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Europium and samarium doped calcium sulfide thin films grown by PLD

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Abstract

Europium and samarium doped calcium sulfide thin films (CaS:Eu,Sm) with different thickness were prepared by the pulsed laser deposition technique using sintered targets. A typical homemade deposition chamber and XeCl excimer laser (308 nm) were employed and the films were deposited in helium atmosphere onto silicon and corning glass substrates. Structural investigations carried out by X-ray diffraction and atomic force microscopy showed a strong influence of the deposition parameters on the film properties. The films grown had an amorphous or polycrystalline structure depending on growth temperature and the number of pulses used, the same parameters affecting the film roughness, the grain shape and dimensions, the film thickness and the optical transmittance. This work indicates that pulsed laser deposition can be a suitable technique for the preparation of CaS:Eu,Sm thin films, the film characteristics being controlled by the growth conditions.

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1. Introduction

Rare-earth-doped alkaline earth sulfides are well-known for their high luminescent yields. As a result, these materials can be used in several applications such as infrared sensors and X-ray radiation imaging plates, optical storage media, and electroluminescent displays [1–3]. Conventional bulk powders of phosphor materials used for display applications normally suffer in resolution while thin film forms can offer significant advantages such as higher resolution, more uniform density and increased thermal stability. However, the preparation of thin films of such compounds is a rather difficult task because of their instability in air and high activation temperature in obtaining luminescent films [4]. As a result, current polycrystalline phosphors thin film exhibit noticeably lower luminescent output than their powder counterparts, a response attributed to deficient stoichiometry and poor crystallinity of the CaS host lattice [5,6]. Therefore, there exists a great challenge in the deposition of sulfur-based phosphors in thin film form exhibiting good stoichiometry, surface morphology and crystallinity.

In this work we present preliminary results related to the deposition of europium and samarium doped calcium sulfide thin films (CaS:Eu,Sm), using the pulsed laser deposition technique. Our investigation is focused on the understanding of the growth mechanisms and this study concerns properties such as the crystallinity, the surface grain size, the roughness and the optical transmittance of the films.

2. Experimental details

The films were grown in a typical pulsed laser deposition (PLD) chamber in inert atmosphere at various temperatures, using a XeCl excimer laser (308 nm) as light source. The

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deposition was carried out onto silicon [1 1 1] and corning 1737F glass substrates. The thickness of the films was measured using an Alphastep profilometer, while, X-ray diffraction (XRD) with a Rigaku diffractometer with Cu Kα X-rays was used for the determination of the crystal structure of the target and the deposited films. Moreover, the surface characterization was performed with an atomic force microscope (AFM) Nanoscope III (Digital Co. Instruments, USA) using normal silicon nitride tips (125 μm) in tapping mode scanning the surface with the oscillating tip in its resonant frequency (200–400 kHz). The surface characteristic parameters RMS, S_{bi}, S_{dr}, S_{fd}, and lateral grain size evaluation were determined using the scanning probe image processor (SPIP image processing software for nano- and micro scale microscopy). The RMS roughness of the surface is then defined as:

$$\mathrm{RMS} = \sqrt{\frac{\sum_{i=1}^{N} (z_i - z_{\mathrm{ave}})^2}{N}},$$

where z_i is the current value of z, z_{ave} the mean value of z in the scan area and N is the number of points. Surface bearing index, S_{bi} is the ratio of the RMS deviation over the surface height at 5% bearing area.

$$S_{\mathrm{bi}} = \frac{\mathrm{RMS}}{Z_{0.05}} = \frac{1}{h_{0.05}},$$

where $h_{0.05}$ is the normalized surface height at 5% bearing area. A larger surface bearing index indicates a good bearing property. For a Gaussian height distribution, S_{bi} approaches 0.608 with increasing number of pixels. The surfaces area ratio, S_{dr}, expresses the ratio between the surface area (taking the z height into account) and the area of the flat xy plane:

