

Pulsed laser deposition of silicate phosphor thin films

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Abstract. Three types of silicate phosphor thin films, emitting in the red-green-blue (RGB) primary colors, were fabricated by pulsed laser deposition, including manganese and lead doped calcium silicate ($\text{CaSiO}_3:\text{MnPb}$) for red color, manganese doped zinc silicate ($\text{Zn}_2\text{SiO}_4:\text{Mn}$) for green color and cerium doped yttrium silicate ($\text{Y}_2\text{SiO}_5:\text{Ce}$) for blue color. A correlation was observed between photoluminescence intensity with film crystallinity and surface morphology. RGB phosphor thin films with excellent color saturation were obtained. Luminescence mechanisms for these phosphor thin films are discussed.

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Phosphors are widely used in fluorescent lamps, cathode-ray tubes (CRT), and *x*-ray intensifier screens. Although the processing of phosphor films is a relatively mature art, recent advances in some new display technologies impose severe new requirements demanding new solutions. For example, in vacuum fluorescent displays (VFD) and field emission displays (FED), the electron accelerating voltage is low, leading to a decrease in phosphorescence efficiencies. To maintain the brightness, high current has to be used, often leading to disastrous results. Unlike the 15–30 kV used in CRT, VFD voltages range from 20 to 100 V, while FEDs run from 300 V to 8 kV at present. Furthermore, these VFDs and FEDs devices are addressed one line at a time, so a given pixel can be excited for many tens of microseconds as opposed to nanoseconds in the usual raster scanning. The conditions of high currents and long addressing times produce severe current saturation and degradation from Coulomb loading. Therefore, considerable phosphor development is required for these new VFDs and FEDs [1].

One proposed solution to the high current problem is the use of phosphors in the thin film form as opposed to powder phosphors used traditionally in CRT. Thin film phosphors should have high contrast ratio, high ambient visibility,

high image resolution, and good heat resistance [2]. Many thin films deposition techniques have been used for phosphor deposition, including sputtering, thermal evaporation and chemical deposition. For any technique to work, it is highly desirable that good quality thin film phosphors that can be deposited at low substrate temperatures. This is because of the use of glass substrates and the temperature-sensitive phosphor materials. Pulsed laser deposition (PLD) technique, which has been quite successful in depositing complex materials such as superconducting oxide thin films, provides a unique process for stoichiometric evaporation of target materials [3]. It should, therefore, be interesting to investigate PLD as a technique for making new types of phosphor thin films and examine their luminescent properties.

In the past, PLD has been employed for the growth of phosphor thin films such as ZnS, SrS, ZnO, YAGG, $\text{Y}_2\text{O}_3:\text{Eu}$ [4–8]. One class of phosphor that deserves special attention is silicate oxide phosphors. They are more chemically stable than sulfide phosphors under high Coulomb loading. As a matter of fact, $\text{Zn}_2\text{SiO}_4:\text{Mn}$, known as the P1 phosphor, is a useful phosphor in CRT applications due to its high efficiency and relatively long persistence. Electroluminescence (EL) devices have been made from the same silicate [9]. Doped silicate phosphor is one kind of complex compound system, which generally consists of four or more elements. Such silicate phosphor thin films may be good materials for PLD studies.

There has been no literature report on silicate phosphor thin film grown by PLD, although sputtering deposition of RE-doped yttrium silicate phosphor has been investigated [10]. In this paper, we describe our work of PLD deposited red-green-blue (RGB) silicate phosphors doped with different transition and rare-earth metals in their thin film form. We shall also correlate their structural, surface morphologies to their luminescent properties [11].

