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Long-Term Cathodoluminescent Characterization of Thin-Film Oxide Phosphors in a Wide Range of Electron Excitation Densities

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ABSTRACT

Long-term processes of cathodoluminescence degradation of thin film phosphors Zn_2SiO_4:Ti and Zn_2GeO_4:Mn were investigated in a wide range of e-beam energies, current and power densities. The time dependencies describing the decreasing of emission intensity have been found. At higher current densities of e-beam irradiation, the specific behavior of long-term degradation processes was observed, which is characterized by rapid initial degradation and a slower long term decrease. The most probable mechanisms are proposed for long-term processes of degradation in the investigated phosphors.

INTRODUCTION

Thin film oxide phosphors are promising for low-voltage field-emission display applications due to their appropriate color coordinates, high efficiency [1,2], and possible increased conductivity [3]. Long-term stability of phosphors is also very important for practical applications, especially for development of field-emission displays with low-voltage excitation (less than 3 keV) where excitation takes place in the near surface layer which is extremely sensitive to degradation. The degradation processes were intensely studied in a series of works [2, 4-10]. Two main mechanisms have been found to be responsible for the decrease of cathodoluminescence (CL) intensity: irreversible loss, caused by physical and chemical reactions, and reversible loss (thermal quenching), caused by thermal heating by the electron beam. Several forms of CL degradation behavior have been found previously [5-8]. Some new forms describing the long-term behavior of a series of thin film oxide phosphors have been found by the authors of the present work [2,10]. Results of more detailed studies of degradation processes are presented in the present work for a wide range of excitation energies, e-beam currents and excitation intensities for the case of phosphors with charged luminescent centers, which are most sensitive to the processes of thermal diffusion quenching.

EXPERIMENTAL

Thin films were deposited by the modified rf-magnetron method [11] with subsequent high-temperature recrystallization at 650-1050°C. CL was measured at continuous electron excitation at 1-3.5 keV, 20-200 μA and beam diameter of 3 mm which corresponds to e-beam current densities of 0.28 - 2.8 mA/cm^2 and power densities from 0.1 to 20 W/cm^2. This mode of

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measurement during 8 hours corresponds to approximately 1500 hours of excitation of a conventional 21-inch kinescope at 25 kV and 1 mA (assuming equal deposited charges per square cm during irradiation). Measurements were made on the laboratory-made prototype CRT with thin film phosphor samples mounted on the faceplate. The laboratory CRT-prototypes were fabricated using standard technology of CRTs fabrication. It included pumping to 10^{-7} Torr with degassing near 400-450C, sealing and consequent gettering. Final residual gases partial pressure was not higher than 10^{-9} Torr. Therefore the influence of residual gases may be considered as negligible. Two methods were used for avoiding possible errors caused by the instability of the e-beam and the photo detector: periodic deflection of the e-beam to the non-irradiated area and simultaneous measurement of e-beam current and energy with subsequent correction of intensity data. Both methods showed good stability and accuracy in long-term measurements of CL intensity.

RESULTS AND DISCUSSION

It was found that at power densities less than 0.5 W/cm^2 most oxide thin films phosphors do not show substantial decrease of CL intensity within the accuracy of measurements (3-5%). A decrease of CL intensity was observed at power densities greater than 1 W/cm^2 and is in a good agreement with the dependence

$$(Io/I - 1) = K \cdot t^{1/2} \qquad (1)$$

that describes a thermal diffusion process [10] of long-term degradation of CL intensity.

At the same time, at higher e-beam power densities in the range of 1-20 W/cm^2 and various current densities and energies, Zn_2SiO_4:Ti phosphors showed distinctive behavior under long-term irradiation which is revealed in a two-stage long-term dependence.

In the case of low excitation energies (< 2 keV) dependence (1) for Zn_2SiO_4:Ti films is linear (figure 1), and quenching (degradation) coefficient K increases from 0.01 to 0.1 with the increasing of current density from 0.28 to 2.8 mA/cm^2.

