# Epitaxial Growth of $NdF_3:Er^{3+}/CaF_2(111)$ by MBE

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Abstract

$Er^{3+}$ doped $NdF_3$ single crystalline thin films with smooth, microcrack-free, and high-crystalline quality were grown on $CaF_2(111)$ substrate at 500℃ by molecular beam epitaxy(MBE). The relationship between subcell and supercell showing the reconstructed $3^{1/2} \times 3^{1/2}$ structure was studied by reflection high-energy electron diffraction(RHEED) investigation. The film surface and the growth mode were examined in situ by RHEED patterns and atomic force microscope(AFM) images ex situ. The crystallinity of film and the lattice mismatch between $NdF_3:Er^{3+}(0002)$ film and $CaF_2(111)$ substrate depending on the $Er^{3+}$ concentration were investigated by X-ray rocking curve analysis.

1. Introduction

Since the first reported growth of fluorides($BaF_2$/InP(001), $BaF_2$/CdTe(001)) by molecular beam epitaxy(MBE)[1], the epitaxial growth of group II fluorides and their alloys on various compound semiconductors has been studied with the strong attention to the fabrication of the actual devices such as semiconductor-insulator-semiconductor(SIS)[2] and metal-epitaxial insulator-semiconductor field-effect transistor(MEISFET)[3] which might be suitable for use in three dimensional intergrated circuits as passivation layers. However, more emphasis has recently shifted to the epitaxial growth of the rare-earth trifluorides[4-6] or rare-earth ion doped fluorides[7-10] by the several advantageous points: (1) The physical properties of the rare-earth trifluorides show that they are water insoluble, mechanically harder, and have significantly smaller thermal expansion coefficients than the group II fluorides. (2) The laser emission by up-conversion of the rare-earth trivalent ions would be available to satisfy the demand for solid state laser sources of the compact blue and green visible light in the field of memory storage. (3) Moreover, the conjuction of rare-earth trifluoride films grown on $CaF_2$ substrate with the semiconductor layers are showing the possibility of the magnificent monolithic waveguide device composed of the laser host and pumping laser diode, utilizing the difference of refractive indices.

However, the study on the growth mode and the crystallinity of rare-earth ion doped fluoride films were not yet investigated sufficiently. In this paper, we report the heteroepitaxial growth of $Er^{3+}$ doped $NdF_3$ film on $CaF_2(111)$ substrate. The growth mode is studied by observing the reflection high-energy electron diffraction(RHEED) patterns and surface morphologies of films with various thickness, and the dependences on $Er^{3+}$ concentration of the film crystallinity and the mismatch between the film and the substrate, are investigated.

2. Experimental Procedures

The growth experiments were performed in a MBE system equipped with $NdF_3$ and $ErF_3$ effusion cells, from which powdered sources of $NdF_3$ and $ErF_3$ were evaporated simultaneously. The base pressure was around $1.0\times10^{-9}$ torr. $CaF_2(111)$ substrates, $20\times20$ mm$^2$ and 1mm thick, were chemically cleaned and mounted on a molybdenum block. The protective oxide and contaminant layers were removed by heating the substrate at 600℃. Epitaxial growth was performed at substrate temperature 500℃. The beam equivalent pressures(BEP) of $NdF_3$ and $ErF_3$ at cell temperature range of 980℃ to 1100℃ were varied from $5.0\times10^{-8}$ to $4.0\times10^{-7}$torr and from $1.0\times10^{-8}$ to $8.0\times10^{-8}$torr, respectively.

The control of these BEP of $NdF_3$ and $ErF_3$ leaded film deposited to various thickness at growth rate of 0.02 to 0.4 μm/h and various $Er^{3+}$ concentration of around 2.1 to 42.3 mol%. The overall thickness of films was determined by scanning electron microscope(SEM) image of the cross-section of films, and the $Er^{3+}$ concentration was determined by electron probe microanalysis(EPMA). The epitaxial relationship and growth mode of the $NdF_3:Er^{3+}$ film were studied in situ by RHEED patterns, which were at regular interval time, and the surface morphology of film was observed by atomic force microscope(AFM). The crystallinity of film and mismatch between film and substrate were investigated by X-ray rocking curve(XRC) analysis for the (0002) reflection of $NdF_3:Er^{3+}$ film and the (111) reflection of $CaF_2$ substrate using a Philips XPert-MRD high-resolution diffractometer with Cu $K_{\alpha 1}$ radiation diffracted by four-crystal Ge(220) monochromator.

