



Cathodoluminescence from Thin Film $\text{Zn}_2\text{GeO}_4:\text{Mn}$ Phosphor Grown by Pulsed Laser Deposition

Lizandra C. Williams,^{a,z} David Norton,^a John Budai,^b and Paul H. Holloway^{a,*}

^aDepartment of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611-6400, USA

^bOak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

Low voltage cathodoluminescent (CL) characteristics of $\text{Zn}_2\text{GeO}_4:\text{Mn}$ thin-film phosphors grown by pulsed laser deposition were investigated. The effects of substrate heating (600–750°C) and substrate type (MgO, Si, and yttria-stabilized zirconia) on the cathodoluminescent properties were studied. A characteristic green emission peak at 540 nm was observed at substrate temperatures of 650, 700, or 750°C. However, the emission was red shifted to 650 nm for a substrate temperature of 600°C. The red shift in emission wavelengths from 540 to 650 nm was attributed to a change in ionic state of the activator from Mn^{2+} to Mn^{4+} . While the spectral position was independent of substrate type, the relative intensities of the cathodoluminescent emission peak varied with both substrate type as well as substrate temperature. At a substrate temperature of 600°C, the crystal structure of the film was mixed polycrystalline and amorphous. However, at substrate temperatures ranging from 650–750°C, the films were only polycrystalline with varying degrees of crystallinity that correlated with the CL intensity.

© 2004 The Electrochemical Society. [DOI: 10.1149/1.1767159] All rights reserved.

Manuscript submitted April 11, 2003; revised manuscript received February 2, 2004. Available electronically June 25, 2004.

Recently, oxide phosphors have gained attention as potential replacements for conventional cathodoluminescent phosphors in low voltage display applications such as vacuum fluorescent displays (VFDs) and field emission displays (FEDs).¹ Conventional sulfide phosphors such as $\text{ZnS}:\text{Cu}$, Al emit gases which may potentially damage the cathode and decompose under electron beam exposure leading to a decrease in luminous efficiency. Both effects can deteriorate the display device.^{1,2} Oxide phosphors are being considered as an alternative since they are more stable in a vacuum environment under irradiation of electrons and may emit fewer harmful gases to compromise the integrity of display devices.¹

Previous research has shown that electroluminescent phosphors may sometimes be used as suitable cathodoluminescent phosphors. One example of this is zinc gallate ($\text{ZnGa}_2\text{O}_4:\text{Mn}$), which has shown promise as an electroluminescent and cathodoluminescent phosphor.^{1,3,4} Zinc gallate has a spinel crystal structure and an optical bandgap of about 4.4 eV.¹ Similarly, zinc germanate has an optical bandgap of about 4.68 eV.⁵ The crystal structure of zinc germanate is rhombohedral. Thin-film zinc germanate doped with manganese ($\text{Zn}_2\text{GeO}_4:\text{Mn}$) has been evaluated as an electroluminescent phosphor,^{5,6} but its cathodoluminescent properties have not been reported.

In this study, the low voltage cathodoluminescent properties of thin-film zinc germanate doped with manganese ($\text{Zn}_2\text{GeO}_4:\text{Mn}$) are examined. Pulsed laser deposition was used to grow $\text{Zn}_2\text{GeO}_4:\text{Mn}$ on magnesium oxide (MgO), yttria-stabilized zirconia (YSZ), or silicon (Si) substrates. The structural properties as well as cathodoluminescence (CL) and photoluminescence (PL) spectra of the films are reported. The variation of the CL emission spectra with film deposition temperature and crystalline quality of film was also studied.

Experimental

A Zn_2GeO_4 ablation target doped with 1.5 atom % Mn was prepared by mixing and ballmilling ZnO , GeO_2 , and MnO_2 powders, which was then calcined in air at 1000°C for 8 h in covered alumina crucibles. The powder mixture was then milled again for 60 min and pressed into 2.5 cm diam targets. The targets were sintered in air at 1250°C for 36 h. In addition, ZnO powder was milled, pressed into targets, and sintered. A $\text{Zn}_2\text{GeO}_4:\text{Mn}/\text{ZnO}$ mosaic target was formed to control the cation ratio of Zn/Ge in the films. The area ratio of the target was 75% $\text{Zn}_2\text{GeO}_4:\text{Mn}$ and 25% ZnO . Single-

crystal (100) MgO, polycrystalline YSZ, and single-crystal Si-(100) substrates were cleaned by a solvent wash in a sonicator prior to deposition.

