Molecular beam epitaxial growth of Eu-doped CaF$_2$ and BaF$_2$ on Si

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The growth of Eu-doped CaF$_2$ and BaF$_2$ thin films on Si(100), (110), and (111) substrates has been realized by molecular beam epitaxy using elemental Eu evaporation. Very bright blue emissions from Eu-doped CaF$_2$ and yellow emissions from Eu-doped BaF$_2$ were obtained in the wavelength range of 400–850 nm at 10 K. Depending on the Si substrate orientation, the zero-phonon line of Eu$^{2+}$ in the CaF$_2$ thin films was shifted by different amounts relative to that of bulk CaF$_2$ due to residual strain in these epilayers. © 1996 American Vacuum Society.

I. INTRODUCTION

Increasing interest in the incorporation of rare-earth (RE) elements in epitaxial thin films of alkaline-earth fluorides is motivated by potential applications in light emitters and solid state microcavity lasers. Growth of these materials on Si substrates offers potential compatibility with Si-based technology. Nd- and Er-doped CaF$_2$ films grown on Si substrates by MBE and that Eu-doped CaF$_2$ /Si substrates using a two-stage growth method. 7 The first stage was deposition of 600 Å of CaF$_2$ and 570 Å of BaF$_2$ at 580 °C. The second stage was rapid thermal annealing at 820 °C, followed by in situ annealing at 1100 °C for a few minutes. For the growth of Eu-doped CaF$_2$ films on Si(110), a 20 Å CaF$_2$ and a 7800 Å Eu-doped CaF$_2$ layer were deposited at 840 °C. These CaF$_2$/Si(110) films always exhibit a ridged and grooved surface morphology. 6 Eu-doped CaF$_2$/Si(111) films were obtained by depositing a 4100 Å CaF$_2$ buffer and a 600 Å Eu-doped CaF$_2$ layer at 700 °C. Eu-doped BaF$_2$ films were grown on Si(100) substrates using a two-stage growth method. 7 The first stage was deposition of 600 Å of CaF$_2$ and 570 Å of BaF$_2$ at 580 °C. The second stage was rapid thermal annealing at 820 °C. This annealing was followed by the deposition of a 4600 Å Eu-doped BaF$_2$ layer at 750 °C.

Figure 1 shows the RHEED patterns recorded during the growth of Eu-doped CaF$_2$ and BaF$_2$ on Si(100) with Eu concentrations of ~4.05 at. % and ~0.93 at. %, respectively. The Eu concentrations were determined in a way described in Ref. 4. A well-defined Si(100)-two-domain (2×1) pattern appears after oxide desorption [Fig. 1(a)]. Diffraction spots, indicative of three-dimensional island growth, were observed after the growth of the Eu-doped CaF$_2$ layer [Fig. 1(b)]. No apparent change in the surface structure of the CaF$_2$ matrix due to Eu incorporation is detected through comparison of the RHEED patterns of the Eu-doped CaF$_2$ layer with those of the undoped CaF$_2$ buffer. However, surface degradation is visible under optical microscopy when Eu concentration exceeds ~7.48 at. % even though the RHEED patterns remain unchanged. Precipitation of Eu at high doping levels may be responsible for the surface degradation. The effect of in situ annealing is evident by comparing the RHEED patterns

II. EXPERIMENT

Growth of Eu-doped CaF$_2$ and BaF$_2$ on Si was carried out in an Intevac Modular GEN II MBE system with a background pressure of ~10$^{-10}$ Torr throughout deposition. The 3-in.-diameter $p$-type Si substrates (Silicon Sense, Inc.) were cleaned using the Shirakaki method. 5 The passivating oxide formed during the ex situ cleaning procedure was thermally desorbed in the growth chamber after several minutes at ~1100 °C. High purity polycrystalline CaF$_2$ and BaF$_2$ were evaporated from graphite-coated PBN crucibles at typical growth rates of 20 Å/min and 19 Å/min for CaF$_2$ and BaF$_2$ with cell temperatures of 1300 and 1180 °C, respectively. An elemental source of Eu was evaporated from a separate low-temperature effusion cell heated to 300–400 °C to give beam equivalent pressures of 3.5×10$^{-10}$–1.9×10$^{-8}$ Torr.

