

Epitaxial Growth of Rare-earth Ion Doped CaF_2 layers by MBE

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Abstract

The rare-earth ions(R^{3+} , $\text{R}=\text{Nd}$, Er) doped CaF_2 layers have been grown on $\text{CaF}_2(111)$ substrate by molecular beam epitaxy. The epitaxial relationship and the crystallinity of $\text{CaF}_2:\text{R}^{3+}$ layers depending on the concentration of R^{3+} were studied by reflection high-energy electron diffraction(RHEED). In aspect of application as buffer layer in semiconductor-related hybrid structure, the lattice displacement between $\text{CaF}_2:\text{R}^{3+}$ layers and $\text{CaF}_2(111)$ substrate was investigated by X-ray rocking curve analysis.

1. Introduction

For last several decades, the deposition of alkaline-earth fluorides(AF_2) such as CaF_2 , SrF_2 and BaF_2 on a variety of semiconductors(Si , Ge , and GaAs) by MBE has been studied[1-7]. These fluorides were used as epitaxial buffers to grow semiconductor-insulator-semiconductor structures, which is a prerequisite for long-ranged three dimensional integrated devices. Recently, the $(\text{Ca}, \text{Sr})\text{F}_2$ or $(\text{Sr}, \text{Ba})\text{F}_2$ solid solutions film have been preferred because the mixture of these fluorides with different lattice constant($\text{CaF}_2=5.46\text{\AA}$, $\text{SrF}_2=5.80\text{\AA}$, $\text{BaF}_2=6.20\text{\AA}$) are able to attain very close matching with basic semiconductor substrates($\text{Si}=5.43\text{\AA}$, $\text{Ge}=5.65\text{\AA}$, $\text{GaAs}=5.65\text{\AA}$) or narrow gap IV-VI semiconductor materials($\text{InP}=5.87\text{\AA}$, $\text{PbS}=5.94\text{\AA}$, $\text{PbSe}=6.12\text{\AA}$, $\text{PbTe}=6.45\text{\AA}$, $\text{CdTe}=6.48\text{\AA}$)[8-11]. Moreover, because the composition of the mixed fluoride buffer layer can be graded across its thickness, the superlattice structure having each interface good-matched between buffer layers and semiconductor layers can be realized.

However, in aspect of application as buffer layer in semiconductor-related integrated circuitry, the MBE-grown rare-earth trifluorides(RF_3) seem to have attracted more attention, because the physical properties of the RF_3 show that they are water-insoluble, mechanically harder, and have significantly smaller thermal expansion coefficients than the AF_2 . Furthermore, RF_3 layer would be available to show laser emission of short wavelength by up-conversion effect, and has the possibility of the magnificent monolithic wave-guide device with staggered structure, $\text{RF}_3/\text{AF}_2/\text{semiconductor-material}$, utilizing the difference in refractive indices of each layer.

To realize more useful semiconductor-related integrated circuitry by combining all aforementioned advantages of AF_2 and RF_3 , the rare-earth ions(R^{3+}) doped AF_2 should be studied sufficiently. In this study, we report the MBE growth of R^{3+} ($\text{R}=\text{Nd}$, Er) doped CaF_2

layers on CaF₂(111) substrate, which was employed as the growing substance because CaF₂ is undoubtedly one of most popular buffer materials and Nd and Er trivalent ions is very useful laser-active center. The epitaxial relationship and surface structure of CaF₂:R³⁺ layers on CaF₂(111) substrates depending on R³⁺ doping concentration were studied, and the lattice displacement between CaF₂:R³⁺ layers and CaF₂(111) substrate was investigated by X-ray rocking curve(XRC) analysis.

2. Experiments

The growth experiments were performed in a Eiko EL 10A MBE system equipped with conventional effusion cells containing boron nitride crucibles, in which powdered sources of CaF₂ and RF₃(R=Nd, Er) respectively were charged and evaporated simultaneously. The base pressure was around 1.0×10^{-10} torr. CaF₂(111) substrates, 20×20 mm² and 1 mm thick, were chemically cleaned and mounted on a molybdenum block. The protective oxide and contaminant layer were removed by heating the substrate at 650 °C. Epitaxial growth was performed at substrate temperature of 600°C for CaF₂:Nd³⁺ layers and 550°C for CaF₂:Er³⁺ layers.