The films were grown using an excimer KrF laser with a wavelength of 248 nm. The energy of the laser was 130 mJ/pulse. The number of pulses and pulse frequency during deposition was 10,000 pulses at 10 Hz, immediately followed by a second cycle of 20,000 pulses at 20 Hz. Four different deposition temperatures (600, 650, 700, and 750°C) were maintained by a substrate heater and a thermocouple attached to the substrate stage. The substrates were allowed to reach the desired temperature before film growth commenced. The oxygen partial pressure in the system was maintained at 100 mTorr during all film growth.

The crystal structure was investigated using X-ray diffraction (XRD) with Cu $K\alpha$ radiation (0.15406 nm wavelength). CL was measured in an UHV chamber using a Kimball Physics EFG-7 electron gun operated at 4 kV and 8.5 μA and an Ocean Optics S2000 optical spectrometer. The detected spectral range was 200 to 850 nm.

Results and Discussion

The XRD data in Fig. 1 show the effect of the deposition temperature on the structural properties for film grown on MgO substrates. At 600°C (Fig. 1d), (223) and (550) weak diffraction peaks for Zn_2GeO_4 are evident indicating that some structural order exists. However, the weak peak intensity and the broad maximum at 2θ of

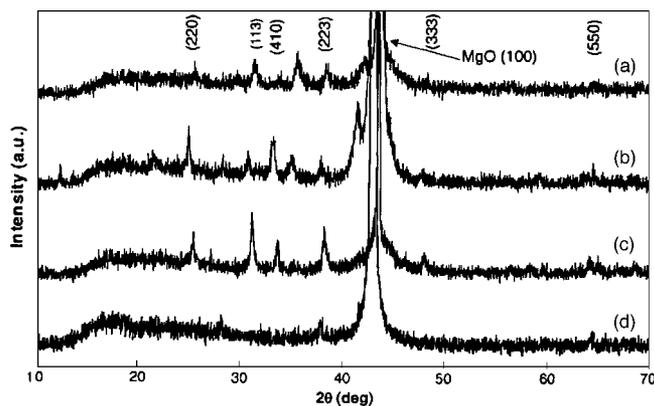


Figure 1. XRD pattern for films grown on MgO substrate at different deposition temperatures: (a) 750, (b) 700, (c) 650, and (d) 600°C.

* Electrochemical Society Active Member.

^z E-mail: lizandra@ufl.edu

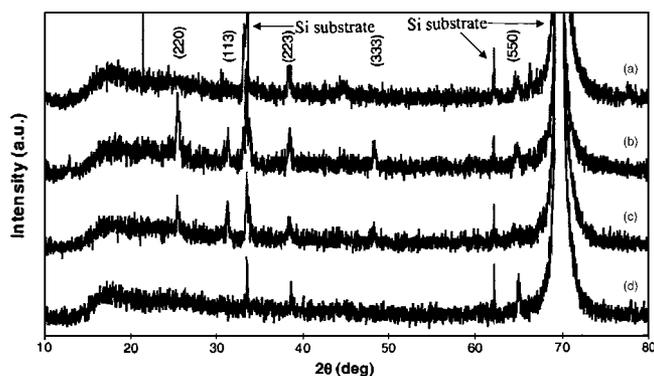


Figure 2. XRD pattern for films grown on Si substrate at different deposition temperatures: (a) 750, (b) 700, (c) 650, and (d) 600°C.

$\sim 18^\circ$ suggest that the majority of the film was amorphous with respect to XRD. The presence of additional Zn_2GeO_4 diffraction peaks in the XRD pattern shown in Fig. 1a-c indicate that the films grown at 650, 700, and 750°C are polycrystalline and exhibit better long-range order. Additional diffraction peaks at 2θ of $\sim 28^\circ$ and 36° for films grown at 750 and 700°C are attributed to an impurity GeO_2 phase. The shoulder diffraction peak at 2θ of $\sim 41^\circ$, detectable only in film grown at 750 and 700°C, also results from the GeO_2 impurity phase. XRD patterns from films grown on Si are shown in Fig. 2, which are comparable to the results for films grown on MgO. At 600°C, the presence of weak (223) and (550) Zn_2GeO_4 peaks and a broad peak at 2θ of $\sim 18^\circ$ in the diffraction pattern indicate that the film structure is mixed amorphous and polycrystalline. Again, the XRD patterns shown in Fig. 2a-c indicate that the films grown at temperatures from 650–750°C are polycrystalline with better long range order. Figure 3 presents the XRD pattern for films deposited on YSZ substrate at different deposition temperatures. For films deposited at 600°C (Fig. 3d), only a weak (550) diffraction peak is present, which indicates that Zn_2GeO_4 is again mixed amorphous and polycrystalline. Additional diffraction peaks from Zn_2GeO_4 were observed from films deposited at higher temperatures. Polycrystalline Zn_2GeO_4 films were formed at 650 and 700°C. The diffraction pattern for the film grown at 750°C (Fig. 3a) reveals a strongly preferred (110) texture.