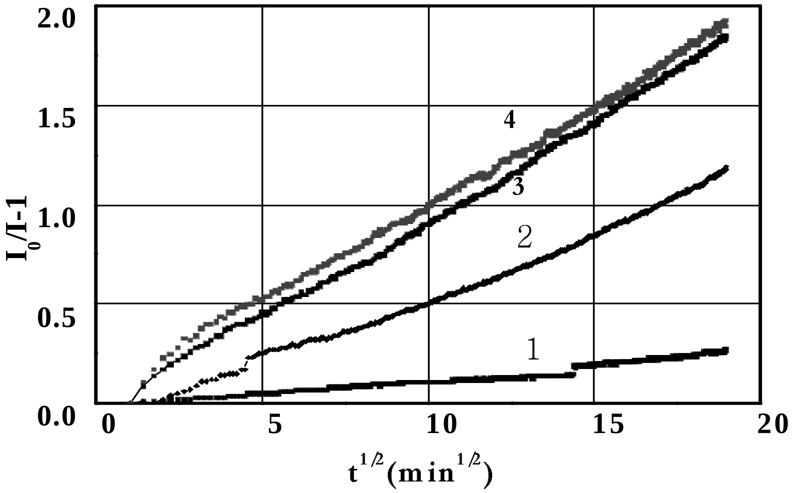

Figure 1. (I_0/I -1) vs. $t^{1/2}$ (min$^{1/2}$) plot of CL intensity of thin-films Zn_2SiO_4:Ti at 2keV and 0.71 mA/cm^2 (1), 1.42 mA/cm^2 (2), 2.12 mA/cm^2(3), 2.83 mA/cm^2(4).

At higher e-beam excitation energies (E > 2.5 keV) long-term behavior differs, though also can be described with dependence (1). It becomes a two-stage structure with a rapid initial decrease with $K = 0.2$-0.4, and a relatively flat region with $K = 0.01$ - 0.06 during consequent long-term period irradiation dose (figure 2). The rate of decrease at the initial stage increases with an increase of e-beam power density and is accompanied by a relative decrease of degradation rate during the final stage. The value of maximal decrease ($Io/I - 1$) at current density of 2.1 mA/cm^2 changes from 1.85 at 2 keV to 1.45 at 3.5 keV.

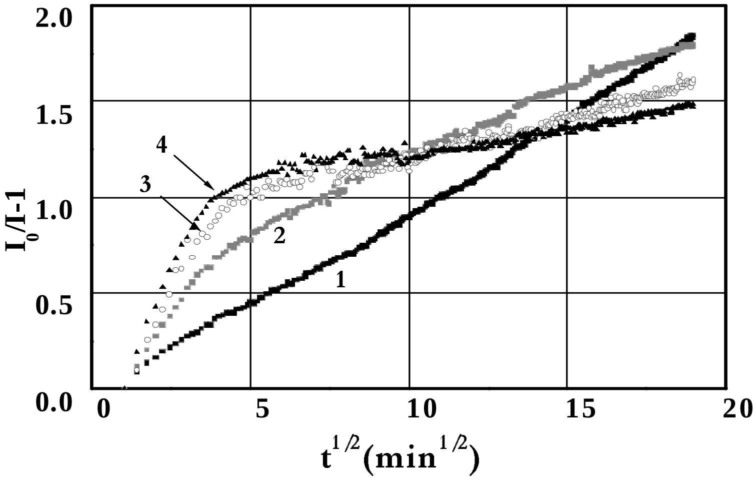

Figure 2. (I_0/I -1) vs. $t^{1/2}$ (min$^{1/2}$) plot of CL intensity of thin-films Zn_2SiO_4:Ti at 2.1 mA/cm^2 and 2 keV (1), 2.5 keV (2), 3 keV (3), 3.5 keV (4).

