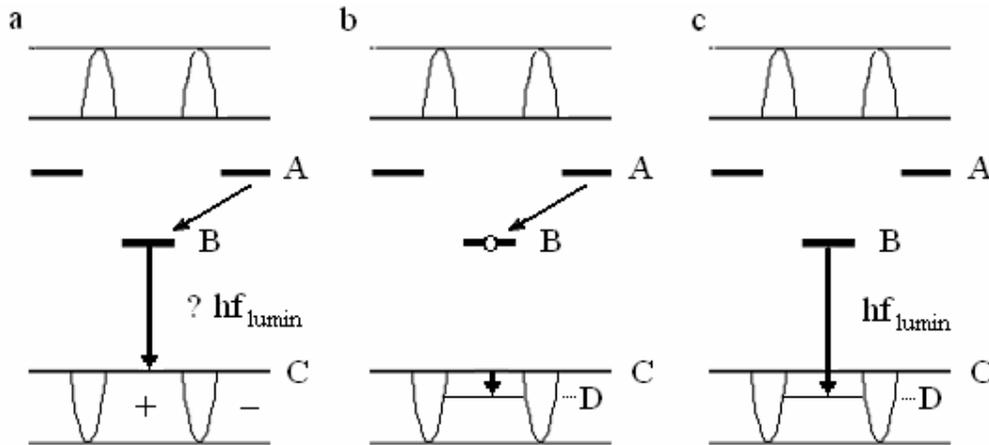


Fig. 2. Luminescent process a) simplified, but incorrect explanation b) transition of an electron from A level to B level connected with excitation of the hole c) luminescent recombination transition of electron to the statistically determined level D

Such process enables strong electron-phonon interaction conditioned by potential barriers. The gained energy by a hole is

$$E_D - E_C = E_A - E_B - W_{\text{phon}}$$

The  $D$  levels show a statistical dispersion (scattering) because the energy of emitted phonons is also statistically determined. An inherent radiative luminescent transition occurs via electron jumping from the discrete level  $B$  on energetically dispersed levels  $D$  of a barrier band with a low mobility at upper edge of a valence band (Fig. 2c). Therefore, relatively broad energy spectrum will correspond to the emitted luminescence photons.

At the upper described mechanism an important role plays an excitation of hole immediately before the process of particular radiative recombination. Just the hole excitation determines by emitted phonons is responsible for a typical bell-bottomed shape and relative broad photoluminescence spectrum profile of chalcogenide glasses.

The scheme shown in Fig. 2 should be achieved by additional analogical transitions as drawn transition  $A \rightarrow B$ . Over the level  $A = A_1$  there are also higher (excited) levels  $A_2, A_3, \dots$  of a given localized region in a forbidden band of semiconductor which are not depicted in Fig. 2. For example, the transition  $A_2 \rightarrow B$  can be accompanied by an excitation of hole inside a barrier region of the valence band. The barrier region is dominant for this process because just the barriers support the strong electron-phonon interaction.

Evidently, the excitations of holes can be caused also by phonons produced at non-radiative  $e-h$  pair recombination. It is not excluded that under certain conditions just this mechanism can dominate. It should be the case when free electron concentration is higher enough. Then the fraction of non-radiative recombination is higher and likewise the phonon production connected with that mechanism.

We remark that phonons are created at non-radiate tunnel electron transition from one region to other one (in which an electron approaches to a hole). These phonons can, also, contribute to the excitations of holes.

## 5. Second exponential tails (region of very low absorption)

Next, we are going to describe the mechanism of formation of second exponential tails, the exponential tails in the region of very low absorption. The absorbed photon has a relatively

small energy in this case. This energy allows only transitions of an electron from the valence band on a discrete energy level  $B$  in its own localization region (Fig. 3). Thus, tunnelling to a neighborhood region does not occur. Such a transition can occur at the temperature  $0\text{ K}$  only if the photon energy is sufficient. Minimum energy necessary for the transition, corresponds to the difference  $E_C - E_B$  (Fig. 3a). If the photon energy exceeds this given minimum energy (Fig. 3b), then an electron from some deeper level of the valence band would participate, e. g. from the level  $D$ . It will be that level, for which the energy difference  $E_D - E_B$  corresponds to the photon energy  $hf$ , so that  $E_D - E_B = hf$ . However, it is obvious that probability of such an absorption will depend on level density on the energy level  $D$ . Since the density of levels in localization regions (clusters) increases in downward direction, the probability of absorption will increase with increasing photon energy. At that, the highest density of discrete levels in the region between barriers is close to barrier peaks, thus, at the lower edge of low mobility band of the valence band. This explains the growth of absorption with increasing photon energy. However, this raises the question: which type of function could it be?