1 Experiment

Commercial phosphor powders ($\text{CaSiO}_3:\text{MnPb}$, $\text{Zn}_2\text{SiO}_4:\text{Mn}$, $\text{Y}_2\text{SiO}_5:\text{Ce}$) were cold-pressed into 1" disks, and sintered at 1000 °C for five hours to make hard enough ceramic

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targets suitable for laser ablation. Pulsed laser deposition experiments were performed on these self-made targets with a 193 nm Lambda Physik ArF excimer laser. In the present experiment, the laser operated at 150 mJ per pulse and at 10 Hz repetition rate. The substrates used for the deposition were either (100) bare silicon substrates or silicon substrates with a thermally grown 1000 Å silicon dioxide on top. The latter was used to simulate the growth of the phosphors on glass substrates. Oxygen pressures used in the experiments varied from 10 mTorr to 200 mTorr. All the films were deposited at a substrate temperature of 300 °C. Annealing was performed on these samples in air at temperatures ranging from 400 °C to 1200 °C.

The as-grown and annealed films were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL) measurements.

2 Results and discussions

The PLD deposited phosphor films were generally 300 nm to 400 nm thick as calibrated by a profiler. It was found that the oxygen pressure during deposition was a crucial factor to obtain luminescent films. With a low oxygen pressure, such as 10 mTorr, the deposited films showed no luminescence even after 1000 °C annealing. This suggests that oxygen deficiency suppresses the luminescence property of silicate phosphors. Luminescent silicate phosphor films were obtained at oxygen pressures from 60 mTorr to 200 mTorr.

The XPS results showed that for all three kinds of phosphors, there was no change of chemical state. The chemical bonding energies remain the same for the film and the target. There is however, a small change in the relative chemical compositions between the target, the as-grown, and the 1000 °C annealed samples. The elemental concentrations of these three kinds of samples, calculated from XPS data, are shown in Table 1. Using $\text{CaSiO}_3:\text{MnPb}$ as example, it can be seen that, although, the concentration of Ca, Si and O deviate from that of stoichiometric CaSiO_3 (which is acceptable for

Table 1. Chemical composition (%) of $\text{CaSiO}_3:\text{MnPb}$, $\text{Zn}_2\text{SiO}_4:\text{Mn}$, $\text{Y}_2\text{SiO}_5:\text{Ce}$ target, as-grown and 1000 °C annealed films (counting from the top)

	C	O	Si	Ca	Mn	Pb
target	2.68	60.56	21.72	13.21	1.60	0.23
as-grown	3.07	60.13	20.16	14.85	1.78	0.02
1000 °C	2.31	58.88	20.26	16.84	1.69	0.02
	C	O	Si	Zn	Mn	
target	5.74	55.85	17.00	19.55	1.86	
as-grown	3.04	58.35	20.30	16.47	1.85	
1000 °C	0.36	55.77	16.41	24.49	2.97	
	C	O	Si	Y	Ce	
target	2.76	62.60	12.48	20.86	1.30	
as-grown	6.74	60.88	10.05	22.03	0.31	
1000 °C	1.94	61.99	15.97	19.19	0.90	

such a complex system), all the elements were well reserved as the target, except for Pb.

Figure 1 shows the XRD θ - 2θ scans for 300 °C as-grown, 800 °C and 1000 °C (5 hours in air) annealed $\text{Zn}_2\text{SiO}_4:\text{Mn}$, $\text{Y}_2\text{SiO}_5:\text{Ce}$, and $\text{CaSiO}_3:\text{MnPb}$ films grown on SiO_2/Si . The increase in crystallinity with an increase in annealing temperature is clearly demonstrated. However, there are three unidentified peaks labeled as ?1, ?2 and ?3. These peaks may result from impurities introduced during high temperature annealing in the furnace. XRD data showed that there is no improvement in using Si substrate over SiO_2/Si in terms of crystallinity.

Figure 2 shows the PL intensity versus annealing temperature for silicate phosphor thin films grown on SiO_2/Si with annealing temperature from 400 °C to 1200 °C. The as-grown and low temperature annealed $\text{Zn}_2\text{SiO}_4:\text{Mn}$ and $\text{CaSiO}_3:\text{MnPb}$ films showed no photoluminescence. The as-grown $\text{Y}_2\text{SiO}_5:\text{Ce}$ film showed a weak photoluminescence. With post-annealing at a temperature of 700–800 °C or higher for five hours in air, the luminescent property improved significantly.

