



Luminescence properties of Mn^{2+} doped Zn_2SiO_4 phosphor films synthesized by combustion CVD

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Abstract

$\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphor films were successfully prepared by a novel combustion chemical vapor deposition (CCVD) method. In the CCVD process, a flammable solution, containing precursor materials, is atomized and sprayed through a specially designed nozzle and ignited to form a combustion flame. This enables crystallized films to be directly deposited onto a substrate in open-atmosphere with no post deposition heat treatment. SEM images indicated that the film deposited at 1200 °C consisted of densely packed particles with a fine grain size of several 100 nm. Strong Photoluminescence (PL) and cathodoluminescence (CL) intensities were observed with $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ samples deposited at a substrate temperature of 1200 °C exhibiting the best crystallinity and highest luminescence. The optimum doping level for films deposited using CCVD was found to be ~4 mol% Mn^{2+} of starting concentration, with a maximum CL luminescence equivalent to 53% of the luminescence measured from a commercial powder phosphor. A relatively fast CL decay with life time about 0.6–0.7 ms was also observed from these films.

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1. Introduction

Mn^{2+} doped Zn_2SiO_4 has been widely used as a green phosphor in cathode ray tubes (CRT),

plasma display panels (PDP), and more recently in thin film electroluminescent (EL) devices, due to its high luminescent efficiency. Thin film products synthesized by sol–gel process [1,2], magnetron sputtering [3], and the charged liquid cluster beam techniques [4] have been recently reported. However, the luminescence from films made by these techniques is relatively weak compared to powder

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samples. In this paper, $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ films were prepared by a novel combustion chemical vapor deposition (CCVD) method [5]. CCVD is a new technique capable of producing films with thickness between 10 nm and 30 μm . In this technique, high-density crystallized films can be directly deposited onto a substrate and no post-heat treatment is needed. The process is performed in the open-atmosphere, offering great flexibility for producing oxide phosphors.

2. Experimental

2.1. Synthesis

The apparatus used in this work was a combustion chemical vapor deposition system, details of which have been reported elsewhere [5,6]. In this process, a flammable solution, containing the precursor materials, is atomized and sprayed through a specially designed nozzle and ignited to form a combustion flame. The nozzle (From Microcoating Technologies, Inc.) is the key component of the system. Methane was used as the fuel gas and oxygen served as the oxidizer for the flame.

The starting solutions were prepared from zinc nitrate, tetraethyl orthosilicate (TEOS), and manganese nitrate. All the chemicals were from Aldrich. In a typical synthesis, 13.3 mmol of $\text{Zn}(\text{NO}_3)_2$ and 6.7 mmol of TEOS were dissolved in 400 ml ethanol to form a 0.05 M solution according to the stoichiometric ratio. Then $\text{Mn}(\text{NO}_3)_2$ was added to the solution and mixed uniformly. The doping concentrations of Mn^{2+} used are 1, 2, 4, 6, and 8 mol% of the Zn^{2+} concentration. After 10 min of vigorous magnetic stirring, the solution was pumped to the nozzle and ignited to form a combustion flame. Complete solubility was essential before pumping the solution through the nozzle. Quartz slides were used as substrates and thin films were deposited when the flame was directed onto the substrate. To determine the optimum deposition temperature, films with 4% Mn^{2+} doping concentration were prepared at substrate temperatures of 750, 900, 1050, and 1200 °C.

2.2. Characterization

All the film samples were analyzed by XRD on a Phillips PW-1800 X-ray diffractometer with $\text{Cu K}\alpha$ ($\lambda = 0.15405$ nm) radiation (40 kV, 30 mA). The surface morphology was studied by scanning electron microscopy (SEM) in a LEO 1530 microscope with an energy dispersive spectroscopy (EDS) attachment. Photoluminescence (PL) and cathodoluminescence (CL) spectra were recorded with a SpectraScan PR705 spectrophotometer. A 254 nm UV lamp was used to excite the film samples for PL measurements. Photoluminescent excitation spectra (PLE) and PL spectra were obtained with a Spex1000 M spectrometer and a 150 W xenon lamp/monochromator combination as the excitation source. Sodium salicylate was used as a reference for the PLE measurements. The CL emission spectra were measured under DC excitation at a low current density of 2.62 $\mu\text{A}/\text{cm}^2$, with a custom Kimball Physics EFG-11 electron gun as the excitation source. Commercial $\text{ZnS}:\text{Cu},\text{Cl}$ was used as the standard green to measure the intrinsic efficiency of films. CL decay measurements were conducted with a photomultiplier tube attached to a CVI 125 mm monochromator under the excitation conditions of 5 kV, 1.1 ms pulses at 72 Hz. All luminescence measurements were performed at room temperature.