Smooth Eu-doped CaF$_2$ films on Si(100) were obtained by growing a 400 Å CaF$_2$ buffer, a 3600 Å Eu-doped CaF$_2$ layer and a 200 Å CaF$_2$ top layer at 580 °C followed by in situ annealing at 1100 °C for a few minutes. For the growth of Eu-doped CaF$_2$ films on Si(110), a 20 Å CaF$_2$ and a 7800 Å Eu-doped CaF$_2$ layer were deposited at 840 °C. These CaF$_2$/Si(110) films always exhibit a ridged and grooved surface morphology. 6 Eu-doped CaF$_2$/Si(111) films were obtained by depositing a 4100 Å CaF$_2$ buffer and a 600 Å Eu-doped CaF$_2$ layer at 700 °C. Eu-doped BaF$_2$ films were grown on Si(100) substrates using a two-stage growth method. 7 The first stage was deposition of 600 Å of CaF$_2$ and 570 Å of BaF$_2$ at 580 °C. The second stage was rapid thermal annealing at 820 °C followed by the deposition of a 4600 Å Eu-doped BaF$_2$ layer at 750 °C.
from the lowest lying ZPLs shown in Fig. 2 arise from the electronic transition vibronic sideband peaking at about 422 nm in each spectrum. While in situ annealing improves the growth morphology by smoothing out the [111] facets on the surface, it does not seem to alleviate the morphological features due to Eu precipitation. Following the deposition of BaF$_2$ at 580 °C, a spotty RHEED pattern with off-angle lines and arrow-head features was observed immediately after the substrate temperature was raised to 1100 °C, signifying the smoothing of the CaF$_2$ surface. Dramatic improvement in the growth morphology was achieved after in situ annealing and the second-stage growth. Diffraction streaks emerged in the RHEED patterns [Fig. 1(e)] and no change due to the incorporation of Eu in the BaF$_2$ lattice was observed.

Figure 2 shows the PL spectra of three Eu-doped CaF$_2$ films grown on: (a) Si(100), −0.77 at. % Eu; (b) Si(110), −4.32 at. % Eu; and (c) Si(111), −0.32 at. % Eu. The spectra were taken at 10 K. Note the relative shifts in energy position of the zero-phonon lines.

shown in Figs. 1(b) and 1(c). Diffraction spots were replaced by sharp diffraction streaks accompanied by Kikuchi lines immediately after the substrate temperature was raised to 1100 °C, signifying the smoothing of the CaF$_2$ surface. While in situ annealing improves the growth morphology by smoothing out the [111] facets on the surface, it does not seem to alleviate the morphological features due to Eu precipitation. Following the deposition of BaF$_2$ at 580 °C, a spotty RHEED pattern with off-angle lines and arrow-head features was observed [Fig. 1(d)], indicating island epitaxy at this stage. Dramatic improvement in the growth morphology was achieved after in situ annealing and the second-stage growth. Diffraction streaks emerged in the RHEED patterns [Fig. 1(e)] and no change due to the incorporation of Eu in the BaF$_2$ lattice was observed.

Figure 2 shows the PL spectra of three Eu-doped CaF$_2$ films grown on Si(100), (110) and (111). A sharp zero-phonon line (ZPL) near 413 nm accompanies a broad vibronic sideband peaking at about 422 nm in each spectrum. The ZPLs shown in Fig. 2 arise from the electronic transition from the lowest lying $\Gamma_8(4f^65d)$ level of Eu$^{2+}$ to the $^8S_{7/2}(4f^{12})$ ground state. The peaks between the vibronic sideband maxima and the ZPLs are associated with the density of states maxima of various optical and acoustic phonons. No emission indicative of a $^5D_0 \rightarrow ^7F_J$ transition of Eu$^{3+}$ was observed in the entire scanned range of 400–667 nm.

