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Growth of $GdCa_4O(BO_3)_3$ thin films by pulsed-laser deposition for nonlinear optical applications

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This paper reports the first results obtained on calcium gadolinium oxoborate $GdCa_4O(BO_3)_3$ (GdCOB) thin films grown on silicon coated with amorphous silica at high temperature by pulsed-laser deposition (PLD). It was found that the chemical composition (*i.e.* Ca/Gd ratio) depends critically on the oxygen pressure used during pulsed-laser deposition (PLD) experiments. The crystallization of thin films about 500 nm thick required a high temperature substrate (750 °C) during the PLD process followed by a post annealing treatment at 800 °C in an oxygen atmosphere. Under these conditions, the layers are polycrystalline and no texturation features have been found. The surfaces of the films are smooth (average roughness: 5-6 nm) with only a few particles or droplets. The refractive index of the films is estimated to be 1.746 at 633 nm, in agreement with the bulk GdCOB value.

Introduction

Several new nonlinear optical materials which have appeared recently have attracted widespread interest due to their large transparency ranges and higher nonlinear coefficients. For example, β-BaB_2O_4 (BBO), $KTiOPO_4$ (KTP) and KH_2PO_4 are commonly used in various nonlinear optical devices, such as parametric oscillators.[1] In 1992, a new series of oxoborates $RCa_4O(BO_3)_3$ (RCOB with R = rare earth atom) was discovered.[2] In particular, crystalline $GdCa_4O(BO_3)_3$ (GdCOB) is transparent in the visible and near infra-red spectral range (300–2600 nm) and its optical properties for frequency doubling are very promising in comparison to other nonlinear optical crystals. The damage threshold is as high[3] as 10^9 W cm^{-2} at 532 nm and the efficiency of the second harmonic generation from the 1064 nm Nd:YAG laser wavelength is higher than 50%.[4]

GdCOB is a congruent melting compound and the crystal is a chemically stable and nonhygroscopic material, with good optical quality. Though single crystals can be grown by the Czochralski method,[5] the synthesis of high quality thin films for integrated optical devices has never been realized. Using such a chemically complex material as a waveguiding thin film requires a deposition technique allowing precise control of the stoichiometry. Nowadays, pulsed-laser deposition (PLD) is a well-known method for growing stoichiometric and well-crystallized thin films at moderate substrate temperatures under a controlled reactive atmosphere. For example, high quality thin films for optical infra-red devices, such as yttrium oxide waveguides doped with rare earths, have been successfully grown by PLD.[6] Thin films for active waveguides or lasing layers have also been obtained on various substrates: E : KTP on KTP,[7] BBO on silicon or sapphire,[8] Nd : YAG on silicon or crystalline YAG,[9] $LiNbO_3$ on sapphire[10] and, recently, $KGd(WO_4)_2$ on sapphire.[11] In the present work, we report the growth and the properties of GdCOB thin films obtained by PLD under an oxygen atmosphere.

Experimental

The PLD thin films were prepared by using an ArF excimer laser (wavelength: 193 nm, repetition rate: 5 Hz, pulse duration: 23 ns). The laser beam was focused onto a rotated $GdCa_4O(BO_3)_3$ ceramic target (focusing diameter: 1 mm) centered in the PLD set-up[12] that leads to a fluence around 1.5 J cm^{-2}. The thin films were deposited onto SiO_2/Si [*i.e.* silicon(100) substrate coated with thermal silicon oxide 0.5 μm thick] for further optical waveguiding investigations and the time of the experiments was fixed to 2 h (*i.e.* 36 000 laser pulses). The target–substrate distance was kept at 3 cm. Substrate temperature and oxygen pressure were varied in the ranges 25 to 750 °C and 10^{-6} to 0.5 mbar, respectively. The thin films were characterized by X-ray diffraction (XRD) using Cu-Kα radiation in the Bragg–Brentano mode, Rutherford backscattering spectroscopy (RBS) using a $^4He^+$ ion beam, and atomic force microscopy (AFM). The optical measurements were investigated by the prism coupling method.[13]

