

# Visible electroluminescence from Eu:CaF<sub>2</sub> layers grown by molecular beam epitaxy on *p*-Si (100)

T. Chatterjee,<sup>a)</sup> P. J. McCann, and X. M. Fang

*Department of Electrical and Computer Engineering and Laboratory for Electronic Properties of Materials, University of Oklahoma, Norman, Oklahoma 73019*

J. Remington and M. B. Johnson

*Department of Physics and Astronomy and Laboratory for Electronic Properties of Materials, University of Oklahoma, Norman, Oklahoma 73019*

C. Michellon

*Centre Universitaire des Sciences et Techniques (C.U.S.T.), Blaise Pascal University, 63006 Clermont-Ferrand Cedex, France*

(Received 18 October 1996; accepted for publication 17 October 1997)

Visible electroluminescence (EL) is observed at room temperature by current injection into Eu:CaF<sub>2</sub> layers containing 7.5 and 8.0 at. % Eu grown by molecular beam epitaxy on lightly doped (100) *p*-type silicon. The EL spectra are broad with peaks near 700 and 600 nm, respectively. Room temperature photoluminescence spectra for the same samples exhibited peaks near 420 nm, with higher doped samples showing a more pronounced long wavelength tail. Although both metal and indium–tin–oxide (ITO) contacts were successfully used for current injection, the best EL intensity stability was achieved with contacts made of a 100 Å thick Al layer covered by a 2500 Å thick ITO layer. © 1997 American Institute of Physics. [S0003-6951(97)01951-7]

A small lattice parameter mismatch (~0.6% at 293 K) makes the CaF<sub>2</sub>/Si heteroepitaxial system a strong contender for multilayer integration of novel device structures on silicon. Recently several groups have successfully grown Nd, Er, and Eu doped CaF<sub>2</sub> layers on silicon using molecular beam epitaxy (MBE).<sup>1–3</sup> In an earlier letter,<sup>4</sup> we reported MBE growth and characterization of Eu:CaF<sub>2</sub> layers having Eu concentrations as high as 7.5 at. % on silicon (100) substrates. Although these Eu concentrations were considerably higher than prior Eu:CaF<sub>2</sub> work, there was no observed quenching of the photoluminescence (PL) from the Eu<sup>2+</sup> ions. This work showed that high concentrations of rare earth ions can be incorporated into MBE-grown CaF<sub>2</sub>, most probably because low MBE growth temperatures inhibit rare earth ion clustering. In this letter, we report visible electroluminescence (EL) from Eu:CaF<sub>2</sub> layers with high Eu concentrations grown epitaxially on silicon using MBE. Operating at less than 25 V, these devices offer a new approach to fabrication of reliable optical devices on silicon.

The Eu:CaF<sub>2</sub> layers studied were grown by MBE on lightly doped (3–7 Ω cm) *p*-type Si (100) substrates as described previously.<sup>4</sup> The layer structure is comprised of a 400 Å CaF<sub>2</sub> buffer layer, a 3600 Å Eu:CaF<sub>2</sub> layer and a 200 Å CaF<sub>2</sub> cap layer. Eu was incorporated into the Eu:CaF<sub>2</sub> layer using a separate effusion cell, allowing variation of the Eu concentration by varying the Eu cell temperature. The substrate temperature was kept at 580 °C during growth, and the growth rate was 20 Å per minute. An *in situ* postgrowth anneal at 1100 °C was carried out for 2 min to improve the surface morphology and crystallinity of the samples.<sup>4</sup> The concentration of Eu in the samples was determined using Eu to CaF<sub>2</sub> beam flux ratios and confirmed using x-ray photoelectron spectroscopy as described elsewhere.<sup>4</sup>

Samples, containing 0, 1.0, 4.1, 7.5, and 8.0 at. % Eu, were prepared for electrical studies by thermally evaporating 450×450 μm<sup>2</sup> Cr/Au (100 Å of Cr and 2400 Å of Au) contacts onto the layer structure using a shadow mask. The back sides of the Si substrates were completely metallized with thermally evaporated aluminum. Following metallization, the samples were annealed in forming gas (80% N<sub>2</sub>, 20% H<sub>2</sub>) for 20 min at 450 °C. Samples for EL studies were prepared by depositing (using dc magnetron sputtering with an Ar plasma) transparent conducting indium–tin–oxide (ITO) contacts either on the bare CaF<sub>2</sub> surface (for the 7.5% Eu layer) or onto a CaF<sub>2</sub> surface covered with approximately 100 Å of thermally evaporated aluminum (for the 8.0% Eu layer). The substrate was kept at 230 °C during the sputtering process and the Ar background pressure was 26 mTorr. The ITO layers were ~2500 Å thick with a sheet resistance of 12 Ω/□ and >80% transmittance over the spectral range in which the EL spectra were obtained. Electrical contact was made to the ITO layer using Pt/Ir probes and the back side (Si substrate) was mounted onto a copper plate with silver paint.