In summary, the XRD data show improved crystallinity in films deposited at $T \geq 650^\circ\text{C}$. The quality of the diffraction peaks was good for films deposited at 650 and 700°C on MgO and Si substrates. This can be correlated with the Zn content in the film.

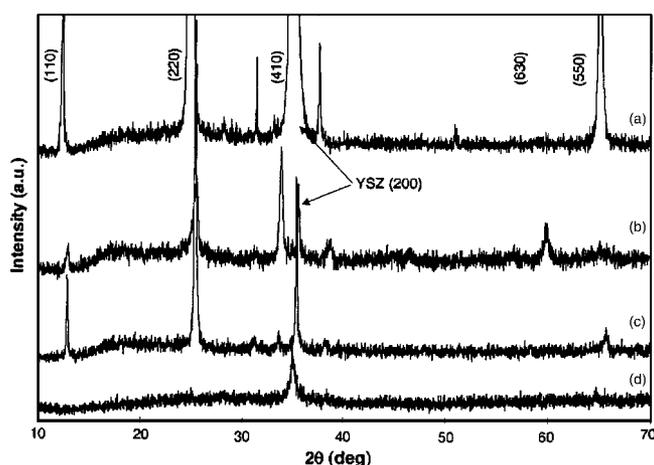


Figure 3. XRD pattern for films grown on YSZ substrate at different deposition temperatures: (a) 750, (b) 700, (c) 650, and (d) 600°C.

Table I. Zn/Ge atomic ratio in deposited $\text{Zn}_2\text{GeO}_4:\text{Mn}$ film vs. deposition temperature on various substrates.

	750°C	700°C	650°C
MgO	0.31	0.60	0.36
Si	0.42	0.47	0.57
YSZ	0.89	0.65	0.44

The Zn to Ge atomic percent ratio was measured using energy dispersive X-ray fluorescence (EDX) with a JEOL JSM 6400 scanning electron microscope (SEM) at a primary beam energy of 5 keV. These ratios, given in Table I, were measured for films deposited at $T \geq 650^\circ\text{C}$. All of the deposited films exhibited a low Zn/Ge ratio, ranging from 0.31 to 0.89, suggesting a Zn deficiency. The absolute values of these ratios are considered to be subject to large errors because the sensitivity factors for the Zn and Ge $L\alpha$ signals used were from look-up tables using different transitions and higher primary beam energies. Neither factor could be accurately corrected by the quantification program. Nonetheless, the relative changes in the ratios correlate well with the changes in the crystalline quality and CL intensities (see below), suggesting that they are valid trends. The fact that the XRD patterns indicate that Zn_2GeO_4 with varying degrees of crystallinities was present is consistent with these ratios having large absolute errors, but accurate trends. As shown in Table I, films deposited on MgO and Si substrates at 650 and 700°C have a higher Zn/Ge ratio than films deposited at 750°C. Because of the low Zn/Ge ratio for films deposited at 750°C on MgO or Si substrates, the crystalline quality decreases. The Zn/Ge ratio is highest (0.89) for the (110) textured film deposited at 750°C on YSZ, and this film has the best diffraction pattern, indicating the highest crystalline quality.

With respect to luminescent properties, the characteristic PL and EL emission wavelength of $\text{Zn}_2\text{GeO}_4:\text{Mn}$ is a broad peak with a maximum at 540 nm.^{5,6} The CL emission spectra for $\text{Zn}_2\text{GeO}_4:\text{Mn}$ on MgO deposited at various temperatures are shown in Fig. 4. The highest 540 nm CL intensity came from films that were grown at 650 and 700°C. For the 600°C sample, no CL emission at 540 nm is noted. Rather, the emission peak has shifted to 650 nm. The CL emission spectra from film deposited onto Si substrates are shown in Fig. 5. CL emission at 540 nm resulted only from the film grown at 750 and 700°C. Films grown at temperatures of 600 and 650°C did not show any detectable CL emission at 540 nm, but did show emission at 650 nm. The CL emission spectra from film deposited onto YSZ are presented in Fig. 6. The highest CL intensity, in this case, results from the film grown at 750°C. In contrast to the results for films grown on MgO and Si, the intensities for CL emission from