From Fig. 2, it can be seen that the photoluminescence of the annealed sample showed increasing PL intensity with annealing temperatures from 800 °C to 1000 °C, and that the

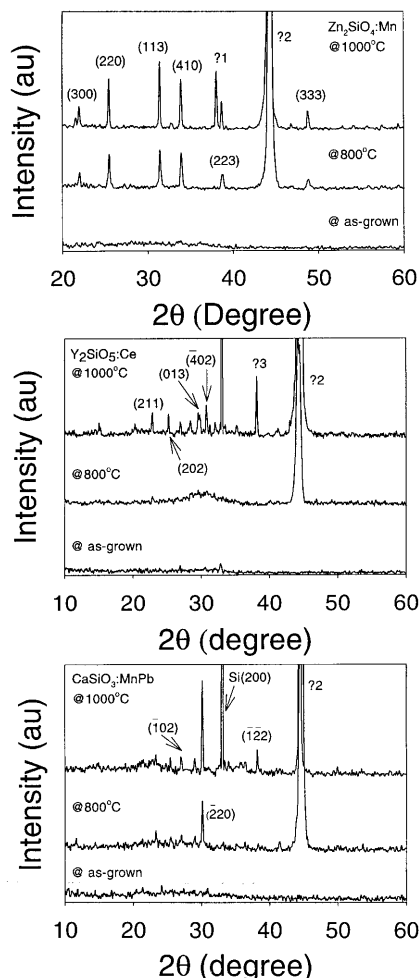


Fig. 1. XRD θ - 2θ scan of 300 °C as-grown, 800 °C and 1000 °C annealed $\text{Zn}_2\text{SiO}_4:\text{Mn}$, $\text{Y}_2\text{SiO}_5:\text{Ce}$, and $\text{CaSiO}_3:\text{MnPb}$ films on SiO_2/Si respectively

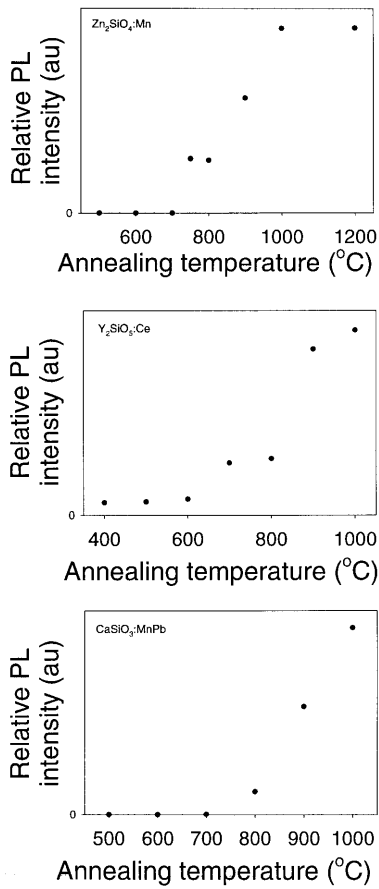


Fig. 2. Relative PL intensity of Zn₂SiO₄:Mn, Y₂SiO₅:Ce, and CaSiO₃:MnPb thin film as a function of annealing temperature respectively from top down

PL intensity tends to saturate with further increasing of annealing temperature. The enhanced luminescence correlated well with the increasing crystallinity at higher annealing temperatures. The phosphor films deposited on Si substrate and SiO₂/Si substrate showed comparable PL intensity after annealing. This result indicates that the luminescence is not sensitive to the substrate material used.

The PL intensity of the thin film as compared to the bulk material was measured. It was found that at low excitation intensity, the thin film is about ~40% as efficient as the bulk. However, the ratio drops to 20% for higher excitation intensities. This result can be explained by the lower saturation threshold in thin film samples.

