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# Photoluminescent and structural properties of CaS:Pb electron beam deposited thin films

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## Abstract

The structural and optical properties of electron beam deposited CaS:Pb thin films were investigated as a function of annealing temperature and lead concentration. X-ray diffraction measurements show weak crystallinity for such layers. Although this improves with higher annealing temperatures, no difference in the grain size could be seen by means of atomic force microscopy. This can be explained by columnar growth or relaxation of strain. At high annealing temperatures (1000 °C for 2 min) and sufficiently high lead concentrations (0.74 at%), a bright blue photoluminescence could be observed. Excitation spectra were acquired showing different excitation bands.

## 1. Introduction

CaS:Pb has, for a long time, been known to exhibit efficient blue photoluminescence (PL) [1].  $\text{Pb}^{2+}$  is a so-called  $S^2$ -ion, having a  $6s^2$  ground state. The  $6s^16p^1-6s^2$  transition is efficient, allowed and luminescent in the UV or blue regions, depending on the host lattice [2].

While some work has been performed on the PL characteristics of CaS:Pb powders, almost no results are available for thin films. A few years ago, CaS:Pb received some attention as a blue emitter for thin-film electroluminescent applications [3, 4], but the possibilities seemed rather limited at that time. Recently, however, promising results of CaS:Pb layers grown by means of ALE (atomic layer epitaxy) have been reported [5].

Rapid thermal annealing (RTA) has already shown to be very effective to improve the brightness of PL and electroluminescence (EL) of SrS:Cu,Ag and CaS:Cu,Ag thin films [6–8]. In the present work, the effects of RTA and lead concentration on the optical and structural properties of CaS:Pb thin films were studied.

## 2. Specimen preparation and experimental data

CaS:Pb layers (thickness about 1200 nm, deposition rate  $2 \text{ nm s}^{-1}$ ) were made by electron beam evaporation (ESV6 electron gun in a Leybold Univex 450 vacuum system) from a pressed pellet of CaS (Cerac 99.99%) and thermal evaporation of elemental lead (Johnson Matthey

& Co) in an alumina crucible. Corning Vycor (Corning 7913), which has high temperature resistance and high UV transparency, was used as a substrate.

The optimum growth condition of CaS:Pb thin films are determined by two conflicting demands. To get a sufficiently high crystallinity, the substrate temperature has to be at least 500 °C. However, because of the low sticking coefficient of lead, low substrate temperatures are necessary to obtain a sufficiently doped CaS thin film. As a compromise a substrate temperature of 250 °C was used. The pressure prior to film deposition was about  $2 \times 10^{-4}$  Pa. During evaporation H<sub>2</sub>S was added up to a pressure of  $6 \times 10^{-3}$  Pa in order to reduce the sulfur deficiency in the CaS thin films. Post-deposition annealing was performed in a RTA unit (AST SuperHeatSystem 1000) at 700–1000 °C for 2 min in a N<sub>2</sub> flow. Alternatively, a classic anneal was performed in a quartz tube furnace at 680 °C for 45 min, also in a N<sub>2</sub> flow. Emission spectra were measured using a microchannel plate intensified optical multichannel analyser (EG&G OMA III). To obtain emission spectra, the films were excited using a pulsed nitrogen laser at a wavelength of 337 nm and a pulse time of 800 ps (PRA LN1000). The maximum energy per pulse was 2.5 mJ. For excitation spectra a high-pressure Hg lamp (125 W) and a UV monochromator (Carl Zeiss M4 QIII) were used. The structural properties and chemical composition of the layers were investigated using x-ray diffraction (XRD) (Siemens D5000 diffractometer) and x-ray photoelectron spectroscopy (XPS) (Perkin Elmer Phi 5500 ESCA system), respectively.

### 3. Results and discussion

#### 3.1. Evaporation of the dopant

In preliminary experiments a tungsten boat was used to evaporate the lead dopant. This led to a problem of the reproducibility of the effective lead concentration: the evaporation rate was difficult to stabilize during the production of the films due to the change of the effective resistance of the crucible upon deposition. A solution was to use a tungsten crucible around an alumina interior covered with a lid having a small hole. In this way, the evaporation rate of the lead dopant was easy to control and was stable during the entire deposition. All dopant concentrations mentioned are effective concentrations, measured with XPS and expressed in atomic percentages.