Room temperature PL spectra were obtained for Eu:CaF<sub>2</sub> samples containing 4.1%, 7.5%, and 8.0% Eu, using the 365 nm line of a Hg lamp as the excitation source. PL spectra from the same samples excited with the 253.7 nm Hg line did not show any features that were different from the 365 nm excitation. The collimated light from the samples (for both the PL and EL spectra) was optically chopped and coupled to a 0.25 m grating monochromator. A Hamamatsu H5704-01 PMT (long wavelength cutoff at 750 nm) connected to a lock-in amplifier was used to record the spectra. Both the EL and PL spectra were corrected for the spectral response of the measurement system which was determined using the measured versus known spectra of a 3200 K black body source.

<sup>a)</sup>Electronic mail: tchatterjee@ou.edu

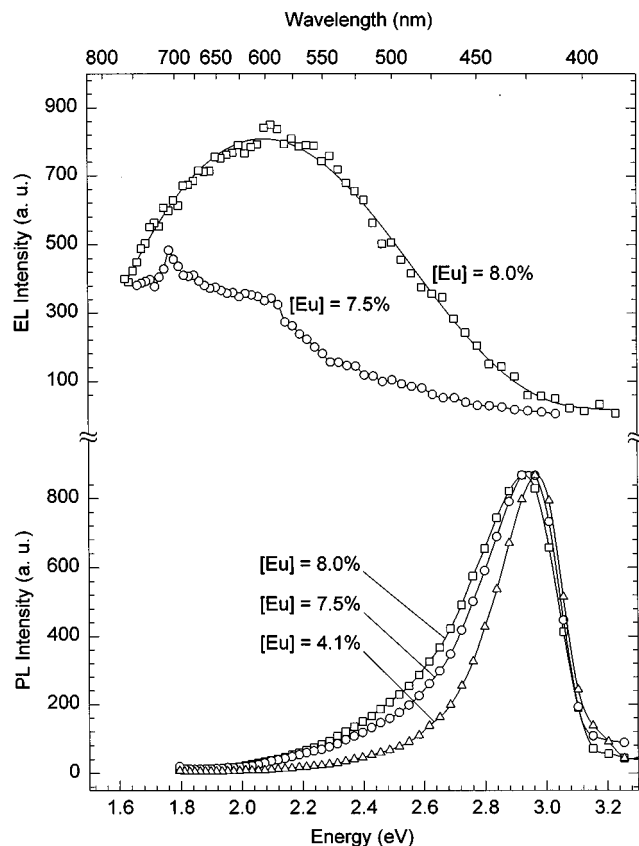


FIG. 1. EL spectra of 7.5% and 8.0% Eu samples and normalized PL spectra of 4.1%, 7.5%, and 8.0% Eu samples are shown in Fig. 1. The EL spectrum of the 7.5% Eu sample was obtained with the ITO electrode held at +14 V relative to the substrate and an injection current of 465 mA, while the 8.0% Eu EL spectrum was obtained with the ITO/Al contact held at -18.5 V relative to the Si substrate and an injection current of 240 mA. The PL spectra of 4.1%, 7.5%, and 8.0% Eu samples were excited with the 365 nm Hg line. The symbols are data points and the curves are regressions on the data.

Figure 1 shows EL spectra for 7.5% and 8.0% Eu samples along with normalized PL spectra for 4.1%, 7.5%, and 8.0% Eu samples. The EL spectrum of the 7.5% Eu sample was obtained with the ITO electrode held at +14 V relative to the substrate and an injection current of 465 mA, while the 8.0% Eu EL spectrum was obtained with the ITO/Al contact held at -18.5 V relative to the Si substrate and an injection current of 240 mA. Note that the 8.0% Eu sample exhibits more intense EL than the 7.5% Eu sample at about half the current level (240 mA versus 465 mA). This difference could be due to the different contact structures between the samples, though the role of slightly higher Eu content cannot be ruled out. The room temperature PL spectra are consistent with previously published low temperature PL spectra for MBE-grown Eu:CaF<sub>2</sub> layers,<sup>4,5</sup> the main difference being that thermal broadening effects completely obscure the zero-phonon line and vibronic sidebands. Note, however, that the 7.5% and 8.0% Eu samples exhibit significant inhomogeneous broadening with more emission between 450 nm and 600 nm than the 4.1% Eu sample. Additional long wavelength features in the PL spectra of Eu<sup>2+</sup> ions in Eu<sup>2+</sup>:Sr<sub>1-x</sub>Ba<sub>x</sub>F<sub>2</sub> and Eu<sup>2+</sup>:Ca<sub>1-x</sub>Ba<sub>x</sub>F<sub>2</sub> mixed fluorides with a few percent Ba was attributed to the strong in-