The SEM images, corresponding to the samples in Fig. 1, are shown in Fig. 3. Surface morphology of the phosphor films grown on SiO₂/Si substrate resembles that of the film grown on Si. It should be noted that the cracks on the SEM picture of the as-grown CaSiO₃:MnPb are due to electron beam induced peeling during SEM photographing. When the AFM data (not shown here) was combined with the SEM data, it was observed that the surface morphology did not change much with lower annealing temperatures (< 800 °C). However, with annealing temperatures higher than 800 °C, the surface becomes a little bit rougher, and the grains become finer. The PL intensity experiences a sharp change from 800 °C for all three kinds of phosphors as shown in Fig. 2. So, the enhanced luminescence is due to the increased crystallinity as well as the rougher surface morphology. These observations are consistent with the fact that luminescence in phosphors is mainly induced on the surface. Finer grains and rougher surfaces are needed for good PL and perhaps cathodoluminescence as well. It should also be noted that the PL intensity and the film crystallinity are not sensitive to the substrate material used.

Reasonably good purity RGB chromaticity was obtained from CaSiO₃:MnPb, Zn₂SiO₄:Mn, and Y₂SiO₅:Ce films by

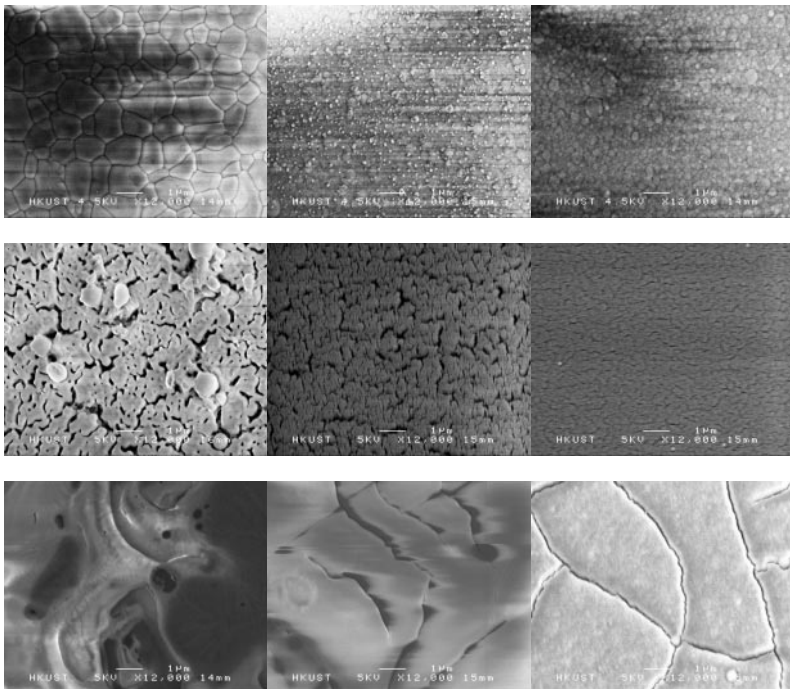


Fig. 3. SEM pictures of 300 °C as grown, 800 °C and 1000 °C annealed (from right to left) Zn₂SiO₄:Mn, Y₂SiO₅:Ce and CaSiO₃:MnPb (from top down) phosphor films respectively

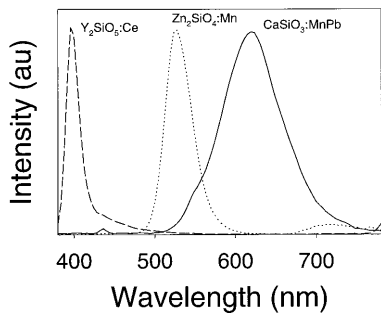


Fig. 4. PL spectrum of red CaSiO₃:MnPb, green Zn₂SiO₄:Mn and blue Y₂SiO₅:Ce phosphor films obtained by PLD

PLD. Figure 4 shows the spectra measured with a Photo Research (model PR650) spectrophotometer. The PL of the CaSiO₃:MnPb, Zn₂SiO₄:Mn, Y₂SiO₅:Ce films peaked at 620 nm, 520 nm and 400 nm respectively. The red tail of Zn₂SiO₄:Mn (green) and Y₂SiO₅:Ce (blue) phosphors are due to unfiltered excitation light source of the xenon lamp. The red emission spectrum of CaSiO₃:MnPb thin film was measured with 193 nm ArF laser excitation. The corresponding CIE chart is shown in Fig. 5. Real images of these RGB phosphor thin films are also shown in Fig. 6 for visual inspection of their chromaticity. Here, the excitation source was a 193 nm ArF laser.

