

# Cathodoluminescence study of erbium in $\text{La}_{1-x}\text{Er}_x\text{F}_3$ epitaxial layers on Si(111)

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Erbium-substituted  $\text{La}_{1-x}\text{Er}_x\text{F}_3$  lanthanum trifluoride epitaxial layers have been grown on Si(111) substrates by molecular beam epitaxy (MBE). Strong near-infrared luminescence, peaked at  $1.54\text{ }\mu\text{m}$ , was observed from such films under electron beam excitation. This cathodoluminescence arises from the intra-4f-shell transitions  $^4I_{13/2} \rightarrow ^4I_{15/2}$  of  $\text{Er}^{3+}(4f^{11})$ . The infrared spectra reveal that MBE-grown  $\text{LaF}_3$  layers on Si(111) crystallize in the hexagonal tysonite structure, typical for bulk  $\text{LaF}_3$  single crystals.

In recent years, the growth and characterization of insulating epitaxial fluoride layers, such as  $\text{LaF}_3$  and  $\text{CaF}_2$ , on semiconductor surfaces (Si, GaAs) has become an active field of materials research. Such epitaxial insulator/semiconductor layers offer new possibilities for novel devices, such as metal epitaxial insulator-semiconductor field-effect transistors (MEISFETs) and three-dimensional staggered structures, which cannot be realized by the traditional  $\text{SiO}_2/\text{Si}$  system.<sup>1</sup> In addition, epitaxially grown single crystalline insulators on semiconductor surface are more adapt for basic studies of the physical properties of insulator/semiconductor interfaces.

Among conceivable candidates, the system  $\text{LaF}_3/\text{Si}(111)$  has attracted much attention.<sup>2,3</sup> For such work, techniques able to characterize the crystalline structure and perfection of the epitaxially deposited fluoride layers are indispensable. Electron diffraction (LEED), x-ray diffraction (ADXRD), and electron energy loss spectroscopy (HREELS) are appropriate techniques and have been successfully applied.<sup>2,4,5</sup> LEED and ADXRD unequivocally proved the presence of the  $\text{LaF}_3$  supercell structure containing six molecules per unit cell.<sup>4</sup> The *c* axis of the  $\text{LaF}_3$  cell is parallel to the [111] direction of the silicon substrate. The two-dimensional hexagonal symmetry cells are displaced from each other by a rotation angle of  $30^\circ$ . Within the instrumental resolution no change in the  $\text{LaF}_3$  lattice parameters could be detected, i.e., the layer was found to be relaxed. But due to rocking curve analysis a high density of lattice defects was observed.<sup>4</sup>

It is the purpose of this letter to show that for the system  $\text{LaF}_3/\text{Si}$  other techniques are also possible. For this we recall that  $\text{LaF}_3$  is a traditional model host crystal for the strongly luminescent trivalent rare-earth (lanthanide) ions.<sup>6,7</sup> Laser action of the systems  $\text{LaF}_3:\text{Nd}^{3+}(4f^3)$  and  $\text{LaF}_3:\text{Er}^{3+}(4f^{11})$  was demonstrated a long time ago.<sup>7,8</sup> Much spectroscopic work has been devoted to the system  $\text{LaF}_3:\text{Er}^{3+}(4f^{11})$ ,<sup>8,9</sup> in order to elucidate the influence of the crystalline electric field (Stark effect) on the characteristic intra-4f-shell transitions of trivalent erbium,  $\text{Er}^{3+}(4f^{11})$ .

In the present study it will be shown that erbium-

substituted  $\text{La}_{1-x}\text{Er}_x\text{F}_3$  layers grown by molecular beam epitaxy (MBE) on silicon (111) substrates are strongly luminescent, in particular in the near-infrared ( $\sim 1.54\text{ }\mu\text{m}$ ) spectral range. This emission is caused by the intra-4f-shell transition  $^4I_{13/2} \rightarrow ^4I_{15/2}$  of  $\text{Er}^{3+}(4f^{11})$ .<sup>8,9</sup> The energy level scheme of the  $^4I_{15/2}$  ground state of  $\text{Er}^{3+}$  in  $\text{LaF}_3/\text{Si}(111)$  derived from these spectra will turn out to be practically identical to that of  $\text{Er}^{3+}$  in bulk  $\text{LaF}_3$  single crystals, which occurs in the hexagonal tysonite structure.<sup>10</sup>

The lanthanide trifluoride layers investigated in this study were grown by molecular beam epitaxy (MBE) on *n*-type Si(111) wafers with a bulk resistivity of 15–30  $\Omega\text{ cm}$ . Since  $\text{LaF}_3$ , as  $\text{ErF}_3$ , evaporates as molecules, the stoichiometry problem is solved automatically. Details of the growth conditions are described elsewhere.<sup>4,5</sup> For doping  $\text{LaF}_3$  with erbium, powdered  $\text{ErF}_3$  (3N) was mixed under pure (4N) powdered  $\text{LaF}_3$  with weight fractions between 0.05 and 0.5%. Since the vapor pressures of  $\text{LaF}_3$  and  $\text{ErF}_3$  are close to each other at the evaporation temperature (1200–1300  $^\circ\text{C}$ ) it is reasonable to assume that the La/Er ratio of the deposited layer will be nearly the same as that of the source.

