Nd:YVO_4 Thin Films Grown by Pulsed Laser Deposition: Effects of Temperature and Pressure on the Grain Morphology and Microstructure

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Nd:YVO_4 thin films were grown by pulsed laser deposition (PLD) on single-crystal *r*-cut sapphire(1102) substrates, and the grain morphology and microstructure of the films were investigated as a function of substrate temperature and oxygen pressure employed during growth. Highly crystalline (200)-oriented films were grown using the following optimized growth parameters: 700−900 °C and 250−350 mTorr of O_2. Below these values, *a*-axis-textured polycrystalline films were formed exhibiting no epitaxial relationship with the sapphire substrate. Scanning electron microscopy studies revealed that the films contain grains that undertake a morphological transformation from spherical to rectangular in the temperature range of 650−670 °C, with the latter being well faceted and having dimensions as large as $1 \times 5\ \mu$m. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) revealed that the films are epitaxial and exhibit a high degree of crystalline perfection because of their 2θ- and ω-FHWM values of 0.06° and 0.12°, respectively. The importance of certain growth parameters, specifically substrate temperature and oxygen pressure, on the microstructure and grain morphology of the films is discussed in detail.

I. Introduction

Yttrium orthovanadate (YVO_4) has sparked great interest in the fields of solid-state chemistry and material science over the past decade because of its potential applications as a polarizer,[1] phosphor,[2,3] and laser material.[4−6] Concerning the latter, Nd:YVO_4 has been reported to be the most efficient laser crystal for diode-pumped solid-state lasers. Compared to single-crystal Nd:YAG, it exhibits a lower lasing pumping threshold and higher slope efficiency, a large emission cross-section at the lasing wavelengths of 1.06 and 1.34 μm, high absorption over a wide pumping wavelength bandwidth, and a large birefringence. These characteristics consequently allow for the emission of a strongly polarized laser.

For these reasons, numerous efforts have been made concerning the synthesis of large, high optical quality single crystals via various single-crystal techniques.[7−11] Nonetheless, in despite of these techniques, there remains some difficulties in growing high quality single crystals of YVO_4 because of its high melting point (1810 °C) and instabilities near this temperature such as oxygen defects and vaporization of V_2O_5 (mp = 690 °C) at high temperatures.[12−14] Low-temperature (<200 °C) hydrothermal synthesis[15] and room-temperature aqueous precipitation reactions[16−18] have been successful for producing nanometer size particulate powders of various rare earth-doped YVO_4; however, these relatively low temperatures are not sufficient for the growth of large single crystals needed for lasing applications. Thus, other low-temperature synthetic routes for the isolation of single-crystal YVO_4 warrant investigation, in particular, in the form of thin films. A better understanding of the fundamental properties (structural and optical) of single-crystal or polycrystalline YVO_4 is needed in order to optimize its potential. Surprisingly enough, there are very few reports of YVO_4 grown in thin film form; in fact, we have found only two reported studies involving sol−gel[18] and MOCVD techniques.[19] Nonethe-

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less, these methods suffer from either a lack of crystallographic orientational control or the incorporation of vanadium-poor or -rich nonstoichiometric phases. In light of these aspects, a synthetic technique, which will allow for the growth of high-quality, stoichiometric, well-textured films, is needed in order to exploit the potential applications of rare earth-doped YVO_4 films may exhibit. Pulsed laser deposition is an attractive synthetic method for the growth of high-quality single crystalline films because it is a simple, relatively cheap and reliable technique, which yields high-quality films of various materials. Moreover, by proper choice of substrate and experimental parameters, one can usually obtain accurate control of the film orientation, morphology, and microstructure of the growing film. Thus, in an attempt to investigate the various fundamental aspects of YVO_4 thin film growth, we have recently carried out a series of work to study the processing structure and morphological relationships of YVO_4 thin films on sapphire substrates.

II. Experimental Section

Target Preparation. A polycrystalline Nd:YVO_4 target was prepared by adding 15 mL of ethanol (95%) to a stoichiometric mixture of Nd_2O_3, Y_2O_3, and V_2O_5 and subsequently mixing in a planetary ball-mill for 2 h. The resultant mixture was then filtered, dried,and heated to 900 °C for 16 h in a platinum crucible and then cooled to room temperature. The powder was ground, mixed, and then uniaxially cold-pressed into a disk-shaped pellet prior to being sintered at 1500 °C in an oxygen atmosphere for 20 h and then cooled to room temperature at a rate of 1 °C/min. The resulting polycrystalline target was pale-orange in color, and powder XRD measurements concluded that the powder was single phase and consistent with the JCPDS data for YVO_4.