Results and discussion

In order to study the topological features of the GdCOB layers, a PLD film was deposited at 650 °C under 0.3 mbar O_2 on the half surface of a SiO_2/Si substrate. Fig. 1a and 1b show AFM images of the uncoated substrate and the 120 nm thick GdCOB thin film, respectively. The thin film surface is strongly homogeneous with only a few particles or droplets. The average roughness of the film is around 6–7 nm, while the substrate is perfectly smooth (roughness: 0.5 nm). These initial results indicate that the growth of GdCOB thin films does not involve strong morphological damage and is not sensitive to the formation of droplets. It should also be noted that the PLD experiments were performed with a laser wavelength (193 nm) corresponding to a strong absorption of the GdCOB ceramic target. Indeed, previous experiments carried out with a

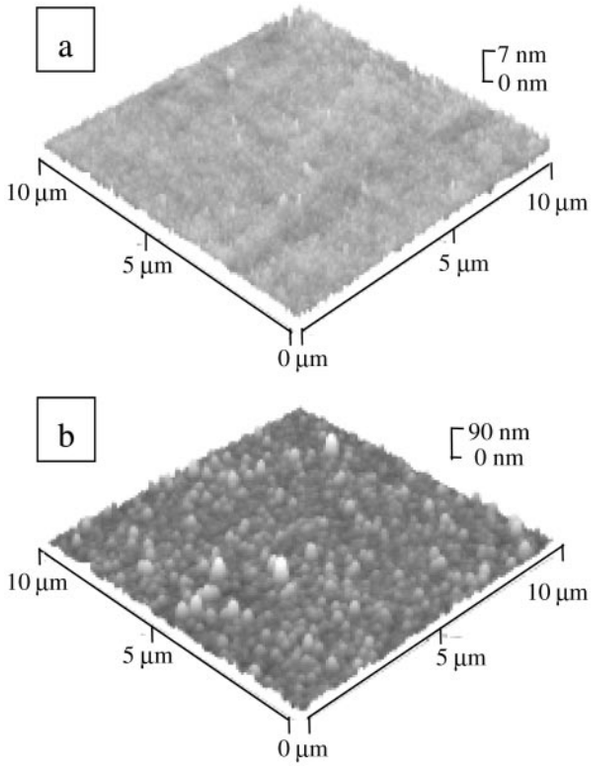

Fig. 1 AFM micrographs of SiO_2/Si substrate (a) and GdCOB thin film deposited on SiO_2/Si at 650 °C under 0.3 mbar O_2 (b).

quadrupled frequency Nd : YAG laser (266 nm) did not lead to good quality thin films.

According to RUMP simulations,[14] the RBS spectra should allow the determination of the thickness and composition of the thin film. Nevertheless, the determination of the boron content in layers from RBS measurements is not accurate. Therefore, the optimization of PLD experimental conditions (*i.e.* oxygen pressure and substrate temperature) is determined mainly by the Ca/Gd ratio. A typical RBS spectrum of a GdCOB thin film grown at 650 °C under 0.3 mbar O_2 is displayed in Fig. 2. The thickness of this film is 520 nm, with a Ca/Gd ratio of 3.8. The abrupt fall of both the Ca and Gd profiles towards the lower energies reveals a smooth and regular film without any macroscopic particles. Moreover, no chemical diffusion feature between the film and the substrate is observed. Fig. 3 shows the Ca/Gd ratios (determined by RBS measurements) depending on the oxygen pressure in the range 10^{-6}–0.5 mbar at constant temperature (650 °C). The strong

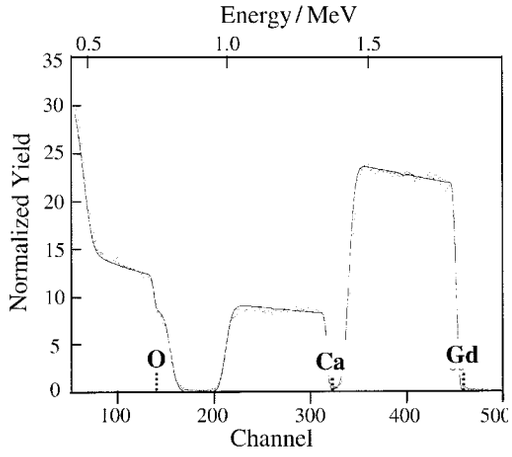

Fig. 2 RBS spectrum of a GdCOB thin film deposited on SiO_2/Si at 650 °C under 0.3 mbar O_2.

