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Fabrication of CaS:Pb blue phosphor by incorporating dimeric Pb^{2+} luminescent centers

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The CaS:Pb phosphor emitting blue electroluminescence (EL) induced by dimeric Pb^{2+} luminescent centers was deposited using the controlled atomic layer deposition technique. The effect of the incorporation method and concentration of Pb^{2+} ions on the color of high luminance CaS:Pb phosphor was investigated at the deposition temperatures of 350 and 400 °C. The blue EL emission at 440–445 nm could be maintained with the Pb concentration ranging from 0.6 to 2.5 mol % contrary to the earlier works that had demonstrated very sensitive dependence of color on Pb^{2+} concentration. The selective incorporation of dimeric Pb^{2+} ions was attributed to the reactivity of tetraethyl lead as Pb precursor as well as the controlled deposition technique. © 2001 American Institute of Physics. [DOI: 10.1063/1.1343478]

The distinct advantages of thin film electroluminescent (EL) devices such as ruggedness, long lifetime, fast response, and wide operating temperature as well as a wide viewing angle, have made EL displays the most reliable display with the longest lifetime among flat panel displays. However, the lack of suitable blue EL phosphor has been one of the big impediments in commercializing full color EL display, although extensive effort has been paid for its development for more than two decades.

A few earlier studies of CaS:Pb, one of the blue phosphors, reported that CaS:Pb was a very efficient photoluminescent phosphor, but not a bright EL phosphor.^{1–3} According to the earlier studies, divalent Pb ions (Pb^{2+}) easily agglomerated, and CaS:Pb phosphor generated luminescence from all of monomer, dimer, and larger agglomerates of Pb^{2+} ions.^{1,2} Furthermore, the luminescence properties were shown to strongly depend on the environmental conditions of Pb^{2+} in a host matrix because Pb^{2+} ion has a s^2 outer electron configuration. Then, the wavelength of EL emission, i.e., the color of CaS:Pb phosphor, continuously changed from UV to green as the concentration of Pb^{2+} increased. The blue EL originated from Pb^{2+} dimer centers could be obtained only by regulating the concentration of Pb^{2+} ions within ranges from 1.0 to 1.5 mol %. The luminance was also much lower than the brightness level required for commercialization.^{2,3}

Contrary to earlier works, the present authors reported that blue CaS:Pb phosphor with high luminance could be deposited using atomic layer deposition (ALD).⁴ The luminance at a voltage of 25 V higher than the threshold voltage L_{25} was higher than 80 cd/m² at 60 Hz, which was the highest luminance amongst blue EL phosphors ever reported.

In this letter, procedures to fabricate CaS:Pb phosphor containing Pb^{2+} ions as the most preferable state for blue emission is introduced utilizing the advantages of the ALD technique to deposit a film layer by layer.^{5,6} Especially, $\text{Pb}(\text{C}_2\text{H}_5)_4$ (tetraethyl lead, TEL) was first used as a Pb pre-

cursor in the deposition of CaS:Pb by the present authors because TEL was expected to easily form a dimeric intermediate state. The dimeric compound of TEL, $\text{Pb}_2(\text{C}_2\text{H}_5)_6$, is known to be isolated as a stable compound via the reaction between TEL molecules.

In the ALD process of CaS:Pb, bis(2,2,6,6-tetramethylheptanedionato)-calcium [$\text{Ca}(\text{thd})_2$] and H_2S were used as the precursors of Ca and S, respectively.⁷ The deposition rate of ALD is defined by the deposited thickness per cycle.^{5,6} For example, one cycle of PbS deposition is composed of the pulses of TEL, N_2 , H_2S , and N_2 purge. The deposition rates of PbS were 0.02 and 0.15 Å/cycle at 350 and 400 °C, respectively, so that PbS layer deposited per cycle was much thinner than one monolayer under the experimental conditions used in this work. The composition and thickness of CaS:Pb layers were determined by Rutherford backscattering spectrometry.

