Determination of recombination parameters of phosphors from cathodoluminescent characteristics

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A simple method to determine recombination parameters of polycrystalline phosphor materials is proposed based on a comparison of a theoretical prediction of cathodoluminescent intensity with experimental characteristics. The obtained parameters are very sensitive to additional treatments of phosphor surface, especially to chemical modification by even small amounts of inorganic oxides.

The proposed method offers a simple and rapid way of controlling recombination parameters of luminescent materials. © 2002 American Institute of Physics. [DOI: 10.1063/1.1508170]

At low-voltage cathodoluminescence (CL), the generation of nonequilibrium charge carriers by the deceleration of primary electrons proceeds in a thin (about several tens of nanometers) surface layer. In this case the majorities of recombinations are nonradiative, and diffusion and drift processes of electrons and holes become very important. The efficiency of phosphors at low energy electron excitation (<1 keV) is determined by the possibility that the nonequilibrium charge carriers, especially the minority ones, can reach the bulk, the less defective part of a phosphor grain. Therefore, such principal parameters as surface recombination velocity, diffusion and drift length, radiative and nonradiative lifetimes, quantum efficiency, and others give important information about the luminescent processes of materials, especially those excited near the surface.

The influence of the aforementioned parameters on the performance of CL phosphors is considered in several publications, but there are some difficulties in the experimental determination of these important characteristics of a material. One is connected with minor details of investigations on polycrystalline samples. Another is the short lifetime of nonequilibrium charge carriers of the studied materials, which complicates the determination of these parameters by direct experimental methods. A CL is a very attractive method for the determination of recombination parameters, since it is very simple to vary the excitation energy of an electron beam. It allows one to control the depth of generation of nonequilibrium charge carriers in a wide range and to alter the influence of surface recombination on CL characteristics.

The aim of this work is to develop a simple method to determine recombination parameters of polycrystalline materials and to understand the mechanism of influence of a coated material on phosphor performances.

The mathematical description of recombination processes in semiconductor materials and their influence on CL characteristics are considered in several articles. But there are some difficulties in the application of the known equations in the analysis of experimental data. One results from the complex aspect of the final mathematical expressions. Second, practically all of the known formulas are obtained for nonequilibrium electrons. But the majority of phosphors are n-type semiconductors where the recombinations processes are determined mainly by properties of minority charge carriers, which are holes.

For a semi-infinite crystalline semiconductor of n type in absence of external electrical fields, the distribution of minority charge carriers (holes) \( \Delta p(z) \) is described by the diffusion equation

\[
\frac{d^2 \Delta p}{dz^2} - \frac{\Delta p}{L_p^2} + \frac{1}{D_p} G(z) = 0,
\]

where \( z \) is the coordinate axis which is perpendicular to the semiconductor surface and is directed to the sample’s bulk, \( D_p \) is the diffusion coefficient of holes in a host material, \( L_p \) is the diffusion-drift length of holes, and \( G(z) \) is the function which describes a distribution of concentration of the nonequilibrium charge carriers in a semiconductor. In our simulations we used the following simple mathematical expression for the description of the aforementioned distribution:

\[
G(z) = \frac{G_0}{z_0} H(z_0 - z),
\]

where \( z_0 \) is the penetration depth of primary electrons, \( G_0 \) is the generation rate of nonequilibrium charge carriers, and \( H(z_0 - z) = \begin{cases} 0, & \text{if } z < 0 \text{ or } z > z_0 \\ 1, & \text{if } 0 < z < z_0 \end{cases} \)

is the Heaviside function. Equation (2) simplifies the final equation and describes well the real processes of charge carriers generation, especially in the case of low energy electron excitation. The procedure of obtaining the solution of Eq. (1) is well known and described by many authors. In the case where the self-absorption of luminescent light is negligible, the following equation is obtained for the distribution of light-emitted intensity \( J(z) \) in a semiconductor volume:

\[
J(z) = G_0 \eta \left[ 1 - \frac{L_p}{z_0} \left( \frac{S_0 L_p}{1 + S_0 L_p} \right) \left[ 1 - \exp \left( - \frac{z_0}{L_p} \right) \right] \right],
\]
where $S_0 = S/D_p$ is the reduced surface recombination velocity, and $\eta$ is the internal quantum efficiency.