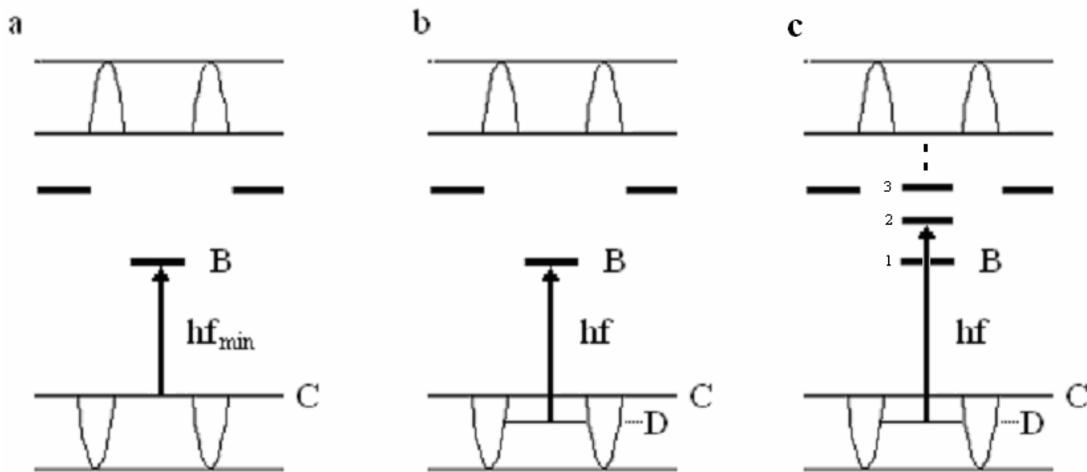


Fig. 3. Arising of second exponential tails of optical absorption a) absorption at minimum photon energy b) absorption at higher photon energy. At suitable conditions the energy  $hf$  can be changed to  $hf + W_{phon}$ .

A similar consideration which we have introduced in the case of a discrete level  $B$  can be applied to another excited levels (Fig. 3c), e.g. 2, 3 (B)... of a given localized region lying over the ground energy level 1 (B). There are possible transitions from levels of a low mobility band (e.g. levels C and D) on higher excited levels. For creation of the exponential tails are responsible all possible transitions from valence band levels of the low mobility to the all possible discrete levels of a given localized region lying inside a forbidden band. Upper mentioned transitions in a real state are affected by temperature trough phonons due to the strong electron-phonon interaction. Under suitable conditions a disposable energy of an electron at a transition is the sum of the both energies: photon and phonon. These phonons may be of “thermal” origin or “optical” one (created during non-radiative recombination).

## 6. The intensification (stimulation) of the radiation

In this part, we are going to discuss the physical substance of the stimulation effect of an additional low energy radiation upon increasing level of photoluminescence.

It is known that if on irradiation by photons with energies from the region of exponential tails (which invokes usual luminescence) some additional low-energy radiation (with energies  $hf$  of quanta from luminescence band up to exponential tail) is applied on chalcogenide glass,

luminescence will boost. At that, this intensification is higher than it should correspond to an unsupported photoluminescence effect of the additional radiation. Thus, some cooperative effect is apparently in question.

We will explain this effect from the point of view of the barrier-cluster model. On irradiation of glass by additional low-energy radiation, there are analogical optical transitions (Fig. 4) as in the case of transitions, which are responsible for the second exponential tails (as they were described in previous paragraph). Figs 4a,b give a true picture of optical transitions in which phonons play no role. The outcome would be only small changes of luminescence level. They would correspond to luminescence in the region of second exponential tails. They could not explain the amplification (stimulation) effect, which we are speaking about. For understanding the intensification (stimulation), the presence of phonons produced in optical way is very important. The concentration of thermal phonons is very low at low temperatures. However, in the considered case, phonons are created also in optical way. They arise at non-radiative recombinations of  $e-h$  couples excited by free electrons (carriers). Phonons arisen in this way will cause an increased absorption of additional radiation in glass.