$$\begin{aligned} S_{\mathrm{dr}} &= \frac{S_{3\mathrm{A}}}{S_{2\mathrm{A}}} \\ &= \frac{\left(\sum_{k=0}^{M-2}\sum_{l=0}^{N-2} A_{\mathrm{kl}}\right) - (M-1)(N-1)\delta x\delta y}{(M-1)(N-1)\delta x\delta y} \\ &\quad \times 100\%, \quad \text{where} \quad A_{kl} \\ &= \frac{1}{4}\left[\sqrt{\delta y^2 + (z_{k,l} - z_{k,l+1})^2}\right. \\ &\quad \left. + \sqrt{\delta y^2 + (z_{k+1,l} - z_{k+1,l+1})^2}\right] \\ &\quad \times \left[\sqrt{\delta x^2 + (z_{k,l} - z_{k+1,l})^2}\right. \\ &\quad \left. + \sqrt{\delta x^2 + (z_{k,l+1} - z_{k+1,l+1})^2}\right] \end{aligned}$$

For a totally flat surface, the surface area and the area of the xy plane are the same and $S_{dr} = 0\%$. The fractal dimension, S_{fd} is calculated for the different angles by analyzing the Fourier amplitude spectrum; for different angles the Fourier profile is extracted and the logarithm of the frequency and amplitude coordinates is calculated. The fractal dimension for each direction is then calculated as 2.0 minus the slope of the log–log curves.

Finally, the optical transmittance of the deposited films was measured using a Varian Cary50 UV/VIS spectrophotometer with Varian data analysis tools.

3. Results and discussions

For the deposition of the europium and samarium doped calcium sulfide (CaS:Eu,Sm) thin films, 11 mm diameter targets were vacuum hot pressed sintered, using commercially available CaS:Eu,Sm powder (Phosphors Technology) of mean particle diameter in the range of 5–10 μm. Several films were prepared under various growth conditions in order to investigate their influence on the film properties. The film growth and quality depend on few fundamental parameters such as substrate temperature, kinetic energy of the deposition flux, the growth rate and the environmental conditions (buffer gas or inert gas).

In general, the substrate temperature affects the film quality in many ways. During the initial stages of the film growth, surface re-evaporation, cluster nucleation, trapping on surface by defects may occur. The mobility of the atoms deposited on the surface is directly dependent on temperature, a dependence which can influence the activation energy of each process. Only selected processes exceeding a certain energy threshold are possible at certain temperatures, while at lower temperatures they are inhibited. In other words, the closer is the temperature of the substrate to the melting temperature of the film, the less the strain and stress in the resulting film, resulting in higher quality of the crystalline lattice. Low substrate temperatures film growth can also enable metastable structures due to a thermal growth. At higher temperatures, film grain boundaries gain mobility inducing surface diffusion and recrystallisation which can result in improved structural properties.

Initially we examined the crystallinity of the films and its dependence on the growth conditions. In order to get a rough control on the target to the film material transfer, X-ray

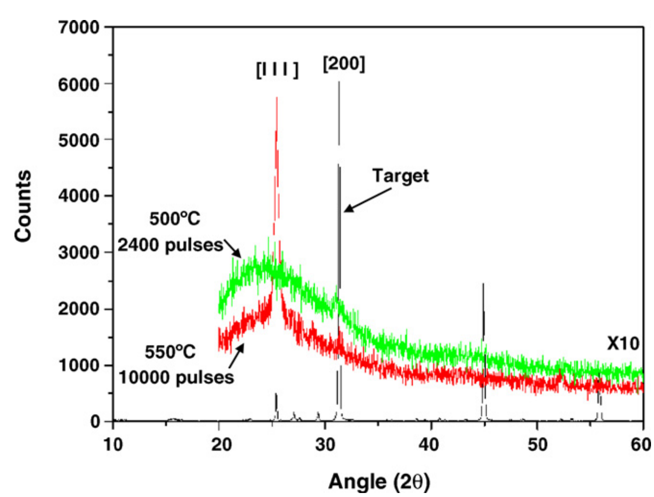

Fig. 1. XRD diffractograms of the CaS:Eu,Sm target and two films deposited at 500 °C, 2400 pulses and 550 °C, 10,000 pulses. The data for the films have been multiplied by 10.