3 Luminescence mechanisms

The PL peak of Y₂SiO₅:Ce (blue) observed in Fig. 4 can be attributed to the 5d → 4f transition of Ce³⁺ [12]. The electron configuration of cerium atom is 4f²5s²5p⁶6s². The Ce³⁺ ion has only one 4f electron, and this explains the two ground state energy levels: in one state, the orbital and spin momenta of the electron are parallel (²F_{7/2}), while in the other state, they are antiparallel (²F_{5/2}). Because of the ground state splitting, this band has a doublet character (see Fig. 4).

The 5d → 4f transitions of Ce³⁺ ion are electric-dipole allowed. As a consequence, the emitting level has a short lifetime, a common property in certain phosphors. For example, a very short lifetime has been reported for CeP₅O₁₄ [13]. An-

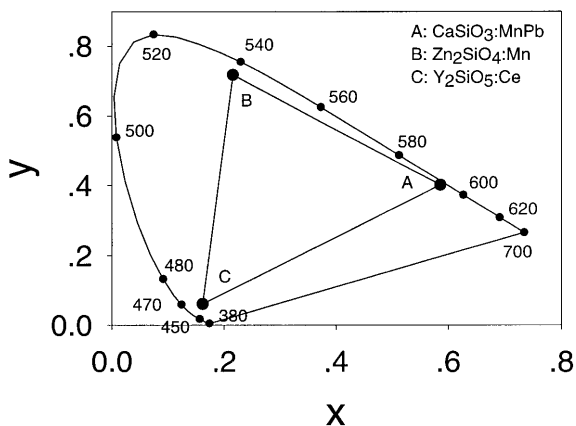


Fig. 5. Chromaticity coordinates of red CaSiO₃:MnPb, green Zn₂SiO₄:Mn and blue Y₂SiO₅:Ce phosphor films obtained by PLD

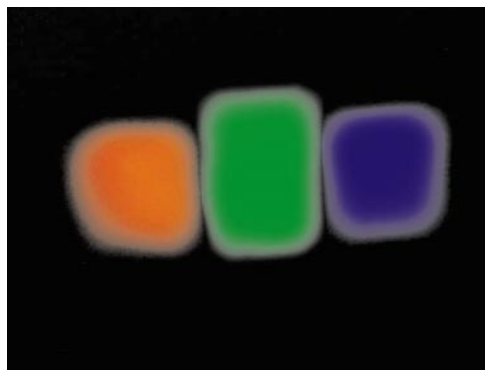


Fig. 6. Real images of CaSiO₃:MnPb, Zn₂SiO₄:Mn, and Y₂SiO₅:Ce phosphor thin films showing the saturated RGB colors. Here, the excitation source was a 193 nm ArF laser

other interesting feature of cerium-based phosphor is that the 5d excited energy levels of Ce³⁺ depend on the host materials. This is because the 4f electron is screened by the outer electron shells. Hence, the 4f electron energy levels are scarcely affected by the crystal lattice. When the electron in the excited 5d state is in the outer shell, its energy levels can be affected by the crystal field. It has been reported that using Ce³⁺ as an activator and various kinds of host materials, emission spectrums from UV to green and red can be obtained [14].

Zn₂SiO₄:Mn is a useful phosphor in CRT applications due to its high efficiency and relatively long persistence. It is generally accepted that the green emission band (centered at about 520 nm) is attributed to the spin flip transition of the d-orbital electron associated with the Mn²⁺ ion [15]. The Mn²⁺ ion has been identified to be located on the two non-equivalent zinc sites in the rhombohedral crystal with a tetrahedral site symmetry [16]. The luminescence is ascribed to the ⁴T₁ → ⁶A₁ transition, a dipole forbidden one according to the selection rules [17]. This is the reason why the luminescence of this phosphor has a relatively long persistence.