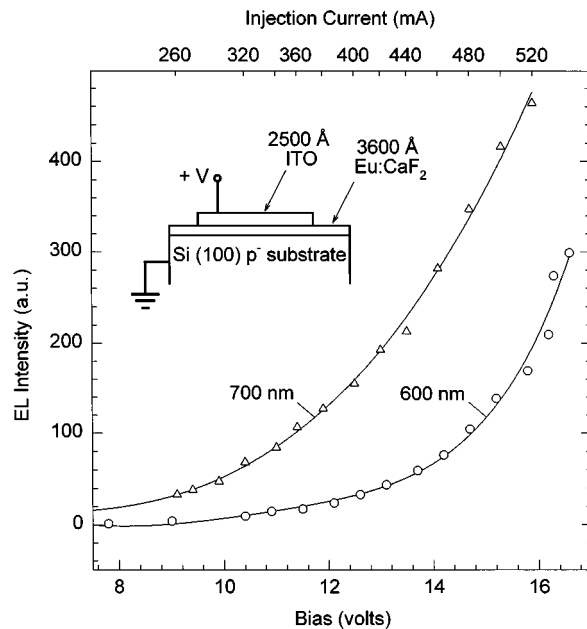


FIG. 2. EL intensity vs bias for the 7.5% Eu sample monitored at 600 nm and 700 nm. The EL spectrum of this sample is shown in Fig. 1. The 700 nm peak is excited at lower voltages than the 600 nm peak. The biasing configuration of the device is shown in the inset.

fluence of a large cation (Ba) near the Eu<sup>2+</sup> ion.<sup>6</sup> The presence of nearest neighbor Eu<sup>2+</sup> ions in our higher doped samples may be responsible for a similar effect.

Figure 2 shows EL intensities at 600 and 700 nm for the sample containing 7.5% Eu as a function of bias voltage. It can be seen that EL emission at 700 nm occurs at lower voltages, indicating that there may be more than one excitation path involved in this system. This sample was tested with the ITO contact biased positive relative to the Si substrate. Although injection current was similar, reversing the polarity of the bias resulted in no detectable optical signal. In contrast, the EL device with ITO/Al contact on the 8.0% Eu samples produced bright EL with contact biased negative relative to the Si substrate while reversing the polarity produced very faint EL. This electrode-material dependence is not understood at this point but may be due to band alignment and interface states affecting current injection efficiency.

EL structures were also fabricated with semitransparent Cr/Au and Al contacts. However the EL intensity from these structures was not stable as compared to the ones with the ITO or ITO/Al contacts, which have been operated for over 24 h (cumulative) at a current injection of 240 mA without any measurable degradation in EL intensity or change in the EL spectrum. The current versus voltage measurements on all the samples prepared for electrical characterization revealed that the Eu:CaF<sub>2</sub> layers were very leaky. It is not clear at this time whether this leakiness is necessary for EL.

The EL spectra in Fig. 1 do not show any similarity with the PL spectra, indicating that EL in these samples may not involve the excitation of Eu<sup>2+</sup> ions. In an Ar ion excitation experiment of bulk Eu:CaF<sub>2</sub> crystals,<sup>7</sup> peaks at 600 and 700 nm in the luminescence spectra have been attributed to Eu<sup>3+</sup> ions, although the PL spectra of these samples was not re-

ported. The features at 600 and 700 nm in the EL spectra may thus be evidence of  $\text{Eu}^{3+}$  ions in our layers. Optical studies of  $\text{Eu}^{3+}$  in  $\text{CaF}_2$  bulk crystal have shown that  $\text{Eu}^{3+}$  ions charge compensated with  $\text{O}^{2-}$  ions at neighboring fluorine ion vacancies have a broad ultraviolet absorption band peaked at 256 nm (Ref. 8) and a corresponding PL peak 600 nm, and that  $\text{Eu}^{3+}$  ions/clusters charge compensated with interstitial fluorine ions have several sharp optical absorption bands near 525, 580, 465, 390, and 400 nm yielding PL peaks near 590, 610, 650, 690, and 700 nm (Ref. 9). The absence of 600 nm PL features in our samples with 253.7 nm excitation suggests the lack of oxygen compensated  $\text{Eu}^{3+}$  centers, but does not exclude the possibility of  $\text{F}^-$  compensated  $\text{Eu}^{3+}$  centers in our  $\text{Eu}:\text{CaF}_2$  layers.