Cathodoluminescence (CL) spectra were taken on a JEOL JSM-840 scanning electron microscope, equipped with an Oxford Instruments cold stage and CL collector. For photon detection in the  $1.5\text{ }\mu\text{m}$  near-infrared range a germanium detector was used.

An overall CL spectrum of a 3000-Å-thick  $\text{La}_{0.95}\text{Er}_{0.05}\text{F}_3$  epitaxial layer on a Si(111) substrate is shown in Fig. 1. In the  $1.5\text{ }\mu\text{m}$  near-infrared spectral range a strong characteristic luminescence spectrum is observed which arises from the intra-4f-shell transitions  $^4I_{13/2} \rightarrow ^4I_{15/2}$  of  $\text{Er}^{3+}(4f^{11})$ . In the visible and near-ultraviolet spectral range further much weaker emissions occur (Fig. 1). The sharp line features arise from higher lying  $4f^{11}$  states of  $\text{Er}^{3+}$ , such as the transitions  $^4S_{3/2} \rightarrow ^4I_{15/2}$  and  $^2H_{9/2} \rightarrow ^4I_{13/2}$  (Refs. 8, 9) of  $\text{Er}^{3+}(4f^{11})$ , whereas the broad background emission in the 300–500 nm spectral region apparently results from other, not rare-earth-related defect centers, in the  $\text{LaF}_3$  host. A more thor-

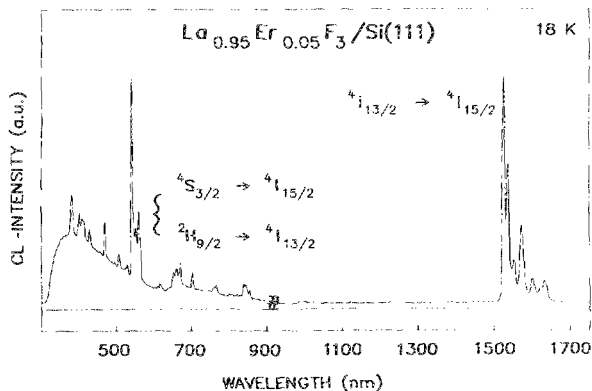


FIG. 1. Cathodoluminescence (CL) spectrum of a  $\text{La}_{0.95}\text{Er}_{0.05}\text{F}_3/\text{Si}(111)$  film grown by MBE on a Si(111) substrate. Electron beam parameters: 20 kV, 750 nA focused on  $0.1 \times 0.1 \text{ mm}^2$ . Note change of photon detector (PMT/Ge) at  $\lambda = 900 \text{ nm}$ .

ough analysis of the very weak spectral emissions in the visible and near-ultraviolet spectral range was not attempted.

The  $1.5 \mu\text{m}$  infrared emission spectrum of the  $\text{La}_{0.95}\text{Er}_{0.05}\text{F}_3/\text{Si}$  layer is shown in Fig. 2 on an expanded spectral scale, and as a function of temperature. The multiplicity of lines results from crystal field splittings of the  $^4I_{15/2}$  ground state and the  $^4I_{13/2}$  excited state whereas the much larger energetical separation between the  $^4I_{13/2}$  and  $^4I_{15/2}$  levels is caused by spin-orbit interaction.

In a crystal field of lower than cubic symmetry, as present at a La substitutional site in the  $\text{LaF}_3$  lattice, the free ion spin-orbit levels  $^4I_{15/2}$  and  $^4I_{13/2}$  split into eight and seven Kramers doublet states, respectively. At sufficiently low temperatures, a maximum of eight luminescence lines

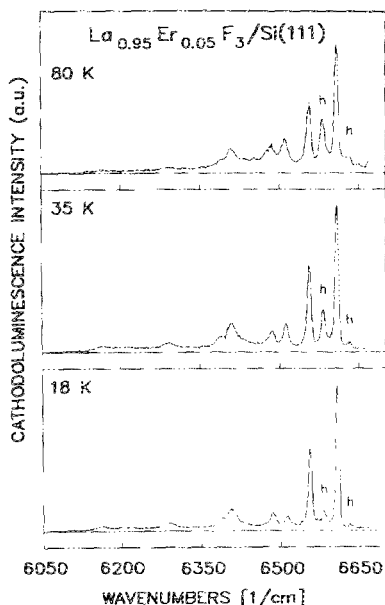


FIG. 2. Cathodoluminescence spectra of  $\text{La}_{0.95}\text{Er}_{0.05}\text{F}_3/\text{Si}(111)$  in the  $1.5 \mu\text{m}$  near-infrared spectral range, as arising from the intra- $4f$ -shell transitions  $^4I_{13/2}$ ,  $^4I_{15/2}$  of  $\text{Er}^{3+}(4f^{11})$ , at different temperatures. Lines labelled  $h$  are caused by thermal population of the first excited  $^4I_{13/2}$  crystal field level at elevated temperatures.

