Effects of ZnS Insertion on the Characteristics of CaS:Pb Thin Film Phosphor

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Abstract

The effects of ZnS insertion on the characteristics of CaS:Pb phosphor were investigated. The intensity of photoluminescence of ZnS inserted CaS:Pb excited by 347nm were increased while that excited by 254nm was unchanged, compared to those of CaS:Pb thin film. The electroluminescent display having ZnS inserted CaS:Pb showed lower threshold voltage and higher efficiency than those of CaS:Pb ELD device.

1. Introduction

Alkaline-earth sulfides have been well known as the luminescent materials for flat panel displays such as electroluminescent display (ELD), plasma display panel (PDP), and field emission display (FED). Especially, thin film alkaline-earth sulfide phosphors based on SrS, deposited by sputtering and atomic layer deposition method, have been intensively investigated for the application of ELD.[1] In the case of CaS based thin film phosphor, however, just several works had been reported.[2]

CaS:Pb phosphor known to emit blue photoluminescence has been studied for the use of low voltage driving FED and ELD.[3,4] The luminescent properties of CaS:Pb thin film phosphor grown by atomic layer deposition (ALD) have attracted much interests since the first report on the high electroluminescence property by this group.[5] The CaS:Pb phosphor, however, showed relatively low luminescence efficiency when fabricated as ELD device. Several efforts such as codoping and rapid thermal annealing have been made to increase the electroluminescent properties, but no significant improvement was obtained.

Previous studies on the photoluminescence excitation (PLE) and PL spectra of ALD grown CaS:Pb phosphor revealed that energy transfer from PbS monomer to the Pb aggregated centers might be the main factor for the blue emission.[6] This led us to consider the addition of ZnS thin film in the CaS:Pb phosphor since ZnS has band-gap of 349.5nm, showing similar value for CaS:Pb monomer absorption peak.

Here, we attempt to elucidate the luminescent mechanism of ZnS containing CaS:Pb phosphor and increase the electroluminescent efficiency of CaS:Pb thin film phosphor.

2. Experimental

CaS:Pb thin films were grown on two different substrates (A and B) by an atomic layer deposition method using bis(2,2,6,6-tetramethylheptanedionato) calcium [$Ca(thd)_2$], H_2S, tetraethyl lead [$Pb(C_2H_5)_4$] as the precursors of Ca, S and Pb, respectively. Substrate A is an aluminum oxide coated Si. Substrate B was prepared by deposition of aluminum oxide and ZnS followed by in-situ annealing at the temperature of 450°C for 6 hours. CaS:Pb films were deposited at the temperature of 380°C. The concentration of Pb dopant was 0.55 atomic %. ZnS thin films were deposited at the substrate temperature of 300°C using diethylzinc and H_2S as the precursors of Zn and S, respectively. Photoluminescent spectra were measured at room temperature by using mercury lamp with wavelengths of 254 and 347nm as excitation sources. The electroluminescent properties were measured by fabrication of standard double insulator EL devices using alumina, deposited by ALD at the temperature of 350°C, as the dielectric layer and ITO and Al as the contact electrodes. The luminance and efficiency were measured using 500Hz AC standard applied voltage waveform with rise and fall times of 2μs and a pulse width of 16μs.

3. Results and discussion

The Figure 1 shows typical photoluminescence spectra of ALD grown CaS:Pb phosphor. The photoluminescence excitation spectrum of CaS:Pb thin film at room temperature consisted of a group of band A and a group of band C. The band peaking at

347 is known to be responsible for the excitation of Pb monomer center.[7] The emission spectrum shows a broad band peaking around 440~450 nm, which depends on the Pb concentration. The emission spectra excited by 347nm showed increased luminescence compared to that excited by 254nm, indicating absorption at 347nm plays an important role for the blue emission.