#### 3.2. Structural properties

From the acquired XRD patterns (not shown) we conclude that the CaS:Pb thin films deposited have only weak crystallinity (low intensity of the main XRD peaks), even after a post-deposition heat treatment. The low substrate temperature during deposition may be the reason for this low quality. However, it is seen that the crystallinity of electron beam evaporated CaS (undoped) thin films remains low, even at higher substrate temperatures (500 °C). The films are preferentially oriented along [220], in agreement with earlier research on CaS:Eu and results from the literature [9].

*3.2.1. Influence of post deposition heat treatments.* Although the intensity of the [200] and the [220] peaks are low, an increase of both peak intensities is visible with increasing annealing temperature. The evolution of the peak width of the main XRD peaks ([200] and [220]) as a function of the annealing temperature is shown in figure 1. It is seen that the peak width decreases with increasing RTA temperature. It can also be seen that the effect of a classic anneal is almost the same as for a RTA treatment at 800 °C for 2 min. Without taking into

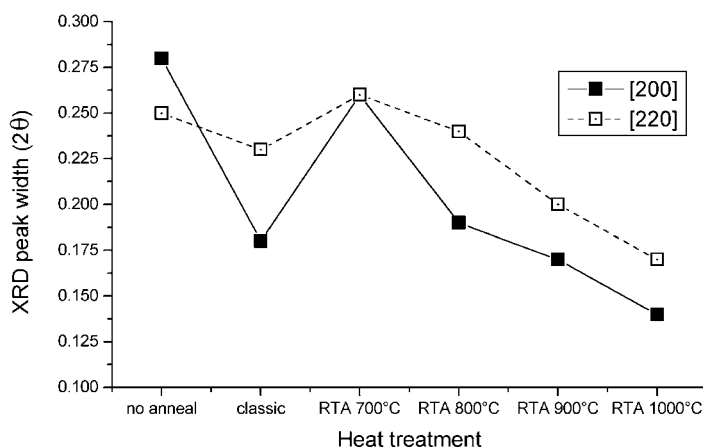


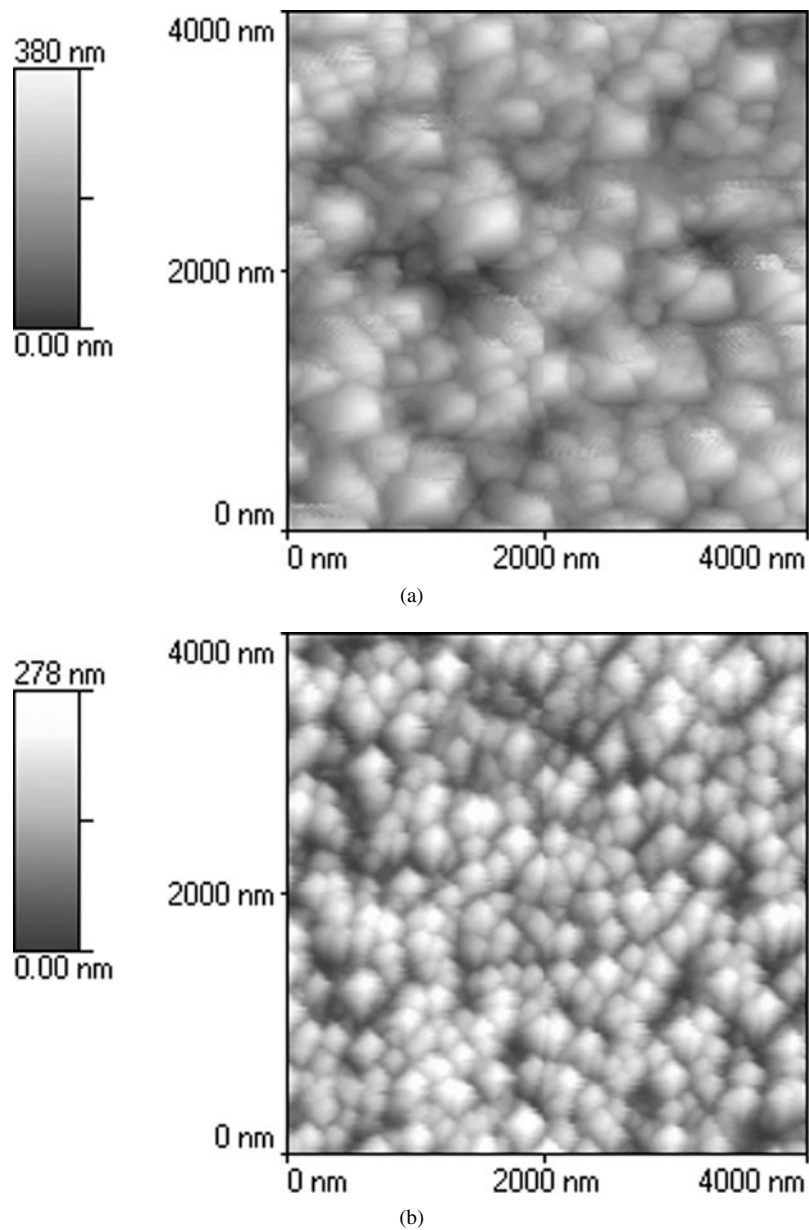
Figure 1. XRD peak width as function of heat treatment.