diffraction measurements were performed on the target (2θ scans) and films ($2\theta - \omega$ scans) with various thicknesses deposited at different temperatures. As it was observed, for temperatures lower than 400 °C all films are amorphous. At higher temperatures, the films deposited for low number of pulses are amorphous, while for a larger number of pulses, the films present a polycrystalline structure with preferential orientation the (1 1 1) reflection plane of CaS, slightly shifted to smaller angles [7]. In Fig. 1 one can see X-rays diffractograms for the target and two films deposited at 500 °C, 2400 pulses (amorphous) and at 550 °C, 10,000 pulses (textured on [1 1 1] preferential orientation). The broadening of the [1 1 1] peak was used for the determination of the crystallite size (d), which is inversely proportional to the full width at half maximum (FWHM) of the peak according to the Scherer's formula:

$$d = \frac{k\lambda}{\cos\theta\sqrt{(\beta^2 - \beta_0^2)}},$$

where β is the FWHM of the peak in radians, β_0 the width introduced by the instrumental broadening, $k = 0.9$, $\lambda = 0.154056$ nm and θ is the peak position. The mean crystallite size calculated from this equation was found to be ~22–23 nm. Finally, it should be mentioned here that for a large

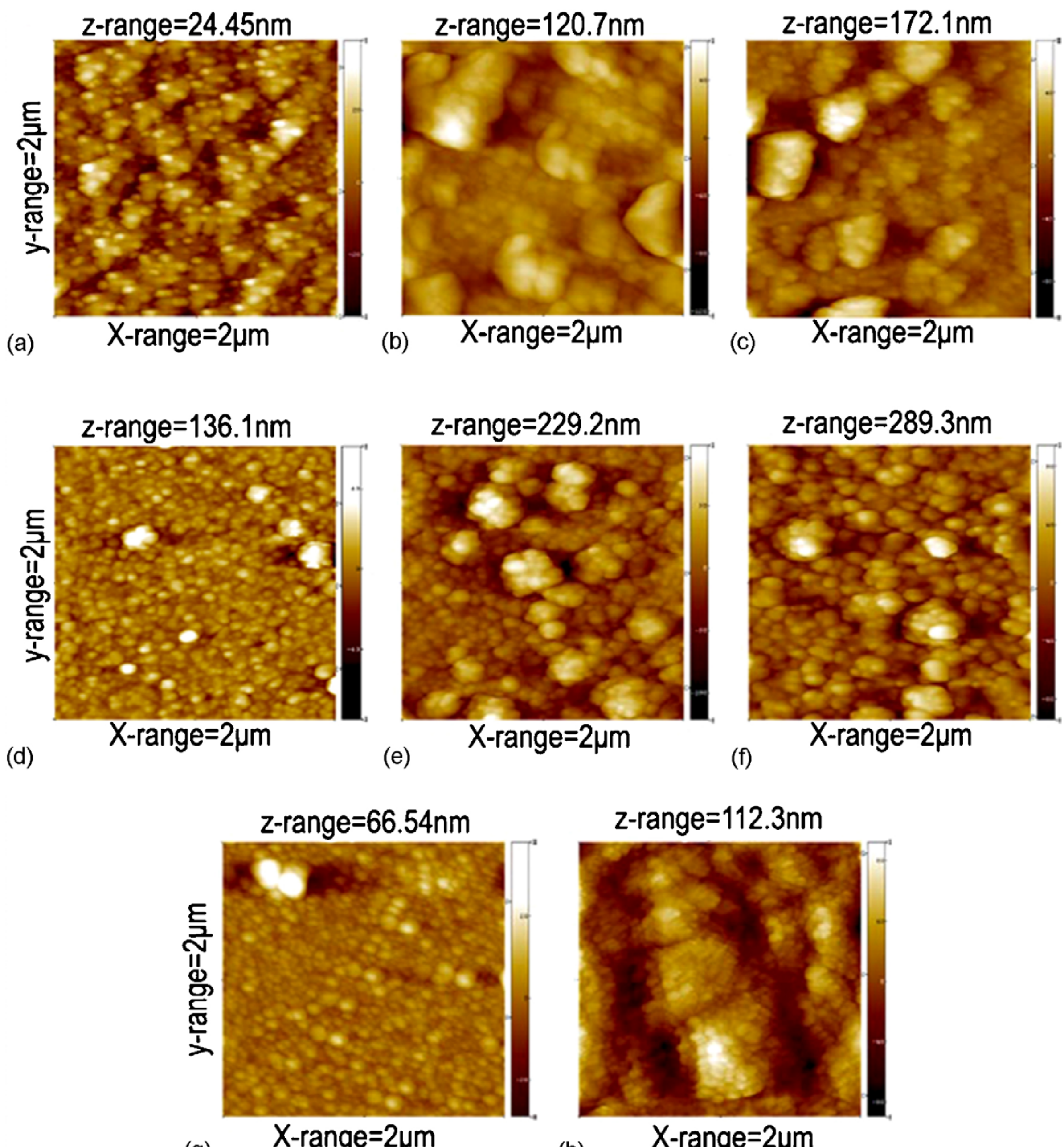

Fig. 2. 2D AFM images of films surface (scan size 2 µm × 2 µm) for films grown at: (i) 200 °C (a) 2000 pulses, (b) 3600 pulses, and (c) 6300 pulses; (ii) 300 °C (d) 2500 pulses, (e) 5000 pulses, (f) 10,000 pulses, and (iii) 500 °C (g) 2500 pulses, and (h) 5000 pulses.

number of pulses and high temperatures, the [2 0 0] peak tends to appear. This behavior is quite important since, as it was stated by other authors [8,9], the [2 0 0]-oriented films usually present better luminescent characteristics than the [1 1 1]-oriented ones. In any case, since good luminescent properties require good crystallinity of the CaS host lattice [5,6], further investigations are required as far as it concerns both the deposition conditions and/or annealing of the deposited films towards the growth of films with improved crystallinity.

