Mechanisms of Energy Loss of Fast Electrons (1-100 keV) in Semiconductors and Dielectrics and Their Impact on Efficiency of Cathodoluminophores

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***Abstract* — The processes of energy loss by electrons in semiconductors and dielectrics are complex and not fully understood to date. These processes determine the mean pair-creation energy. Its value is important for many technical applications such as scintillators, betavoltaics, cathodoluminescence, etc. The main channels of energy losses can be as follows: impact ionization, excitation of collective oscillations of high energy (plasmons) or low energy (phonons).**

***Index Terms* —cathodoluminescence, electron energy loss, impact ionization, pair creation energy, plasmon.**

I. INTRODUCTION

The processes of energy loss by electrons in semiconductors and insulators define the average energy cost of creating of electron-hole pairs. This value is important for many technical applications such as scintillators, betavoltaics, cathodoluminescence, etc. We are interested in the last of these processes for the development of cathodoluminescence devices [1,2]. Nowadays, the energy efficiency of cathodoluminophores does not exceed 20-25% [3-6].

The host matrix of a luminophore, a wide gap semiconductor or dielectric, absorbs the energy of fast electrons and transforms it into the energy of electron-hole pairs, which subsequently thermalize and excite the luminescence centers when captured by them. The main losses of the initial energy (more than 60%) occur during the thermalization stage. The total efficiency can be approximately presented in the following form [4]

$$\eta = (1-r)\frac{\langle hv \rangle}{\beta E_g} \tag{1}$$

where r is the reflection coefficient of electrons, which is usually small (~1% or less); $<h\nu>$ is the mean energy of the emitted photon, E_g is the forbidden gap of the host matrix, and β is a coefficient, which characterizes the mean energy of generation of the electron-hole pair. Starting from the experimental data, this coefficient is usually taken as β ~ 2.5–3 (see, for example, [7]). It is essential to use cathodolumonophores with minimal energy value required for an **e-h** pair generation. The search for such cathodoluminophores can be purposeful and effective only when the processes occurring in the material are clear.

II. THE PROCESSES OF ENERGY LOSS

The complicated process of interaction of fast electrons with the energy within the range of 1–100 keV with dielectrics and semiconductors is not still clear in details. In the published data related to cathodoluminescence two theories of creation of **e-h** pairs by fast electrons are presented.

The first model (a model of impact ionization proposed by Yu.M. Popov [3]) describes an avalanche process of generation of secondary fast electrons and holes by the primary electron. When their energy exceeds the threshold value of impact ionization $\mathbf{E_i}$ they in turn can generate secondary electrons and holes. The $\mathbf{E_i}$ value is greater than $\mathbf{E_g}$ due to the condition of conservation of the energy and momentum; it is defined by the zone structure of the material and for direct gap semiconductors when the approximation of the effective mass is valid

$$E_i = E_g(1+\frac{m_e}{m_e+m_h}) \tag{2}$$

where $\mathbf{m_e}$ and $\mathbf{m_h}$ are the effective masses of the electrons and holes, respectively. Electrons and holes with $\mathbf{E} < \mathbf{E_i}$ cannot knock out electrons from the valence band, and their energy is spent for the heating of the crystal lattice. Therefore, the excess energy of all electrons in the conduction band and holes in the valence band from the band edge to $\mathbf{E_i}$ is lost for thermalization. Integrating the energy of electrons and holes within the limits from zero to the threshold value one can estimate the mean energy per electron-hole pair. It is shown in [3] that this value is weakly sensitive to the energy distribution of the secondary electrons and holes. At the uniform energy distribution **β~3** for the direct gap semiconductors where effective masses of electrons and holes are approximately equal – this is valid for many cathodoluminophores used as host materials. This **β** values correlate well with the experimental data [7] (see Fig.1), as well as $\mathbf{E_i}$ values determined in the experiments on photon multiplication.

Note that in the theory of impact ionization variations of the zone structure, energy gap values, effective masses of electrons and holes lead to the variation of the threshold of impact ionization and of the energy integral values. The threshold energy can exceed $\mathbf{E_i}$. by the optical phonon energy $\mathbf{E_{ph}}$ when the characteristic time of phonon generation is comparable with the characteristic time of