account strain in the layers, a decrease in the XRD peak width is attributed to an increase in grain size. Therefore we also investigated the layers using atomic force microscopy (AFM) (figures 2(b) and 2(c)). Very small grains are visible on the surfaces of the thin films (estimated diameter 20–30 nm). There is no effect of annealing on the visible grain size, which is quite remarkable considering the XRD results. Also, it should be mentioned that the layers have a large surface roughness (300 nm or 25% of the thickness of the thin films). It is possible that after the annealing process grain growth occurred in depth, leading to some kind of columnar growth. However it is also possible that the decrease in the peak width is due to the relaxation of strain in the CaS:Pb thin films after annealing, because this also influences the size of the XRD peak width. Because AFM is a surface technique, no details can be seen in the bulk of the layer. Cross section scanning electron microscopy (SEM) or TEM will therefore be performed in the future to learn more about the internal structure of the CaS:Pb layers.

**3.2.2. Influence of lead concentration.** No effect was seen in the XRD peak height and peak width with changing lead concentration. Figures 2(a) and 2(b) show AFM images of an undoped CaS thin film and a CaS:Pb thin film respectively. For the undoped CaS layer a grain size of 500 nm is estimated, while for the CaS:Pb thin film a grain size of 30 nm is seen. This is a very important result which obviously limits the possibilities of CaS:Pb for thin-film EL. Indeed, large grains are necessary for EL, in order to limit electron scattering at grain boundaries. If some sort of columnar growth appears in CaS:Pb, EL in these layers are expected to be efficient. If this is not the case, solutions have to be searched in order to increase the grain size, such as codoping with Ag [7]. Possibly lead acts as a nucleation centre at the initial stages of layer formation, leading to too many individual (small) crystallites. Again, the large roughness of the layers is to be noted.

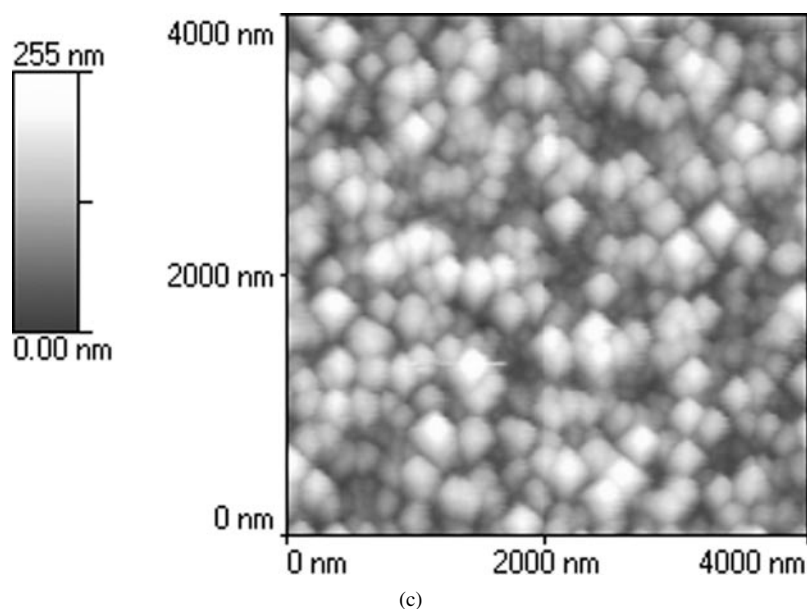
### 3.3. Emission

**3.3.1. Influence of post-deposition treatments.** No PL emission was visible in unannealed CaS:Pb thin films. The PL spectra of differently annealed layers are shown in figure 3. From this figure it can be seen that the PL intensity is increasing with increasing RTA temperature. A classic anneal (at 680 °C) gives an emission intensity which is comparable with the films annealed at 800 °C for 2 min.