AFM analysis revealed that all films displayed granular morphology with high roughness. Since crystallinity could be improved by post deposition annealing treatment [6], even low temperature grown films with low crystallinity may be interesting for future applications due to their surface appearance. Fig. 2 shows the evolution of the surface morphology with increasing number of pulses for three growth temperatures: 200 °C (a) 2000 pulses, (b) 3600 pulses, (c) 6300 pulses, 300 °C (d) 2500 pulses, (e) 5000 pulses, (f) 10,000 pulses; 500 °C (g) 2500 pulses, and (h) 5000 pulses. The scan size of these images is 2 μm × 2 μm and z-range increases with increasing number of pulses. In order to fully characterize the surface evolution as a function of growth parameters, the RMS, S_{dr}, S_{bi} and S_{fd} parameters were analyzed. Surface RMS of the films grown on corning glass was found to be systematically slightly higher than that for films grown under similar conditions onto silicon and is increasing with increasing number of pulses. An example of the surface RMS variation is shown in Fig. 3a for films with different thickness grown at 200 °C. Moreover, it was found that an increase in growth temperature leads apparently to a decrease of surface RMS, a behavior that can be explained by the increased mobility of the species on the surface and, consequentially better packing of material in better formed grains. Close values for surface RMS were reported also by Day et al. [10] for undoped CaS thin films grown by atomic layer deposition technique. This observation is sustained also by the variation of S_{dr} with number of pulses, from 31.6 to 10.6 for 200 °C and from 44.0 to 14.4, respectively for 300 °C as shown in Fig. 3b. The decreasing trend with

