Enhanced stability of light-emitting performances of phosphors under low energy electrons

Sergey A. Bukesov and Duk Y. Jeon
Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 373-1 Kusong-dong, Yusong-gu, Daejeon 305-701, Republic of Korea

Burtrand I. Lee
School of Materials Science and Engineering, Olin Hall, Clemson University, Clemson, South Carolina 29634-0971

(Received 12 September 2005; accepted 2 November 2005; published online 12 December 2005)

Here we demonstrate the experimental evidence of an unusually high stability of emission characteristics of phosphor screens by the intensive bombardment by low-energy electrons. The explanation of the observed emission stability is based on the assumption that the low-energy electrons enhanced the electrical conductivity of the phosphor which initiated the improvement of the light-emitting performances. © 2005 American Institute of Physics. [DOI: 10.1063/1.2142291]

Low operating voltages (<1 kV) are very attractive for the modern information displays. In this case the necessary brightness of a luminescent screen is normally achieved by applying an electron beam with a high current density. Fast degradation of light-emitting materials under high-density excitation is one of the main concerns, which makes high working voltages for commercial cathodoluminescent (CL) devices preferable.

The reduced stability of phosphors by the high-density electrons is claimed by the data obtained in both standard testing systems and cathode ray tubes (CRTs). However, the aging characteristics for vacuum fluorescent displays (VFDs) operated at low voltages and high current densities revealed that the high brightness of phosphor screen have been maintained in a continuous operating mode for more than 10 years. There is no reasonable explanation for this phenomenon.

The goal of this work is to reveal the mechanism of the unusual behavior observed in CL aging of the phosphors under the bombardment by low-energy electrons with high current density.

We investigated commercial red, green, blue (RGB) phosphors in VFDs of experimental constructions at different operating modes. A special attention was given to the characteristics of sulfide phosphors, which usually demonstrate low stability under the electron bombardment.

Our experimental results confirm the enhanced stability of the phosphors by the intense bombardment of low-energy electrons. However, these results differ from the previously reported data. Figure 1 shows aging characteristics of RGB phosphors with charge dose accumulated on the phosphor screen. The theoretical data calculated by Pfahnl’s law usually describe the aging of the phosphors well for CL devices operating at high voltages. Figure 2 shows the degradation characteristics of ZnS:Ag,Al phosphor at several display operating voltages. According to our results, the Coulombic degradation of the phosphor is reduced at low applied voltages that are quite different from the data reported by other researchers, for example.

Figure 3 shows the dependence of normalized CL brightness of the Zn2SiO4:Mn phosphors with different mean particle size on the charge dose accumulated on the screen. The degradation characteristics of the phosphors with submicron size are initially the same as for the bulk samples. However, after 200 h of the display operation we observed an unusual growth of CL brightness of the submicron size phosphors. The initial CL brightness of bulk samples was higher than the submicron ones, but after 1000 h of the electrons bombardment, the fine particle phosphors became brighter. The charge doses passing through the phosphor screen during our experiment were extremely huge. For CRT it will take more than 200 years to collect this amount of charge! Pfahnl’s law describes well the degradation of the bulk samples, but the behavior of submicron size Zn2SiO4:Mn phosphor is difficult to explain by the known theories.

The known theories for degradation of phosphors in CL devices deal with high accelerating voltages of primary electrons and do not take into account the characteristics of low-energy electron excitation. The main peculiarity of the display operating at low voltages is removing the electrical...
charge of primary electrons from the screen through the phosphor layer. Obviously, the electrical conductivity of a phosphor composition plays an important role.

The total power applied to low voltage CL display is distributed between the power of electron beam and that dissipated in a phosphor layer. The last one is usually converted to Joule heating. The CL brightness of a phosphor screen is separated in a phosphor layer. The last one is usually converted into Joule heating. The CL brightness of a phosphor screen is presented by both the cathode matter and the residual gas in the atmosphere. This power is specific for CL devices operating at low voltages and high current densities and it is the main reason for their reduced brightness.

By substituting the Equation (1) to Pfahnl’s law, the equation describes aging of the CL brightness derived below

$$B = \frac{B_0}{1 + CN} = k(\frac{U_0 - R_L}{1 + CN})$$

where $C$ is the “burning” parameter of material, $N$ is the total number of electrons hitting on the exposed area of 1 cm$^2$.

Thus the CL brightness of a display depends on the current density and electrical resistance of the phosphor screen. The resistance of a phosphor can be changed under the electron bombardment. The reasons for these changes are the following: decomposition of a phosphor and contamination of the phosphor surface by components of the display atmosphere. These two physical processes can be described separately.

The changes in the resistance of a phosphor layer result from the electron-stimulated contaminations of the surface by both the cathode matter and the residual gas in the atmosphere. This can be described by the following empirical formula:

$$R_L = R_{ph} + (R_{S} - R_{ph}) \tanh(\omega I t),$$

where $R_{ph}$ is the resistance of the phosphor composition, $R_S$ is the resistance of the contaminants deposited on a phosphor surface, $t$ is the operating time, and $\omega$ is the coefficient which characterizes the phosphor surface contamination. Both characters and relative value of electron-stimulated changes of the electrical resistance of phosphor layer are determined by the difference between resistance of the deposited contaminants and that of phosphor composition ($R_S - R_{ph}$).

