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Pulsed-laser deposition of a Nd:$KGd(WO_4)_2$ waveguide in Ar and O_2 environments

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ABSTRACT Thin-film Nd-doped potassium gadolinium tungstate (Nd:KGW or $KGd(WO_4)_2$) waveguides are deposited on $(1\bar{1}02)$sapphire or (100)YAG substrates by KrF laser ablation of potassium-rich ceramic targets in Ar and O_2. The dependence of the stoichiometry, crystallinity and waveguide properties of the films on the environmental gas pressure and substrate temperature is studied. Highly textured crystalline (110) KGW films are grown. An optical waveguide loss as low as 3 dB/cm is obtained for the films grown in Ar. The as-grown films are optically active. Upon annealing at 900 °C in air, the crystallinity and the properties of the emission spectra are dramatically improved.

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1 Introduction

Planar and channel waveguide lasers are of great interest for laser physics, integrated optics, photonics, optical communications, laser and Raman spectroscopy, ellipsometry, range finders, etc. From this point of view, potassium gadolinium tungstate [KGW or $KGd(WO_4)_2$] doped with Nd, Er or Yb ions may play an important role in some of these fields. Diode pumping [1–4], a lower threshold and a higher slope efficiency (by a factor of two) than Nd:YAG [3, 5, 6], and ultra-low-threshold stimulated Raman scattering [7, 8] are advantages of this material.

Although some high-optical-quality thin films and waveguides produced by pulsed laser deposition (PLD) have been reported, the technique presents numerous difficulties. To date, Nd-doped YAG [9] and GGG [10] have been successfully grown. Recently, the growth and study of Nd:KGW films on $(1\bar{1}02)$sapphire, (100)Si, (100)MgO, (100)YAG and (100)YAP has been reported [11–15]. A single-crystal target was used for ablation in these studies. However, the films were usually K deficient due to potassium preferential scattering in the plasma, which provokes a non-desired Gd_2WO_6 (GW) crystalline phase growth. Although the K deficiency can be compensated for, when deposited at higher O_2 pressure (1 mbar), it causes a rough surface and high absorption of the films.

In this paper we will describe the growth of highly textured crystalline Nd:KGW thin films on r-cut $(1\bar{1}02)$sapphire or (100)YAG substrates in Ar or O_2 environments using K-rich ceramic targets. The latter compensate for the K deficiency in the films, which allows us to decrease the gas pressure. Moreover, better results are obtained when depositing films in Ar. Rutherford backscattering (RBS) measurements, X-ray diffraction (XRD) analyses, PL measurements and waveguide propagation measurements have been made. Improvement of the films with post-annealing has also been accomplished.

2 Experimental

2.1 *Preparation of a* K*-rich ceramic target*

The ceramic targets were prepared by mixing WO_3, K_2CO_3, Gd_2O_3 and Nd_2O_3 in various ratios. The mixture was homogenized for 1 h, pressed to 4–7 MPa at room temperature to form a pellet, and then heated at a temperature between 760 and 800 °C for 4 h to remove the carbon and the water absorbed by K_2CO_3. Afterwards, the pellets were ground, pressed again at 6–10 MPa to form targets and dried at 150 °C for 4 h. The as-prepared targets were very hygroscopic and were stored in a dry atmosphere. During this procedure, some quantity of potassium loss is also anticipated. The subsequent K content was analyzed using an EDX technique equipped with environmental scanning electron microscopy (XL-30 ESEM-FEG, Philips). A target with the ratio of potassium N_K to tungsten N_W content $N_K/N_W = 1.30$, the stoichiometric value being 0.5, has been used for ablation in this study.

2.2 *Pulsed-laser deposition*

The pulsed laser was a KrF excimer laser (LPX150, Lambda Physik) operating at $\lambda = 248$ nm, $f = 20$ Hz, $\tau = 27$ ns. The laser beam was focused onto the ceramic target inside the vacuum chamber at an incident angle of 45° with the fluence, E, between 1.2 and 1.5 J/cm^2. The target and substrate separation, d_{T-S}, was 4 cm. The Nd-doped KGW thin films were deposited on single-crystal $(1\bar{1}02)$sapphire or (100)YAG substrates heated between $T_{sub} = 600$–800 °C

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by a resistive heater. The deposition has been carried out in vacuum ($< 10^{-4}$ mbar) and at the pressure of $P(\mathrm{Ar\,or\,O_2}) = 5 \times 10^{-3}$–0.1 mbar. Both target and substrates were rotated to ensure better film quality. A deposition rate of approximately 8.5 nm/min was obtained. The thickness of the films was in the range 0.3 to 1.0 μm, depending on the deposition time. The as-deposited films were annealed using an electrical furnace in air at 900 °C for 1 h.