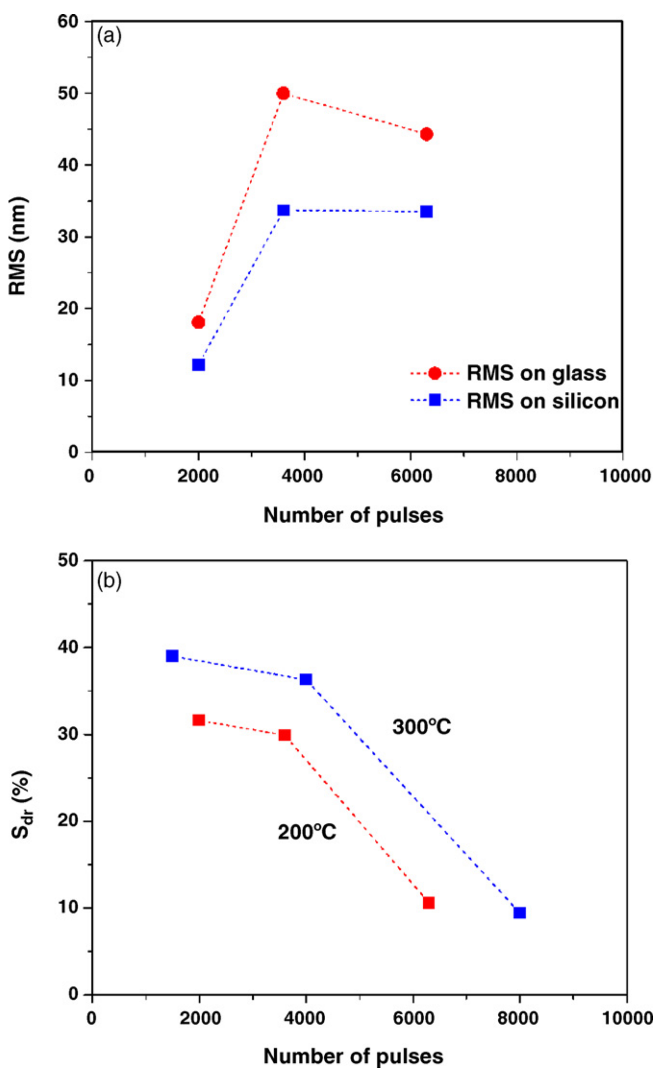

Fig. 3. Variation of surface parameters with number of pulses and growth temperature: (a) RMS for films grown at 200 °C on silicon and Corning glass and (b) S_{dr} for films grown at 200 and 300 °C.

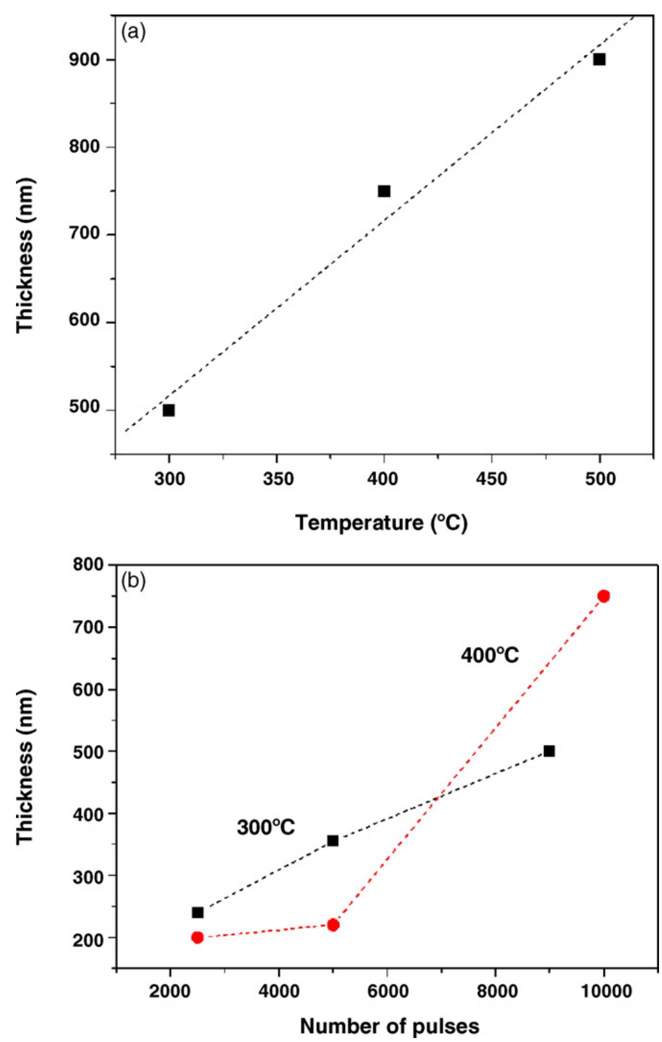

Fig. 4. (a) Variation of films thickness with deposition temperature for 10,000 pulses under similar growth conditions and (b) variation of films thickness with number of pulses for two growth temperatures, 300 °C and 400 °C.