The energy levels of Zn₂SiO₄:Mn are depicted pictorially in Fig. 7. ⁴T₁ and ⁶A₁ represent the excited state and ground state of Mn²⁺ respectively. The bandgap of zinc silicate is about 5.5 eV. The threshold E_T, which is the smallest photon energy that could excite a ⁶A₁ electron to CB of zinc silicate,

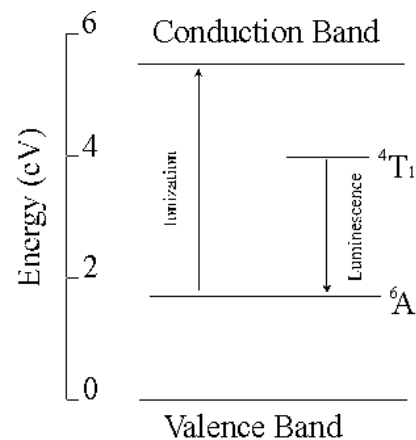


Fig. 7. Schematic energy band diagram of manganese-doped zinc silicate

is about 3.9 eV [18]. The photo-excited ionization of Mn^{2+} can be represented by the following equation:



Here, $h\nu$ is the energy necessary for the photoexcitation of Mn^{2+} , which is just E_T . The 6A_1 state of Mn^{2+} is about 1.6 eV above the valence band of zinc silicate. The 4T_1 state of Mn^{2+} is 2.38 eV above the 6A_1 state of Mn^{2+} , which could be inferred from the photoluminescence spectra of $\text{Zn}_2\text{SiO}_4:\text{Mn}$ in Fig. 4. When photons with energies higher than 3.9 eV are absorbed by Mn^{2+} ions, the ground state electrons of Mn^{2+} (d^5) can be excited to the conduction band (CB) of zinc silicate. These free electrons rapidly relax to different centers in the lattice. Some recombine immediately with ionized Mn^{3+} centers producing an initial population of excited Mn^{2+} centers in the 4T_1 excited state; the remainder of the CB electrons are captured by traps. When the excited state electron relaxes to the ground state, a photon is emitted.

The luminescence mechanism of $\text{CaSiO}_3:\text{MnPb}$ is much more complex than $\text{Zn}_2\text{SiO}_4:\text{Mn}$. The luminescence centers involve not only Mn^{2+} ions, but also Pb^{4+} ions. Although no reports were found on the luminescence mechanism of $\text{CaSiO}_3:\text{MnPb}$, probably due to a sensitized luminescence mechanism [19]. In the case of the sensitized mechanism, the Pb centers perform the double function of: (1) introducing new absorption bands in the UV region around 254 nm, and (2) creating an emission band in the 280 nm to 420 nm region (peaking at approximately at 350 nm), essentially exciting the Mn activator centers to luminescence.

4 Conclusions

In summary, RGB primary silicate phosphor thin films were fabricated on both Si and SiO_2/Si substrates by pulsed laser deposition. Films deposited at a substrate temperature of 300 °C showed no photoluminescence. Subsequent annealing at 800–1000 °C in air produced strong red, green, and blue photoluminescence for all three colors. It is expected that these silicate phosphor thin films should have applications in low voltage cathodoluminescence for field emission displays and in electroluminescence displays.

In view of the fact that annealing is needed for the luminescence to occur, in situ deposition at low temperature is probably not a useful technique for silicate phosphor deposition. Thus a major advantage of PLD, that of stoichiometric deposition, is not applicable. Additionally, since high temperature annealing has to be used, it will be difficult to deposit these phosphors on glass substrates directly. Thus, much further work is needed to obtain good quality thin film phosphors at low temperatures. Perhaps in situ PLD at higher temperatures may be one possibility.

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