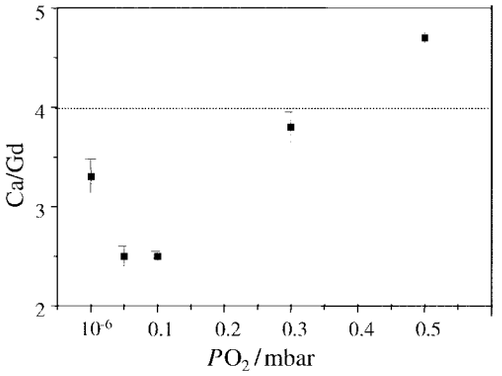

Fig. 3 Ca/Gd ratio *versus* oxygen pressure for a thin film deposited on SiO_2/Si at 650 °C.

influence of the oxygen pressure on the thin film composition can be seen. The minimum value of Ca/Gd is reached for the $P_{O_2} = 0.05$–0.1 mbar range. Nearly stoichiometric thin films (corresponding to Ca/Gd = 4) are obtained at 0.3 mbar oxygen pressure. This behavior, the chemical composition depending on the oxygen pressure, typical of complex oxides, has been observed previously.[15] This phenomenon is due to both the different sticking coefficient connected with the volatility of the species which are incorporated in the film during growth and the different spatial distribution of the species in the plume during laser ablation.

The crystalline structure of GdCOB thin films grown at various temperatures (room temperature to 750 °C) was investigated by XRD measurements in the diffraction angle range 2θ 10–65°. It appears that, even at the highest temperature allowed in our PLD system (750 °C), the films are not crystalline. In order to induce crystallization, a post-annealing treatment at 800 °C under an oxygen atmosphere was employed on films grown at 650 °C. The $\theta/2\theta$ pattern of this post-annealed GdCOB film (Fig. 4) displays a polycrystalline structure without texturing features. All peaks of the XRD pattern can be indexed according to the crystallographic data of GdCOB bulk material (monoclinic biaxial and centric C_m space group with $Z = 2$, $a = 8.095$, $b = 16.018$, $c = 3.558$ Å and $\beta = 101.26°$).[4] The general conclusion from RBS and XRD analyses is that a faithful stoichiometric transfer occurs for an oxygen pressure of 0.3 mbar and a good crystalline structure requires temperatures as high as 800 °C.

Finally, the value of the refractive index has been obtained by using *m*-lines spectroscopy at 633 nm. As a result of the thinness of our films (140 nm for the film grown at 700 °C under 0.3 mbar O_2), only one TE mode is observed. Therefore, by using the thickness value deduced from RBS measurements, the refractive index is estimated to 1.746. This value obtained for our thin films is in agreement with that for bulk GdCOB.[3]

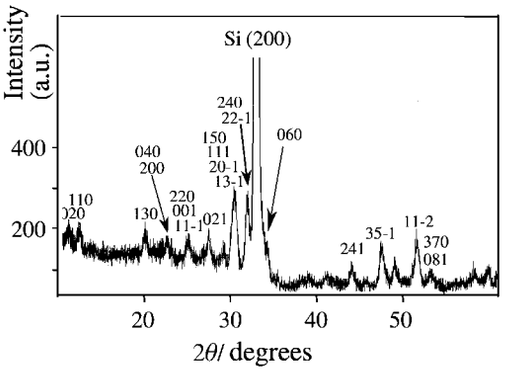

Fig. 4 XRD pattern (Cu-Kα) of a GdCOB thin film deposited on SiO_2/Si at 650 °C and post annealed at 800 °C under an oxygen atmosphere.

Conclusion

Smooth, stoichiometric, polycrystalline, monophasic GdCOB thin films may be grown under 0.3 mbar oxygen pressure on Si(100) coated with SiO_2 *via* the PLD process at a moderate substrate temperature (650 °C), followed by post annealing at 800 °C under an oxygen atmosphere. Future experiments should involve improvements aimed at synthesizing GdCOB thin films of high crystalline quality and with oriented and heteroepitaxial growth features with the substrate allowing optical waveguiding and nonlinear effects.

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