It is useful to compare our results with an earlier study of an  $\text{Eu}:\text{CaF}_2$  EL device on ITO-coated glass substrates using  $\text{ZnS}$  and  $\text{Y}_2\text{O}_3$  buffer layers and a thermally evaporated  $\text{Eu}:\text{CaF}_2$  layer.<sup>10</sup> In that work, the EL device, which appears to have been operated with ac voltages of  $\sim 100$  V, exhibited a strong emission around 420 nm and a weak broad emission around 590 nm. The position and shape of the 590 nm feature in their EL spectrum is similar to our EL spectra, possibly due to a common origin of this feature. PL spectra of their material with 365 nm excitation showed the 420 nm luminescence associated with  $\text{Eu}^{2+}$  ions but did not show any emission in the 590 nm range. This suggests that electric fields and/or electron impact are necessary for obtaining the lower energy emission around 590 nm. The excitation of  $\text{Eu}^{3+}$  requires less energy ( $\sim 2.5$  eV) than  $\text{Eu}^{2+}$  ( $> 3.1$  eV), as evident from optical absorption spectra of these two centers in  $\text{CaF}_2$ .<sup>9,11</sup> The absence of peaks at 420 nm in our EL spectra (Fig. 1) suggests that the electric fields involved are unable to produce electrons with kinetic energies suffi-

cient to excite  $\text{Eu}^{2+}$ . Therefore it seems possible that EL from our  $\text{Eu}:\text{CaF}_2$  layers may be due to the impact excitation of  $\text{Eu}^{3+}$  ions charge compensated with interstitial fluorine ions.

We have demonstrated room temperature visible electroluminescence using MBE-grown  $\text{Eu}:\text{CaF}_2$  layers on silicon which produces visible luminescence peaked at around 600 nm. The ability to generate this luminescence using relatively small dc voltages makes this system promising for Si-based display applications. Future work, however, is needed to clearly understand the EL mechanism and to understand the origin of current leakage in order to reduce operating currents and increase brightness.

The authors thank Denton McAllister for technical assistance. This work was supported by NSF EPSCoR under Grant Nos. OSR-9108771 and OSR-9550478.

<sup>1</sup>C. C. Cho, W. M. Duncan, T. H. Lin, and S. K. Fan, *Appl. Phys. Lett.* **61**, 1757 (1992).

<sup>2</sup>E. Daran, R. Legros, A. Munoz-Yague, C. Fontaine, and L. E. Bausa, *J. Appl. Phys.* **76**, 270 (1994).

<sup>3</sup>N. S. Sokolov and N. L. Yakovlev, *Solid State Commun.* **76**, 883 (1990).

<sup>4</sup>X. M. Fang, T. Chatterjee, P. J. McCann, W. K. Liu, M. B. Santos, W. Shan, and J. J. Song, *Appl. Phys. Lett.* **67**, 1891 (1995).

<sup>5</sup>X. M. Fang, T. Chatterjee, P. J. McCann, W. K. Liu, M. B. Santos, W. Shan, and J. J. Song, *J. Vac. Sci. Technol. B* **14**, 2267 (1996).

<sup>6</sup>C. Dujardin, B. Moine, and C. Pedrini, *J. Lumin.* **54**, 259 (1993).

<sup>7</sup>K. Aono, M. Iwaki, and S. Namba, *Nucl. Instrum. Methods Phys. Res. B* **32**, 231 (1988).

<sup>8</sup>S. M. Dhopte, P. L. Muthal, V. K. Kondawar, and S. V. Moharil, *J. Lumin.* **54**, 95 (1992).

<sup>9</sup>R. J. Hamers, J. R. Wietfeldt, and J. C. Wright, *J. Chem. Phys.* **77**, 683 (1982).

<sup>10</sup>N. Miura, T. Ishikawa, T. Sasaki, T. Oka, H. Ohata, H. Matsumoto, and R. Nakano, *Jpn. J. Appl. Phys., Part 2* **31**, L46 (1992).

<sup>11</sup>J. F. Owen, P. B. Dorain, and T. Kobayasi, *J. Appl. Phys.* **52**, 1216 (1981).