Thin Film Deposition. Nd-doped yttrium orthovanadate thin films were grown on single-crystal ($1\bar{1}02$)-oriented sapphire substrates by pulsed laser deposition (PLD). The substrates, with typical sizes of $5 \times 5 \times 0.5$ mm^3, were first ultrasonically cleaned in acetone and then alcohol before being mounted to the heater block with silver paint. The films were deposited by ablating the prepared target using a 248 nm KrF excimer laser at a laser energy density of 1.6 J/cm^2 and a pulse rate of 2 Hz. The laser beam was focused through a quartz window onto the rotating target at a 45° oblique incidence, and the substrate was set at a distance of 5 cm parallel from the target surface. The depositions were carried out at substrate temperatures ranging between 500 and 900 °C and from vacuum (5×10^{-3} mTorr) to oxygen partial pressures of 450 mTorr. After deposition was completed, oxygen was bled into the PLD chamber to a static value of 500 mbar and the films were cooled to room temperature at 10 °C/min. All films deposited, regardless of the temperature or oxygen pressure used during growth, were shiny and transparent, indicating the absence of oxygen defects, which typically discolor the films black and opaque.

Characterization. Crystalline phase identification, mosaicity, and determination of out-of-plane lattice parameters of the deposited films were carried out by X-ray diffraction (XRD) using a Seiffert XRD-3000 diffractometer, while the in-plane orientation of the films was determined by asymmetrical diffraction performed on a Philips X-Pert MRD four-circle diffractometer. Both diffractometers were equipped with Cu Kα_1 radiation ($\lambda = 1.5405$ Å). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were done using a JEOL 2010 electron microscope, working at 200 kV ($C_s = 1$ mm) in order to verify the quality and morphology of the films. Samples were prepared by scratching the film from the substrate with a diamond tip and dispersing the crystallites onto a carbon-coated grid. Surface characteristics and grain size of the films was investigated by scanning electron microscopy (SEM) on a Phillips XL 30 series scanning electron microscope. The micrographs were acquired from the Nd:YVO_4 films using an accelerating voltage of 7 kV and magnification values up to 28000×.

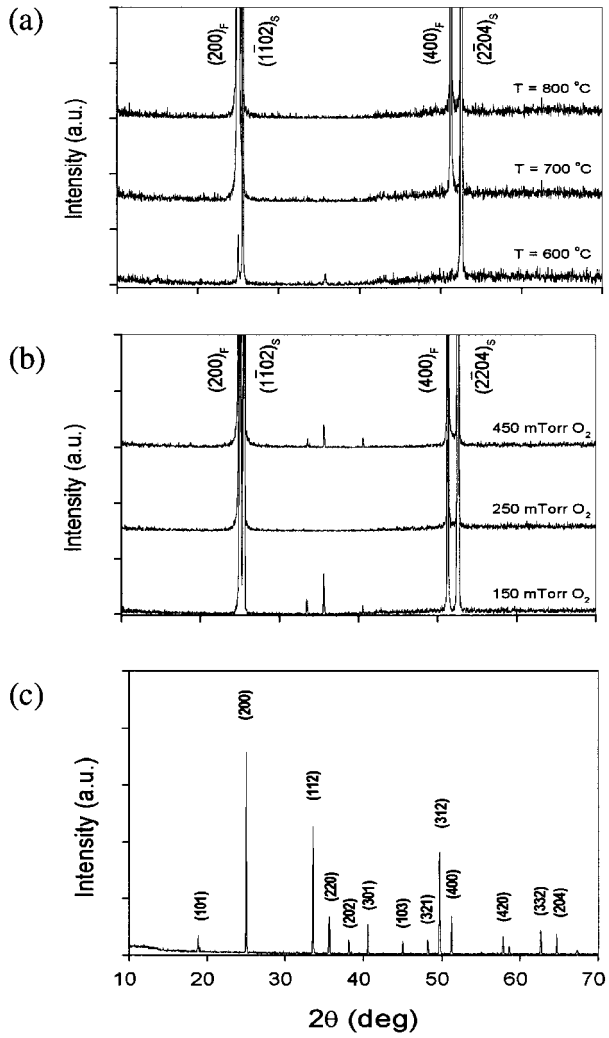

Figure 1. XRD patterns (magnified to show the low intensity peaks) for the Nd:YVO_4 films with a thickness of 2000 Å grown on sapphire($1\bar{1}02$) (a) at different substrate temperatures and a fixed oxygen pressure of 350 mTorr and (b) in different oxygen gas pressures at a fixed substrate temperature of 800 °C. (c) XRD powder pattern of the Nd:YVO_4 ablation target.

