Developing High-Efficiency Zn$_2$SiO$_4$ : Mn Thin-Film Phosphors for Flat-Panel Cathodoluminescent Displays

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Abstract

Zn$_2$SiO$_4$:Mn thin films were produced and studied for their potential application as thin-film phosphors for high-resolution flat-panel cathodoluminescent displays. Crystallized films with improved electrical conductivity were obtained after conventional and rapid thermal annealings in an N$_2$ environment at 850 to 1100 °C for 0.25 to 60 min. A maximum cathodoluminescent efficiency of 1.3 lm/W was achieved under dc excitation at 1500 V. The luminescent emission from these thin films peaked around 525 nm. The decay time of these films was controlled in the range of 2 to 10 ms by variation of the deposition and annealing parameters. Because their fast response time overcomes the long decay limitation of the Zn$_2$SiO$_4$:Mn powder phosphor, these thin films will be suitable for practical display applications.
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1. Introduction

Developing appropriate phosphors has been one of the key issues in the advancement of flat-panel cathodoluminescent (CL) displays such as field-emission displays (FEDs). Over the years, conventional cathode ray tube (CRT) displays and vacuum fluorescent displays (VFDs) have provided important applications for highly efficient sulfide and oxide powder phosphors [1,2].

Present flat-panel CL displays (i.e., FEDs) are based on the currently available phosphor technologies, which are adapted to commercial powder phosphors [3]. However, flat-panel CL displays have limited space between electrodes and preferably operate under low voltage and high current. These displays therefore usually confront high current saturation, heat dissipation, phosphor decomposition, and cathode emitter contamination; these conditions seriously affect the lifetime of the device. A highly efficient and stable form of phosphor such as crystallized thin films is most desirable to meet these challenges.

Compared to conventional phosphor films made by powder settling, thin-film phosphors made by chemical vapor deposition (CVD) and crystallization would have the advantages of high electrical and thermal conductivities, a high energy saturation limit, and high screen contrast and resolution. A high-efficiency oxide thin-film phosphor would be especially ideal, since oxides are generally less volatile than sulfides, so that there would be less out-gassing. Thin-film phosphors are also unlikely to release particles that could contaminate the cathodes.

Zn$_2$SiO$_4$:Mn is one of the known efficient green light-emitting phosphors. Its powder form, Mn-doped willemite (originally designated P1), was widely used in oscilloscope and radar screens. After the luminescent decay time was improved from nearly 30 ms to a few milliseconds, Zn$_2$SiO$_4$:Mn found application in flat-panel plasma displays [4]. During the last few years, rf magnetron sputtered Zn$_2$SiO$_4$:Mn thin films have been produced and studied for electroluminescent (EL) displays [5,6]. Increasing the Mn doping concentration was found to produce high EL luminance and sub-millisecond decay time. However, increasing the Mn concentration also tends to result in a significant reduction in the luminescence and lifetime of the phosphor [7].

We report here the recent development of Zn$_2$SiO$_4$:Mn thin films using metal organic chemical vapor deposition (MOCVD) and annealing treatment. We carried out a series of studies, including investigations of processing conditions, micromorphology, postdeposition treatment, and the CL performance of these thin films. Our investigations have emphasized the reproducible production of films and their application as high-efficiency and high-stability thin-film phosphors for flat-panel CL displays.
2. Experiment

2.1 Growth of Zn₂SiO₄:Mn Thin Films

Zn₂SiO₄:Mn thin films were grown on n-type, (111) oriented Si and indium tin oxide (ITO) coated glass substrates by low-pressure MOCVD. Figure 1 is a schematic of the 8-in. rotation-disk low-pressure MOCVD system used in this study. The system uses a vertical high-speed rotation-disk reactor (up to 1000 rpm), with multiple gas injectors on its top flange and a separate oxygen injector directly above the sample platter. The samples are heated by a radiative heater underneath the platter.

During the growth process, the temperature and mass flow rates were monitored and controlled by computer. Diethylzinc (DEZn), tetraethyl orthosilicate (TEOS), and tricarbonyl (methylcyclopentadienyl) manganese were used as precursors. Argon and oxygen gases were used as carrier and oxidant, respectively. The growth temperature was between 250 and 700 °C, and the growth rate was controlled at about 1 µm/hr. The final thickness of the films used in this investigation ranges from 0.5 to 1 µm. The stoichiometry and doping concentration were controlled by adjustments to the processing parameters during the CVD process. After the deposition, the films were treated by conventional furnace annealing.
(CFA) in an N₂ environment and by rapid thermal annealing (RTA) in Ar at 850 to 1100 °C. The annealing time varied from 15 s for RTA up to 60 min for CFA.

Crystallized Zn₂SiO₄:Mn films were obtained as a result of these annealing treatments. The electrical conductivity of the film was found to be significantly improved compared to the as-grown films. We carried out structural and micromorphological studies using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), Rutherford backscattering (RBS), and x-ray diffraction. Figures 2 and 3 show an SEM micrograph and the corresponding x-ray diffraction spectrum of a crystallized Zn₂SiO₄:Mn thin film. The x-ray diffraction data revealed the willemite structure with a

Figure 2. SEM micrograph of RTA-processed Zn₂SiO₄:Mn thin film.

Figure 3. Corresponding x-ray diffraction spectrum of RTA-processed Zn₂SiO₄:Mn thin film.
preferred (220) orientation. Although some pinholes were found in the crystallized films after CFA treatments longer than 30 min, the RTA-processed films maintained a smooth surface morphology. The Mn concentration was estimated below 0.5 percent per mole from the processing condition. The RBS study could not provide the exact Mn concentration because of the overlap of Zn and Mn signals. A layer of ZnO was also found on the Zn$_2$SiO$_4$:Mn film surface.

