Two-dimensional growth of lattice matched Nd-doped (Gd,Lu)₂O₃ films on Y₂O₃ by pulsed laser deposition

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This letter focuses on epitaxial growth of a 1- μm -thick lattice matched Nd-doped monocrystalline (Gd,Lu)₂O₃ film deposited on a {100} oriented Y₂O₃ substrate by pulsed laser deposition. Layer-by-layer growth indicated by *in situ* reflection high energy electron diffraction was observed up to film thicknesses of 100 nm. The subsequent growth behavior could be explained by a multilevel growth mode. Thus, the growth mode was two-dimensional and epitaxial. Lattice matching of up to 99.3% was achieved. The evolution of the structural and topographical properties of the films was verified by *ex situ* x-ray diffraction analysis and atomic force microscopy, respectively. © 2008 American Institute of Physics. [DOI: 10.1063/1.2967870]

Optically active waveguiding devices based on thin film technology are promising for the development of integrated optical devices. Various reports show different functional planar waveguide lasers based on rare earth (RE)-doped dielectric oxide thin films.^{1–3} RE-doped sesquioxides belong to the most attractive active media for solid-state lasers due to their relatively low phonon energies, high thermal conductivities, and mechanical stabilities. Recently, laser operation with a slope efficiency of 80% has been achieved for Yb-doped Lu₂O₃ in the thin disk laser setup, which is known to be the most efficient Yb-doped thin disk laser reported so far.⁴ As high peak cross-section can rather be obtained in crystalline than amorphous media and as crystalline materials usually exhibit a better thermal conductivity compared to their amorphous counterparts, the fabrication of thin films with monocrystalline quality is desired. Pulsed laser deposition (PLD) is a promising fabrication technique for this purpose due to the high kinetic energies of the particles impinging onto the surface. Two-dimensional (2D) layer-by-layer growth of homoepitaxially grown sesquioxide films has been shown recently.⁵ In order to obtain a high positive difference of the refractive indices between the film and the substrate, and thus a waveguiding thin film, heteroepitaxial growth is necessary. For instance, heteroepitaxial growth of Sc₂O₃ thin films on Y₂O₃ substrates leads to lattice stress and a three-dimensional growth behavior due to the influence of the high lattice mismatch.⁵ In order to reduce the scattering losses at small crystallites in micrometer-thick films and at their surfaces, the films should be monocrystalline and the surface should be as flat as possible. Therefore, 2D epitaxial growth is beneficial. Hence, here the authors report on lattice matched film growth of (Gd,Lu)₂O₃ on Y₂O₃. Codoping of Gd and Lu has already been proven to be a promising method to increase the refractive index of KY(WO₄)₂ films.⁶ In this letter the PLD technique allowing a stoichiometric material transfer is used to obtain perfect lattice matching by replacing the Y³⁺ ions in the Y₂O₃ host lattice with a mixture of the smaller Lu³⁺ and the larger Gd³⁺ ions. Here the authors demonstrate the two-dimensional heteroepitaxial

growth by PLD of a 0.5 at. % Nd-doped (Gd,Lu)₂O₃ monocrystalline film of 1 μm thickness.

Prior to the growth procedure, an epitaxial grade polished {100} oriented Y₂O₃ substrate with the dimensions of 10×10×0.5 mm³ was annealed in air at 900 °C for 1 h. This thermal treatment of Y₂O₃ {100} results in steps and nearly atomically smooth terraces. While the step heights were determined by atomic force microscopy (AFM) to be approximately 5 Å, which corresponds to one monolayer (ML) of Y₂O₃ (cf. Ref. 5), the widths of the terraces were nearly 100 nm. After transferring the annealed substrate into the PLD vacuum chamber, it was treated at about 900 °C for 30 min at an oxygen pressure of $P_{\text{O}_2} = 10^{-2}$ mbar, which led to the removal of contaminations on the surface. For ablation, a focused KrF excimer laser beam ($\lambda = 248$ nm, $\tau = 20$ ns) irradiated a sintered (Nd_{0.005}, Gd_{0.479}, Lu_{0.516})₂O₃ ceramic target with a laser fluence of approximately 1.5 J/cm². The deposition was carried out at a substrate temperature of 900 °C and an O₂ pressure of about 9×10^{-3} mbar, and the target-substrate distance was 9.5 cm. The substrate was heated with seven fiber coupled 20 W laser diodes.

For the *in situ* investigation of the growth behavior, a high pressure reflection high energy electron diffraction (RHEED) system at 25 keV electron beam energy is used. Thereby, the incident electron beam irradiates the substrate in a grazing angle which fulfills the off-Bragg condition. Figure 1(a) shows the RHEED pattern of the annealed Y₂O₃ {100} substrate in the direction with the incident electron beam along the <010> azimuth. The RHEED pattern indicates an atomically flat surface demonstrated by the circular reflec-

FIG. 1. RHEED patterns (a) of an annealed Y₂O₃ {100} substrate with the incident electron beam along the <010> azimuth and (b) of the monocrystalline 1- μm -thick film.