3. Results and discussion

3.1. Phase formation

The dependence of the crystal structure and crystallinity of $\text{Zn}_2\text{SiO}_4:\text{Mn}$ phosphor films prepared by CCVD were investigated as a function of deposition temperature. This temperature was monitored by measuring the substrate temperature, which was controlled by adjusting the distance between the nozzle and substrate. Fig. 1 shows the XRD patterns of $\text{Zn}_2\text{SiO}_4:4\%\text{Mn}^{2+}$ samples deposited at different temperatures and compared with the standard pattern of the will-emite zinc silicate phase (Card No: 72-1856). This data indicates that the crystallinity of the films increased with deposition temperature. While the

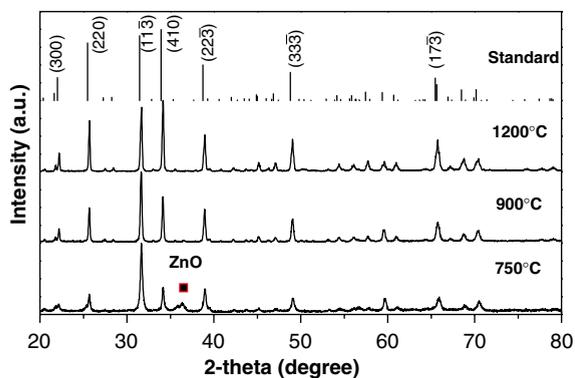


Fig. 1. Standard XRD pattern of Zn_2SiO_4 and $\text{Zn}_2\text{SiO}_4:4\%\text{Mn}^{2+}$ samples prepared at temperatures between 750 and 1200 °C.

willemite phase was formed at low deposition temperature as 750 °C, the (002) diffraction peak of a ZnO impurity phase was also detected, indicating that the reaction was not fully completed at this temperature. The higher background of the XRD pattern may imply that some amorphous phases existed. The body color of this film was dark. When the deposition temperature was raised above 900 °C, a pure willemite phase was formed and the film exhibited a white body color. At 1200 °C, all the diffraction peaks were well defined, and the position and intensity of all the peaks agreed very well with the standard pattern.

3.2. Surface morphology

The surface morphology of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ films were investigated by SEM. Fig. 2 shows the images of a film deposited at 1200 °C on a quartz substrate. The film was fine and relatively dense, but not quite uniform all over the surface. Near the outer region, the film consists of densely packed particles with grain sizes between 100 and 200 nm, while in the central region, the well crystallized grains were around 500–800 nm. This is believed to be related to the non-uniform distribution of temperature and mass flow in the combustion flame.

The surface morphology was also sensitive to the deposition conditions. Except for the deposi-