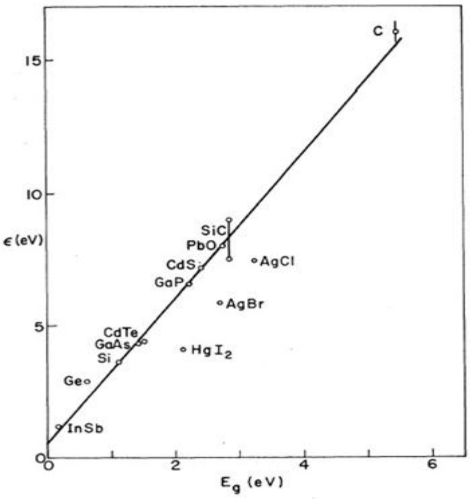

Fig. 1. Experimental values of the mean pair-creation energy [7].

impact ionization, and the electron with great probability can descend below the genuine threshold $\mathbf{E_i}$ before it generates one more **e-h** pair. Therefore, strictly speaking, the upper integration limit can be $\mathbf{E_i}$ + $\mathbf{E_{ph}}$ or the conduction band top. It depends on which of the values is less; e.g., the conduction band in ZnS is narrow, less than 1.5$\mathbf{E_g}$. However, in many cases this does not considerably influence the total mean pair-creation energy value. For the majority of substances that are used as host substances of cathodoluminophores the reliable and detailed data related to the zone structure are absent. For example, in individual cases for alkali halides the available date provide $\mathbf{E_i}$ values close to $\mathbf{E_g}$ and **β~2** [8]; this agrees with the experimental data [7].

As another theory of **e-h** pair creation, a plasmonic model can be named [9]. After Bohm and Pines works [10] the ideas became widespread that the energy loss of fast electrons in substances occurs due to the generation of plasmons (Langmuir's oscillations of the electron gas in solids). In particular, for a long time the theories of the secondary emission were based on these ideas. The energy of the quantum of these oscillations (plasmons) amounts to

$$E_p = \hbar e \sqrt{\frac{n}{m_e \varepsilon_0}} \tag{3}$$

where **n** is the electron concentration (the concentration of conduction electrons in metals or that of valence electrons in semiconductors is usually taken), **e** is the electron charge, $\mathbf{m_e}$ is the electron effective mass, and $\boldsymbol{\varepsilon_0}$ is the dielectric constant of vacuum. For semiconductors the energy of plasmons, longitudinal oscillations of valent electrons relative the ion core, usually amounts to ~ 14–17 eV (for high-frequency mode). The low-frequency mode caused by the conduction electrons cannot play a substantial role in the energy loss by fast electrons, since the concentration of the conduction electrons is low; the energy of low-frequency plasmons is also small (~ 0.01-0.1 eV).

However, low-frequency plasmons can contribute into the energy losses, especially at high excitation densities when the density of conduction electrons increases; here, since the energy of low-frequency plasmon is low, it cannot decay via the generation of an **e-h** pair and presents the energy losses per se. The plasmonic model assumes that the total energy of primary electrons is spent for generation of plasmons, and each of them subsequently generates an **e-h** pair, since the plasmon energy is greater than $\mathbf{E_g}$. Correspondingly, the total difference between $\mathbf{E_p}$ and $\mathbf{E_g}$ is losses. From this model an obvious recommendation follows to use substances with low plasmon energy as cathodoluminophore bases. Unfortunately, this did not allow one to find substances with the efficiency exceeding those for known since the 1940s conventional ZnS-based materials.

However, each of the hypothesis - 1) the total or almost total energy of primary electrons is spent for generation of plasmons; 2) each plasmon decays with creation of only one electron-hole pair – is not obvious and should be proved.

The data related to the characteristic electron energy loss spectra (EELS) in thin films of metals were presented as unambiguous substantiation of the first hypothesis. In these spectra wide peaks with energies that approximately coincide with the plasmon energies calculated according to Eq. (3) were observed. However, these peaks are not unique or pronounced even for metals, not to mention semiconductors and dielectrics; the process of losses itself is multistep and complicated. Therefore, these experimental data cannot give a definite evidence of the plasmonic theory in its initial form.

The plasmon decay into an **e-h** pair was postulated, though the possibility of this decay is not obvious. Really, despite the plasmon energy $\mathbf{E_p} > \mathbf{E_g}$, the great number of electrons participate in plasmonic oscillations. As a result, the energy of each of them is insignificant; therefore, to realize the possibility of the energy transfer of the plasmon spread over the area with dimensions of the order of the Debye radius a certain mechanism for 'concentration of energy' is necessary to transfer it to an individual electron. It is stated in several textbooks on the solid state physics that the transformation of plasmon energy into the energy of motion of individual particles is not possible [11]. Nevertheless, it turned out that the plasmon decay with creation of an **e-h** pair is possible, though as V.L. Ginzburg has shown is not trivial. It occurs due to acceleration of the electron by a plasma wave field and is analogous to the reverse Vavilov–Cherenkov effect [12]. Fig. 2 illustrates the plasma oscillation in the solid excited by a fast charged particle [13].