2.3 *Characterization of the films*

The composition of the films was analyzed by means of an ion-beam analyzer (IBA-9900, Shimadzu). To determine the crystallographic structure before and after annealing, XRD analysis with Cu K_α radiation (RAD-C, Rigaku) was used in the θ–2θ Bragg–Brentano geometry. The waveguide losses were measured by recording the attenuation of the scattered light ($\lambda = 633$ nm) along with the propagation path. Film-prism coupling was used for introducing the He-Ne laser into the film. The scattered light was measured by a CCD camera. The PL measurements were performed at room temperature using an OMA 2000 Digital Triple Grating Spectrograph (Q8381A, Advantest), and a 810-nm line of fiber-coupled laser diodes (OPC-A002-808-FC/150, Opto Power) were used for pumping.

3 Results and discussion

3.1 *Composition and crystallographic characterization*

The RBS analysis revealed that the K content strongly depends on the growth conditions. At about 5×10^{-3} mbar oxygen pressure it reaches the stoichiometric value of $N_\mathrm{K}/N_\mathrm{W} = 0.5$, and further increases with pressure. However, better crystallinity of the films is observed for deposition at one order of magnitude higher pressure $P(\mathrm{O_2}) = 0.05$ mbar. This may be understood since the excess of potassium will promote KGW crystal growth and suppress GW crystal growth. Furthermore, $N_\mathrm{O}/N_\mathrm{W} = 4.0 \pm 0.4$ is approached only in vacuum and increases with oxygen pressure rise. It has similar behavior to potassium with the temperature change. $N_\mathrm{Gd}/N_\mathrm{W} = 0.50 \pm 0.05$ does not depend on $P(\mathrm{O_2})$ or temperature. The Nd content cannot accurately be determined via RBS due to the low percentage concentration and the proximity of the Nd signal to that of Gd in the spectrum. However, it is estimated by EDS analyses to be 0.15 at. % and we believe that it is preserved at the same quantity during deposition as Gd. The errors given correspond to the dispersion of the data for different films grown under similar conditions or to the experimental error in the determination of the atomic content by RBS.

When films are deposited in Ar, this does not influence the $N_\mathrm{K}/N_\mathrm{W}$ compared with the same pressure of O_2. However, the best crystalline and single-oriented KGW films were obtained at a pressure of $P(\mathrm{Ar}) = 0.05$ mbar at $T_\mathrm{sub} = 700$ °C. It has been well explained that the need for some gas environment is mainly to prevent K from scattering in the plasma for stoichiometric transfer, and not for further improvement of the oxygen content of the film.

Figure 1 shows the XRD scans of films, deposited on $(1\bar{1}02)$sapphire at $P(\mathrm{O_2}) = 0.05$ mbar and different substrate temperatures. It is obviously seen that the film growth strictly depends on the substrate temperature. A clear (110)KGW crystal phase appears only around 700 °C. This temperature is found to be 50 °C higher than the optimum one evaluated in [12], but equal to those reported in [15]. At temperatures below 650 °C, the films are amorphous. Subsequently, at temperatures higher than 750 °C, the non-desired monoclinic GW crystal phases grow dominantly. Over 900 °C, film formation cannot be obtained due to re-evaporation. Although this optimum temperature does not change, the crystallinity of the thin films is better each time when deposited on $(1\bar{1}02)$sapphire compared with (100)YAG.