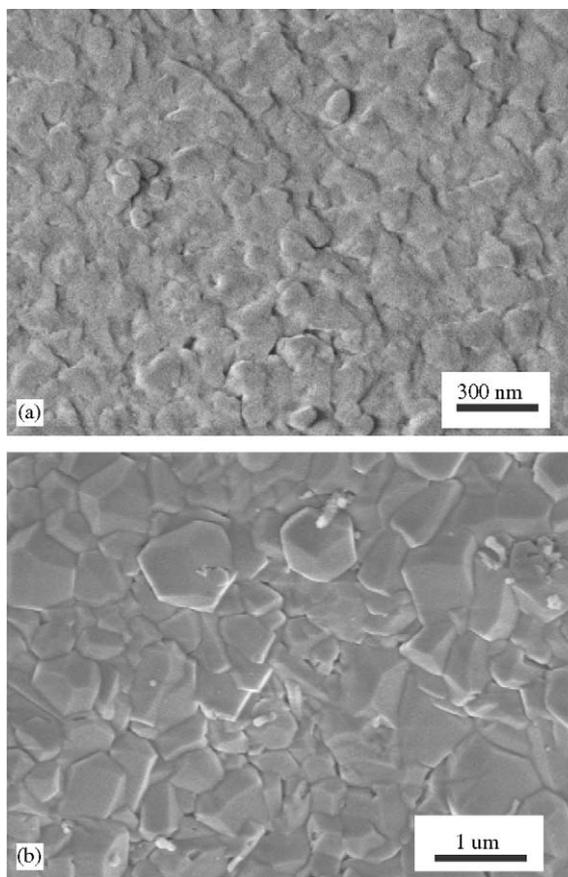


Fig. 2. SEM images of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ film deposited on quartz glass at 1200 °C: (a) outer region and (b) central region.

tion temperature, other major parameters such as solution concentration, flow rate, nozzle temperature, fuel gas/oxygen ratio, precursor and solvent, all have an effect on the film quality. Thus, to obtain the desired film microstructure, the deposition parameters must be carefully adjusted, and a combination of these parameters should be optimized.

3.3. Photoluminescence properties

As shown these films exhibited bright green luminescence when irradiated by 254 nm UV light. Fig. 3 shows the photoluminescence emission spectra of $\text{Zn}_2\text{SiO}_4:\text{Mn}$ films with 4 mol% Mn content as a function of deposition temperature.

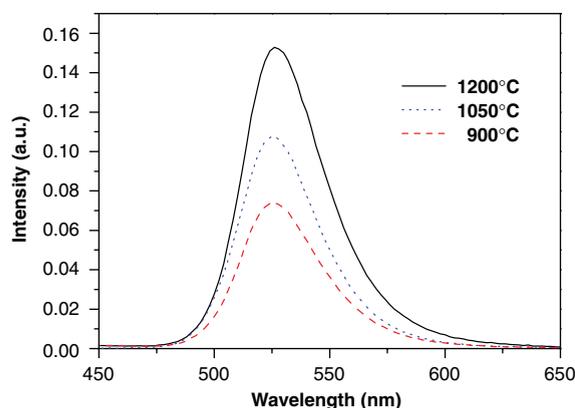


Fig. 3. PL spectra of $\text{Zn}_2\text{SiO}_4:4\%\text{Mn}^{2+}$ samples prepared at temperatures between 900 and 1200 °C.

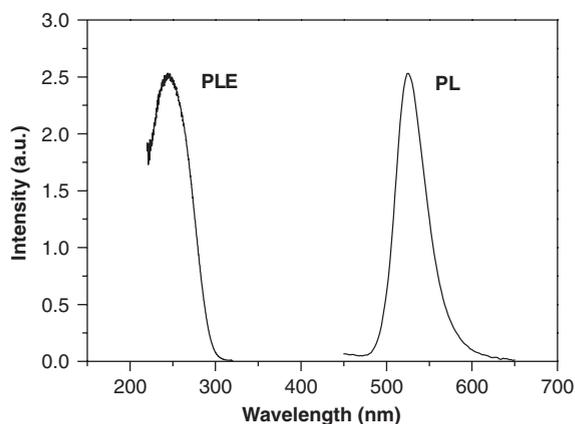
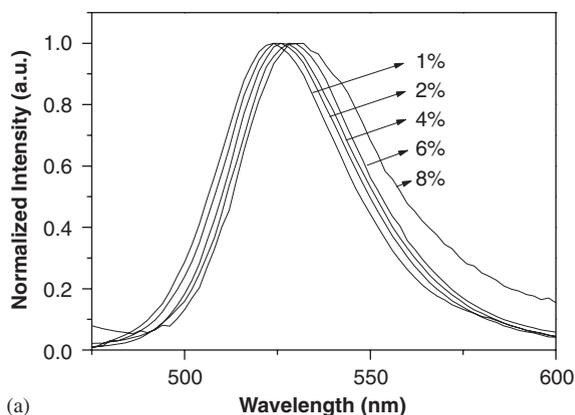


Fig. 4. PL and PLE spectrum of a typical $\text{Zn}_2\text{SiO}_4:2\%\text{Mn}^{2+}$ film.