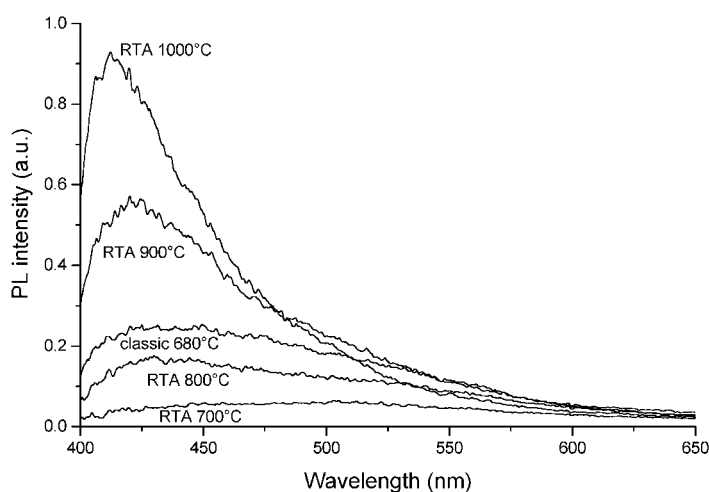


**Figure 2.** (a) AFM image of undoped CaS thin film (RTA 900 °C, 2 min), (b) AFM image of CaS:Pb (0.26 at%) (RTA 900 °C, 2 min), (c) AFM image of CaS:Pb (0.26 at%) (no anneal).

The emission spectrum of CaS:Pb ([Pb] = 0.74 at.%) after classic anneal yields CIE (Commission International de l'Eclairage) colour coordinates (0.216, 0.248) corresponding to unsaturated green–blue. Upon increasing the RTA temperature from 700 °C to 1000 °C, the CIE colour coordinates shift from (0.271, 0.326) (white) to (0.180, 0.125), which is purple blue. In the literature the blue emission in CaS:Pb has been mainly attributed to lead dimers [1, 4]. Lead monomers are thought to be responsible for UV emission while higher lead aggregates

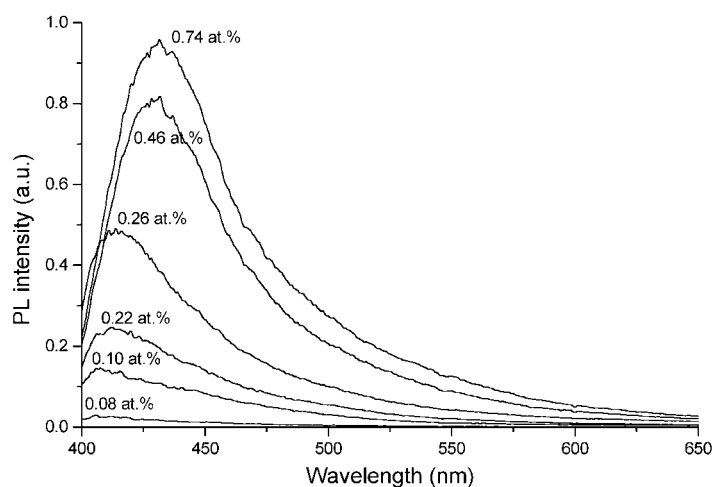


(c)

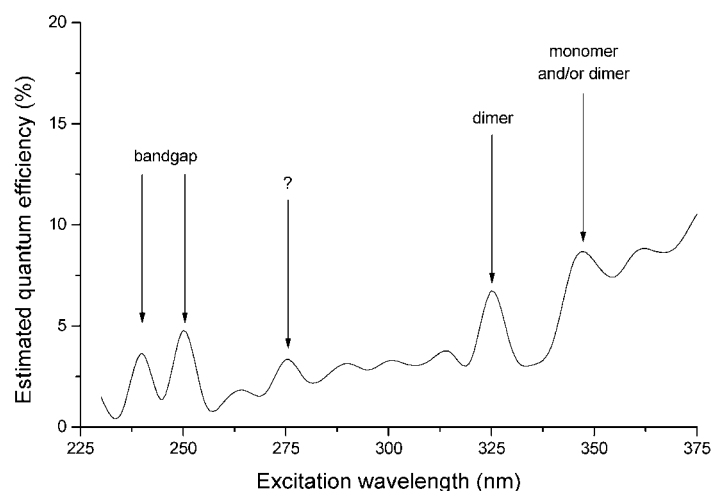
**Figure 2.** (Continued)**Figure 3.** PL emission spectra of CaS:Pb (0.26 at.%) as function of annealing conditions (excitation source pulsed N<sub>2</sub> laser).

yield green emission. It is possible that in the present case the higher lead aggregates are destroyed by a high annealing temperature and the blue emission centres are activated.