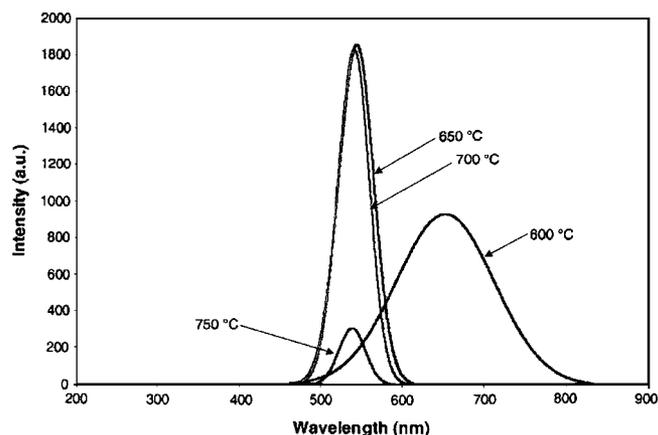


Figure 4. CL emission spectrum of $\text{Zn}_2\text{GeO}_4:\text{Mn}$ on MgO substrate at various deposition temperatures.

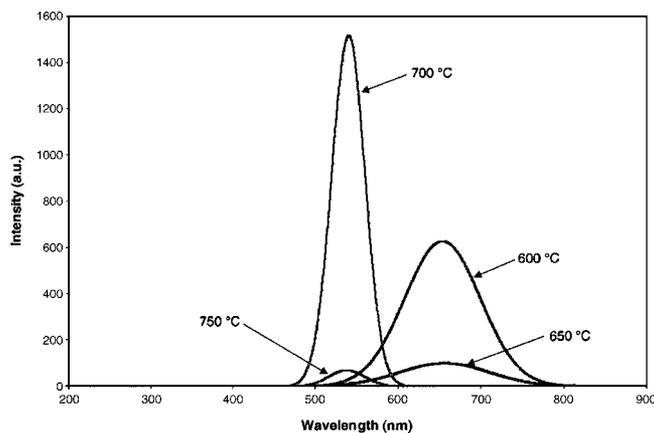


Figure 5. CL emission spectrum of $\text{Zn}_2\text{GeO}_4:\text{Mn}$ on Si substrate at various deposition temperatures.

the films deposited at 700 and 650°C on YSZ are less than that from the film grown at 750°C. There was no CL response at 540 nm from the film grown at 600°C, but again the emission peak was shifted and broadened to 650 nm.

A relationship between the CL emission maximum intensity and the film crystal quality and stoichiometry is obvious. The film with the best CL emission intensity at 540 nm was the (110) textured film grown on the YSZ substrate at 750°C, which also exhibited the best crystal quality. The films deposited at 700 and 650°C on MgO , which were determined to have good crystal quality and Zn/Ge ratios ~ 0.5 also exhibited the highest CL emission intensities at 540 nm for films deposited on this substrate. For films deposited on the Si substrate, the CL emission was also highest for the film with the best crystal quality which again correlated with higher Zn/Ge ratios. The fact that higher Zn/Ge ratios lead to brighter CL emission is consistent with observation of better crystallinity for the Zn_2GeO_4 crystal structure.

The highly textured film grown on the YSZ substrate at 750°C had the highest crystallinity, highest Zn/Ge ratio, and the best CL properties. It has been suggested that grain boundaries may limit the luminescent performance of a phosphor,⁷ which is consistent with emission from more randomly oriented polycrystalline film being lower when compared to the textured film on YSZ.