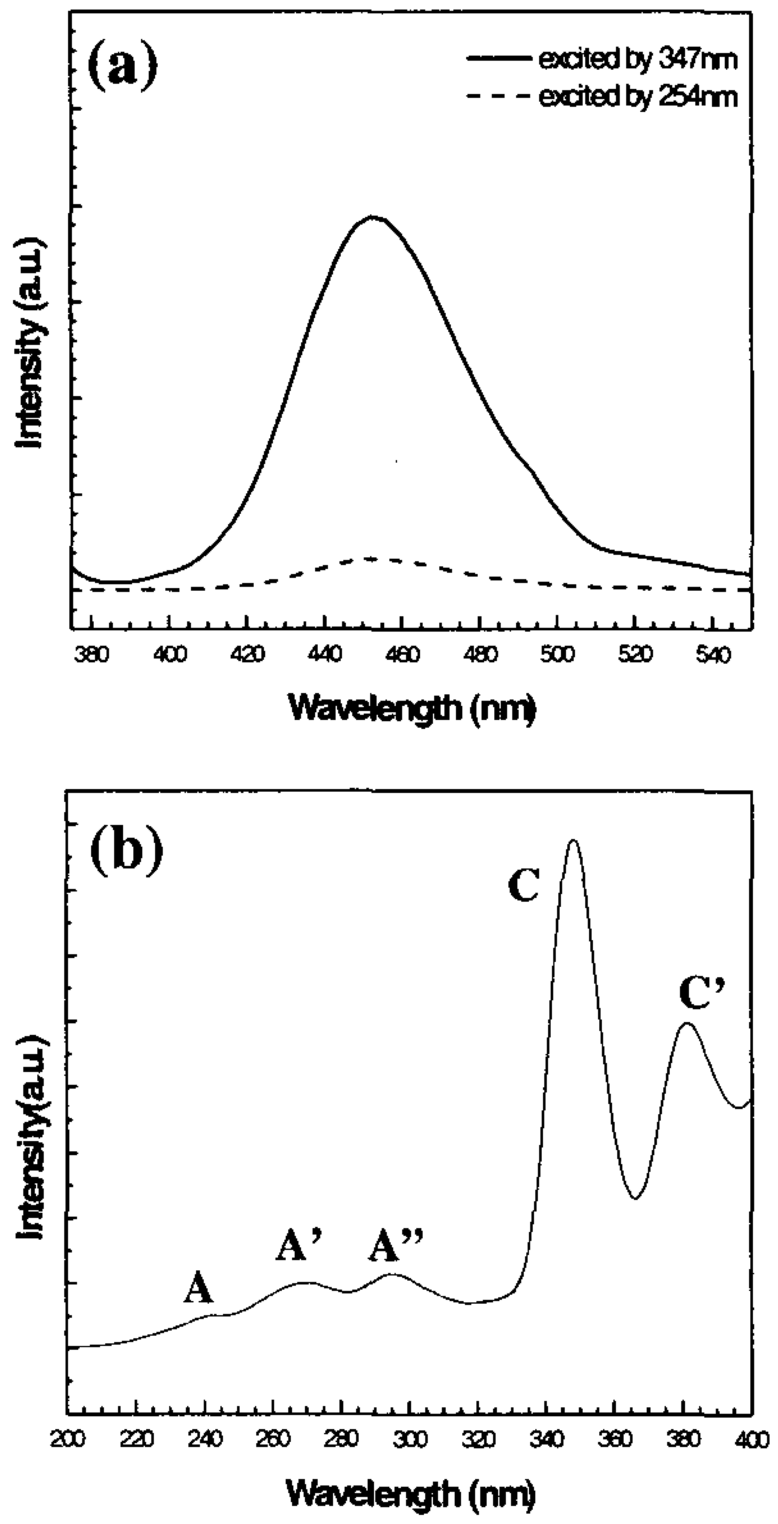


Figure 1. (a) PL spectra of ALD grown CaS:Pb phosphor; (b) photoluminescence excitation (PLE) probed at 455nm of ALD grown CaS:Pb.

Figure 2 shows PL spectra of ALD grown CaS:Pb and ZnS/CaS:Pb thin films excited by 254nm and 347nm. When ZnS is deposited under CaS:Pb layer, emission spectra excited by 254nm of CaS:Pb and ZnS/CaS:Pb phosphor showed similar intensity while PL excited by 347nm shows significant difference in luminescence intensity with same position of emission peak. The addition of ZnS layer increased not only the emission intensity excited by 347 nm, but increased the excitation intensity. Figure 3 shows photoluminescence excitation (PLE) of blue emission (450nm). The excitation spectra of ZnS/CaS:Pb phosphor also shows increased intensity at 347 nm, indicating that efficient energy absorption at 347 nm could enhance the energy transfer to the active blue-emitting Pb center.