In the case of Zn_2GeO_4:Mn thin films, the linear behavior of dependence (1) is observed at current densities not greater than 0.28 mA/cm^2 and excitation energies of 1.5-2 keV (figure 3).

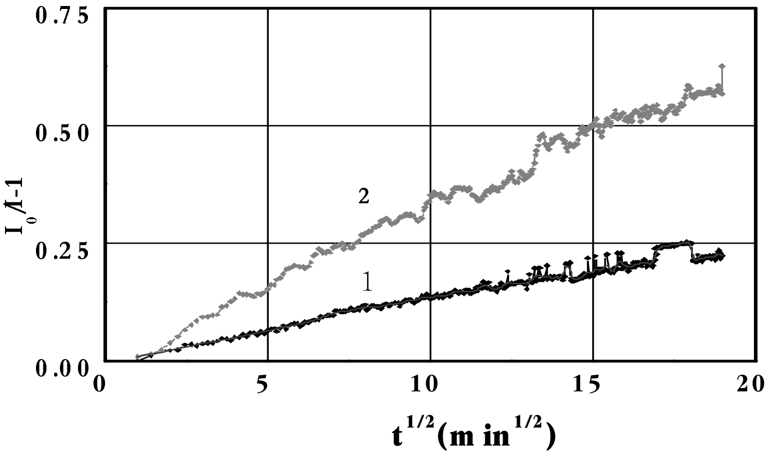

Figure 3. (I_0/I -1) vs. $t^{1/2}$ (min$^{1/2}$) plot of CL intensity of thin-films Zn_2GeO_4:Mn at 0.28 mA/cm^2 and 1.5 keV (1); 2. keV (2).

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At higher current densities it becomes a two-stage (figure 4) dependence. At e-beam energy of 1 keV the value of the maximum decrease (*Io*/*I* – 1) in Zn_2GeO_4:Mn thin films is 0.25, 0.35 and 0.70 at current densities 0.7, 1.4 and 2.1 mA/cm^2, respectively. After the region with rapid decrease, stabilization of intensity or even its partial increase (buildup) is observed. At energies higher than 1.5 keV such stabilization of intensity was not observed.

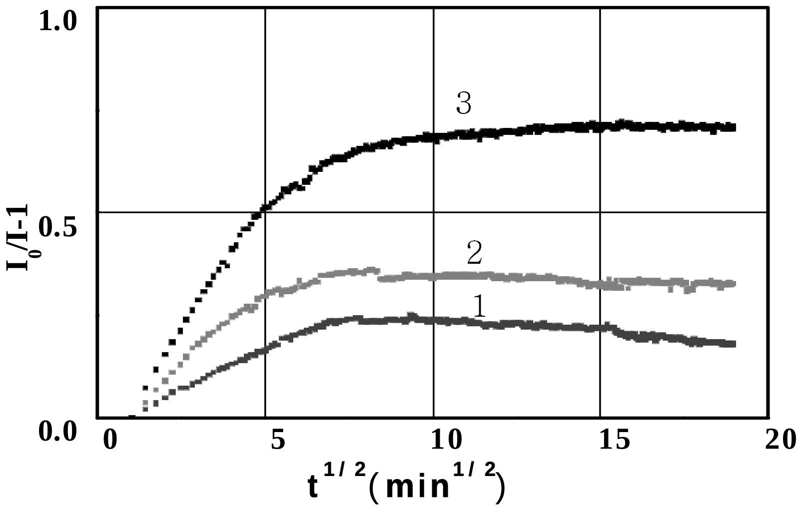

Figure 4. (I_0/I -1) vs. $t^{1/2}$ ($min^{1/2}$) plot of CL intensity of thin-films Zn_2GeO_4:Mn at 1 keV and 0.71 mA/cm^2(1), 1.42 mA/cm^2 (2), 2.12 mA/cm^2 (3).