III. Results and Discussion

Film Structure as a Function of Temperature and Oxygen Pressure. To determine the optimized growth conditions for highly crystalline Nd:YVO_4 films, a systematic study of the effects of oxygen pressure and substrate temperature on film formation was carried out in detail. Figure 1a shows the Nd:YVO_4 films with a thickness of 2000 Å grown at various temperatures and a fixed oxygen pressure of 350 mTorr. For comparison, we have also shown the powder XRD pattern of the target material Nd_x:$Y_{1-x}VO_4$ (where $x = 0.02$) (Figure 1c). As can be seen from Figure 1, the film grown at 600 °C contains grain orientations corresponding to the (200) and (220) planes of tetragonal YVO_4, displaying

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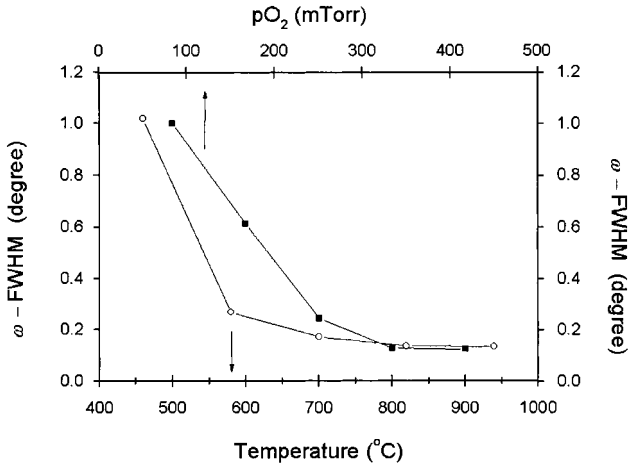

Figure 2. FWHM values of the (200) XRD peak in theYVO$_4$ films as a function of substrate temperature (open circles) and oxygen pressure (solid squares) during deposition. The partial pressure of oxygen was fixed at 350 mTorr during the depositions for the temperature study while the substrate temperature was maintained constant at 800 °C for the pressure study.

weak diffraction peaks located at 24.98° and 35.67°, respectively, which correspond exactly to the values observed in bulk YVO_4. It is clear that the preferred growth orientation of the film is along the [100]-direction; however, when the standard power diffraction intensity is used to normalize observed peak intensities, the volume fraction of the (220) peak was estimated to be approximately 1%. When the substrate temperature is increased to 700 °C the film becomes entirely (100)-oriented giving rise to an intensity increase of the (200) and (400) peaks by 1 order of magnitude (Figure 1b). No diffraction peaks attributed either to other orientations in YVO_4 or foreign phases were observed within the accuracy of the measurement in the 2θ scan range of 10−70°. Films grown at substrate temperatures above 700 °C remain highly oriented in the [200]-direction and show a slight improvement in crystallinity as can be seen by the FWHM values presented in Figure 2. Thus, although the increase in substrate temperature improves the texture and crystallinity of the films, it does not play a key role in the orientation of the films. Moreover, the *a*-axis orientation (i.e., *c*-axis in the plane of the film) is an important result for lasing applications since the absorption coefficient of Nd:YVO_4 is higher when the pump polarization is oriented parallel (π) to the *c*-axis, as opposed to perpendicular (σ), since this results in stronger lasing effects.