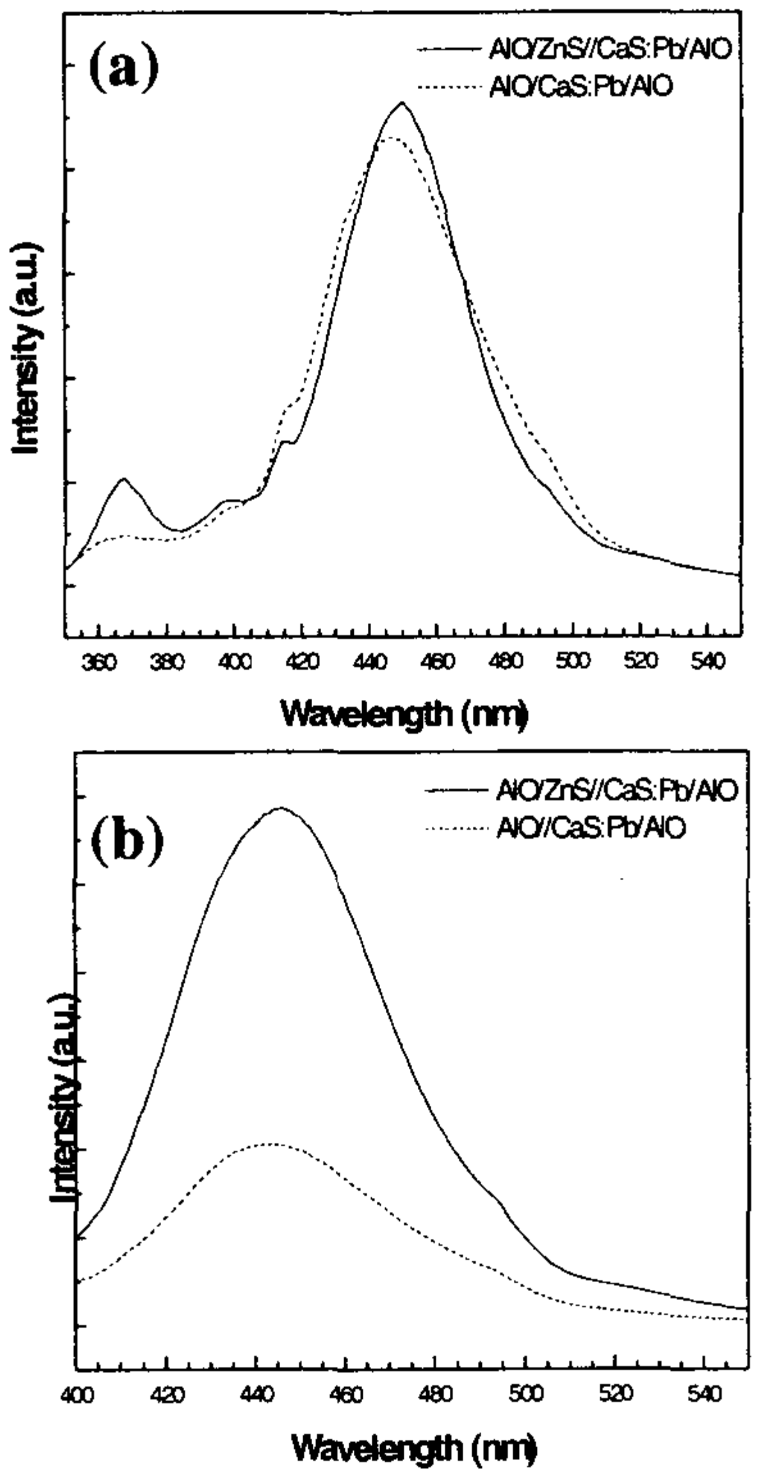


Figure 2. PL spectra of CaS:Pb and ZnS/CaS:Pb thin films ; (a) excited by 254nm, (b) excited by 347nm.