2.2 Cathodoluminescent Characterization

Characterization of the CL performance of crystallized Zn$_2$SiO$_4$:Mn thin films was carried out in a high-vacuum operation system. A Kimball Physics thermionic electron gun that operates both in dc and ac mode was used to excite the phosphor samples. The total electron current injected into the sample was collected by a Faraday cup on the back side of the sample holder and measured by an electrometer. The luminance was measured by Pritchard 1980A and 1980B photometers. Synchronized video signals were analyzed by a digital oscilloscope and a computer for a study of the luminescent decay. Figure 4 is a schematic of the CL characterization system.

CL spectroscopic data of all the phosphor samples were taken by a Gamma Scientific radiometer, which provides an accuracy within 1 nm. Commercial Zn$_2$SiO$_4$:Mn and ZnS:Cu,Al,Au powder phosphors were also electrophoretically deposited into phosphor films as standard references for comparison.

Figure 4. Schematic of system used for cathodoluminescent performance study.
3. Results and Discussion

3.1 Cathodoluminescent Performance

The CL performance of thin-film phosphors has been the focus of several previous investigations. (Among these are our own studies of over 10 thin-film phosphors including ZnO:Zn and ZnGa2O4:Mn.) Although promising results have been obtained in some of these studies [8], increasing efficiency generally remains a serious concern. In contrast, our crystallized Zn2SiO4:Mn thin films have demonstrated very encouraging CL performance. Under the excitation of a dc electron beam that was biased with an accelerating voltage of 1500 V, the luminance value reached 500 cd/m² at a current density of 0.32 mA/cm². The luminous efficiency, calculated as the total luminance per unit injected power density, was found to be 1.3 lm/W at a current density of 10 mA/cm². Figure 5 shows the CL behavior of a crystallized Zn2SiO4:Mn thin-film phosphor.

From our measurements of other phosphor samples under similar operating conditions, the performance of this Zn2SiO4:Mn thin film is nearly equivalent to 25 percent of the performance of its powder-type phosphor, or about 15 percent that of the best commercially available ZnS:Cu,Al,Au powder phosphor. Compared to other thin-film phosphors, such as ZnO:Zn, the Zn2SiO4:Mn thin film gives a luminance more than 10 times higher and has significantly better aging characteristics during the CL operation. Figure 6 shows comparisons of the CL performance of Zn2SiO4:Mn thin-film phosphor to that of commercial ZnS:Cu,Al,Au powder phosphor and ZnO:Zn thin-film phosphor.

Figure 5. Cathodoluminescent performance of crystallized Zn2SiO4:Mn thin-film phosphor.
3.2 Spectroscopic and Decay Performance

The luminescent emission of a Zn$_2$SiO$_4$:Mn phosphor, as studied earlier [9], is ascribed to the transition between the spin-orbit components of the $^4T_1$ excited state and the $^6A_1$ ground state of Mn$^{2+}$. The selection rule for this forbidden transition results in a long decay time for the luminescence. In our measurements, the CL emission spectrum of the Zn$_2$SiO$_4$:Mn thin film was found to be centered around 525 nm with a full width at half maximum (FWHM) of 40 nm. Figure 7 shows such a typical CL spectrum. Satisfactory chromaticity of this green emission was obtained. For these
films, we measured the shift of the spectrum under different annealing treatments. The CL emission spectrum exhibited a blue shift as the film was treated with higher temperatures or longer annealing times. This shift is due to the slight change of the Mn$^{2+}$ excited state inside the host crystal field. Such spectral behavior is shown in figure 8.

The luminescent decay behavior of Zn$_2$SiO$_4$:Mn thin-film phosphors was studied under a 30-µs pulsed electron-beam excitation. The CL signal from the thin film was digitized and measured by an oscilloscope and a computer. The decay time is calculated as the point when the luminescence decreases to 10 percent of the maximum value. It was found that the luminescent decay time of the thin film changed with the annealing condition. A range in decay time of 2 to 10 ms was measured after the Zn$_2$SiO$_4$:Mn thin-film samples were treated under the conditions described in section 2.1.

Figure 9 shows the decay behavior under three different postdeposition CFA treatments. Under CFA annealing at 1100 °C, the decay time was found to increase from 1.98 ms after 15 min to 8.58 ms after 30 min. The decay time decreased back to 3.75 ms when the annealing time was extended to 60 min. Since we did not change the Mn doping concentration, the variation of the decay time was an effect only of the host crystal structure of the thin film after the annealing. The same effect to the emission spectrum can also be seen in figure 8. As the decay time was shortened, the luminance was also found to decrease.

The response time of these Zn$_2$SiO$_4$:Mn thin films is suitable for VGA display applications, whose typical scan rate is about 14 ms. However, further efforts are needed to produce similar Zn$_2$SiO$_4$:Mn thin films on a glass substrate.
4. Summary

Our Zn$_2$SiO$_4$:Mn thin films, deposited by MOCVD and treated by CFA and RTA, have demonstrated the highest CL luminance and efficiency of over 10 thin-film materials that we have measured so far, including ZnO:Zn and ZnGa$_2$O$_4$:Mn. The decay time of the Zn$_2$SiO$_4$:Mn thin film was controllable by the postdeposition annealing treatment, as well as by the Mn concentration. As a result, the response time is shown to be adequate for high-speed display applications, which was not the case for the conventional
Zn$_2$SiO$_4$:Mn powder phosphor. These thin films are promising for application to FEDs and other CL devices. As we continue to improve the crystal quality of the thin film and increase the CL output, this study may also shed light on the mechanism of the Zn$_2$SiO$_4$:Mn luminescent process.

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