R³⁺ doping concentration was confirmed by electron probe microanalysis(EPMA). The overall thickness of CaF₂:R³⁺ layers were determined by step profiler. The crystallinity, epitaxial relationship and the surface structures of CaF₂:R³⁺ layers were studied in situ by RHEED patterns, which was shown at regular interval time by using electron beam gun of 15keV energy. The layer thickness for each RHEED pattern was calculated through the data of the overall thickness of layer and growth time on the assumption that the growth rate is constant during overall deposition. The lattice displacement between CaF₂:R³⁺ layers and CaF₂(111) substrates was calculated by XRC analysis for (111) reflection of CaF₂ substrate using a Philips XPert-MRD high-resolution diffractometer with Cu K_α radiation diffracted by four-crystal Ge(220) monochromator.

3. Result and Discussion

The RHEED patterns obtained from CaF₂:R³⁺/CaF₂(111) structure for $[\bar{1}\bar{1}0]$ and $[11\bar{2}]$ azimuths of CaF₂ substrate are presented in Fig. 1, which show the dependence of layer crystallinity on the substrate temperature and the R³⁺ doping concentration up to ~50 mol%. For all CaF₂:R³⁺ layers, in the very initial growth stage sharp elongated streaky patterns with well-defined Kikuchi bands were obtained which provided evidence of the good crystallinity of the CaF₂:R³⁺ layer and the flatness of its surface on the atomic scale. For the CaF₂:Nd³⁺ layers(up to ~50 mol%) grown at 600°C and the CaF₂:Er³⁺ layers(up to ~40 mol%) grown at 550°C, the spacing between the streaks in both azimuths corresponds to electron diffraction from a surface with (1 × 1) structure which coincides with the structure of bulk CaF₂ crystals(Fig. 1(a)). Such simple RHEED pattern, (1 × 1), is characteristic of the surfaces of other alkaline-earth fluorides(SrF₂, BaF₂). However, CaF₂:Nd³⁺ layers of above ~30 mol%