A red shift in wavelength of emission from green to red has also been noted in Mn-doped ZnGa_2O_4 phosphors.⁸ It was reported that Mn^{4+} ions in the octahedral sites led to red emission, while Mn^{2+} ions that occupied the tetrahedral sites in the spinel structure re-

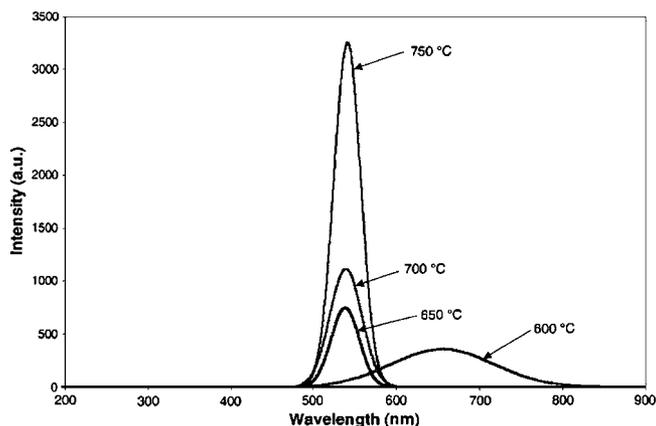


Figure 6. CL emission spectrum of $\text{Zn}_2\text{GeO}_4:\text{Mn}$ on YSZ substrate at various deposition temperatures.

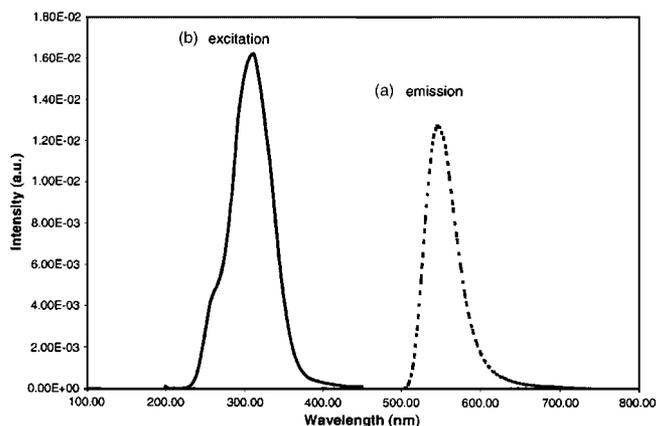


Figure 7. (a) Green emission spectrum of $\text{Zn}_2\text{GeO}_4:\text{Mn}$ excited with 325 nm radiation and (b) excitation spectrum monitored at 545 nm.

sulted in green emission.⁸ At 600°C, where the $\text{Zn}_2\text{GeO}_4:\text{Mn}$ films exhibit mixed short and long-range order, the dominant CL emission was at 650 nm. It is postulated that the Mn^{4+} ions are responsible for red emission at 650 nm. The rhombohedral crystal structure of Zn_2GeO_4 has only tetrahedral sites.⁹ Therefore, a change in substitution site must occur to accommodate the change in valency of Mn in $\text{Zn}_2\text{GeO}_4:\text{Mn}$. The Mn^{4+} ions may substitute for Ge^{4+} at the lower temperature. This substitution is possible since the ionic radii of both ions are 0.39 Å.¹⁰ At higher deposition temperatures (650, 700, and 750°C), the films develop a polycrystalline structure and the Mn^{2+} ion gains enough energy to move into the expected tetrahedral site and substitute for Zn^{2+} . This is again possible since the ionic radii of these atoms are close, 0.60 Å vs. 0.66 Å for Zn^{2+} and Mn^{2+} , respectively.¹⁰ The Mn^{2+} activator ions resulted in emission at 540 nm, as expected.

The excitation wavelengths for the Mn^{2+} and Mn^{4+} ions in ZnGa_2O_4 were different.⁸ The photoluminescence (PL) emission and the excitation (PLE) spectra for a Zn_2GeO_4 sample that emits green light are shown in Fig. 7. The emission excited with 325 nm radiation showed a peak at 545 nm. The excitation spectrum, monitored at 545 nm, exhibited an excitation peak at 310 nm with a small shoulder at 265 nm. The results are similar to what has been noted for a green emission from $\text{Zn}_2\text{GeO}_4:\text{Mn}$.⁵ The PL emission and excitation spectra for Zn_2GeO_4 samples that have longer wavelength emission are shown in Fig. 8. The PL emission for these samples, when excited with 325 nm radiation, results in a broad peak at 625

