



Electron Beam Induced Degradation of CaS:Pb Thin Film Phosphor Grown by Atomic Layer Deposition

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The effects of electron (e)-beam irradiation on the luminescent and the materials properties of CaS:Pb films were investigated using structural and compositional analysis techniques. Continuous e-beam irradiation on CaS:Pb thin film for 180 min resulted in an approximately 60% decrease of cathodoluminescence (CL) intensity. Transmission electron microscopic analysis indicated that e-beam irradiation induced the precipitation of Pb. The decrease of CL intensity by e-beam irradiation was mostly caused by the decrease of Pb^{2+} luminescent center ion concentration due to the precipitation of Pb. E-beam irradiation also resulted in heavy carbonaceous contamination on the surface. The thickness of the carbonaceous layer was approximately 10 nm.

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Manuscript submitted August 8, 2002; revised manuscript received October 15, 2002. Available electronically December 31, 2002.

Alkaline-earth sulfides have been studied as luminescent materials for cathode ray tube and flat panel displays (FPDs). The thin film processes of the materials have become important to meet the requirements of high-resolution FPDs such as low-voltage field emission displays (FEDs) and thin film electroluminescent (EL) displays. For the application to low-voltage FEDs, the study on degradation and surface contamination of thin film phosphor due to electron (e)-beam irradiation is essential because the penetration depth of the e-beam, *i.e.*, illuminating film depth, is quite shallow compared to that of an e-beam accelerated by high voltage. However, the e-beam-induced damage of thin film phosphors has not been examined in view of FED application.

Earlier works reported that the CaS:Pb phosphor had been a very efficient photoluminescent phosphor.¹ Pb^{2+} ion can be incorporated easily into CaS due to the isomorphism of the crystal structures of CaS and PbS. The previous work accomplished by using conventional deposition techniques such as e-beam evaporation had reported that dimer and larger aggregate centers tend to form abundantly in the lattice with increasing concentration of Pb^{2+} ions.^{1,2} Contrarily, the present authors reported that the size of aggregates could be controlled by changing the deposition sequence of CaS and PbS, and that blue EL emission peaked at 440-445 nm and could be maintained with the Pb concentration ranging from 0.3 to 1.3 atom % by using a controlled atomic layer deposition (ALD) technique.³ Longer wavelength emission can be also obtained by controlling the incorporation method of Pb^{2+} ions into the CaS host matrix.³ The authors also presented that CaS:Pb phosphor revealed high-luminance blue cathodoluminescence (CL).⁴

In the present work, the effect of e-beam irradiation was investigated on CL and materials properties of CaS:Pb phosphor deposited by the controlled ALD. First, the dependence of CL intensity and wavelength of the CaS:Pb thin film phosphor was studied with the e-beam irradiation time. Then, the materials degradation induced by e-beam irradiation was clarified using structural and compositional analysis techniques.

In the ALD of CaS:Pb thin films, $\text{Ca}(\text{thd})_2$ (thd is 2,2,6,6-tetramethyl-3,5-heptanedionate), H_2S , and $\text{Pb}(\text{C}_2\text{H}_5)_4$ were used as the precursors of Ca, S, and Pb, respectively. The deposition temperature was 390°C and the reactor pressure was approximately 4 Torr during ALD. E-beam irradiation and CL measurement were carried out in a vacuum chamber of 10^{-6} Torr. The acceleration voltage and the current density of the e-beam were 1 kV and 25 $\mu\text{A}/\text{cm}^2$, respectively. The films were characterized using Auger electron spectroscopy (AES), X-ray diffraction (XRD), X-ray pho-

toelectron spectroscopy (XPS), and transmission electron microscopy (TEM). In the preparation of a TEM specimen, methyl alcohol and isopropyl alcohol were used to avoid the hydration of the CaS:Pb phosphor during the grinding and dimpling process. The specimen was cooled using liquid nitrogen to eliminate heating effect during TEM observation. The composition of the films was determined using Rutherford backscattering spectrometry (RBS) and energy dispersive X-ray spectroscopy (EDX).