The increase of O_2 pressure during the deposition yields similar effects on the crystallinity of the Nd:YVO_4 films as temperature, however, has shown to have a more profound effect on the microstructure of the films. For instance, when the oxygen pressure is incresed from 50 to 450 mTorr, the intensity of the (200) diffraction peak significantly increases; however, the microstructure of the films alters as the pressure in raised. When the Nd:YVO_4 films are grown under low (<250 mTorr) and high (>350 mTorr) oxygen partial pressures, mixed films with (200)-, (112)-, (220)-, and (301)-textured grains were grown albeit the strong preferential (200) texture in all pressure regions studied (Figure 1b). On the contrary, in the intermediate pressure range of 250−350 mTorr, single-oriented films were grown and no evidence of other grain orientations were observed. The presence of mixed films at low and high pressures can be explained as follows: an increase in oxygen pressure induces an increased number of density outgrowths on the film surface during growth as a direct result of cluster formation of ablated species in the laser plume. Upon arrival on the film surface, these clusters may act as nucleation sites for the growth of grains with different orientations, specifically the (112)-, (220)-, and (301)-grain orientations, resulting in a polycrystalline film with preferred orientation along the [200]-direction. On the contrary, at low oxygen pressures the plume species undergo less collisions and interactions with the background gas in the plume during flight to the substrate and, consequently, have more kinetic energy when they reach the surface of the growing film. Nonetheless, at lower deposition pressures, the plume species spend less time in the plume; therefore, the kinetic energy conserved in flight is wasted during surface interactions because the next incoming plume quickly bombards the surface species before they can settle into a preferred orientation. This was observed in the XRD data of films, having identical thickness, which revealed an enhancement of film crystallinity when the oxygen pressure was increased. The improved quality of the growing film is due to a longer relaxation time for the growth species on the film surface to form large particulates and, more time for these particulates to migrate on the growing film surface before being covered by the material generated from the next laser pulse.[20]

The mosaicity of the films was characterized by measuring the corresponding rocking curve (ω-scan) of the (200) diffraction peak. Figure 2 shows the resulting values of the full-width at half-maximum (FWHM) of the (200) diffraction peak as function of substrate and oxygen gas pressure. It is clear from these data that the FWHM values decrease upon increasing substrate temperature and O_2 pressure and present the most significant improvements of film quality in the temperature and pressure ranges of 500−700 °C and 50−150 mTorr O_2, respectively. For instance, at high temperatures and O_2 pressures the rocking curve is comprised of an extremely sharp Gaussian shape peak with a full width at half-maximum (FWHM) in the range of 0.12−0.17°. It should be noted that a FWHM value of 0.12° was recorded for the sapphire substrate and, thus this value can be considered as the instrumental broadening of the diffractometer. This extremely small FWHM value implies very little tilting of the (200) planes with respect to the substrate and further reinforces the high crystalline quality of the films.

Grain Morphology as a Function of Oxygen Pressure and Temperature. It is clear from the SEM analyses of the different films that the oxygen pressure and substrate temperature employed during growth play key roles in the resulting grain size and shape. Parts a−c of Figure 3 show the change in grain morphology as a function of oxygen pressure corresponding to the films presented in Figure 2b. We have observed that in the entire pressure regime studied throughout our investigation that there exist two main pressure zones that correspond to different grain mor-

(20) *Pulsed Laser Deposition of Thin Films*; Chrisey D. B., Hubler, G. K., Eds.; Wiley & Sons: New York, 1994; p 456.

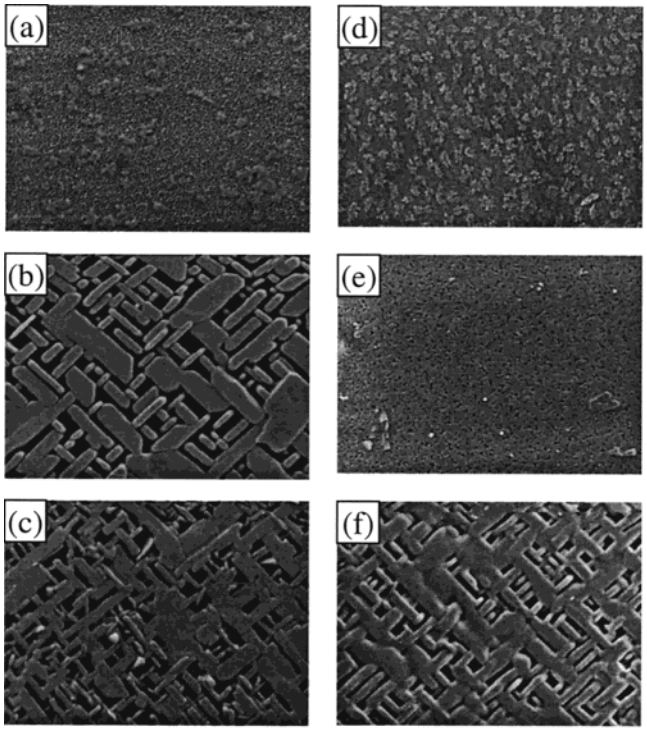

Figure 3. Scanning-electron microscopy photographs (magnification: 14000×) of YVO_4 films grown on sapphire ($1\bar{1}02$) substrates at oxygen pressures of (a) 150 mTorr, (b) 250 mTorr, and (c) 450 mTorr at a fixed substrate temperature of 800 °C and at substrate temperatures of (d) 600 °C, (e) 700 °C, and (f) 800 °C at a fixed oxygen pressure of 350 mTorr.