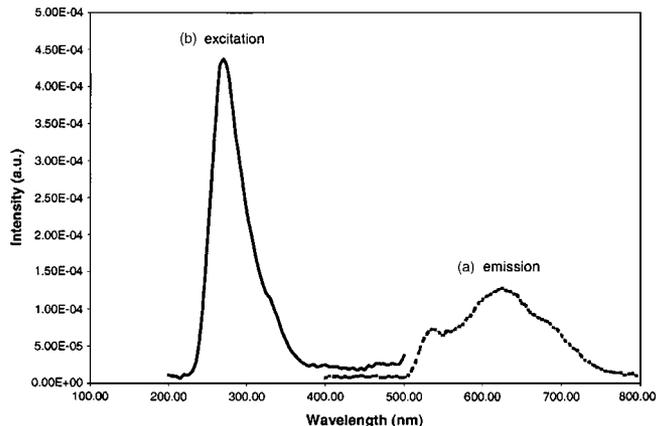


Figure 8. (a) Red emission spectrum of $\text{Zn}_2\text{GeO}_4:\text{Mn}$ excited with 325 nm radiation and (b) excitation spectrum monitored at 625 nm.

nm with a smaller peak showing at 535 nm. The excitation spectrum, monitored at 625 nm, exhibited a peak at 270 nm with a small shoulder at 330 nm. The difference in excitation spectra for green (540 nm) and red (650 nm) luminescence indicates that excitation of different states are responsible for each type of emission. This is consistent with the Mn ion exhibiting different valence states and substituting for either Zn or Ge, depending upon the temperature during deposition.

Conclusions

Zn₂GeO₄:Mn was successfully pulsed laser deposited onto MgO, Si, and YSZ substrates and the cathodoluminescent and photoluminescent properties of the film were characterized. The characteristic green emission peak for the Zn₂GeO₄:Mn phosphor film was observed at 540 nm for films deposited at $T \geq 650^\circ\text{C}$. The intensity of the cathodoluminescence varied with the deposition temperature, being high from films deposited at 650-700°C for MgO and Si substrate samples, and being highest for films deposited at 750°C for YSZ substrate samples. The film deposited at 750°C onto YSZ had a strongly preferred (110) texture and the largest Zn/Ge atomic ratio of 0.89. All other films that resulted in the characteristic green CL emission at 540 nm were more randomly polycrystalline. The numerical value of the ratio of Zn/Ge ratio was discussed and concluded to have large errors, but to accurately represent trends in the change in concentrations of Zn and Ge with deposition parameters. Higher ratios were shown to be consistent with improvement in crystallinity and CL intensity.

A shift to red emission at 650 nm was noted for all films grown at 600°C. This shift in emission is attributed to a change in the valence state of the activator from Mn²⁺ to Mn⁴⁺. A distinct differ-

ence was noted in the PL excitation spectra, indicating that different excited states are responsible for green and red emissions. The change in valence state was suggested to result from a change in the substitution site for the Mn ion. The Mn²⁺ ion substitutes for the Zn²⁺ in Zn₂GeO₄:Mn, resulting in green emission. However, when the Mn⁴⁺ ion substitutes for the Ge⁴⁺ ion, the emission is red-shifted to 650 nm.

Acknowledgments

This work has been sponsored by DARPA grant MDA 972-93-1-0030 through the Phosphor Technology Center of Excellence, ARO grants DAAD 19-00-1-0002 and DAAD 19-01-1-0603, and by Oak Ridge National Laboratory. The authors wish to thank Dr. Nigel Shepherd for assistance in obtaining PL data.

University of Florida assisted in meeting the publication costs of this article.

References

1. S. Itoh, H. Toki, K. Morimoto, and T. Kishino, *J. Electrochem. Soc.*, **138**, 1509 (1991).
2. S. Itoh, T. Kimizuka, and T. Tonegawa, *J. Electrochem. Soc.*, **136**, 1819 (1989).
3. T. Minami, T. Maeno, Y. Kuroi, and S. Takata, *Jpn. J. Appl. Phys., Part 2*, **34**, L684 (1995).
4. L. E. Shea, R. K. Datta, and J. J. J. Brown, *J. Electrochem. Soc.*, **141**, 2198 (1994).
5. J. S. Lewis and P. H. Holloway, *J. Electrochem. Soc.*, **147**, 3148 (2000).
6. J. P. Bender, J. F. Wager, J. Kissick, B. L. Clark, and D. A. Keszler, *J. Lumin.*, **99**, 311 (2002).
7. Y. E. Lee, D. P. Norton, and J. D. Budai, *Appl. Phys. Lett.*, **74**, 3155 (1999).
8. C. F. Yu and P. Lin, *J. Appl. Phys.*, **79**, 7191 (1996).
9. D. T. Palumbo and J. J. J. Brown, *J. Electrochem. Soc.*, **117**, 1184 (1970).
10. *CRC Handbook of Chemistry & Physics*; 78th ed., D. R. Lide, Editor, CRC Press, Boca Raton, FL (1997).