As can be seen from the results obtained, the long-term dependence of CL of Zn_2GeO_4:Mn and Zn_2SiO_4:Ti thin film phosphors show both similar and different behavior. The common feature for both Zn_2GeO_4:Mn and Zn_2SiO_4:Ti films is the existence of the two types of long-term dependencies:

type 1 – linear dependence, characteristic for low current densities and e-beam energies;

type 2 – two-stage long-term dependence with rapid degradation at initial stage.

The difference in long-term behavior of Zn_2GeO_4:Mn and Zn_2SiO_4:Ti thin films is that in the case of Zn_2GeO_4:Mn type 1 is limited by lower currents and energies (0.28 mA/cm^2, 1.5-2 keV) as compared to Zn_2SiO_4:Ti films (0.28-2.8 mA/cm^2, 2 keV).

From basic analysis of phenomena in solids and phosphors, one may consider degradation processes to be caused by the following main mechanisms:

- temperature quenching of luminescence centers dependent only on the temperature of a sample (power or current density);
- external quenching of luminescence due to generation of free carriers trapped by the trap centers; this component also depends on non-uniformity of electron distribution in the sample, their space diffusion (drift), and trapping parameters;
- generation of defects under electron bombardment which behave as the centers of nonradiative recombination both in the volume or at the surface of phosphor;
- surface reactions (this process may be considered as special case of generation of nonradiative recombination centers on the phosphor's surface).

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Based on results obtained, the most probable mechanisms for long-term stability may be:

- intrinsic temperature quenching, which is indicated by increase of degradation coefficient with increase of current density at the same excitation energy;
- generation of nonradiative recombination centers in near-surface area, which is indicated by increase of degradation rate at higher excitation energies;

Let's discuss the possibility of mechanism of nonradiative recombination centers generation. The probability of generating defects by direct impact is small at the e-beam energies used (< 4 keV) because such energies are much less than the defect generation threshold. However, the defects may be generated by means of below-threshold mechanisms as well. In fact, several mechanisms of defect generation at below-threshold energy levels are known: multiple ionization [12] , decomposition of self-trapped holes [13], radiation-enhanced reactions [14]. Indeed, these mechanisms have been found in a series of materials [15, 16], and in particular under electron excitation [17].

When nonradiative recombination centers are generated in the near-surface region, the process of diffusion of free carriers generated in volume to nonradiative recombination centers, as well as the process of radiation-enhanced diffusion of defects take place, and degradation of CL intensity is proportional to $t^{1/2}$ [15]. Stabilization of luminescence degradation observed in Zn_2GeO_4:Mn can be explained as attaining equilibrium between generation of nonradiative recombination centers and their annealing.

Existence of the rapid stage of defects generation in Zn_2GeO_4:Mn at lower currents compared to Zn_2SiO_4:Ti correlates with the fact that the temperature of Zn_2GeO_4:Mn thin films formation (crystallization) is lower than that of Zn_2SiO_4:Ti.

CONCLUSIONS

It was found that at power densities less than 0.5 W/cm^2 most of the oxide thin film phosphors do not show substantial decrease of CL intensity. Decrease of CL intensity was observed at e-beam power energies higher than 1 W/cm^2 and is in a good agreement with the dependence $(Io/I - 1) = K \cdot t^{1/2}$ which describes a thermal diffusion process.

At higher energy densities of e-beam irradiation (in the range of 1 - 20 W/cm^2) and various current or power densities the specific behavior of long-term degradation processes in Zn_2SiO_4:Ti and Zn_2GeO_4:Mn was found which reveals as rapid degradation at the initial stage and a slow consequent decrease of intensity.

The most probable mechanisms responsible for long-term processes of degradation in the investigated phosphors are caused by internal thermal quenching due to heating by the e-beam as well as generation of nonradiative recombination centers in the near-surface area. This mechanism is in agreement with results presented in [7,8] where the chemical modification of the phosphor surface had been observed.

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