The CaS:Pb thin films deposited by ALD were highly stoichiometric contrary to the films deposited by e-beam evaporation.² The 10 nm thick Al_2O_3 film-deposited Si wafers were used as substrates. Materials analysis showed that 0.5-1.0 atom % of oxygen was contained in the CaS:Pb phosphor while carbon was not detected. Oxygen is thought to be incorporated from the Ca precursor, $\text{Ca}(\text{thd})_2$, containing oxygen.

Figure 1 shows the dependence of CL intensity of 200 nm thick CaS:Pb films on the e-beam irradiation time. The CL intensity decreased to approximately 40% of initial intensity after continuous e-beam irradiation for 180 min. The continuous beam irradiation must accelerate the degradation of phosphor films compared to a pulsed e-beam irradiation. The previous work had reported that the

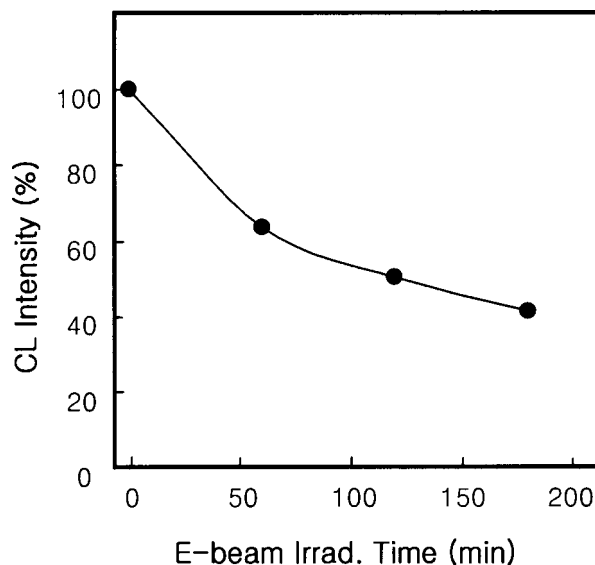


Figure 1. Dependence of CL intensity of 200 nm thick CaS:Pb film on the time of e-beam irradiation.

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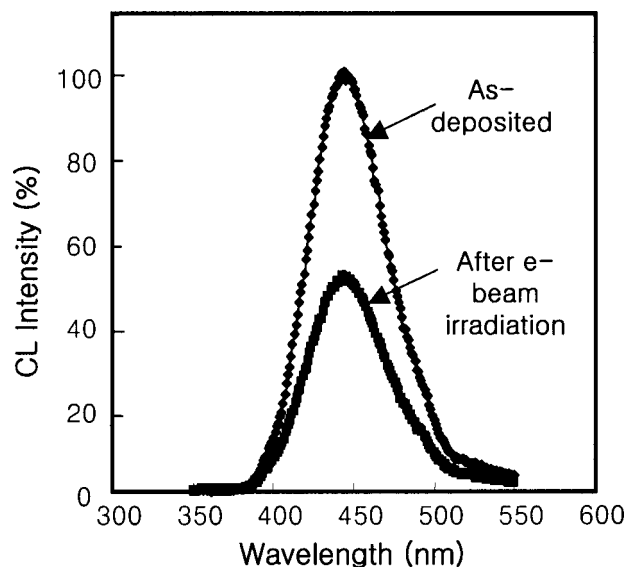


Figure 2. CL spectra of as-deposited CaS:Pb film compared to that obtained after decrease of 50% CL intensity.

decrease of CL intensity of CaS:Pb thin film phosphor had been slower than that of a ZnS:Ag,Cl powder phosphor (a commercial product) under the same experimental condition.⁴