3. Results and Discussions

Fig. 1 shows the RHEED patterns for an $Er^{3+}$ doped $NdF_3$ film with various thickness along the $[1\bar{1}0]$ and $[2\bar{1}\bar{1}]$ azimuthal direction on the $CaF_2(111)$ substrate. In the initial growth stage(Fig. 1a), sharp elongated streaky patterns with well-defined Kikuchi bands were obtained, suggesting very smooth surface morphology. A hexagonal symmetry was confirmed for the $Er^{3+}$ doped $NdF_3$ film by observation that the same pattern of RHEED showed up at every $60^o$ rotation of the stage, which were related to the $3^{1/2}\times3^{1/2}$ reconstructed structure. This reconstruction indicates well-matched heteroepitaxial growth with smooth surface morphologies on a cubic $CaF_2(111)$ substrate which provides hexagonal closed packed arrays of constituent atoms with an equivalent lattice parameter of $a_{CaF2}/2^{1/2}$ = 3.8629Å which is similar to the lattice parameter of hexagonal structure $NdF_3$(a =4.0540 Å) having $P6_3/mmc$ space group. However, as film thickness increased over around 2000Å, RHEED patterns started to be degraded showing the spot superimposed in the streaky line broadened(Fig. 1b) and finally reconstructed structure disappeared. The appearance of this spot indicates that three-dimensional growth forming islands on the flat surface is starting, where the electron beam is diffracted by penetrating through islands. This typical conversion to the three-dimensional island growth was more apparently ascertained by observaion of AFM images depending on the various thickness(Fig. 2), which show that the smooth surface(rms = 3.29Å) in the initial stage changes to rough surface(rms = 17.87Å) having the hexa-shaped islands of around 200Å diameter. As the quantitative indicator of the surface roughness, root-mean-square(rms) roughness extracted measurements was used, which yields information about the vertical magnitude of the roughness features although rms value denotes no information about lateral size of surface and is variable with scan size.

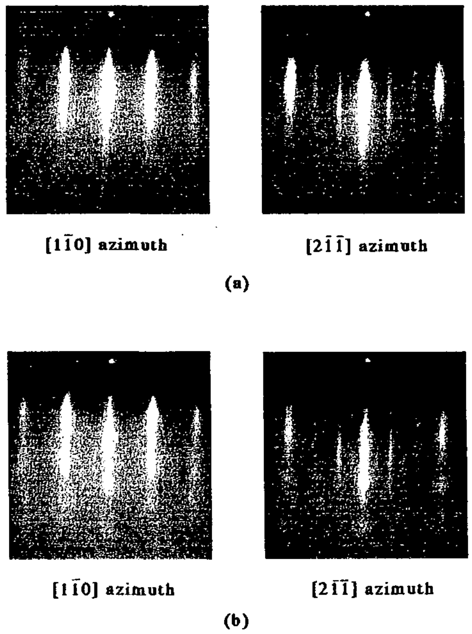


Fig. 1. RHEED patterns for [110] and [211] azimuth in $NdF_3:Er^{3+}/CaF_2(111)$ epitaxial growth depending on film thickness(t): (a) t = 400Å, (b) t = 2000Å.

(a) (b)

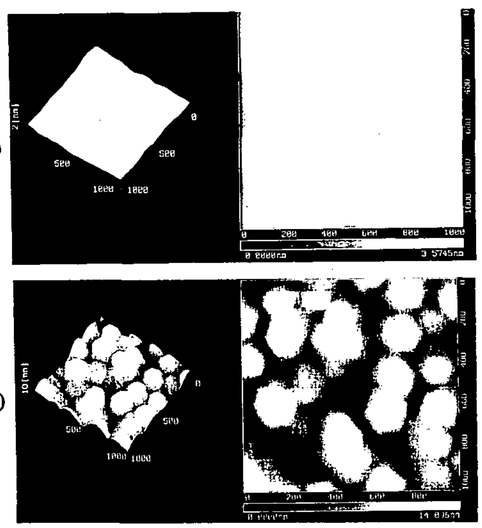

Fig. 2. AFM images showing the surface morphologies of $NdF_3:Er^{3+}$ film depending on film thickness(t): (a) t = 400Å, rms = 3.29Å, (b) t = 8000Å, rms = 17.87Å.