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FIG. 2. (a) RHEED intensity behavior during the continuous growth (left) and interval growth (right) of the first 100 nm of the $(\text{Gd},\text{Lu})_2\text{O}_3$ film on a $\{100\}$ oriented yttria substrate. (b) presents the RHEED intensity behavior during the continuous growth before reaching the thickness of 1 μm .

tions occurring on the first-order Laue circle. A (1×1) reconstruction of the ordered Y_2O_3 surface is observed as for Sc_2O_3 substrates (cf. Ref. 5). During the growth of the first 100 nm of the Nd-doped $(\text{Gd},\text{Lu})_2\text{O}_3$ film no change in the symmetry and spacing of this RHEED pattern is observed, indicating an epitaxial film growth in the $\langle 100 \rangle$ direction. The continuous deposition has been performed using a pulse repetition rate of 1 Hz. The observed RHEED intensity oscillation of the specularly reflected spot confirms 2D layer-by-layer growth, as shown in the left part of Fig. 2(a). One oscillation period corresponds to the deposition of one ML. The number of pulses needed per ML has been estimated to be about 102, so that the deposition rate is estimated to be approximately $0.05 \text{ \AA/s}$. Furthermore, the pulsed laser interval deposition (PLID) technique has been utilized in order to sustain 2D layer-by-layer growth for a long time and thereby reduce the probability of multilevel 2D growth formation (cf. Ref. 7). Therefore, after the amount of material of 102 pulses has been deposited in a short time interval (pulse repetition rate of 50 Hz) as a deposition packet, the deposition has been stopped for a certain recovery time. On the right side of Fig. 2(a) the RHEED intensity during PLID of two MLs is shown. Here, for the illustration of the layer-by-layer growth mode, one deposition packet consists of half a ML (51 pulses). While the deposition of one packet leads to a decrease in the intensity, the deposition of two packets leads to a complete recovery.

During the first 100 nm of film thickness, the film has been grown continuously and in the interval growth mode as well, since the target properties change during the growth so that the amount of pulses needed to deposit one ML changes. The exact amount has been calculated during the continuous growth and has been utilized for the interval growth. At about 100 nm the RHEED oscillation is damped more and more and vanishes. This behavior can be explained by an increase in the surface roughness and, thus, a premature nucleation of the adatoms, causing a multilevel 2D growth. In this case, the diffusion length of the adatoms is too small to reach the step edges and overcome the Ehrlich-Schwoebel barrier^{8,9} of the terraces. The following deposition of up to 1 μm of thickness has been carried out in the continuous deposition mode with a pulse repetition rate of 1 Hz. While no change in the symmetry of the RHEED pattern has been

FIG. 3. AFM images of the 1- μm -thick $(\text{Gd},\text{Lu})_2\text{O}_3$ film, where (b) represents a higher resolved detail of (a). The height profiles were taken along the white lines indicated in the images.

observed during the growth, the reflections on the first-order Laue circle become more streaky. This indicates an epitaxial 2D multilevel film growth in the $\langle 100 \rangle$ direction. Figure 1(b) shows the RHEED pattern of the monocrystalline 1- μm -thick film. This multilevel structure of the surface is demonstrated by the AFM measurements in the noncontact mode, as shown in Fig. 3. One can verify that the step heights are still in the ML range and the widths of the terraces are less than half as wide as before deposition. The rms roughness has been determined to be approximately $7 \text{ \AA}$, a remarkable surface flatness for a 1- μm -thick heteroepitaxially grown monocrystalline dielectric film. Regarding the RHEED intensity during that time, a relaxation after each pulse has been observed. This quasi-step-flow growth [Fig. 2(b)] can be explained by the smaller terrace width, permitting the adatoms to diffuse to the step edges. The growth mode is not a real step-flow growth, since in that case this behavior should have already been observed during the initial growth of the first 100 nm.^{10,11}

The grade of crystallinity of the 1- μm -thick film has been investigated by *ex situ* x-ray diffraction (XRD) with copper $K\alpha$ radiation. This XRD analysis confirms a highly textured monocrystalline film growth in the $\{100\}$ orientation (Fig. 4). Figure 4(a) displays a θ - 2θ scan in the range of $2\theta=20^\circ, \dots, 70^\circ$ and demonstrates that the film is not grown in any other direction not defined by the substrate. Figure

FIG. 4. (a) XRD spectrum (θ - 2θ scan) of the 1- μm -thick $(\text{Gd},\text{Lu})_2\text{O}_3$ film grown on $\{100\}$ oriented yttria substrate in the range of $2\theta=20^\circ, \dots, 70^\circ$ and (b) a high resolution scan of the $\{600\}$ diffraction peaks resulting from the $K\alpha$ emission.

4(b) shows the high resolution scan of the $\{600\}$ diffraction peaks of the film resulting from the $K\alpha$ emission. Therein, the $K\alpha_1$ substrate diffraction peak appears at 51.7° and the film diffraction peak appears at 51.2° . A shift of 0.5° and thus a lattice matching of 99.3% can be estimated. The full width at half maximum (FWHM) of the film peak, corresponds to the FWHM of the substrate peak, indicating a monocrystalline growth (the XRD setup has a resolution of 0.04° FWHM, corresponding to crystallite sizes of 350 nm). This is consistent with the RHEED measurements mentioned above.

In summary, the growth of a nearly lattice matched (99.3%) monocrystalline 1- μm -thick film of $(\text{Nd}_{0.005}, \text{Gd}_{0.479}, \text{Lu}_{0.516})_2\text{O}_3$ on an yttria $\{100\}$ substrate by PLD was demonstrated. The monocrystallinity was confirmed by means of XRD and RHEED measurements, respectively. Layer-by-layer growth was observed up to film thicknesses of 100 nm, while the following growth behavior could be explained by a mixture of a step-flow-like and a multilevel growth mode. The latter one was proven by additional AFM measurements after the growth. The rms roughness was determined to be approximately 7 Å. Merging of two components with perfect solubility has been proven to be a good method to obtain nearly perfect lattice matching. A

slight increase in the amount of Lu^{3+} ions and thus a reduction in the amount of Gd^{3+} ions should lead to even flatter surfaces in the future.

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