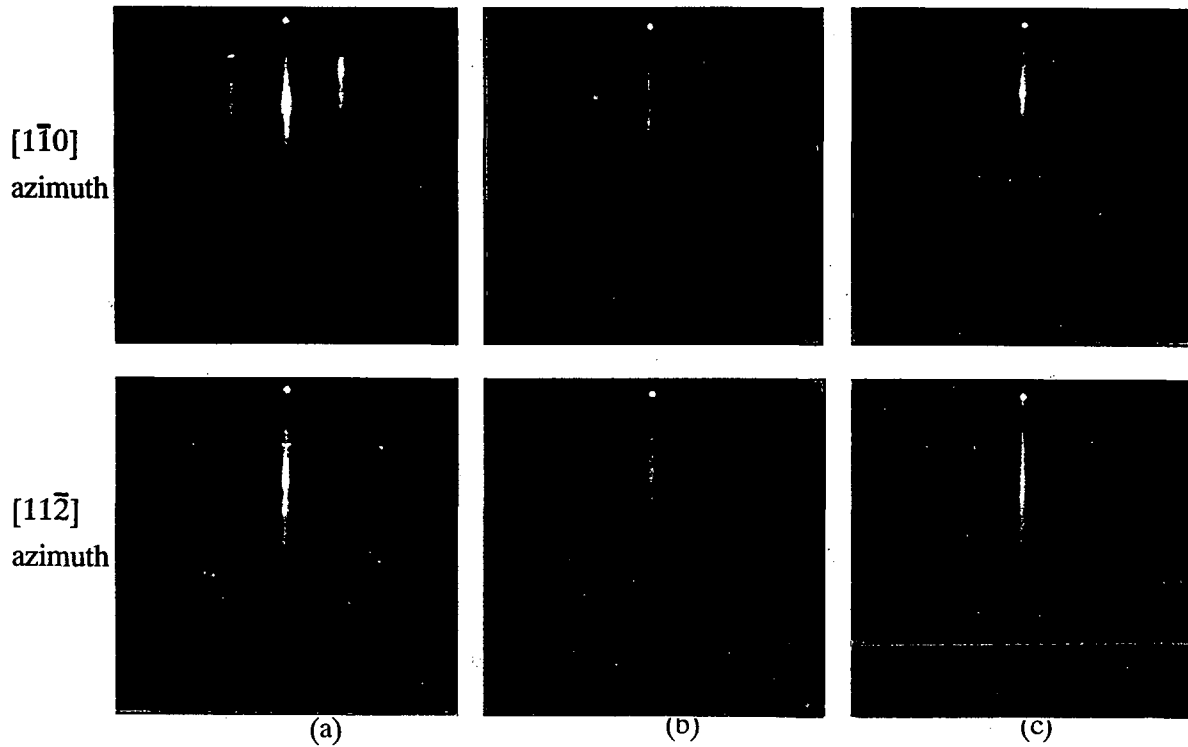


Fig. 1. RHEED pattern of (a) CaF₂:R³⁺(R=Nd, Er) layer in initial growth stage, (b) CaF₂:Nd³⁺ layer(layer thickness : ~300Å, doping concentration : ~35 mol%, growth temperature : 550°C), and (c) CaF₂:Er³⁺ layer(layer thickness : ~2000Å, doping concentration : ~45 mol% , growth temperature : 550°C).

doping concentration, begin to be gradually degraded to show (1 × 1) pattern with ring, which indicate that the lattice of layer composed of tysonite structure of NdF₃ and fluorite structure of CaF₂ immiscible with each other became disordered severely corresponding to the increase of layer thickness. This immiscibility of NdF₃ and CaF₂ in MBE growth is also proved by observation that the CaF₂:Nd³⁺ layers grown at substrate temperature of below 600°C would show ring pattern even in initial growth stage and by small amount Nd³⁺ doping(Fig. 1(b)). Fig. 1(c) shows the RHEED patterns obtained for [1 $\bar{1}$ 0] and [11 $\bar{2}$] azimuths from CaF₂:Er³⁺ layer with Er³⁺ doping concentration ~50 mol%. In this range containing stoichiometric composition, the RHEED pattern of CaF₂:Er³⁺ layer have distinct additional features which show the presence of (2 × 2) reconstructed surface structure. These are fractional order streaks spaced by 1/2 of the main streak spacing on zeroth Laue zone in both azimuths. For the deposition in near middle range of solid solution Ca_{1-x}Er_xF_{2+x} layers(0.4<x<0.5), there is two remarkable natures comparing that of other ranges of Er³⁺ doping concentration. One is that (2 × 2) pattern was always preceded by (1 × 1) pattern which was sustained for deposition of around 200Å thickness. The other is that the well-defined (2 × 2) pattern which was sustained showing sharp streaks began to be degraded and was converted to spotty patterns over around 4000Å thickness. These natures indicates probably that the thickness limitation of good solubility between CaF₂ and ErF₃ would be exist in epitaxial system as expected although the

incorporation of ErF_3 to CaF_2 layer could be more miscible without the co-existence of respective phases when comparing that of NdF_3 to CaF_2 layer. Over this thickness of $\text{Ca}_{1-x}\text{Er}_x\text{F}_{2+2x}$ layers ($0.4 < x < 0.5$), the lattice relaxation by formation and propagation of misfit dislocations, which provides the three-dimensional islands with rough flatness in atomic scale, was over-accumulated and exceedingly distorted, therefore, each phase of CaF_2 and ErF_3 in $\text{Ca}_{1-x}\text{Er}_x\text{F}_{2+2x}$ layer could become prone to form.

Fig. 2 shows reciprocal lattice set of the subcell and supercell corresponding to RHEED patterns of (1×1) and (2×2) , which would explain the relationship between supercell lattice and subcell lattice which was formed on hexagonal base provided by (111) plane of fluorite structure.

Fig. 3 shows the lattice displacement between $\text{CaF}_2:\text{R}^{3+}$ layer and $\text{CaF}_2(111)$ substrate along the $[111]$ growth direction, which was calculated from angular difference ($\Delta\theta$) of X-ray rocking curves for (111) reflection between layer and substrate. In the range over ~ 40 mol% there is large shift of lattice displacement which attributed probably to immiscibility of RF_3 with CaF_2 , as shown by observation of RHEED pattern. Nevertheless, this result of X-ray rocking curve analysis for (111) reflection is characterized by the linearity that

