Blue-Emitting CaS:Pb Thin Film Electroluminescent Devices Fabricated by Controlled Atomic Layer Deposition

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Abstract

Lead-doped calcium sulfide(CaS:Pb) thin film electroluminescent devices were deposited using atomic layer deposition(ALD). CaS:Pb is a very promising blue phosphor showing very high luminance and the color coordinate close to the blue of cathode ray tube. The luminance, L_{25}, of CaS:Pb(1.6 mol.%) EL device was higher than 80 cd/m^2 at a driving frequency of 60Hz. The color coordinates of blue EL emission of CaS:Pb deposited by ALD are consistent with the Pb concentration ranging from approximately 0.5 to 3 mol.%.

Introduction

Electroluminescent(EL) display can be briefly described as the most reliable flat panel display of the simplest structure among flat panel displays. In spite of the well-known advantages, EL display has not been assured to be preferable full color display because of the lack of blue EL phosphor. Thus extensive effort has been concentrated on the study of blue EL phosphors for more than one decade since 1980's.

Calcium sulfide has been considered to be advantageous as the host material of color display phosphors due to the wider band-gap and larger lattice constant than those of ZnS. However, CaS has not been frequently studied for blue EL phosphors compared to SrS having similar band-gap, lattice constant, and crystalline structure to those of CaS. The reason can be explained that it is difficult to deposit stoichiometric CaS film of high crystallinity using conventional physical deposition techniques, such as evaporation and sputtering, etc.[1,2].

A few earlier works had reported that the CaS:Pb phosphor had generated luminescence from monomer, dimer, and larger agglomerates of Pb^{2+} ions and the wavelength of peak maximum of EL spectrum had depended on the concentration of Pb^{2+} in CaS:Pb phosphor, and then the color had been continuously changed from ultraviolet to green by increasing the concentration of Pb^{2+} ion [1,2]. The blue EL emission at approximately 450 nm had been assigned as an emission from dimers and had been predominant at a concentration below 1 mol.% [2] or ranging from 1.0 – 1.5 mol.% [3]. The luminance had not exceeded a few cd/m^2 with a driving frequency of 1 kHz [1, 3].

Recently, the present authors reported that Pb-doped CaS was a very promising blue phosphor showing very high luminance and the color coordinate close to the blue of cathode ray tube [4]. In this work it is presented that the color coordinates of blue EL emission of CaS:Pb were consistent with the Pb concentration ranging from approximately 0.5 to 3 mol.% in contrast to the earlier works. The results indicates that the color, i.e., the state of Pb^{2+} ion, is almost consistent as long as the crystallinity is not considerably degraded by the excess amount of Pb in CaS matrix.

Experiment

In the present work, the phosphor and insulating layers of CaS:Pb EL devices were deposited using atomic layer deposition (ALD) technique. The deposition temperature of CaS:Pb layer was in the range of 350 to 400°C. The precursors of Ca, S, and Pb were bis(2,2,6,6-tetramethylheptanedinato)-calcium, hydrogen sulfide, and tetraethyl lead, respectively. The insulating layer used in the double insulating thin film EL devices was aluminum oxide deposited using ALD.

Results and Discussion

The composition of CaS layer grown in the present work was quite stoichiometric. The microscopic observation of CaS and CaS:Pb films illustrated that the ALD-grown CaS forms well developed cubic structure and the size of the crystallites was almost identical to the thickness of the film. Especially, the great improvement of the EL characteristics was accomplished by using tetraethyl lead as Pb-precursor compared to earlier works using coordination compounds of Pb [3,5].

Table 1 presents that the color of CaS:Pb EL devices is independent of the concentration of Pb ranging from 0.6 to 2.5 mol.%. The CIE color coordinates (x, y) are in the range of x=0.14 - 0.15 and y=0.10 - 0.12. The controlled growth of Pb^{2+} dimer is considered to be attributed to the reaction behavior of precursor, tetraethyl lead, used in the deposition. Even at a Pb concentration lower than 0.1 mol.%, the UV peak induced from the monomer of Pb^{2+} ion was very small in the EL spectrum of CaS:Pb EL device.