According to the previous works describing the preparation of CaS:Pb phosphor film, the wavelength of Pb^{2+} emission was sensitively changed by varying the binding states or the environment of the luminescent ions due to Pb^{2+} ion with s^2 outer shell electron configuration.^{1,2} In the present work, the peak positions of CL spectra of CaS:Pb (0.5 atom %) and CaS:Pb (0.8 atom %) films were not shifted even after the CL intensities were decreased to 40 and 50% of the initial values by e-beam irradiation, respectively. Figure 2 shows the CL spectrum of as-deposited CaS:Pb (0.8 atom %) film in comparison with that obtained after decreasing CL intensity down to the 50% level by e-beam irradiation. This result indicates that the binding state of each luminescent center ion illuminating CL was not changed by e-beam in the host matrix.

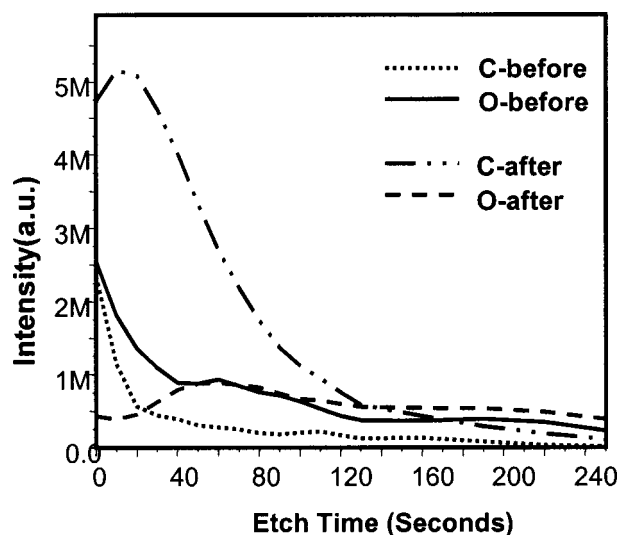


Figure 3. AES depth profile showing C contamination on CaS:Pb surface region by e-beam irradiation for 60 min, compared with that of a nonirradiated CaS:Pb surface.