It is worth discussing the growth mode of heteroepitaxial film of rare-earth trifluoride, $NdF_3:Er^{3+}$ in our experiment, in more detail. First of all, it was brought to the conclusion that unambiguously the growth of $NdF_3:Er^{3+}$ film on $CaF_2(111)$ substrate was performed on the basis of well-known Stranski-Krastanov growth mechanism[11], which is characterized by the fact that after initial two-dimensional growing layers free of dislocation and with high strain, i.e. pseudomorphic, are formed up to a "critical thickness", subsequent layers are grown three-dimensionally reducing the strain energy by forming and propagating misfit dislocations, i.e. lattice relaxation, or by begining to developing three-dimensional islands. Because the value of critical thickness($T_c$) is dependent on the various facors such as lattice mismatch between film and substrate, magnitude of adhesion, elasticity of the layer and supersaturation(substrate temperature), and furthermore is determined wide erroneously, it seems to be hard to represent the exact value of $T_c$. Nevertheless, it might be possible to show the dependence on $Er^{3+}$ concentration of $T_c$, which was determined roughly by checking the appearance time of the spot in the streaky line of RHEED pattern and calculating later through the data of the overall thickness of film and growth time on the assumption that the growth rate is constant during overall deposition. Fig. 3 shows that the incorporation of $Er^{3+}$ up to around 4 mol% concentration increases $T_c$, while in more concentration decreases. Also $T_c$ for the incorporation of $Er^{3+}$ up around 18 mol% has larger than that for undoped $NdF_3$. It can be interpreted that the incorporation of $Er^{3+}$ with smaller ionic size to $NdF_3$ layer relieves the strain energy of overlayer zone by reducing somewhat the mismatch between pseudomorphic growing layers and substrate, therefore, the thickness pertaining to "saturated strain energy", by which the epitaxial system becomes most unstable in the two-dimensional growth and is enforced to find new growth mode, i.e. three-dimensional growth with increase of surface energy, is larger. But in the case of severe $Er^{3+}$ incorporation because the lattice of layers is exceedingly distorted due to high-disorientation or formation of $ErF_3$ cluster, $T_c$ is very short. Also it is worth remarking that our $NdF_3:Er^{3+}/CaF_2(111)$ epitaxial films have been successfully grown in two-dimensional mode as compared with the report by R.Strümpler et al.[12] that in the $LaF_3/Si(111)$ epitaxial system the three-dimensional islands were observed at 150Å thick film by scanning electron microscope. The rocking curves for the (111) reflection of $CaF_2$ substrate are sharp with a full-width at half maximum(FWHM) of around 50 arcsec irrespective of $Er^{3+}$ concentration, while those for the (0002) reflection of the $Er^{3+}$ doped $NdF_3$ film were broad with around 250 arcsec reasonably due to the mismatch of the lattice constants between film and substate with different crystal structure. Moreover, it was observed that with increase of $Er^{3+}$ concentration, the FWHM of films was larger up to 380 arcsec and the rocking curve had very off-symmetric shape. This further broadening of the rocking curve for (0002) reflection of $NdF_3:Er^{3+}$ film was reasonably attributed to the lattice disorientation by the additional stress loaded from the $Er^{3+}$ ions. Also, if it is considered that the MBE growth system is thermodynamically under the non-equilibrium state of high supersaturation, this

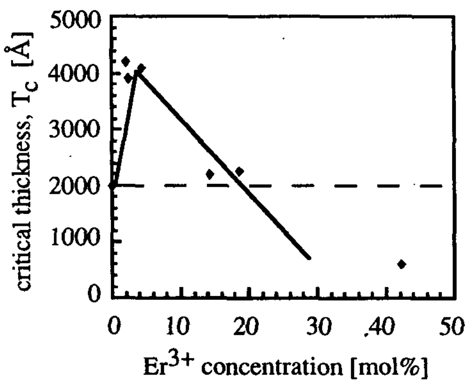


Fig. 3. The dependence of critical thickness($T_c$) of pseudomorphic layer on $Er^{3+}$ concentration in $NdF_3:Er^{3+}/CaF_2(111)$ epitaxial growth.