In principle, the decay of a plasmon into more than a single **e-h** pair is possible; at least for surface plasmons the published data indicate that the decay into two **e-h** pairs can occur. The transfer of the plasma energy to a fast electron is also possible; it leads to the appearance of so-called High Energy Satellites in the EELS spectra.

Therefore, almost over half a century two alternative versions have existed for the description of the processes that occur in the solid under the action of fast electrons. In the Soviet literature the first approach dominated; only N.P. Soshchin in the 1970s developed a modified version of the plasmon approach [14]; in the foreign literature the second approach was developed. Note that these approaches developed in a parallel manner; the scientists

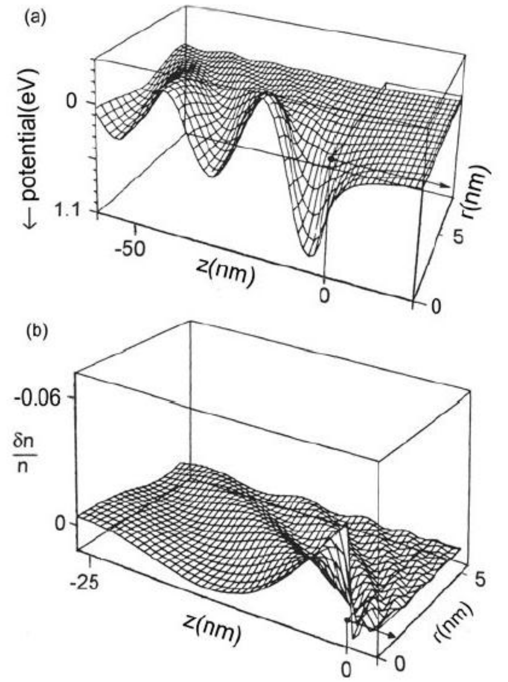

Fig. 2. Response of the medium with the plasmon enegy $\mathbf{E_p}$ = 25 eV to the motion of 100 keV charged particle. (a) Scalar potential; (b) corresponding variation of the electronic density. The particle moves along the z axis [13].

adhered to one of the directions did not argue, comment and as if do not pay attention that the other branch exists. Several authors that discussed both models [15] did not give their preference to one of them and did not propose how they can exist together. Evidently, the proposed concepts do not exclude each other; each of them is valid, but no one gives a complete description of the processes that occur in the solid when it interacts with electrons with energies in the range of 100–10 000 eV.

Nowadays when the EELS method is widely used, a great quantity of data have been accumulated related to the mechanisms of primary energy losses by fast electrons. EELS allows one to investigate inelastically scattered (initially monochromatic) electrons that underwent discrete energy losses at their reflection from the solid surface or after passing through a thin solid film. The energy losses are named characteristic, since their magnitude does not depend on the energy of initial electrons; it is characteristic for the given material. These losses are associated with various processes in the solid surface or volume, such as excitation of quasiparticles (phonons and plasmons), one-particle excitations of valence electrons (intraband and interband transitions), ionization of core atomic levels, etc. The entire spectrum of typical losses is schematically presented in Fig. 3. The mechanisms of losses are indicated near the respective peaks. As can be seen in the figure, the losses linked with plasmons and interband transitions (impact ionization) are the most intensive; a greater plasmon peak height does not allow one to conclude that exactly this channel of losses dominates, since all peaks are rather diffused. In the majority of cases the transitions from core levels of the lattice atoms lead to Auger processes and generation of hot electrons that in turn can generate plasmons or **e-h** pairs.

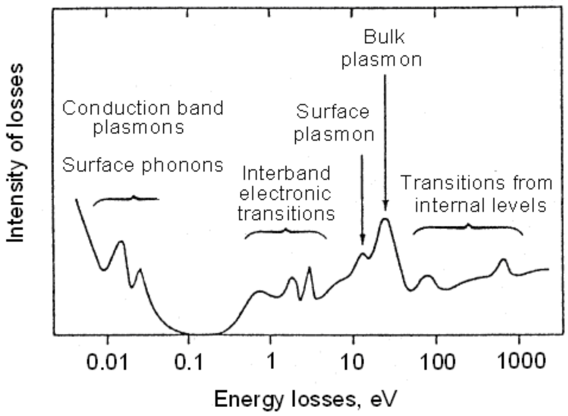

Fig. 3. Qualitative view of the spectrum of characteristic losses of the electron energy in the solid [16]. The main sources of losses and their energies are indicated.