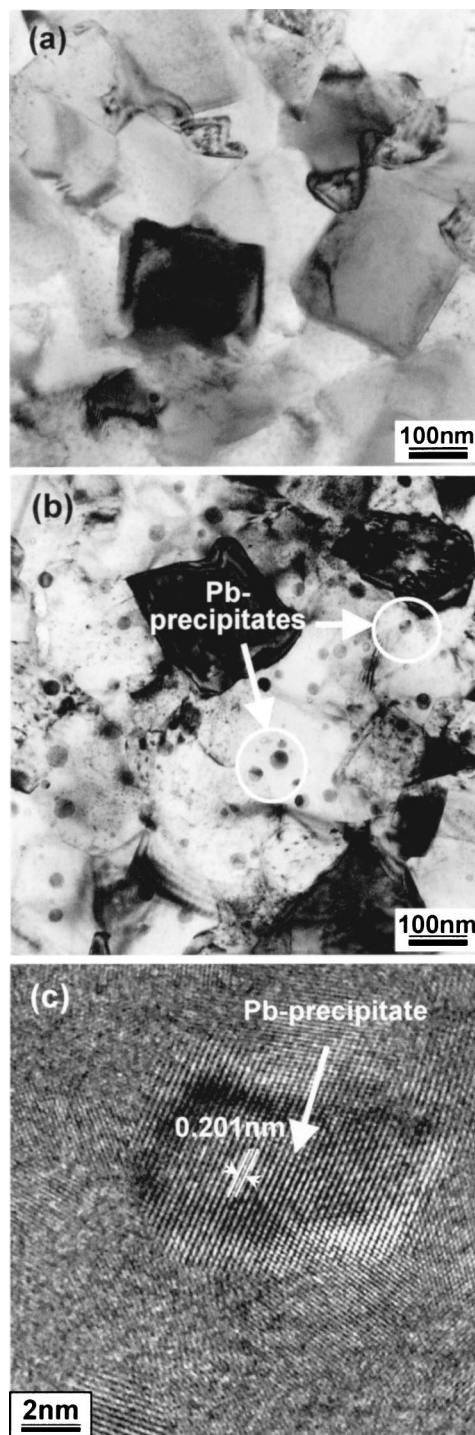


Figure 4. (a) Plan-view TEM image of as-deposited CaS:Pb film, (b) plan-view TEM image of e-beam irradiated CaS:Pb (Pb precipitates are indicated by arrows), and (c) high-resolution image showing a trace of Pb precipitate (the interplanar spacing of 0.201 nm corresponds to the {220} plane of CaS host).

The analyses of CaS:Pb thin films were carried out to clarify the reason for the CL intensity decrease. XPS and RBS study indicated that the content of Pb was not changed by e-beam irradiation (the data not shown here). The results revealed that the out-diffusion of Pb was not induced by e-beam irradiation contrary to the effect of rapid thermal annealing.⁵ However, surface analyses using XPS and AES indicated that the e-beam irradiated surface of the CaS:Pb film was heavily contaminated by a carbonaceous (C-) compound. Figure

Table I. The concentration of constituents in CaS obtained using EDX before and after e-beam irradiation for 180 min.

Sample description	Element	Grain	Grain boundary	Large area
As-deposited CaS:Pb	Ca	50.0	49.5	48.3
	S	49.0	49.9	50.9
	Pb	1.0	0.6	0.8
E-beam irradiated CaS:Pb for 180 min	Ca			48.4
	S			50.9
	Pb			0.7

3 shows the depth profile of e-beam irradiated surface in comparison with that of as-deposited CaS:Pb film. The AES depth profiles (sputter rate ~ 0.1 nm/s) indicated that 60 min of e-beam irradiation produced a C contamination layer of 10 nm. The thickness was not sensitively changed by varying the irradiation time. Only in view of penetration depth of electrons, the C contamination was not thought to be a main reason of the CL intensity decrease, because the penetration depth of the e-beam into CaS:Pb film was deeper than 100 nm under the experimental conditions used in this work as reported in the previous work.⁵ However, the effect of surface electron-hole recombination on luminance efficiency is very important in the case of an acceleration voltage as low as 1 kV.⁶ Further study on the surface recombination effect is being carried out to clarify the contribution of C contamination on CL degradation of a CaS:Pb phosphor.

Generally, the source of C contamination has been considered to be the carbon-containing residue in the phosphor that was incorporated during the preparation of phosphor materials. However, in the present work, the source of carbon might be residual gas or some contaminant in the vacuum chamber of 10^{-6} Torr, because the CaS:Pb film deposited by ALD did not contain a detectable amount of carbon. The residual gas molecules containing carbon might adsorb easily on reactive sites produced by e-beam irradiation, and then give rise to a C layer by continuous e-beam. The C layer was also observed even on the surface of bare Si wafer after 60 min of e-beam irradiation under the same experimental condition.

Structural analysis using XRD and TEM was carried out to observe the structural degradation induced by e-beam irradiation of a thin film phosphor. However, the XRD data did not show any considerable change after e-beam irradiation. To clarify the degradation in view of microstructure, CaS:Pb films degraded by continuous e-beam for 180 min was studied using TEM (Philips TECNAI F20 and Philips CM20T/STEM, 200 kV).