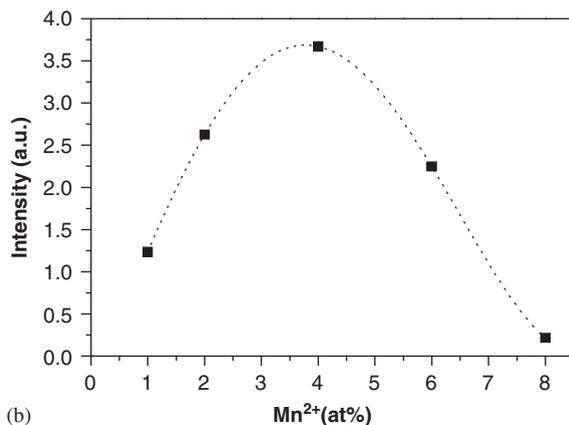
The luminescence intensity increased with deposition temperature. This was attributed to higher crystallinity and the fact that high deposition temperatures promoted the substitution of manganese for zinc in the willemite structure. The emission intensity from the sample deposited at 1200 °C was 47% higher than that from the sample deposited at 1050 °C, and 109% higher than that of the sample deposited at 900 °C. In contrast, the emission from the 750 °C sample was undetectable under the same conditions.

Fig. 4 shows the typical PL and PLE spectra of $\text{Zn}_2\text{SiO}_4:2\%\text{Mn}$ samples prepared at 1200 °C. The emission peak is centered at 524 nm with a half maximum width of 42 nm. This is the typical emission observed from Mn^{2+} doped $\alpha\text{-Zn}_2\text{SiO}_4$ phosphors and is attributed to the ${}^4\text{T}_1({}^4\text{G}) \rightarrow {}^6\text{A}_1({}^6\text{S})$ transition in the Mn^{2+} dopant centers [1]. The excitation spectrum consists of a strong excitation band ranging from 220 to 300 nm with a maximum at ~ 247 nm.

Fig. 5 compares the PL spectra of the films as a function of Mn^{2+} doping concentration. As shown in Fig. 5(a), with increasing Mn^{2+} doping concentration from 1% to 8%, the emission peak shifted to a slightly longer wavelength, from 524 to 532 nm. Fig. 5(b) shows the peak PL intensity as a function of manganese concentration. The highest measured PL intensity of films occurred near 4 mol% Mn^{2+} . Above this manganese concentration quenching led to decreasing PL intensity.



(a)



(b)

Fig. 5. (a) Normalized PL spectra of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ films doped with 1, 2, 4, 6, and 8% Mn^{2+} and (b) PL intensity as a function of Mn^{2+} concentration.

3.4. Cathodoluminescence properties

Fig. 6(a) shows the CL spectra obtained from $\text{Zn}_2\text{SiO}_4:4\% \text{Mn}$ samples prepared at different temperatures and excited by 10 keV electrons. Films prepared at 900 °C and above exhibited a broad green emission band whose intensity increased with increasing deposition temperature, consistent with the PL results. Yellowish green emission, which was too weak to see under the UV excitation, was detected from the film deposited at 750 °C. Apart from the main emission band, a weaker band was observed at $\sim 580 \text{ nm}$, indicating that the phase structure is not pure at this