phologies of the films. In the oxygen pressure range of 0−250 mTorr, the films contain a dense structure of nanometer-sized spherical and irregular-shaped surface clusters (Figure 3a) approximately 0.5 μm in diameter, giving rise to films having a corrugated characteristic. At a deposition pressure of approximately 250 mTorr O_2, the films undergo a remarkable transformation of grain morphology as shown in Figure 3b. An increase in average grain size by 3 orders of magnitude is observed and accompanied by a dramatic change in morphology from spherical to highly faceted rectangular-shaped crystallites oriented 90° from each other forming a crisscross morphology. Films grown in the pressure zone above 250 mTorr of oxygen present the same characteristic; however, as is clearly seen in Figure 3c, at pressures above 400 mTorr, other grain morphologies begin to grow within the voids created by the inefficient packing of the 90° orientation of the rectangular grains. These irregular shaped crystallites are related to the (112)-, (200)-, and (301)-grain orientations that are observed in the XRD pattern in Figure 1b.

Parts d−f of Figure 3 present a similar change in grain morphology as a function of temperature and correspond to the films shown in Figure 1a. Below 650 °C, the films exhibit the same dense structure of nanometer-sized spherical grains and irregular-shaped surface clusters (Figure 3d) as observed in Figure 3a (i.e., film grown at 800 °C and 150 mTorr O_2). Films grown under identical conditions but at a temperature of 700 °C yielded grains of larger size and different morphology. It is evident from the SEM image in Figure 3e that the grains begin to adopt a more nonspherical shape; however, the crystallized surface particulates

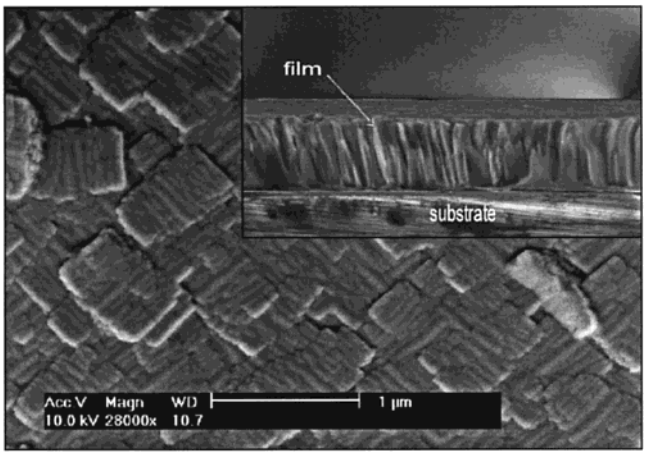

Figure 4. SEM image showing the plan view of a 10,000 Å thick YVO_4 film. The inset shows the cross-sectional view clearly illustrating the columnar grains in the films.

observed in the film grown at 650 °C are still present, nonetheless, in a much lower concentration. Moreover, there still remains spherical-shaped grains embedded within the network of large grains and may be associated with the extra diffraction peak observed in the corresponding XRD pattern (Figure 1a). Above 750 °C, the films become homogeneous in morphology revealing the same rectangular-shaped grains as was observed for films grown at 800 °C and 250 mTorr O_2 (Figure 3b). The rectangular grains exhibit a length of 1−4 μm and a width range between 0.3 and 1.5 μm (Figure 3f). The corresponding XRD pattern (Figure 1a) now displays a highly textured film yielding only the (200) reflection of tetragonal YVO_4, however, the films still contain a high density of voids present between the individual crystallites. These voids, along with the 90° orientation of the grains, are characteristics which could be detrimental for the optical properties of the film (i.e., waveguiding, lasing) because of the undesirable scattering or trapping of phonons. This hypothesis is currently being investigated and will be reported in a follow-up to this report. It should be mentioned that other deposition parameters (i.e., laser fluence, deposition rate and target-substrate distance) were investigated in efforts to coalesce the large elongated microcrystals into a single, void-free film. However, regardless of these efforts, all of the films grown employing these different parameters consistently showed the same high-density voids. We have observed that as the film thickness increases above 10 000 Å (Figure 4) the voids disappear as the rectangular grains coalesce forming individual *blocks* with average dimensions of 0.75 μm × 0.50 μm. These blocks are constructed from approximately 10−12 individual rodlike grains (∼500 nm × 60 nm) per block and show the same crisscross pattern as the micro-sized rectangular grains observed in the 2000 Å thick films.