Figure 1 illustrates the cross-sectional schematic diagram of the CaS:Pb film deposited by ALD. The controlled ALD proceeded by repeated alternate deposition of CaS (thickness: T_{CaS}) and PbS (thickness: T_{PbS}) layers. T_{CaS} was much bigger than T_{PbS} because the content of Pb in CaS:Pb was to be less than a few mol %. The PbS layer with thick-

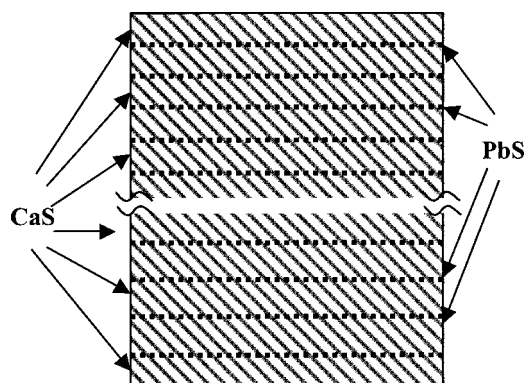


FIG. 1. Schematic cross-sectional diagram of CaS:Pb phosphor deposited by ALD.

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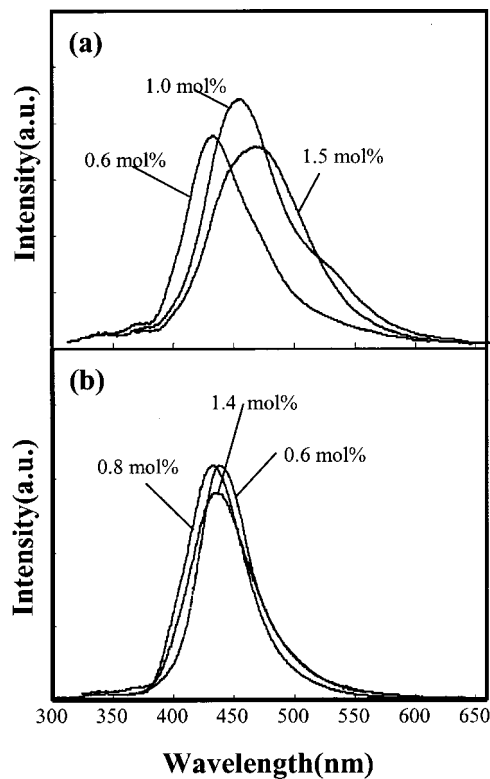


FIG. 2. (a) EL spectra of CaS:Pb EL phosphors containing 0.6 mol % (A), 1.0 mol % (B), and 1.5 mol % (C) of Pb^{2+} , deposited at 350 °C; (b) EL spectra of CaS:Pb EL phosphors containing 0.6 mol % (D), 0.8 mol % (E), and 1.4 mol % (F) of Pb^{2+} , deposited at 400 °C.

ness T_{PbS} was deposited by one or several cycles of PbS deposition to be much thinner than one monolayer of PbS. The total thickness of CaS:Pb phosphor layer was n times of the sum of T_{CaS} and T_{PbS} if alternate deposition was repeated by n times.

In order to investigate the effect of the incorporation method on the color of CaS:Pb phosphor, CaS:Pb films were deposited by varying Pb^{2+} concentration in two different methods and at two different temperatures, 350 and 400 °C. The concentration of Pb^{2+} ions in CaS:Pb can be increased by increasing T_{PbS} sandwiched between CaS layers of a fixed thickness (i.e., bigger T_{PbS} with fixed T_{CaS} and total thickness). In the ALD process, T_{PbS} can be increased only by increasing the number of cycles of PbS deposition because the deposition rate is constant at a given temperature. Alternatively, the content of Pb^{2+} can also be increased by inserting the PbS layers of a fixed value of T_{PbS} with a constant cycle number between CaS layers more frequently (i.e., smaller T_{CaS} with fixed T_{PbS} and total thickness). The data in Fig. 2, Table I, and Table II clearly demonstrate differences in the color of CaS:Pb EL when the concentration of Pb is increased by two different methods.

TABLE I. The Commission Internationale de l'Eclairage (CIE) color coordinates of CaS:Pb EL devices deposited by ALD at 350 °C.

Sample ID	Pb^{2+} (mol %)	T_{PbS} (Å)	PbS (number of cycles)	CIE color coordinates (x, y)
A	0.6	0.04	2	(0.17, 0.13)
B	1.0	0.08	4	(0.17, 0.18)
C	1.5	0.12	6	(0.18, 0.20)

TABLE II. The CIE color coordinates of CaS:Pb EL devices deposited by ALD at 400 °C.