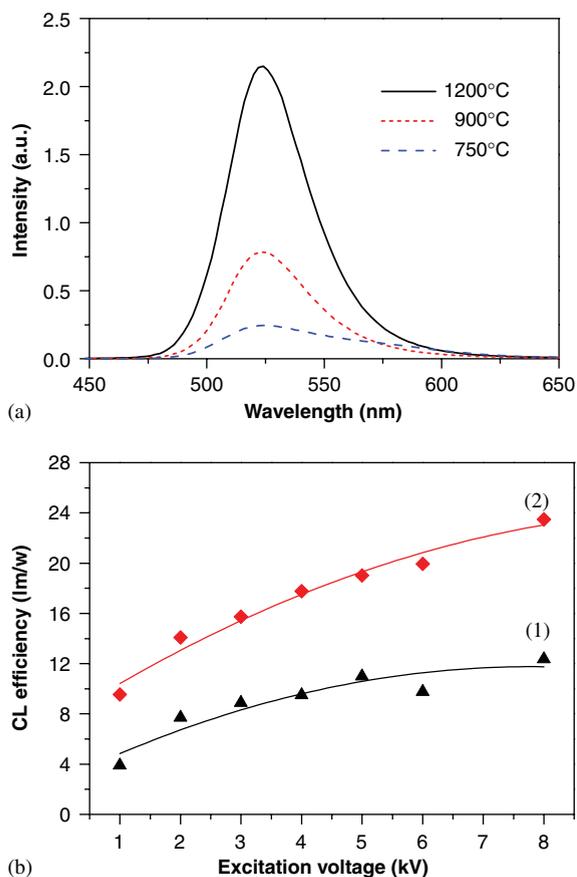


Fig. 6. (a) CL spectra of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphor films prepared by CCVD and (b) CL efficiency of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ as a function of electron voltage; $\text{Zn}_2\text{SiO}_4:4\%\text{Mn}^{2+}$ film prepared by CCVD at 1200 °C (1); commercial powder phosphor (2).

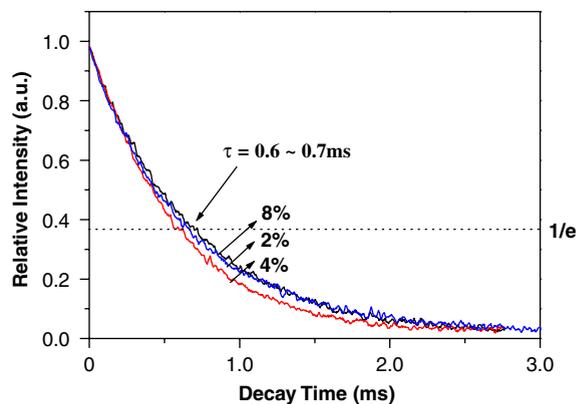


Fig. 7. Decay curves of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphor films prepared by CCVD.

deposition temperature. This may correspond to the emission of Mn^{2+} in $\beta\text{-Zn}_2\text{SiO}_4$, which transforms to $\alpha\text{-Zn}_2\text{SiO}_4$ above 900 °C [7]. Impurity phases such as ZnO may also be responsible for this different emission color.

Fig. 6(b) compares the CL efficiency of a $\text{Zn}_2\text{SiO}_4:4\%\text{Mn}^{2+}$ phosphor film prepared at 1200 °C with a commercial $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphor (RCA 33-W-2J). It was found that at an excitation energy of 8 kV the film has a CL efficiency of 12.4 lm/w, which is approximately 53% of the maximum luminescence measured from the reference powder phosphor. This result is significantly better than for thin films synthesized by the sol-gel method [1,2].

The CL decay curves of $\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ films with various doping concentration are shown in Fig. 7. These curves indicated that the life time ($\tau_{1/e}$) of films prepared by CCVD is about 0.6–0.7 ms. It is much shorter than the life time of the commercial powder phosphor, which is $\sim 4.5 \text{ ms}$. Defects and fine grain size in the films prepared by CCVD may be responsible for this fast decay.

4. Conclusions

$\text{Zn}_2\text{SiO}_4:\text{Mn}^{2+}$ phosphor films were successfully prepared by combustion CVD. The film consisted of densely packed particles with a fine grain size of several 100 nm. Strong PL and CL luminescence

intensities were observed, with a maximum CL luminescence equivalent to 53% of the luminescence measured from a commercial powder phosphor. A relatively fast CL decay with life time about 0.6–0.7 ms was also observed from these films.

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References

- [1] R. Selomulya, S. Ski, K. Pita, C.H. Kam, Q.Y. Zhang, S. Buddhudu, *Mater. Sci. Eng. B* 100 (2003) 136.
- [2] Z. Ji, K. Liu, Y. Song, Z. Ye, *J. Cryst. Growth* 255 (2003) 353.
- [3] A.H. Kitai, X. Ouyang, in: *Proceedings of SID '94 Symposium*, San Jose, CA, USA, 1994, p. 572.
- [4] M. Cich, K. Kim, H. Choi, S.J. Hwang, *Appl. Phys. Lett.* 73 (1998) 2116.
- [5] A.T. Hunt, W.B. Carter, J.K. Cochran, *Appl. Phys. Lett.* 63 (1993) 266.
- [6] Y. Liu, J. Dong, M. Liu, *Adv. Mater.* 16 (2004) 353.
- [7] C.C. Lin, P. Shen, *J. Non-Cryst. Solids* 281 (1994) 171.