EELS provides a certain representation of the structure of primary energy losses by fast electrons; however, an ‘invisible’ multistage process of final energy transformation of thermalized **e-h** pairs and phonons is not shown in EELS. Excitons are also generated, but for simplicity we will not treat them as a separate category, especially because the exciton energy differs no more than by 5–10% from the energy of the thermalized **e-h** pair (that is $\mathbf{E_g}$), and the share of excitons generated due to the bombardment of the solid by fast electrons does not usually exceed 10%.

One fast primary electron with the energy ~10 keV can generate hundreds of plasmons and secondary hot electrons; each of them can also generate an avalanche, and plasmons can decay into two or more pairs; electrons or holes can also possess energy exceeding the impact ionization threshold at that. These processes do not virtually influence EELS, though influence the pair-creation energy value.

These processes can be schematically presented in the following way (Fig. 4).

Finally, the **e-h** pairs thermalize by the transfer of the excessive energy to the lattice; in this way the entire energy of primary electrons transforms into the energy of thermalized **e-h** pair (equal to $\mathbf{E_g}$) and phonons.

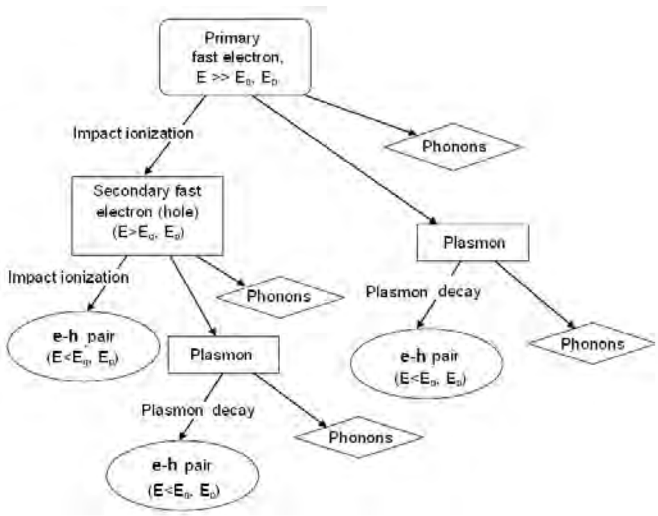

Fig. 4. Schematic view of the cascade loss of the fast electron energy.

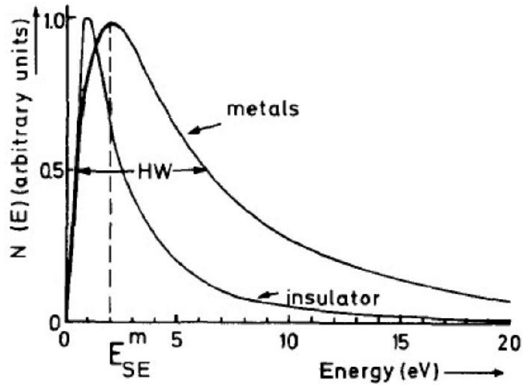

Fig. 5. Typical spectra of secondary electrons in metals and dielectrics [17].

The relative intensities of the channels depend on the parameters of the specific material - $\mathbf{E_g}$, $\mathbf{E_i}$, the concentration of valence electrons, effective masses $\mathbf{m_e}$ and $\mathbf{m_h}$, zone structure, etc., as well as on the energy of primary electrons. These intensities can apparently depend on the excitation current density, since it influences the concentration of conduction electrons. Finally this defines the energy value of **e-h** pair generation. The attempts were made to determine the input of various channels using the theory of secondary emission.

It is possible to say that in the solid a population of electrons exists whose energy spectrum is qualitatively similar to the spectrum of secondary electrons (Fig. 5), but it is shifted to the left by the electron affinity energy. The unobservable spectrum of ‘internal secondary’ electrons is only qualitatively similar to the experimental one even in the right-hand side, since electrons that form it arrive from various depth; correspondingly, their energy loss is different, and this introduces distortions in the spectrum.

However, even for a comparatively simple case of metals such as aluminum the results provided by various researchers are strongly different; according to certain models a plasmon channel plays the main role in the spectrum formation [18], according to other models – an impact ionization channel [18]. Therefore, this illustrates that the problem is not finally solved.

With appearance of various metamaterials it becomes possible not only to search suitable highly effective materials among natural substances, but to create materials with specified properties, in particular, with the appropriate zone structure. However, it is necessary to understand which properties should possess the material that can be used as an efficient cathodoluminophore.

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