The electroluminescence of CaS:Pb EL devices strongly depends on the crystallinity of CaS:Pb layer. The degradation of color and luminance at a Pb concentration higher than 3 mol.% can be explained to be due to the degradation of crystallinity of CaS matrix because there is approximately 20 % of lattice mismatch between CaS and PbS. The electroluminescence of Pb^{2+} ion of $6s^2$ outer electron configuration is easily influenced by environmental conditions in host material.

Table 1. The CIE color coordinates of CaS:Pb EL devices deposited by ALD.

Pb concentration (mol%)	CIE color coordinate(x, y)	
	x	y
0.6	0.15	0.11
0.8	0.14	0.10
1.0	0.15	0.11
1.4	0.15	0.10
2.0	0.15	0.11
2.5	0.14	0.12

Figure 1 illustrates the EL spectra of CaS:Pb EL devices containing Pb of 0.6, 0.8, and 1.4 mol.%. The differences between the EL peaks are shown to be in the order of experimental error. In contrast to those of earlier works, the EL spectra show narrow single peaks of electroluminescence of Pb^{2+} ion and the shape and position do not sensitively depend on the Pb concentration.

The best results on the luminance of CaS:Pb EL devices were obtained with the Pb concentration of 1.0 to 2.0 mol.%. The luminance, L_{25}, of CaS:Pb(1.6 mol.%) EL device was approximately 80 cd/m^2 at a driving frequency of 60Hz as shown in Fig. 2. The high luminance blue EL of CaS:Pb promoted the expectation to full color EL display although further investigations on the reliability including luminous efficiency and aging behavior, etc., and the process compatibility of CaS:Pb EL devices are still in progress. The luminous efficiency and aging behavior strongly depended on the choice of insulating layers in CaS:Pb EL devices of double insulating structure.

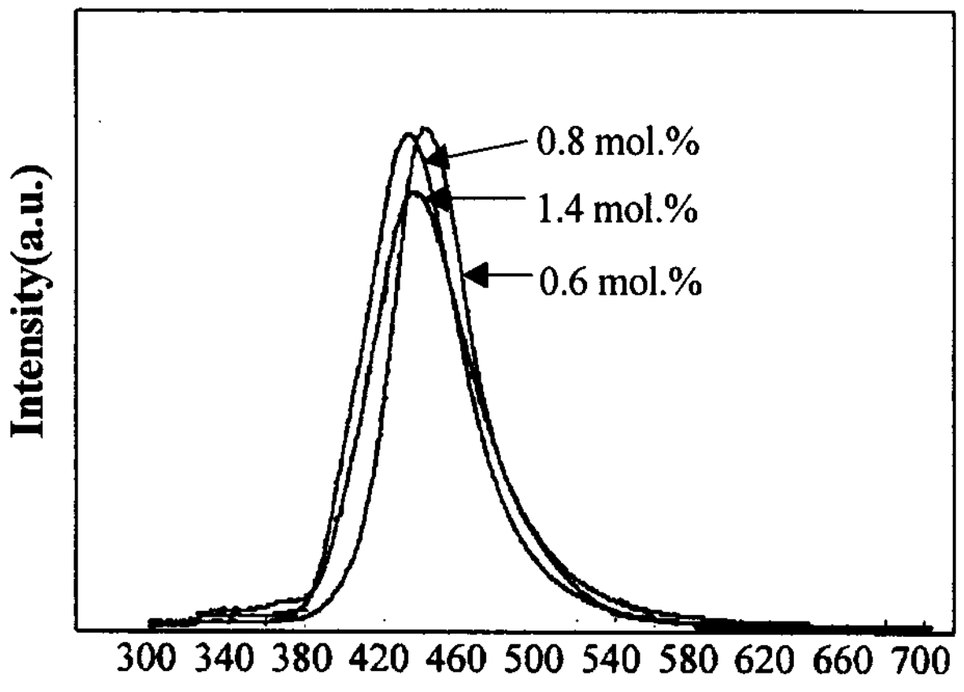

Figure 1. EL spectra of CaS:Pb EL devices grown using ALD.