Sample ID	Pb^{2+} (mol %)	T_{PbS} (Å)	PbS (number of cycles)	CIE color coordinates (x, y)
D	0.6	0.15	1	(0.15, 0.11)
E	0.8	0.15	1	(0.14, 0.10)
F	1.4	0.15	1	(0.15, 0.10)
G	2.5	0.15	1	(0.14, 0.12)

First, the concentration of Pb^{2+} ion was increased by increasing T_{PbS} , i.e., the number of PbS cycles, for CaS:Pb EL devices A–C at the deposition temperature of 350 °C. As listed in Table I, both T_{PbS} and the number of cycles in samples B (1.0 mol % of Pb) and C (1.5 mol %) were approximately 2 and 3 times larger than those of sample A (0.6 mol % of Pb), respectively. The result showed that the color coordinates were moved from (0.17, 0.13) to (0.18, 0.20) with increasing Pb concentration from 0.6 to 1.5 mol %. The EL spectra of samples A–C in Fig. 2(a) also demonstrated that EL peaks were shifted from blue to greenish blue as increasing Pb content. The results indicate that the larger agglomerates of Pb^{2+} ions were formed by higher Pb concentration if the content of Pb^{2+} was increased by incorporating thicker PbS layers in the CaS/PbS laminated structure at a deposition temperature. This result is consistent with the earlier works showing that the emitting color of CaS:Pb changed continuously from UV to green with increasing Pb content by using conventional deposition methods.^{1–3}

Second, the Pb content in CaS:Pb phosphor was increased by incorporating the PbS layers of a fixed thickness more frequently into CaS host matrix at the temperature of 400 °C. The thickness T_{PbS} was 0.15 Å incorporated by one cycle of PbS deposition. Figure 2(b) illustrates the EL spectra of CaS:Pb EL devices, D, E, and F containing 0.6, 0.8, and 1.4 mol % of Pb, respectively. The spectra reveal only blue EL peaks centered at 440–445 nm in contrast with the result shown in Fig. 2(a). The color coordinates were also almost constant as (0.15, 0.10) with Pb concentration ranging from 0.6 to 2.5 mol % as listed in Table II. These results indicate that deep blue EL emission could be obtained with Pb concentration ranges much wider than the range of 1.0–1.5 mol % reported by earlier works. When the PbS layer was deposited by one cycle and the deposition rate was much lower than one monolayer per cycle, the formation of larger aggregates could be suppressed regardless of Pb^{2+} concentration in CaS:Pb unless the Pb content is too high to maintain the crystallinity of phosphor layer.

EL spectra in Fig. 2 also demonstrate a fact of significance to this study. In the samples with Pb content of 0.6 mol % and T_{PbS} much thinner than one monolayer, UV peaks attributed to Pb^{2+} monomers were not observed. The UV peaks were not detected even from the samples containing Pb less than 0.2 mol % (the data not shown here).

These results in Fig. 2(b) and Table II are not in accordance with the earlier works carried out using PbCl_2 , PbBr_2 , $\text{Pb}(\text{thd})_2$, and lead diethyldithiocarbamate as Pb precursors which reported the presence of UV peaks at low concentration of Pb and the strong dependence of color on Pb content.^{3,7} In the present results, the absence of UV peaks

should be perceived as evidence supporting the distinct reactivity of TEL to induce the preferable incorporation of Pb^{2+} ions as dimeric centers. TEL molecules are shown to easily form a dimeric intermediate state during the ALD process and help incorporate Pb^{2+} ions in a CaS host matrix as dimeric centers.

The data listed in Tables I and II also indicate that the color of CaS:Pb phosphor more strongly depended on the cycle number of PbS deposition rather than T_{PbS} . Colors of samples A–C shifted to green compared to the samples D–G, although the T_{PbS} of samples A–C were thinner than those of samples D–G as shown in Tables I and II. The reason must be because the numbers of cycles for samples A–C were larger than those of samples D–G, and the repeated cycle of PbS deposition enhanced the formation of agglomerates.

The method described in this letter to increase the content of luminescent centers without causing deterioration of blue color is very useful to fabricate high luminance phosphor unless the content of the luminescent center is high enough to deteriorate the crystallinity of the phosphor layer. Especially, the choice of a proper precursor of Pb (TEL) was very effective in selectively incorporating dimeric Pb^{2+} ions. This fabrication method was successfully used to fabricate

CaS:Pb blue phosphor of the luminance L_{25} higher than 80 cd/m^2 at 60 Hz that was several tens of times higher than the earlier results of CaS:Pb EL devices.^{2,3}

In summary, blue EL emission peaked at 440–445 nm could be maintained with the Pb concentration ranging from 0.6 to 2.5 mol % by controlling the incorporation method of Pb^{2+} ions in CaS host matrix. The reactivity of TEL as a Pb precursor, to easily form dimeric intermediate state during ALD process, was very effective to selectively incorporate Pb^{2+} dimer centers.

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