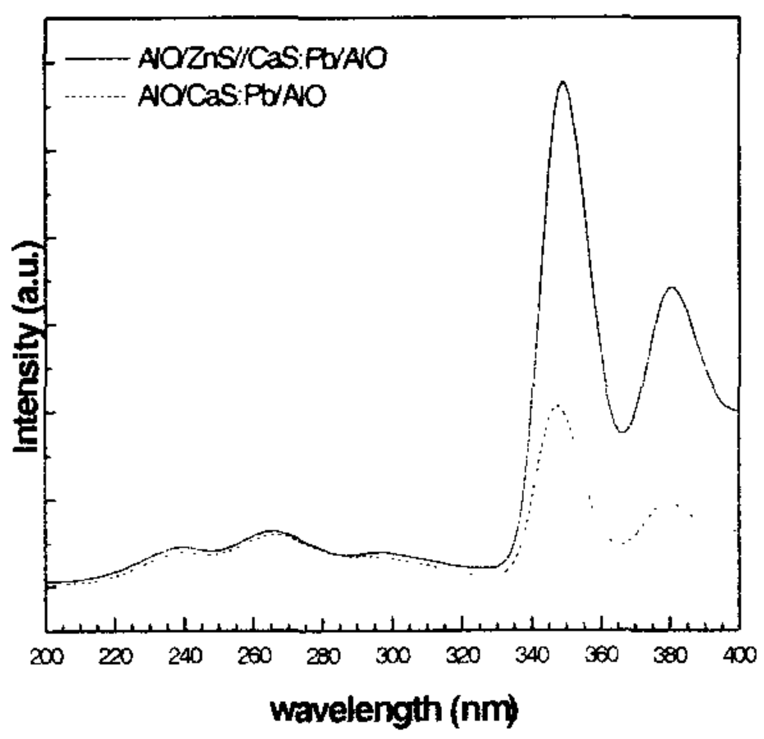


Figure 3. Photoluminescence excitation (PLE) spectra of CaS:Pb containing thin film phosphor probed at 450nm.

We investigated the effect of ZnS layer on the electroluminescence of CaS:Pb phosphor. One of the main drawback of CaS:Pb blue phosphor might be high clamping filed, which results in high driving voltage. The high clamping filed of blue phosphor prevents us from fabricating ELD with thick phosphor. Since the insertion of ZnS layer induces increase of phosphor layer, we need to optimize the ZnS thickness. Although ALD growth gives relatively thin dead layer compared to other deposition method, it is important to obtain improved crystallinity of CaS:Pb phosphor from the early growth stage to have high luminance. Therefore, ZnS layer having good crystallinity would be proper for the insertion layer of ELD. We carried out XRD analysis of ALD grown ZnS layer deposited on the Al_2O_3 coated Si wafer. The XRD patterns in Figure 4 showed that ZnS has hexagonal structure and good crystallinity with thickness of 75 nm.