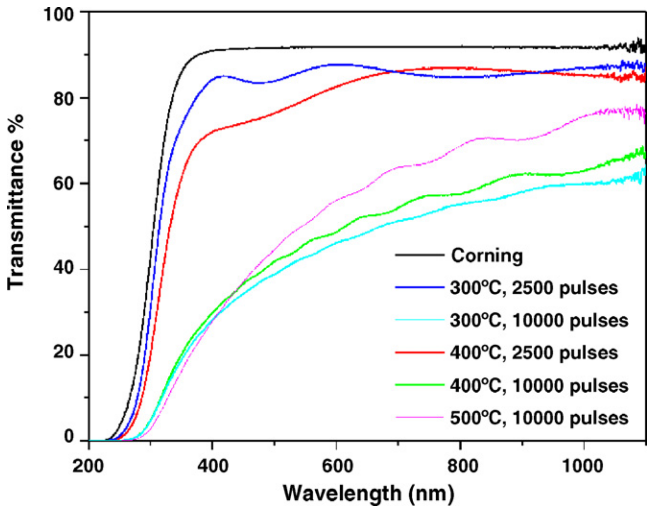

Fig. 5. Variation of the film transmittance as a function of the substrate temperature and the number of pulses.

increasing thickness suggests an improvement of the surface homogeneity and planarity. Moreover, S_{bi} was determined to be in the range 0.538–0.628, values which denote quite small deviations from an ideal Gaussian distribution characterized by a S_{bi} value of 0.608. Finally, the S_{fd} values were varying between 2.74 and 2.90 for all the films without any evident correlation with number of pulses number and temperature.

The lateral dimensions of structure features on the films surface were determined to be in the range 30–60 nm. With increasing thickness of the film and growth temperature, we observed a clear tendency for the formation of grain agglomerations with dimensions around 400–600 nm. As it can be seen in Fig. 2, the evolution of agglomeration appearance with number of pulses is very interesting. While at low number of pulses the grains have a polyhedral shape, the grains become round and agglomerate in cloud like structures at higher number of pulses. These structures are still present but more compact at higher temperatures. This tendency can explain the unexpected increase of the film thickness with the deposition temperature for 10,000 pulses under similar growth conditions, as presented in Fig. 4a. By forming the cloud like agglomerations, the thickness of films increases due to a film volume increase, the density decreasing. As a consequence of this polyhedral to round grain transition, surface ratios S_{dr} decrease with increasing number of pulses (Fig. 3b). The variation of the film thickness as a function of the number of pulses for two growth temperatures (300 and 400 °C) is presented in Fig. 4b. As it can be seen, for small number of pulses, the thickness is lower for higher temperatures and increases with pulse number in a nonlinear way.

Finally, the UV–VIS transmittance of films was recorded and is shown in Fig. 5. As it can be seen, increased number of pulses induces a decrease of films transmittance due to the increased thickness. The variation of the transmittance is ranging between 90–95% at 2500 pulses and 65–75% at 10,000 pulses for the same range of temperatures. As it can also be seen from Fig. 5, the transmittance increases as a function of substrate temperature, being about 65% for films grown at 300 °C, about 75% for films grown at 400 °C and 85% for films grown at 500 °C.

4. Conclusions

Europium and samarium doped calcium sulfide thin films (CaS:Eu,Sm) of various thicknesses were prepared using the pulsed laser deposition technique at different substrate temperatures. Structural investigations showed that the films grown had a granular morphology with high roughness and can have an amorphous or polycrystalline structure depending on growth temperature and the number of pulses used. The increase of the number of pulses was found to determines an increase of RMS value, to improve the surface homogeneity and planarity and to alter the optical transmittance in the visible region. On the other hand, the increasing growth temperature was found to decreases the film surface RMS and to increase the surfaces area ratios. Finally, for films grown with 10,000 pulses, the increasing of the growth temperature resulted in an increasing of the film thickness and the optical transmittance. The work indicates that pulsed laser deposition can be a suitable technique for the preparation of CaS:Eu,Sm thin films.

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