Based on the similar nature of the electron-stimulated changes in electrical conductivity of a phosphor composition and its Coulombic degradation (Pfahnl’s law), we propose the following formula for aging of the electrical resistance of a phosphor composition:

$$R_{ph} = \frac{R_{ph0}}{1 + CN},$$

where the $R_{ph0}$ is the resistance of a phosphor layer before degradation. This formula describes the decrease of phosphor resistance by the decomposition process of the matrix stimulated by the electron beam. By substituting Eq. (3) into Eq. (2), the ultimate equation for CL brightness becomes

$$B = \frac{k[IU_0 - R_L(R_{ph} + (R_{S} - R_{ph}) \cdot \tanh(\omega I t))]}{1 + CN},$$

where

$$R_{ph} = \frac{R_{ph0}}{1 + CN}.$$
the decrease of CL brightness related to the degradation of a phosphor composition. It is described by the denominator rising from the Pfahnl’s law.

The second process is described by the numerator in Eq. (5). The resistance of a phosphor is normally decreased with the electron beam irradiation. It rises from the formation of various defects in phosphor matrix where the metal ions and high conductive oxides can be produced by electron-stimulated processes. The Ba signals observed on the phosphor surface are ascribed to the barium compounds evaporated from the phosphor surface.9–12,14,15 The Ba signals observed on the phosphor surface are ascribed to the barium compounds evaporated from the phosphor surface.9–12,14,15 The Ba signals observed on the phosphor surface are ascribed to the barium compounds evaporated from the phosphor surface.9–12,14,15

The results of the Auger electron spectroscopy (AES) analysis on the phosphor surface. The ZnS:Cu,Al and ZnGa2O4:Mn green emitting phosphors in VFD devices are shown in Table I. Continuous operation of the VFDs for about 2000 h results in the increase of Zn and Ba signals on the phosphor surface and the decrease of O signals. The observed increase of the Zn concentration on the phosphor surface results from the decomposition of the phosphor matrix stimulated by electron irradiation where the volatile oxygen compounds can be released from the surface.9–12,14,15 The Ba signals observed on the phosphor surface are ascribed to the barium compounds evaporated from the phosphor surface.9–12,14,15 Increase of Ba concentration on the phosphor surface after aging also improves its conductivity.

Decrease of the electrical resistance of a phosphor is accompanied by the increase of electron beam power that plays a positive role for maintaining the brightness of a phosphor screen. This effect is specific only for the CL devices operating at low voltages and high current densities. It brings the main difference to the degradation processes of light-emitted performances of phosphors at low- and high-energy electrons. At low current densities and for the compositions with high electrical conductivity, the proposed Eq. (5) approaches Pfahnl’s law.

We applied our model for the simulation of the degradation processes of a phosphor screen. Theoretically simulated curves together with experimental results are presented in Figs. 2 and 3. As the figures show, the real processes of phosphor aging are in good agreement with the data simulated using the proposed model. Equation (5) describes well the experimentally observed behavior of Zn2SiO4:Mn phosphor with submicron grain size.

We found a parameter that seems to be critical for maintaining of phosphor screen brightness at high density of electron excitation. It is the electron stimulation which increases the electrical conductivity of the phosphor composition. The influence of phosphor conductivity on CL performance is especially sufficient when the display device is operated at low-voltage and high-current density. The main reason for the difference in the Coulombic degradation of phosphor characteristics must be attributable to the electron bombarding of low-energy electrons or of high-energy electrons. Our results confirm the high stability of luminescence compositions to the prolonged electron bombardment even at low voltages and high current densities.

The authors acknowledge 21st Century Frontier R&D Program funded by the Ministry of Science and Technology of the Korean government.

TABLE I. The results of the Auger electron spectroscopy analysis for ZnS:Cu,Al and ZnGa2O4:Mn phosphors mixed with 10% In2O3 in VFD devices after electron irradiation for 2 (1) and 2000 (2) h. The aging mode of the VFD devices: Uo=280 V, Io=5 mA.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Phosphor</th>
<th>Zn</th>
<th>Ga</th>
<th>O</th>
<th>S</th>
<th>In</th>
<th>Ba</th>
<th>Si</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ZnGa2O4:Mn</td>
<td>11.1</td>
<td>18.2</td>
<td>60.1</td>
<td>6.8</td>
<td>2.8</td>
<td>2.8</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>ZnGa2O4:Mn</td>
<td>30.1</td>
<td>6.1</td>
<td>48.6</td>
<td>7.2</td>
<td>6.1</td>
<td>6.1</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>ZnS:Cu,Al</td>
<td>7.0</td>
<td>...</td>
<td>40.2</td>
<td>26.0</td>
<td>1.8</td>
<td>4.2</td>
<td>18.1</td>
<td>0.8</td>
</tr>
<tr>
<td>2</td>
<td>Coated with SiO2</td>
<td>32.6</td>
<td>...</td>
<td>11.2</td>
<td>41.7</td>
<td>...</td>
<td>11.2</td>
<td>1.8</td>
<td>0.2</td>
</tr>
</tbody>
</table>