Several oxide and sulfide phosphors with an average grain size of 3 $\mu$m, were investigated in vacuum fluorescent displays of experimental construction in a wide range of voltages. Some of the phosphors were coated with a small amount, less than 1 wt%, of inorganic oxides by high temperature decomposition of corresponding salts or their solutions. The mechanism of influence of surface modifiers on phosphor performance is not well understood yet although this method is very promising for phosphor improvement.

For the estimation of recombination parameters of the investigated samples, Eq. (3) is compared with the experimentally recorded integrated intensity of CL at a constant power of electron beam. The latter requirement is important for maintaining a constant value of generation rate of nonequilibrium charge carriers $G_0$ during all the experiments. Peka et al. proposed this approach for the investigation of GaAs single crystals.

A typical experimental dependence of the CL intensity of a phosphor on the penetration depth of primary electrons is presented in Fig. 1. These characteristics are described well by Eq. (3) for a wide range of voltages. At surface excitation (low-energy electrons), where we can take into account only the first three terms in Taylor’s series for the exponential function, Eq. (3) becomes linear

$$J(z) = \frac{1}{2} G_0 \eta \frac{S_0 z_0^2 + 2}{S_0 L_p + 1}.$$  \hspace{1cm} (4)

The point of intersection of $J(z)$ in Eq. (4) with the abscissa axis ($z_0$) is $S_0 = -2z_0$. Thus, a surface recombination velocity can be found by extrapolation of the linear part of the experimental curve (Fig. 1, broken line) to the abscissa axis. In the case where a penetration depth of electrons becomes larger than the diffusion-drift length of nonequilibrium holes ($z_0 > L_p$), which takes place at high voltage excitation, Eq. (3) is simplified

$$J(z) = G_0 \eta \left[ 1 - \frac{L_p}{z_0 S_0 + L_p} \right].$$  \hspace{1cm} (5)

Equation (5) is saturated to the value of $J_{\text{max}} = G_0 \eta$ with the increase of $z_0$. The linear Eq. (4) can be rewritten as a normalized CL intensity $J/J_{\text{max}}$. This curve intersects an ordinate axis at the point of $(J/J_{\text{max}}) = (1 + S_0 L_p)^{-1}$. The extrapolation of experimentally measured characteristic to the ordinate axis gives the value of $(J/J_{\text{max}})$, which allows one to determine the diffusion-drift length of holes $L_p$ by using the latter mathematical expression. Other parameters can be estimated by the comparison of the theoretical dependence described by Eq. (3) with experimental data.

Special attention was paid to the estimation of the penetration depth of primary electrons, especially at low voltages, because a systematic error in calculating values is possible and it depends on the chosen formula. The majorities of the known formulas are obtained for high-energy electrons and their approximations for low energy ones are not correct sometimes. In our calculations we selected a simple equation, which well describes the penetration depth of electrons in a wide range of their energies: $\rho z_0 = 10^{-2}E^{3/2}$, where $\rho$ is the density of matter (g/cm$^3$), and $E$ is the energy of electrons (kV).

Table I presents the recombination parameters calculated for some phosphor compositions. The results are in good agreement with data obtained in other works. Our proposed method is very sensitive to additional treatments of a phosphor surface, especially to its chemical modification or coating. As is shown from the data in Table II, the modification of phosphors by inorganic oxides changes their recombination parameters noticeably. The decrease of the diffusion-drift length of nonequilibrium charge carriers after phosphor modification is related with the buildup of strong internal electrical fields, which decelerates the migration of the minority charge carriers to the surface of a phosphor grain. On the other hand, for the holes which migrate to bulk, the less defective part of a phosphor, these electrical fields are accelerative. The number of recombination centers in bulk involved in the luminescent process, is increased in this case. In our opinion it is the main reason of enhanced CL efficiency of phosphors after surface modification.