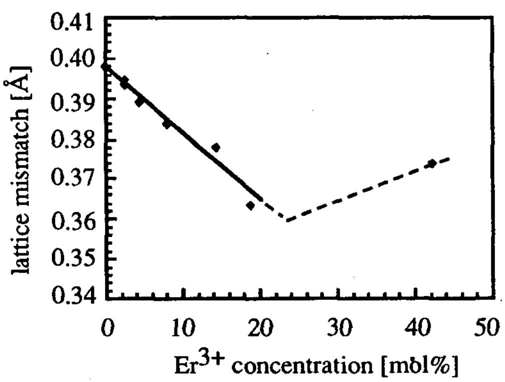


Fig. 4. The lattice mismatch between $NdF_3:Er^{3+}$ film and $CaF_2$ substrate along the [111] direction depending on $Er^{3+}$ concentration.

effect of $Er^{3+}$ incorporation on the FWHM of films might be interpreted by the possibility that on the severe doping concentration of $Er^{3+}$ the molecule of $ErF_3$ is prone to form the its near-orthorhombic structure, at least in the short range possibly, in the $NdF_3$ film of hexagonal structure.

The orientational relationship confirmed is [111]$CaF_2$‖[001]$NdF_3$ and [110]$CaF_2$‖[100]$NdF_3$, where the magnitude of the lattice mismatch between the $CaF_2$(111) substrate and $NdF_3$(0001) film along the [110] direction of the $CaF_2$(111) substrate is estimated to be 4.7% by comparing the periodical spacing of the equivalent planes of $CaF_2$(111) substrate along the [110] direction($a_{CaF2}/2^{1/2}$ = 3.8629Å) with a lattice constant of $NdF_3$, $a_{NdF3}$(= 4.0540Å). Fig. 4 shows the dependence on the $Er^{3+}$ doping concentration of the lattice mismatch between $NdF_3$(0001) film and $CaF_2$(111) substrate along the [111] direction, i.e. normal direction to $CaF_2$(111) substrate evaluated from the difference between the X-ray reflection angles of $CaF_2$ (111) plane and $NdF_3$ (0002) plane. Because the ionic radius of $Er^{3+}$ (0.89Å) is less than that of $Nd^{3+}$ (1.04Å), the doping of $Er^{3+}$ ions, which occupy the $Nd^{3+}$ ion position substitutionally, leads to shrinkage of hexagonal unit cell of $NdF_3$ (0001) film and consequently decreases the lattice mismatch along the [110] direction which is planar direction more meaningful in epitaxial growth. But it was observed that at higher concentration of $Er^{3+}$, the slope of mismatch plot was turned up, probably due to the similiar reasons as described above.

## 4. Summary

The monocrystalline $NdF_3$:$Er^{3+}$ films were grown on $CaF_2$(111) substrate heteroepitaxially by the MBE system. The observation of RHEED pattern in situ and of AFM image ex situ indicated that the pseudomorphic layer of film grown two-dimensionally in the initial stage was converted to hexa-shaped island layer by three-dimensional growth mode. Furthermore, the incorporation of $Er^{3+}$, to a certain extent, made the thickness of pseudomorphic layer larger. The X-ray rocking curves of $CaF_2$ (111) reflection and $NdF_3$:$Er^{3+}$ (0002) reflection showed that with $Er^{3+}$ doping concentration, FWHM of film became larger and the mismatch between the film and the substrate along the planar direction on the substrate was decreased. It was apparently shown that the $Er^{3+}$ incorporation of certain small extent to $NdF_3$ made the mismatch between film and substrate smaller, therefore provided film of good smooth surface although that extent of $Er^{3+}$ concentration was different between the investigation of critical thickness of pseudomorphic layer($T_c$) and the investigation of lattice mismatch.

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