Figure 4 shows plan-view TEM images of an e-beam irradiated CaS:Pb film in comparison with that of as-deposited CaS:Pb film. The low magnification TEM image of Fig. 4a shows a typical plan-view image of as-deposited CaS:Pb film. Contrarily, randomly distributed dark spots (diam 1-30 nm) were observed in the e-beam irradiated sample as shown in Fig. 4b. The spots were rapidly evaporated while increasing the magnification, *i.e.*, the current density of the e-beam. The round-shaped dark spots are considered to be Pb precipitates because Pb has low melting point and high vapor pressure compared to other metals relevant in this experiment.⁷ Melting and eruption of Pb nanocrystals during TEM observation had been

observed and explained to be induced by thermal and charging effect of the e-beam.⁷ The high resolution TEM image in Fig. 4c shows the trace of a Pb precipitate that was taken just after eruption of Pb by the focused e-beam irradiation. The results in Fig. 1 and 4 indicated that CL degradation by e-beam irradiation was mainly due to the formation of Pb precipitates because the metallic Pb precipitates did not contribute to the CL emission.

A possible mechanism to form the Pb precipitates could be the neutralization of S^{2-} ions to S^0 in PbS ionic bonding through Auger electron transition induced by e-beam irradiation.⁸ Then ionic bonded Pb^{2+} ions are released from the network bonding in ionic lattice. Under the local repulsive electrostatic interaction produced by secondary and Auger electron excitation in the illuminated area, the Pb ions can be moved from their original sites and neutralized by electrons. The earlier work had reported also that oxidized Pb^{2+} ions easily formed metallic precipitates by e-beam irradiation.⁷

Table I shows the concentration of constituents in CaS:Pb thin film before and after e-beam irradiation. The concentration was obtained during TEM observation using EDX. As listed in Table I, the concentration of Pb ions inside a grain of as-deposited CaS:Pb film was higher than that in the grain boundary. However, only the average Pb concentration of the e-beam irradiated sample could be obtained over a large area because the Pb precipitates were rapidly evaporated by the focused e-beam during analysis. The average Pb concentration of the e-beam irradiated sample (0.7 atom %) was a little lower than that of the as-deposited sample (0.8 atom %), and the slight decrease of Pb content is thought to happen during TEM analysis. The results implied that e-beam irradiation did not eliminate Pb atoms from the phosphor layer but induced the precipitation of metallic Pb.

In summary, the degradation of CaS:Pb thin film phosphor caused by e-beam irradiation was investigated on luminescent and materials properties. The concentration of Pb was not decreased but the CL intensity was decreased to 40% of initial intensity by 180 min of e-beam irradiation. The present study clarified for the first time that the decrease of CL intensity was caused by the reduction of Pb^{2+} -luminescent center ions, *i.e.*, by forming the metallic Pb precipitates.

Acknowledgment

The authors would like to thank Dr. S.-Y. Kang for his support in the CL measurement. The Korea Ministry of Information and Communications financially supported the accomplishment of the present work.

References

1. S. Asano, N. Yamashita, and Y. Nakao, *Phys. Status Solidi B*, **89**, 663 (1978).
2. N. Yamashita, *J. Phys. Soc. Jpn.*, **53**, 2400 (1984).
3. S. J. Yun, Y. S. Kim, and S.-H. K. Park, *Appl. Phys. Lett.*, **78**, 721 (2001).
4. S. H. K. Park, S.-Y. Kang, J.-W. Byun, K.-S. Suh, Y. I. Kang, and S. J. Yun, in *Proceedings of the International Display Research Conference, IDW/Asia Display '01*, Society for Information Display, p. 1099, Oct 16-19, 2001.
5. S. J. Yun, S. H. K. Park, J.-W. Byun, and K.-S. Suh, in *Proceedings of Information Displays Manufacturing Conference 02*, Society for Information Display, p. 277, Jan 29-31, 2002.
6. C. J. Summers, in *Proceedings of the 3rd International Display Workshops '96*, Society for Information Display, p. 13, Nov 27-29, 1996.
7. Z. W. Pan, Z. R. Dai, and Z. L. Wang, *Appl. Phys. Lett.*, **80**, 309 (2002).
8. N. Jiang, J. Qiu, and J. Silcox, *Appl. Phys. Lett.*, **77**, 3956 (2000).