The rectangular morphology of the grains observed at high temperatures and pressures indicates that the grains were grown at substantially different rates along different crystallographic directions. In fact, these results are in good agreement with attachment energy calculations performed for different crystallographic plans of YVO_4 single crystals grown by several techniques, i.e., Czochralski (CZ), top seeded solution growth

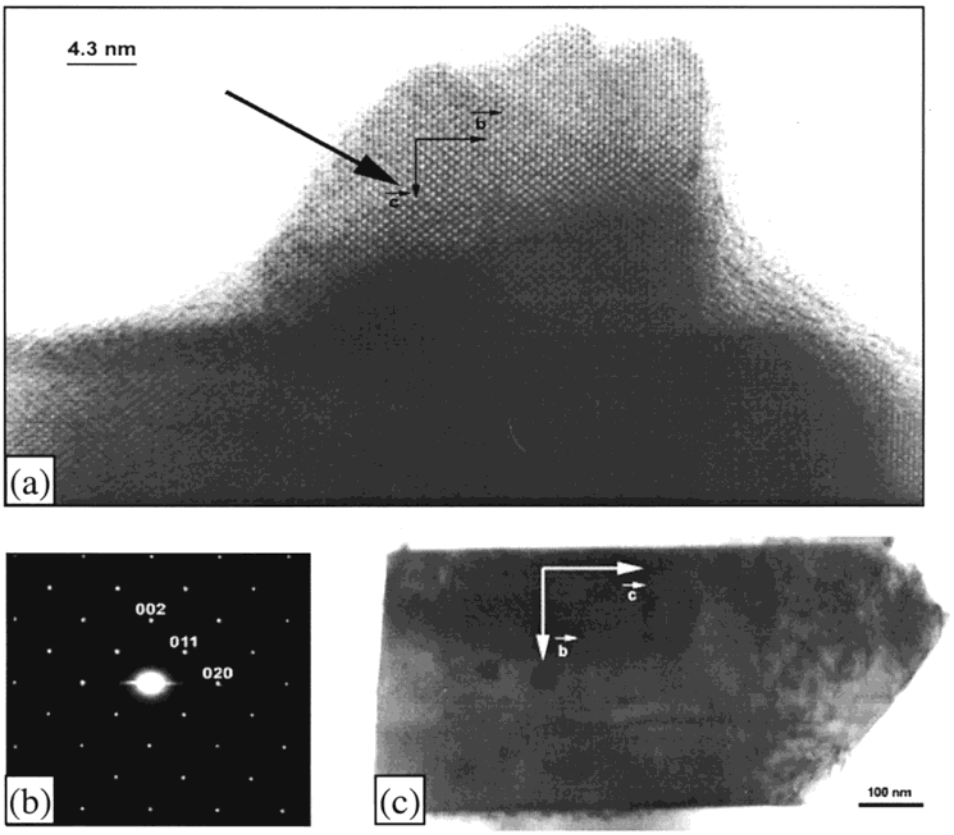

Figure 5. (a) High-resolution image taken along the [100] direction and (b) the electron diffraction (ED) pattern of an individual grain from a (200)-oriented YVO_4 film grown on sapphire ($1\bar{1}02$). (c) TEM image of the same YVO_4 microcrystallite illustrating the rectangular morphology.