**TABLE I.** Recombination parameters calculated for some phosphor compositions: $S/D$ is the reduced recombination velocity, $L_p$ is the diffusion-drift length of holes in a decelerating electrical field, $\tau$ is the lifetime of nonequilibrium holes, and $\eta$ is the quantum efficiency.

<table>
<thead>
<tr>
<th>Phosphor</th>
<th>$S/D$ (cm$^{-1}$)</th>
<th>$L_p$ (cm)</th>
<th>$\tau$ (s)</th>
<th>$\eta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO:Zn</td>
<td>$8.0 \times 10^5$</td>
<td>$1.7 \times 10^{-6}$</td>
<td>$1.2 \times 10^{-11}$</td>
<td>$6.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>ZnO:Zn modified by 0.5 wt % WO$_3$</td>
<td>$9.3 \times 10^5$</td>
<td>$3.2 \times 10^{-7}$</td>
<td>$3.9 \times 10^{-10}$</td>
<td>$2.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>ZnS:Cu:Al</td>
<td>$1.7 \times 10^6$</td>
<td>$1.9 \times 10^{-6}$</td>
<td>$2.7 \times 10^{-11}$</td>
<td>$2.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>ZnS:Cu:Al modified by 0.5 wt % SiO$_2$</td>
<td>$2.3 \times 10^7$</td>
<td>$7.3 \times 10^{-7}$</td>
<td>$4.1 \times 10^{-12}$</td>
<td>$4.0 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

**TABLE II.** Recombination parameters calculated for phosphors modified by inorganic oxides: $S/D$ is the reduced recombination velocity, $L_p$ is the diffusion-drift length of holes in a decelerating electrical field, $\tau$ is the lifetime of nonequilibrium holes, and $\eta$ is the quantum efficiency.

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Based on the obtained data we can calculate the values of electrical fields in a surface region of a phosphor grain. The dependence of the diffusion-drift length of nonequilibrium holes upon the intensity of a decelerating electric field is given as follows:

\[ L_p = \left( c^2 + L^{-2} \right)^{1/2} + c \]

where \( L \) is the diffusion length of holes, \( c \) is the grad \( (E/kT) \), \( E \) is the intensity of the electrical field, \( T \) is the temperature, and \( k \) is the Boltzmann's constant. The data of simulation of internal electrical fields for ZnO:Zn phosphor with or without surface modification of WO₃ are presented in Fig. 2. As the figure shows, the modification enforces the electrical fields in a phosphor grain. These data well confirm our supposition about the role of surface modifiers as a source of high intensity electric fields in the surface region. It occurs due to dynamic charging of a phosphor surface during its continuous bombardment by primary electrons. The amount of charge, which is temporarily collected on a phosphor surface, depends on its electrical conductivity and can be changed after coating. The ZnO:Zn phosphor is a semiconductor with high intrinsic electrical conductivity. There is a big difference between the surface conductivity of pure ZnO:Zn and that of the modified one. The dynamic charging of this phosphor surface increases significantly after it is coated with WO₃, which usually has low conductivity. The aforementioned is the main reason for the great sensitivity of luminescent characteristics of surface treated phosphors, especially at low energy electron excitation. The recorded increase of CL brightness of ZnO:Zn phosphor after the coating is achieved 3–4 times in our experiments.

We see inorganic oxides with low intrinsic electrical conductivity as effective modifiers for high conductive phosphors. These oxides can maintain a high dynamic charge on a phosphor surface at low energy electron bombardment that enforces internal electrical fields. Among the promising materials are the insulator-type oxides such as MgO, SnO₂, and WO₃.

The proposed method offers a simple and rapid way of controlling the main parameters of luminescent materials. The obtained results confirmed the existence of strong electrical fields in a phosphor surface region after its coating with inorganic oxides. The values of recombination parameters are very sensitive to the presence of a small amount of a coated material on the phosphor surface, which makes the proposed method unique and promising for material investigation.

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