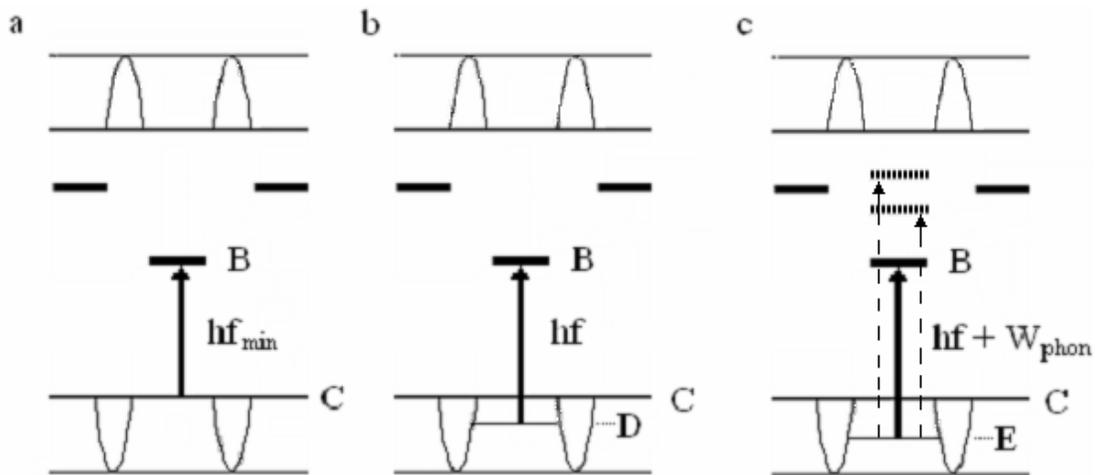


Fig. 4. Absorption of stimulating low energy radiation which intensifies luminescence  
 a) absorption of photon with minimum energy necessary for a transition b) absorption in the case of higher photon energy c) absorption with energy participation of phonon (of optical or thermal origin).

The heart of phonon stimulation consists in the fact that on optical transitions, in the presence of phonons (Fig. 4c), an electron takes not only the photon energy, but also the phonon energy; i. e. the sum  $hf + W_{\text{phon}}$  of these two energies. In this way, the starting level of an electron at optical transition onto the resultant discrete level  $B$  shifts deeper into the valence band in the barrier region – for example from the  $D$  level to the  $E$  level. It is a shift towards the region of increased state density, which results in increasing absorption of additional radiation. The increased absorption of additional radiation causes, in turn, increasing luminescence because practically all  $e-h$  couples created by additional radiation recombine through luminescence. After all, it is well known that also the "pure" absorption in the region of second exponential tails is accompanied by luminescence, the course of which coincides quite well with the course of absorption.

The stimulation effect of additional radiation upon luminescence can obviously be still intensified by increased temperature owing to thermal phonons.

Similar transitions may occur at higher photon energies also onto higher (excited) discrete energy levels within the given localization region; they are not depicted in the figure. The amplification cooperative effect, what we are speaking about, and which is considerably more expressive, would be not explained here.

To understand of an amplification (stimulation) effect of a low energy radiation the existence of phonons is very important. Here, we are speaking of phonons of an optical source. At low temperatures the concentration of thermal phonons is very low. At higher energies an electron can arrive on higher (excited) discrete energy levels in a given localized region (Fig. 4).

## 7. Conclusion

The appearance of a wide bell-shaped luminescence band in non-crystalline semiconductors, before all in chalcogenide glasses, is explained using the barrier-cluster model. A model for the origin of the second exponential tails of optical absorption is proposed as well. Apart from it, the mechanism of the intensification effect of additional low-energy radiation upon the resultant luminescence level has been clarified. We suppose that there are important arguments in support of the barrier-cluster model of a non-crystalline solid.

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