It was noticed that the ZPLs in Fig. 2 were shifted by different amounts relative to bulk CaF$_2$. The ZPL positions and shifts are listed in Table I. The energy shifts in the ZPLs can be attributed to the residual thermal-induced tensile strain in the CaF$_2$ layers because of the higher thermal expansion coefficient of CaF$_2$ (19×10$^{-6}$/deg) relative to Si (2.5×10$^{-6}$/deg). Since the CaF$_2$ layers in our case are much thicker than the critical thickness for growth on Si (~10 nm), 8 most of the compressive strain in the CaF$_2$ layers due to the larger lattice constant of CaF$_2$ compared with Si substrate would be relieved at the growth temperature.

It has been demonstrated that Eu$^{2+}$ incorporated into CaF$_2$ films grown on Si(111) substrates can be used as a sensitive probe of elastic strain in the grown layers. 8,9 It is known that with uniaxial stress along [100] or [110], the ZPL of Eu$^{2+}$ in bulk CaF$_2$ crystals is split into a doublet and that with uniaxial stress along [111], the ZPL is not split but only shifted to longer wavelengths. 10 In general, the in-plane

![Fig. 1. RHEED patterns along the [011] and [001] azimuths recorded after: (a) desorption of oxide from Si(100) substrate; (b) deposition of a 3600 Å Eu-doped CaF$_2$ layer; (c) in situ annealing at 1100 °C for 2 min; (d) deposition of a 570 Å BaF$_2$ layer; (e) second-stage growth of 4600 Å Eu-doped BaF$_2$ layer.](image)

![Fig. 2. Photoluminescence spectra of Eu-doped CaF$_2$ films grown on: (a) Si(100), −0.77 at. % Eu; (b) Si(110), −4.32 at. % Eu; and (c) Si(111), −0.32 at. % Eu. The spectra were taken at 10 K. Note the relative shifts in energy position of the zero-phonon lines.](image)

**Table I. Energy shift of zero-phonon lines (ΔE) and estimated strain (ε$_i$) obtained from the CaF$_2$ films grown on Si substrates with different orientations.**

<table>
<thead>
<tr>
<th>Substrate orientation</th>
<th>ZPL position (nm)$^*$</th>
<th>ΔE (cm$^{-1}$)</th>
<th>ε$_i$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(100)</td>
<td>413.4</td>
<td>−22</td>
<td>0.83</td>
</tr>
<tr>
<td>(110)</td>
<td>412.7</td>
<td>19</td>
<td>0.24</td>
</tr>
<tr>
<td>(111)</td>
<td>412.2</td>
<td>48</td>
<td>0.38</td>
</tr>
</tbody>
</table>

$^*$Zero-phonon line (ZPL) of Eu$^{2+}$ in bulk CaF$_2$ is at 413.01 nm.
strain, induced by the lattice-mismatched epitaxial growth, can be decomposed into uniaxial and hydrostatic contributions. Assuming that CaF$_2$ films heteroepitaxially grown on Si(100)- , (110)- , and (111)-oriented substrates are under planar tensile strain, the relationship between in-plane strain $e_{ij}$ and energy shift $\Delta E$ of the ZPL can be expressed as follows:

$$
(100) \quad e_{ij} = a \Delta E \ (\text{cm}^{-1}), \quad a = \frac{C_{11}}{2(A + 2B)(C_{11} + 2C_{12})(C_{11} - 2C_{12})} = -3.79 \times 10^{-4}, \\
(110) \quad e_{ij} = b \Delta E \ (\text{cm}^{-1}), \quad b = -\frac{C_{11} + 2C_{12} + 4C_{44}}{(A + B)(C_{11} + 2C_{12})(C_{11} + 2C_{12} + 12C_{44})} = 1.31 \times 10^{-4}, \\
(111) \quad e_{ij} = c \Delta E \ (\text{cm}^{-1}), \quad c = -\frac{C_{11} + 2C_{12} + 4C_{44}}{12A(C_{11} + 2C_{12})C_{44}} = 7.94 \times 10^{-5},
$$