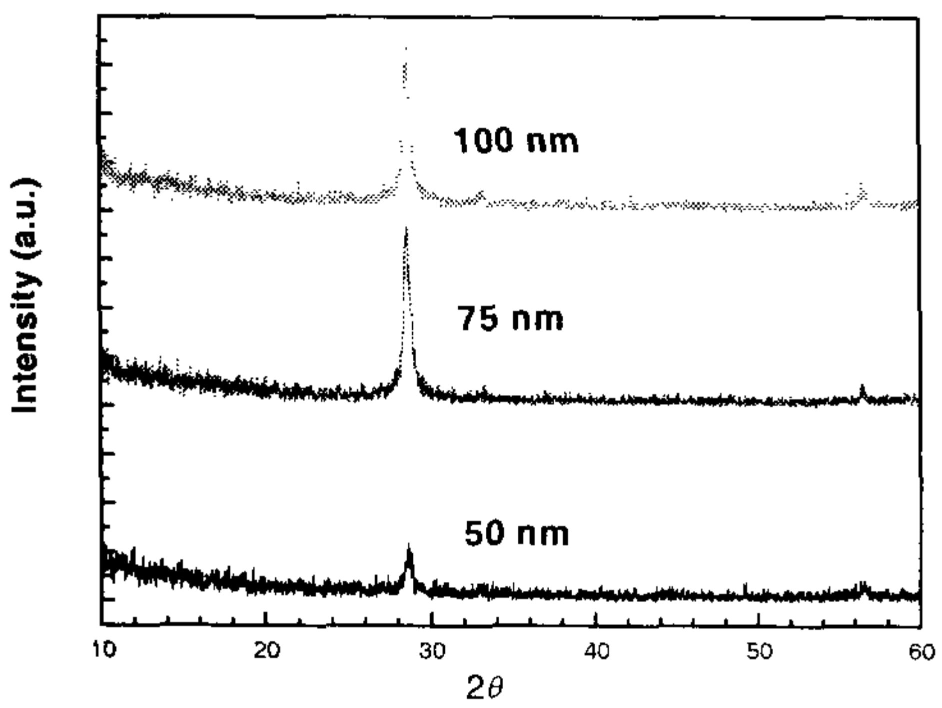


Figure 4. X-ray diffraction patterns of ZnS thin film deposited on the Al_2O_3 coated Si substrate.

Figure 5 shows L-V curves of CaS:Pb containing ELDs. All ELDs showed color coordinate of (0.16,0.16). Although insertion of ZnS layer causes increase of phosphor thickness, the threshold voltage of ELD including ZnS layer was rather decreased compared to that of CaS:Pb device. The ELD consisted of just CaS:Pb layer shows shallow turn-on and lower luminance compared to those containing ZnS layer. In addition, the efficiency of ELDs containing ZnS layer was increased by three or four times according to the thickness of ZnS layer compared to ELD of CaS:Pb single layer.

The mechanism of ELD is quite different from the photoluminescence and there is no direct clue for the changed ELD property. The structural change for the ZnS containing CaS:Pb phosphor that may affect the ELD property was investigated to clarify the increased ELD properties. Figure 6 shows surface morphologies of 28nm thick CaS:Pb thin film that deposited on the amorphous Al_2O_3 thin film and crystalline ZnS thin film. CaS:Pb deposited on the crystalline ZnS film showed columnal structure, indicating ZnS affects early stage growth of CaS:Pb.