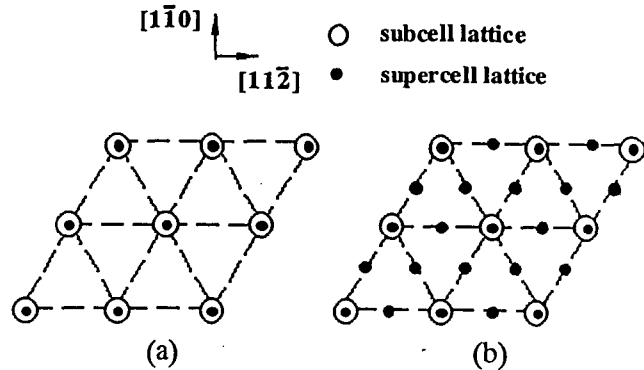


Fig. 2. Schematic diagrams showing the reciprocal lattice sections corresponding to RHEED patterns of $\text{CaF}_2:\text{R}^{3+}$ ($\text{R}=\text{Nd}, \text{Er}$) layers: (a) (1×1) , (b) (2×2) surface structure.

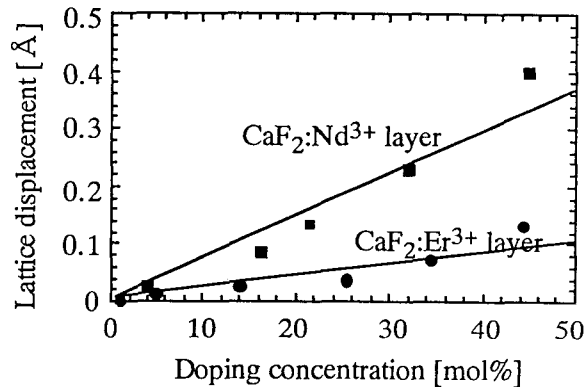


Fig. 3. Lattice displacement between $\text{CaF}_2:\text{R}^{3+}$ ($\text{R}=\text{Nd}, \text{Er}$) layer and CaF_2 substrate along $[111]$ direction depending on doping concentration.

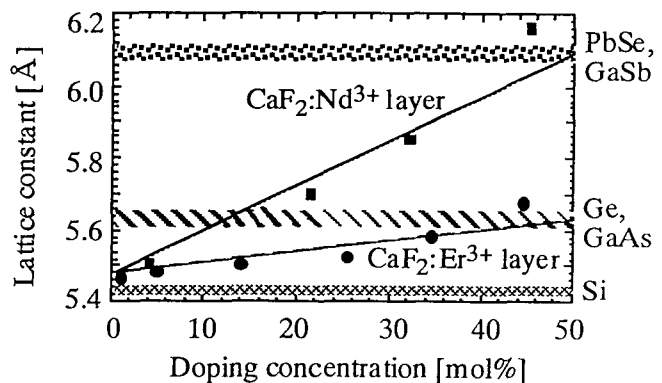


Fig. 4. Lattice constant of $\text{CaF}_2:\text{R}^{3+}$ ($\text{R}=\text{Nd}, \text{Er}$) layer and semiconductor materials

is characterized by the linearity that

the lattice constant of CaF₂:R³⁺ layers increases continuously depending on R³⁺ doping concentration. The increment of lattice constant of CaF₂:Nd³⁺ and CaF₂:Er³⁺ layer corresponding to 1 mol% incorporation of Nd³⁺ and Er³⁺ is estimated to be 0.0124Å and 0.0033Å respectively, which allows for CaF₂:Nd³⁺ layer and CaF₂:Er³⁺ layer to well-match with various semiconductor materials(Fig.4).

4. Summary

The CaF₂:R³⁺(R=Nd, Er) layers up to ~50 mol% doping concentration have been grown on CaF₂(111) substrate by molecular beam epitaxy. By the observation of RHEED pattern, it was shown that CaF₂:Nd³⁺ layers have only (1 × 1) surface structure and CaF₂:Er³⁺ layers have (1 × 1) and (2 × 2) surface structure. ErF₃ could be mixed well with CaF₂ to provide solid solution layer with good crystallinity up to ~4000Å layer thickness, whereas the incorporation of NdF₃ to CaF₂ degraded the crystallinity of CaF₂:Nd³⁺ layers due to immiscibility of each other above ~30 mol% doping concentration. The lattice constant of CaF₂:Nd³⁺ and CaF₂:Er³⁺ layers increased linearly depending on doping concentration of Nd³⁺ and Er³⁺, which propose the availability as buffer layer well-matching with various semiconductor.

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