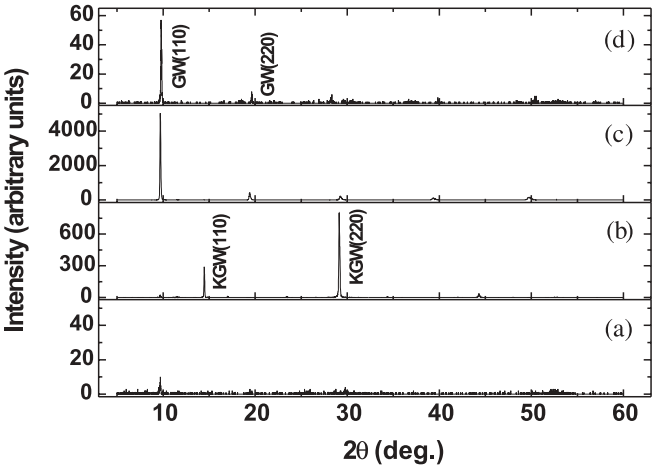

FIGURE 1 XRD spectra of films, deposited on $(1\bar{1}02)$sapphire at $P(\mathrm{O_2}) = 0.05$ mbar and different substrate temperatures: a) 660 °C; b) 720 °C; c) 770 °C; d) 840 °C. The monoclinic KGW and GW crystalline phases are indicated

The crystallinity of the as-grown films on both the different substrates is dramatically improved by annealing. Not only does the crystallinity of the KGW phases improve, but also KGW phases appear from the amorphous films. The latter phenomenon occurs except in the case of films deposited in vacuum, which have smaller than the stoichiometric amount of potassium. It is worth pointing out that even if the films de-

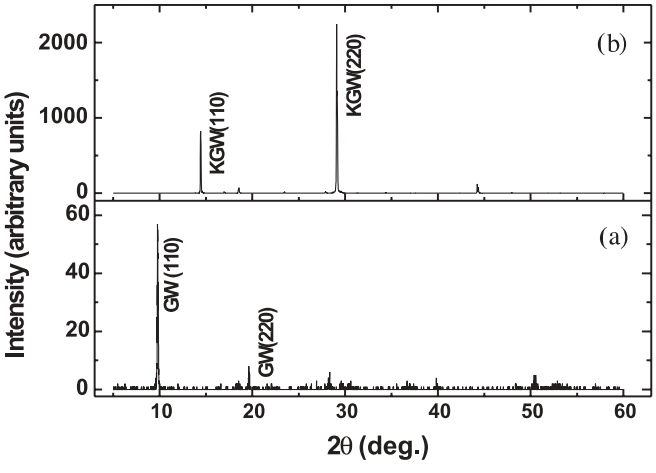

FIGURE 2 XRD spectra of the as-deposited film on $(1\bar{1}02)$sapphire at $T_\mathrm{sub} = 840$ °C and $P(\mathrm{O_2}) = 0.05$ mbar - a) and b) after annealing

posited on $(1\bar{1}02)$sapphire consist of GW crystalline phases, these disappear and transform into the single-oriented KGW crystalline phase after annealing, as shown in Fig. 2. This phenomenon is connected with the excess of potassium presenting in the film as an amorphous phase, and re-crystallization, which occurs during the annealing. In contrast, the films deposited on (100)YAG substrates have some polycrystalline KGW mixed with the GW phases after annealing. These improvements are observed both for films deposited in Ar and O_2 environments.

3.2 *Optical properties*

Figure 3 shows the influence of T_{sub} on the optical waveguide propagation losses for the as-grown and annealed films deposited on $(1\bar{1}02)$sapphire in $P(\mathrm{Ar}) = 0.05$ mbar as well as for annealed films deposited in $P(\mathrm{O_2}) = 0.05$ mbar. In all cases, the propagation losses increase with the temperature rise. The values for the annealed films are slightly higher than those (about 3 dB/cm) for the as-grown ones. However, in all cases they are far better than the values for the films deposited in oxygen, as well as those reported in [15]. We believe that this reduction in optical waveguide losses is caused by improvement of surface roughness, which is directly connected with the influence of the lower gas pressure.