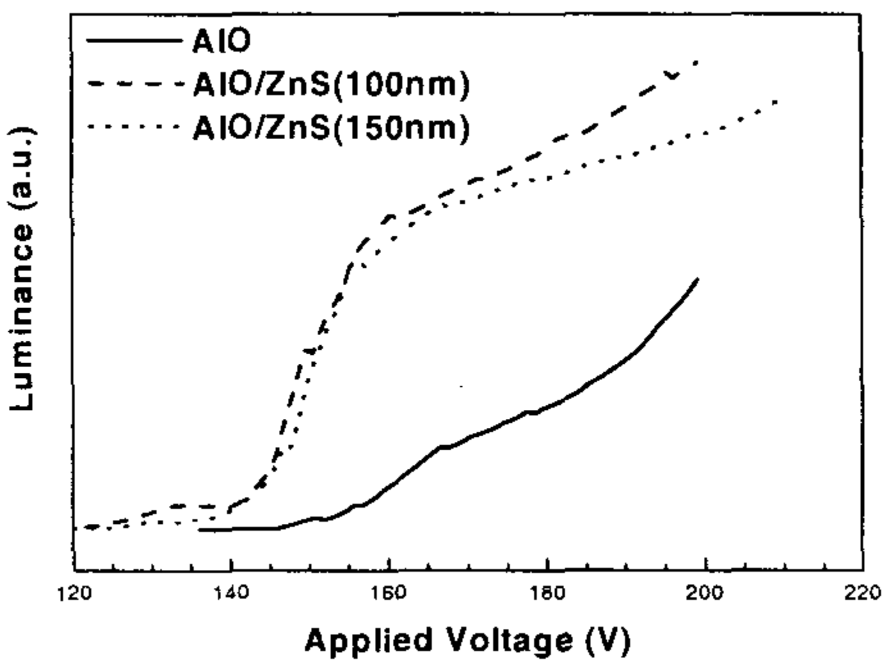
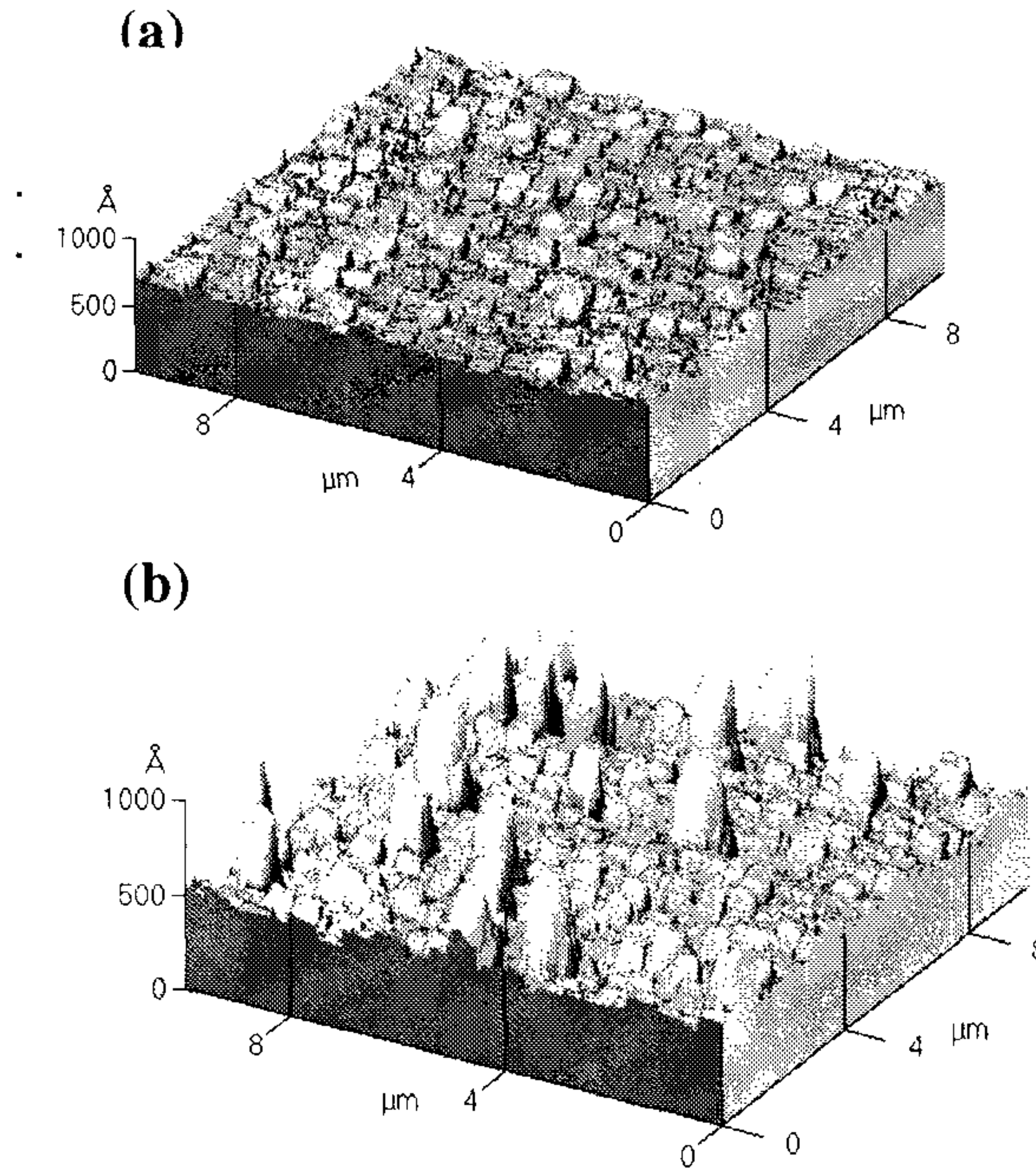


Figure 5. L-V graphs for the CaS:Pb ELD, 100nm thick ZnS containing CaS:Pb ELD, and 150 nm thick ZnS containing CaS:Pb ELD.



	$R_{p\text{-}v}$	Rms. rough.	Aver. rough	Surface area
a	344 Å	37.9 Å	29.0 Å	100.2μ^2
b	842 Å	91.1 Å	59.0 Å	100.3 μ^2

Figure 6. AFM images of 28 nm thick CaS:Pb phosphor thin film deposited on the (a) amorphous Al_2O_3 and (b) 150 nm thick ZnS thin film.

4. Conclusion

Insertion of ZnS layer under the CaS:Pb thin film phosphor enhance the photoluminescent and electroluminescent properties. Although the mechanism for the improvement of ELD characteristics is not clearly understood yet, this shows new approach for the development of thin film phosphor.

5. References

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