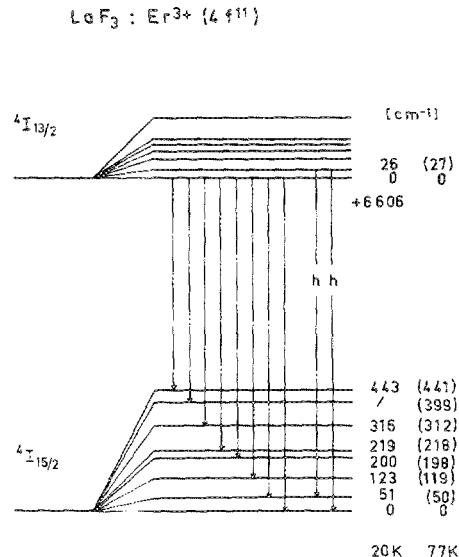


FIG. 3. Crystal field splittings of the  $^4I_{15/2}$  and  $^4I_{13/2}$  states of  $\text{Er}^{3+}(4f^{11})$  in MBE-grown  $\text{La}_{0.95}\text{Er}_{0.05}\text{F}_3/\text{Si}(111)$  layers. Values in parentheses refer to  $\text{Er}^{3+}(4f^{11})$  in bulk  $\text{LaF}_3$  single crystals (see Refs. 8 and 9).

is therefore expected to occur. At elevated temperature, the higher lying crystal field levels of the luminescent state  $^4I_{13/2}$  become thermally populated and additional "hot" luminescence lines ( $h$ ) appear in the spectrum, as illustrated in Fig. 2.

The level scheme derived from these CL spectra is shown in Fig. 3. Also included in this figure are the corresponding crystal field splittings of  $\text{Er}^{3+}(4f^{11})$  in bulk  $\text{LaF}_3$  single crystals, as determined by Krupke and Gruber<sup>8,9</sup> a long time ago. A close correspondence is seen to exist. This demonstrates that the structure of our MBE-grown  $\text{LaF}_3/\text{Si}(111)$  layers is very similar to that of bulk  $\text{LaF}_3$ . The same conclusion has been reached from an analysis of the LEED and ADXRD data.<sup>4</sup>

The spectral width of the erbium-induced luminescence lines in our  $\text{La}_{1-x}\text{Er}_x\text{F}_3/\text{Si}(111)$  epitaxial layers is  $\sim 3 \text{ cm}^{-1}$ . No significant thermal line broadening was observed up to 80 K; see Fig. 2. This highly exceeds corresponding values typical for rare-earth activated bulk single crystalline ionic hosts, where the linewidth may be well below  $0.1 \text{ cm}^{-1}$ , at sufficiently low temperature. The discrepancy might arise from a crystalline strain broadening of the  $4f$  levels, induced by the  $\sim 7\%$  lattice mismatch between the  $\text{La}_{1-x}\text{Er}_x\text{F}_3$  epitaxial layer and the silicon substrate.

We mention that additional information on the crystalline structure and perfection of the epitaxial  $\text{LaF}_3:\text{Er}^{3+}$  layers could also be obtained by electron spin resonance (ESR; 9.5 GHz). An ESR line at  $g = 8.14(8)$ , accompanied by weaker  $^{167}\text{Er}$  hyperfine structure satellites was observed when the external magnetic field was normal to the  $\text{La}_{1-x}\text{Er}_x\text{F}_3/\text{Si}(111)$  interface.<sup>11</sup> This ESR spectrum is very similar to that inferred from ESR data reported a long time ago<sup>12</sup> for  $\text{Er}^{3+}(4f^{11})$  in bulk, hexagonal  $\text{LaF}_3$  single crystals, for  $H \parallel c$ .

In conclusion, we have observed strong near-infrared

intra-4*f*-shell luminescence of  $\text{Er}^{3+}(4f^{11})$  in erbium-doped  $\text{LaF}_3$  layers grown by MBE on silicon substrates. Details of the optical spectra reveal that the crystalline structure and perfection of these layers is comparable to that of bulk  $\text{LaF}_3$  single crystals. We finally point out that the system  $\text{La}_{1-x}\text{Er}_x\text{F}_3/\text{Si}(111)$  bears some potential for novel, silicon-based, optoelectronic devices, operating at  $1.54\ \mu\text{m}$ .<sup>13</sup>

We wish to thank Martina Baeumler for providing the ESR data.

<sup>1</sup> See e.g., F. J. Himpsel, U. O. Karlsson, F. R. McFeely, J. F. Morar, D. Rieger, A. Taleb-Ibrahimi, and J. A. Yarmoff, *Mater. Sci. Engineer. B* **1**, 9 (1988).

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