(TSSG), and laser heated pedestal growth (LHPG).[21] The calculations showed that crystal growth along the *c*-axis of the unit cell is approximately four times faster than in the *a*- and *b*-axes because of the higher attachment energies of Y^{3+} and V^{5+} cations to the O^{2-} anion along the [001]-direction of the unit cell. As a result, an elongated crystal morphology is formed as we have observed in our SEM and TEM studies previously described. The isotropic nanosize grains observed at lower substrate temperatures and oxygen pressures is likely due to a lack of sufficient kinetic energy of the surface species during the crystallization process of the growing film. Although the nucleation density is very high there is not enough of thermal energy on the substrate surface to create supersaturation. To confirm this hypothesis, an as-grown film having spherical grains, deposited at low temperatures, was annealed in oxygen for 1 h and then immediately examined by both SEM and XRD. The SEM results showed that the grain size increased by 3 orders of magnitude accompanied by a change in the grain shape from spherical to rectangular, and the film showed the same crisscross morphology observed in the as-grown films grown above 700 °C. The XRD also revealed an increase in the intensity of the (200) peak as well as a decrease in the FHWM from 0.83 to 0.25° indicating an increase in grain size as was apparent from the SEM investigation undertaken on the film. Moreover, the small (220) diffraction peak present in the original film was no longer present in the annealed film indicating that the elevated annealing temperature increases the mobility of the film species allowing them to settle into the most stable grain orientation, i.e., the (200) orientation.

Transmission Electron Microscopy and Determination of Epitaxial Relationship between Nd:YVO$_4$ Film and Sapphire Substrate. The electron diffraction study was performed on an optimized film grown at 800 °C and 250 mTorr O_2. The reconstruction of the reciprocal space carried out confirms that the cell parameters are close to the bulk ones and are in agreement with the space group $I4_1/amd$ of the bulk material. The high-resolution image of a fragment of the film is shown in Figure 5a along with the corresponding electron diffraction pattern of the crystallites (Figure 5b). It can clearly be observed from the thin areas (outer edges of the image) of the crystallite that the films are highly uniform throughout the entire surface area showing no evidence of defects. The sharp and intense spots in the ED pattern indicate the high crystalline quality of the sample and the observed reflections of this pattern can be indexed using the tetragonal lattice of YVO_4. The [100] high-resolution image shown in Figure 5a is from a thin part of an individual crystallite, [100]- or [010]-oriented with respect to the electron beam, and is in agreement with the orientation deduced from the XRD data. In the center part of this image (black arrow in Figure 5a), a centered rectangular array of bright spots, separated 7.10 Å along one direction and 6.30 Å along the other direction perpendicular to the first one is observed. These observed values correspond to the *b*- and *c*-axes of YVO_4 and are in close agreement with the

(21) Ermeneux, F. S. Ph.D. Thesis, Universite Claude Bernard, Lyon, France, 1999.

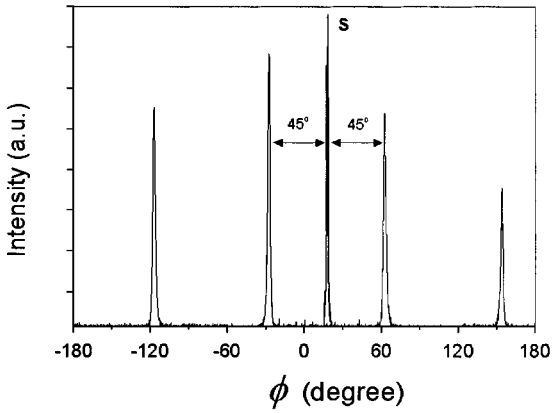

Figure 6. X-ray ϕ-scan in the full 360° range for the (200) reflection for a YVO_4 film grown using the optimized deposition parameters (T_s = 800 °C; pO_2 = 0.250 mTorr; 1.5 mJ/cm^2; 2 Hz; d = 50 mm) on a sapphire($1\bar{1}02$) substrate. The figure shows that the directions of the (200) grains in the film are tilted 45° to the principal axis (labeled S) of the substrate surface lattice.

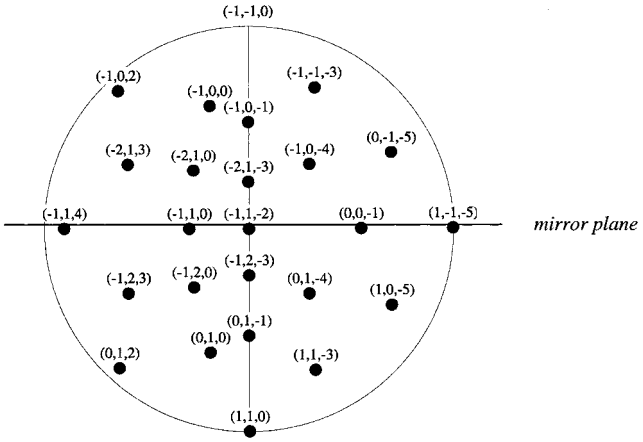

Figure 7. Simulated pole figure of *r*-cut sapphire displaying both the nonrotational symmetry and the mirror plane parallel to the *c*-axis.