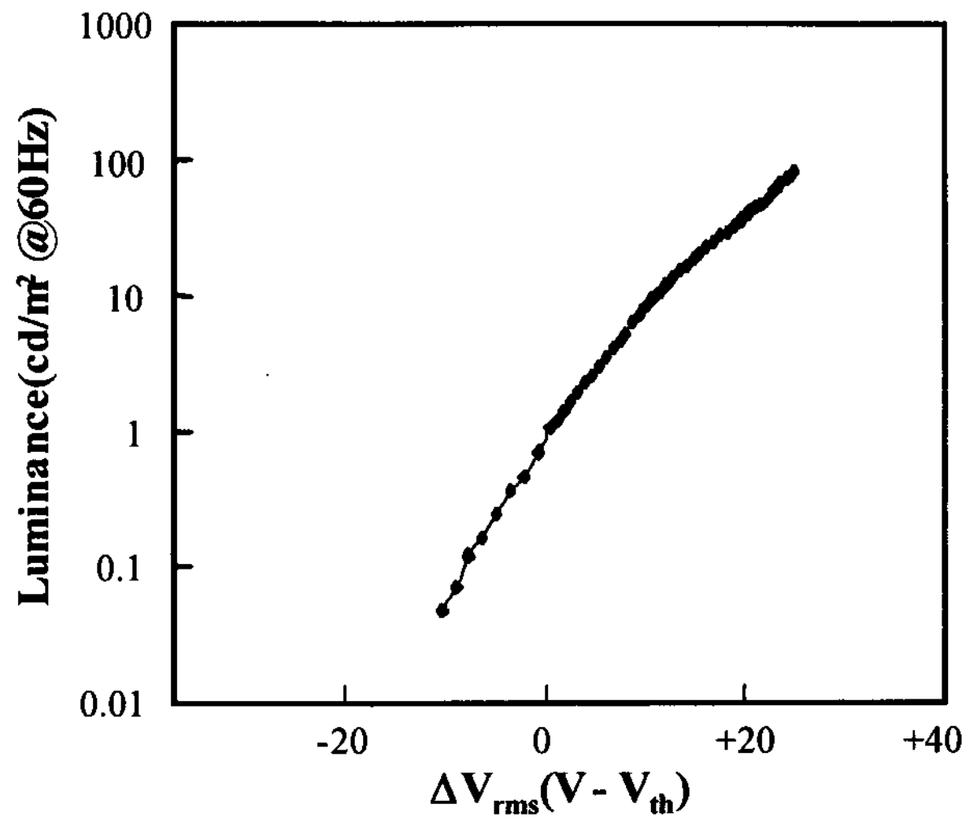

Figure 2. The luminance-voltage curve of CaS:Pb (1.6 mol.%) EL device with driving frequency of AC 60 Hz

Conclusion

Lead-doped calcium sulfide(CaS:Pb) deposited using ALD is a very promising blue phosphor showing very high luminance and the color coordinate close to the blue of cathode ray tube. The luminance, L_{25}, of CaS:Pb(1.6 mol.%) EL device was higher than 80 cd/m^2 at a driving frequency of 60Hz. The color coordinates of blue EL emission of CaS:Pb deposited by ALD are consistent with the Pb concentration ranging from approximately 0.5 to 3 mol.%. The controlled growth of Pb^{2+} dimer is considered to be attributed to the reaction behavior of precursor, tetraethyl lead, used in the deposition.

Acknowledgement

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