Synthesis and Characterization of Mn$^{2+}$ Doped Zn$_2$SiO$_4$ Phosphor Films by Combustion CVD Method

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Outline

- Introduction
  - Zn$_2$SiO$_4$:Mn$^{2+}$ phosphor
  - Combustion CVD process

- Objectives

- Experimental Procedures

- Results and Discussions

- Conclusions

- Future Work
Zn$_2$SiO$_4$·Mn$^{2+}$ Phosphor Properties

Application as Green phosphor
- Lamp
- CRT
- PDP
- EL

Synthesis of Zn$_2$SiO$_4$·Mn$^{2+}$ films
- Sol-gel process (R. Selomulya et al)
- Magnetron sputtering (A. H. Kitai et al)
- Charged liquid cluster beam technique (M. Cich et al)
Combustion CVD Process (A.T. Hunt et al)

Fuel gas/oxygen ratio, flow rate

Oxygen and fuel gas

Nozzle configuration, nozzle temperature

Flammable precursor solution

Solution concentration, flow rate

Spray distance

Substrate or collector

Deposition temperature

Nozzle

Flame

Fabricate: 10nm~30μm film; ~50nm powder
Schematic of CCVD Process

- Flow Controller
- Solution Pump
- Filter
- Nozzle
- Substrate
- Control & Data Acquisition
Combustion CVD Setup
CCVD Advantages

- Cost-effective
- Rapid process
- Easy to operate
- Great flexibility
- Compositional homogeneity
Objectives

- To prepare efficient luminescent phosphor films using a Combustion CVD process.

- To characterize the microstructure features of the prepared films.

- To evaluate the optical properties of the prepared films.
Preparation Process

Zn(NO₃)₂, TEOS, Mn(NO₃)₂ and Ethanol
Aqueous solution

O₂, CH₄
Gas

Atomization

Ignition

Deposition for ~10 min

Zn₂SiO₄·Mn²⁺ Film
(~20 µm in thickness, ~15mm in diameter)

All chemicals Soluble in ethanol

Products are limited to oxides
Characterization Methods

- XRD
- SEM
- PL and PLE
- CL and CL Efficiency
- CL Decay
Standard XRD pattern of Zn$_2$SiO$_4$ and Zn$_2$SiO$_4$:4%Mn$^{2+}$ samples prepared at temperatures between 750 and 1200°C.
Surface Morphology

SEM images of Zn$_2$SiO$_4$:Mn$^{2+}$ film deposited on quartz glass at 1200°C

Outer region
100~200nm grains

Central region
500~800nm grains

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

PLE band ranged from 220 ~ 300 nm with a maximum at ~247 nm

PL band centered at 524 nm with a half maximum width of 42 nm

Typical PL and PLE spectra of Zn$_2$SiO$_4$:2%Mn films prepared at 1200°C
PL as a function of Mn\textsuperscript{2+} concentration

(a) Normalized PL spectra of Zn\textsubscript{2}SiO\textsubscript{4}:Mn\textsuperscript{2+} films

(b) PL intensity as a function of Mn\textsuperscript{2+} concentration
Cathodoluminescence spectra and efficiency

Left) CL spectra of Zn$_2$SiO$_4$;Mn$^{2+}$ phosphor films prepared by CCVD

Right) CL efficiency of Zn$_2$SiO$_4$;Mn$^{2+}$ as a function of electron voltage
(1) Zn$_2$SiO$_4$;4%Mn$^{2+}$ film prepared at 1200°C; (2) commercial powder phosphor
CL Decay curves of Zn$_2$SiO$_4$ with Mn$^{2+}$ concentration from 2~8%

Commercial phosphor
$\tau_{1/e} = \sim 4.5$ms

Films by CCVD
$\tau_{1/e} = \sim 0.7$ms
Conclusion

- Zn$_2$SiO$_4$:Mn$^{2+}$ phosphor films were successfully prepared by combustion CVD.
- The films were well crystallized at deposition temperature of 1200 °C and showed highest luminescent efficiency.
- The films consisted of densely packed particles with a fine grain size of several hundred nanometers.
- 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.
Future Work

- Further optimization of this deposition technique and its extension to other oxide phosphor systems.

- Prepare multi-layer phosphor films with controlled color and refractory index.

- Investigate the possibility of building automatic combinatorial material synthesis system using CCVD technique.