where $C_{ij}$ are the elastic constants of CaF$_2$, $A = -0.45 \ \text{cm}^{-1} \ \text{kg}^{-1} \ \text{mm}^{-2}$ and $B = 0.28 \ \text{cm}^{-1} \ \text{kg}^{-1} \ \text{mm}^{-2}$. Using the above expressions, we can estimate the in-plane strain for the Eu-doped CaF$_2$ layers. The results are listed in Table I. The strains obtained for the CaF$_2$ layers grown on Si(111) and (110) are close to the one ($\sim 0.3 \ %$) measured at liquid helium temperature for films not under stress at room temperature. This suggests that these CaF$_2$ films may have undergone almost complete relaxation at room temperature, probably through the glide of dislocations on available {100} slip planes. Due to the lack of such gliding planes, strain relief is less effective in CaF$_2$/Si(100) films, resulting in a larger strain value.

The dependences of the integrated emission intensities of both the vibronic sideband and the ZPL on Eu concentration for Eu-doped CaF$_2$/Si(100) films are shown in Fig. 3. The intensity of the vibronic sideband increases as the Eu concentration increases. At relatively low concentrations, the intensity of the ZPL also increases with Eu concentration. When the Eu concentration exceeds $\sim 1.64$ at. %, however, a noticeable decline in the PL intensity is observed similar to those reported for Nd-doped CaF$_2$/Si films. Such emission quenching seems to be characteristic of rare-earth-doped CaF$_2$ epilayers on Si and may be attributed to nonuniform distribution of rare-earth ions during growth caused by dislocations and other crystal defects.

Very bright and broad “yellow” emission was obtained from epitaxial BaF$_2$ films grown on Si(100) with Eu concentration of $\sim 0.93$ at. % (Fig. 4). As a comparison, a PL spectrum from a Eu-doped CaF$_2$ film on Si(100) is also shown in Fig. 4. The structureless feature in the emission spectra of Eu$^{2+}$ in BaF$_2$ compared with the ones in CaF$_2$ has been attributed to the static Jahn–Teller effect. As shown in Fig. 4, the emissions of Eu$^{2+}$ in CaF$_2$ and BaF$_2$ cover a broad wavelength range from 400 nm to 850 nm. Since BaF$_2$ can be readily grown on CaF$_2$, two-color (blue and yellow) light emitters may possibly be developed from Eu-doped stacked BaF$_2$/CaF$_2$ films on Si.

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**Fig. 3.** Dependence of the integrated emission intensities of vibronic sideband and zero-phonon line on Eu concentration for Eu-doped CaF$_2$/Si(100) films.

**Fig. 4.** Photoluminescence spectrum taken at 10 K showing strong yellow emissions from a Eu-doped BaF$_2$ film on Si(100) with a Eu concentration of $\sim 0.93$ at. %. A photoluminescence spectrum from a Eu-doped CaF$_2$ film on Si(100) with a Eu concentration of $\sim 0.77$ at. % is given as a comparison.
III. CONCLUSION

In summary, the growth of Eu-doped CaF$_2$ thin films on Si with different orientations and Eu-doped BaF$_2$ layers on Si(100) have been achieved by MBE using an elemental Eu source. Smooth surface morphology is obtained for Eu-doped CaF$_2$ and BaF$_2$ on Si(100) using in situ annealing and two-stage growth techniques. Very bright blue to violet luminescence in Eu-doped CaF$_2$ films and yellow luminescence in Eu-doped BaF$_2$ layers have been observed. Energy shifts in the ZPL for three differently oriented CaF$_2$ layers have been used to estimate the in-plane thermal strain in the epilayers.

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