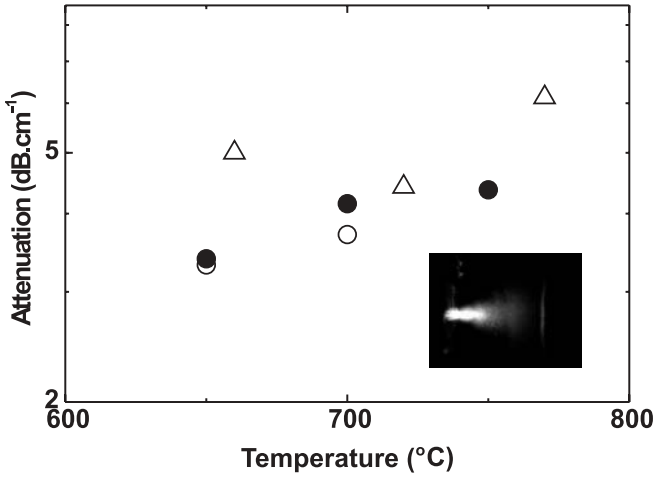

FIGURE 3 Optical waveguide propagation losses of the films deposited on $(1\bar{1}02)$sapphire as function of T_{sub}: ○ - as-grown at $P(\mathrm{Ar}) = 0.05$ mbar; and ● - after annealing; △ - $P(\mathrm{O_2}) = 0.05$ mbar, annealed. The insert shows waveguide propagation of the He-Ne laser light into the film

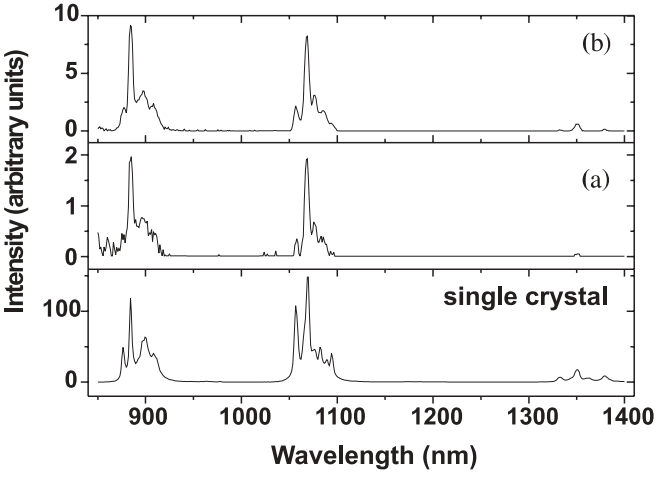

FIGURE 4 Photoluminescence spectra of thin Nd:KGW film: a) as-grown and b) after annealing. Growing conditions are $T_{sub} = 700\,^{\circ}\mathrm{C}$ and $P(\mathrm{Ar}) = 0.05$ mbar. The PL spectrum of Nd:KGW single crystal is also indicated for comparison

PL spectra of the as-grown and afterwards annealed film are shown in Fig. 4. It was deposited at $T_{sub} = 700\,^{\circ}\mathrm{C}$ and $P(\mathrm{Ar}) = 0.05$ mbar. The emission spectra intensity increases by a factor of five after annealing, as indicated in Fig. 4a and b. However, the intensities of the emission peaks of the film are more than an order of magnitude lower compared with those of the single crystal (as shown in Fig. 4 single crystal): the spectrum of the Nd:KGW laser crystal is also given for comparison here. As the film has only about 0.5 μm thickness, its lower emission intensity is mainly due to the excited active volume. The emission spectra have similar features, with the exception of a small broadening of the emission peaks in the case of the films. This is caused by large lattice mismatches between KGW films and $(1\bar{1}02)$sapphire substrates, which induce stresses and distortions to the Nd^{3+} site inside the KGW crystal. The PL intensities are very small or sometimes not observed from the films consisting of GW or consisting of the amorphous phase.

4 Conclusions

Highly textured crystalline (110)KGW films are grown. The crystallinity of KGW is better when deposited on $(1\bar{1}02)$sapphire compared with (100)YAG. We have demonstrated that non-desired GW formation can be suppressed at a temperature around 700 °C and at an excess K content. The films grown in an Ar environment have far better quality with respect to the crystallinity and optical properties than those grown in oxygen. The optimum growing conditions were evaluated to be: $P(\mathrm{Ar}) = 0.05$ mbar, $d_{T-S} = 4$ cm and $T_{sub} = 700\,^{\circ}\mathrm{C}$ with a K-content higher than the stoichiometric one. Upon annealing, the crystallinity dramatically improves due to the re-crystallization of the excess potassium presenting as an amorphous phase. The waveguide losses are improved by the use of Ar, and reach a value as low as 3 dB/cm. Further effort is needed to obtain laser action from the waveguide structure, which is the subject of forthcoming research.

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