**3.3.2. Influence of lead concentration.** Figure 4 shows the change in the PL spectrum of CaS:Pb as a function of lead concentration. It can be seen that the PL intensity increases with increasing lead concentration and the peak wavelength shifts from 410 to 430 nm. There is a minimal change in emission colour. While this may seem odd at first sight, it is a result of the rapidly decreasing eye sensitivity at these low wavelengths.



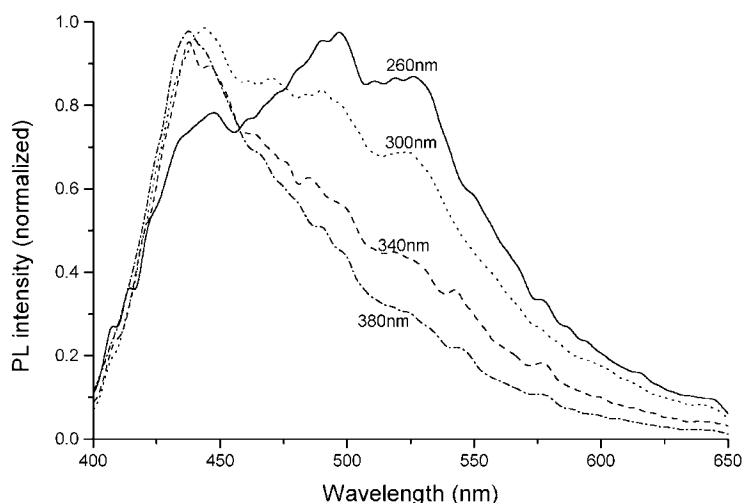
**Figure 4.** PL emission spectra of CaS:Pb (RTA 1000 °C, 2 min) as function of lead concentration (excitation source pulsed N<sub>2</sub> laser).



**Figure 5.** PL excitation spectrum of CaS:Pb (0.74 at.%, RTA 1000 °C during 2 min) (excitation source Hg lamp).

### 3.4. Excitation

Excitation spectra were acquired using a high-pressure Hg lamp, a UV monochromator, and appropriately filtered detectors to measure both the PL intensity and the intensity of the excitation source. Figure 5 shows the total PL intensity (estimated quantum efficiency) as a function of the excitation wavelength. Different excitation bands can be seen, corresponding to several emission centres (according to Asano *et al* [1]). The bands around 240 nm and 250 nm are due to bandgap excitation. The 325 nm band is thought to originate from dimer excitation, while the band around 350 nm is thought to originate from monomer and dimer excitation. It is not clear yet which centre is responsible for the minor excitation band around 275 nm.



**Figure 6.** PL emission of CaS:Pb (0.74 at.%, RTA 1000 °C during 2 min) as function of excitation wavelength (excitation source Hg lamp).

Emission spectra at different excitation wavelengths were also acquired, and are shown in figure 6. The spectrum changes with the excitation wavelength. For example at 260 nm excitation the spectrum has a green emission band around 500 nm, which is of the same intensity as the emission band around 420 nm. However upon excitation at 380 nm the blue emission has gained intensity compared with the green emission, which makes it evident that different emitting centres are involved in the PL spectrum of the CaS:Pb layers.

#### 4. Conclusion

CaS:Pb thin films can be grown with electron beam evaporation, although the crystallinity is not optimal. At sufficiently high annealing temperature and lead concentration an intense PL emission was achieved. The corresponding emission spectrum was deep blue upon excitation lower than the band gap energy, but showed a green component upon band gap excitation. Prospects for the extension to electroluminescent devices are quite favourable, presumed that evidence can be found for columnar grain growth. If this is not the case it will be necessary to find a way to increase the grain size, possibly using codopants (e.g. Ag). Excitation spectra show different bands in agreement with earlier results on CaS:Pb powder phosphors.

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