bulk values of 7.12 and 6.29 Å, respectively. Simulated images were calculated varying the focus value and the thickness of the crystals, using the positional parameters given in ref 22. The comparison between simulated and experimental images allows us to correlate this array of bright spots with the low electron density area of the structure (i.e., close to −600 Å, the Scherzer value, for this microscope). The observation of different areas of the microcrystal shows that such an array of bright spots is maintained throughout the crystallite. Again, this confirms the very good crystallization as well as the absence of extended defects and the elongation direction of the crystals with respect to the crystallographic axes. For example, the *c*-axis of the cell is along the longest length of the crystals while the *a*- *or b*-axis is along the shortest length of the crystals (Figure 5c) and structurally confirms our previous suggestion of the growth rate of the crystallites with respect to the unit cell axes. The longest dimension of the crystallites indeed corresponds to the shortest lattice parameter, and implies that the growth is faster along the most compact direction of the structure.

The in-plane orientation was investigated by performing phi scans on a X-ray four-circle diffractometer. The films were aligned such that the ϕ axis of rotation was parallel to the surface normal and then the ϕ scan of the (220) reflection was performed for the (200)-oriented grains of the film. In the full 360° range the film presents four sharp peaks (average FHWM = 0.92°) separated from each other by 90° suggesting 4-fold rotational symmetry (Figure 6). However, for (200)-oriented Nd:YVO_4 films one would expect to observe only two peaks, separated by 180°, as a result of the 2-fold rotational symmetry of the (200) growth plane. For this reason, the four peaks observed most likely correspond to two separate 2-fold rotational axes and would be in good accordance with the 90° tilt of the rectangular grains observed in the SEM analysis presented in Figure 3. The phi scan of the sapphire substrate taken on the ($\bar{3}30$) reflection shows one diffraction peak (dotted curve) shifted 45° with respect to the (200) Nd:YVO_4 grains. The single peak observed is due to the nonsymmetrical surface (depicted from the pole figure in Figure 7) of the R-plane of sapphire and thus should promote the growth of epitaxial films with a single in-plane variant. Therefore, the observed tilt in the (200)-oriented grains of the films cannot be caused by rotational symmetry since it does not exist, thus other factors such as reflection symmetry must be taken into consideration. Upon examining the simulated pole figure of the sapphire R-plane (Figure 7), it is evident that there is indeed a mirror plane located along the [$1\bar{1}0\bar{5}$] direction (*c*-axis) of the substrate surface, which might result in the 45° tilt observed in the phi scans between the film and substrate (see Figure 6).

(22) X-ray Powder Diffraction Data Card, JCPDS 76-0341.

Conclusions

Nd:YVO_4 thin films have been grown on sapphire-($1\bar{1}02$) substrates by pulsed laser deposition. The results show that the most pertinent parameters for the growth of highly textured (200)-oriented films are the substrate temperature and oxygen pressure employed during the deposition. At elevated growth temperatures (>700 °C) and oxygen pressures (250−350 mTorr), the films were consistently highly crystalline, epitaxial with respect to the sapphire substrate and consisted of micro-size rectangular grains representative of (200)-oriented Nd:YVO_4. On the contrary, at low temperatures and pressures of O_2, the films were consistently well textured out-of-plane along the [200]-direction but, however, were polycrystalline in-plane giving rise to a nonepitaxial relationship with the substrate. Moreover, the grain size decreases by 3 orders of magnitude, giving rise to nanometer-size spherical crystallites. Although the (200) film orientation is favorable for most lasing applications, i.e., the *c*-axis in-plane, the crisscross nature of the (200) grains may pose detrimental effects on the transmission of optical waves because of the anisotropic optical properties of bulk YVO_4. Therefore, the growth of either (i) epitaxial films with coherently aligned (200)-oriented grains or (ii) *c*-axis oriented films is probably necessary to ensure efficient optical properties of the YVO_4 films. Despite the fact that the latter would lead to less intense lasing as mentioned earlier, we have investigated, but nevertheless were unsuccessful in finding experimental conditions to modify the surface energy and promote the

(001) film orientation. Thus, other nonexperimental options involving the use of miscut substrates or buffer layers are currently under investigation for the growth of Nd:YVO_4 films with the above-mentioned characteristics, and the results will be reported at a later time.

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