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Growth of Nd:YAG films by the pulsed laser deposition method

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Abstract

This work presents X-ray diffraction results about the structural properties of thin yttrium aluminum garnet films doped with neodymium. For this purpose, series of samples on silicon substrates were made by the pulsed laser deposition method at various deposition conditions. Successful growth was achieved as long as the substrate temperature was maintained at least at 450 °C. Applied bias was found to exert a detrimental effect on the quality of the films. Laser-produced plasma plume of Y_2O_3 investigations by means of time-of-flight mass spectrometer were also performed.

Keywords: Lattice parameters; X-ray diffraction; Pulsed laser deposition; Yttrium oxide

1. Introduction

In the last 20 years, the pulsed laser deposition (PLD) method has been successfully applied in the production of high-quality thin films of different crystals on various substrates [1]. The film properties were found to depend both on the substrate temperature and the kinetic energy of a plasma flux [2]. The deposition of thin yttrium aluminum garnet (YAG) films on Si substrates was also intensively studied. As a result, the substrate temperature during growth process was thought to surpass 600 °C in producing structures of proper quality at reasonably high growth rate [3–5]. The next step was the modification of the method to reach same or even improved deposit crystallinity under less demanding deposition conditions (substrate temperature, in particular). For this purpose, external polarization was employed to increase the kinetic energies of the incident particles [3]. When realized, successful deposition of a single-crystal YAG at 500 °C became achievable. In this study, further experiments were carried out under more precisely controlled conditions, which showed that growth process occurs even without external polarization and at substrate temperatures as high as 450 °C.

Thin YAG films on Si substrates possess some interesting structural features, which could be observed in their X-ray diffraction (XRD) spectra. The stresses are characterized by relative difference in lattice constants between reference single-crystal YAG and the investigated one.

Generally, there are two possible sources of the stresses:

(1) Structural differences between the two crystals (silicon—cubic diamond-type lattice with $a_{Si} = 5.43$ Å, YAG—Ia3d structure with $a_{YAG} = 12.008$ Å), which lead to a considerably high lattice mismatch (9.6%) defined as a misfit factor ($MF = (|a_{YAG} - 2a_{Si}|/a_{YAG}) \times 100$ [%]).

(2) Defects introduced during growth process, number of which may depend on deposition conditions.

Thus, for the minimization of the stresses, it is reasonably to optimize all the process parameters and particularly the substrate temperature since it controls the entire kinetics of the process.

2. Experimental details

The reported experiments were carried out in a standard PLD system described elsewhere [2,3]. The stainless steel high-vacuum chamber (evacuated down to a

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pressure of 10^{-5} mbar by a diffusion pump) was equipped with a rotating target (18 rpm) onto which an excimer laser beam (XeCl, $\lambda = 308$ nm, $f = 10$ Hz, $\tau = 20$ ns, fluence 5 J/cm^2) was focused. The target was filled with powders of Al_2O_3, Y_2O_3 and Nd_2O_3 made by Aldrich Chem. Co. The evaporated materials were deposited onto electrically heated Si(1 1 1) substrates of 250 μm thickness maintained approximately 4 cm above the target. Substrate temperature was measured with a Pt-PtRh10 thermocouple. The thickness of the resulted YAG layers was typically 200–400 nm, depending on the number of laser shots. The mean growth rate reached approximately 17 nm per 1000 laser shots.

For the analysis of the plasma plume formed by the ablation of the Y_2O_3 target we have used an ion time-of-flight (TOF) mass spectrometer (Comstock, model TOF-101) with an intake aperture. The resolution of the TOF spectrometer (6.25 ns) was high enough to resolve the spectra of ablated targets, that were detected shot-to-shot by the tandem microchannel plate detector (MCP). The signal composed of a train of pulses was amplified and passed to the input of the real-time multichannel scaler (RTMS) [6]. In our experiment, the distance D between the target and the intake aperture of the spectrometer was set at 1.5 cm.

XRD spectra were recorded using a D5000 SIEMENS powder diffractometer with Cu Kα radiation (1.54051 Å) in the θ–2θ mode. The 2θ angle was varied over the range extending from 28 to 35°.

3. Results and discussion

3.1. TOF spectra of Y_2O_3

The TOF spectra of the ablated Y_2O_3, Nd_2O_3 and Al_2O_3 were presented in previous work [3]. In this article, we have investigated the energy distributions of positive particles in the plasma plume obtained during the ablation of the Y_2O_3 target. Fig. 1 shows the TOF spectra for different potential barriers (U_B) between the free-drift tube and the MCP in the spectrometer. Our results indicate, that $Y_2O_3^+$ ions possess extreme energies in the plasma plume.

3.2. XRD analysis of $Y_3Al_5O_{12}$ layers

The obtained results clearly prove that the substrate temperature plays the key role during the PLD of thin YAG films. As mentioned previously, the presented experiments were carried out at temperatures covering a rather wide range from 20 to 620 °C. The temperature was found to be at least as high as 450 °C in order to achieve substantial crystal growth, which followed from the fact that no XRD peak was recorded for samples deposited at lower temperatures. On the contrary, no upper limit of its value was established even if the substrate was heated up to 620 °C.

Fig. 2 shows changes in the measured lattice constants of the substrate (a_{Si}, Fig. 2a) and of the deposited thin YAG film (a_{YAG}, Fig. 2b) depending on the substrate temperature T_{sub}. Note that both plots cover different T_{sub} ranges (540–620 and 450–620 °C, respectively). Obviously, the observed changes in the lattice constants are directly related to the stresses induced in the structure. According to Fig. 2a, the measured a_{Si} values decrease with increasing temperature, which clearly attests to successive contraction of the substrate. Additionally, the plot of the a_{Si} intersects the single-crystal Si lattice constant 5.43 Å at approximately 550 °C indicating, that the stresses induced in the substrate change from tensile into compressive. On the other hand, stresses in the covering film are always tensile (Fig. 1b). In spite of that, data presented in Fig. 2a and b appear to be complementary when analysed in the same range of temperatures. However, both Young's moduli of silicon and the substrate are higher than those of YAG and this results in a stronger distortion of the growing film rather than the substrate (relative distortion is ≈0.2 and 2.2% for the substrate and the deposit, respectively).

Additional analysis of recorded XRD patterns proves that the a_{Si} values in Fig. 2a correspond to interplanar distances d_{111} parallel to the substrate normal. Let us assume that crystallinity of the silicon is nearly perfect (i.e. its structure is almost defect-free). This means that the contraction of the sample along its normal must be accompanied with its in-plane elongation, i.e. the substrate is at the same time compressed and stretched. In the case of YAG (Fig. 2b), a similar result is not attainable. Here, it must be taken into consider that in the range investigated four XRD YAG-related peaks indexed as follows can be found: YAG(4 0 0), YAG(4 1 1), YAG(3 3 0) and YAG(4 2 0), contributing to the presented a_{YAG} values. However, precise examination clarifies that all the means are within 1.6% of its standard deviations. Such consistency of results obtained for different crystal orientations may attest to homogeneous stresses in the film on account of introduced point defects. Additionally, a_{YAG} values are found to decrease slightly with increasing temperatures (when ranged from 540 to 620 °C) approaching the single-crystal YAG lattice constant (12.003 Å). Thus, it can be conclude, that on stress-relief behaviour in the sample can be attributed to increased thicknesses of the deposit.

Taking into consideration the pulsed character of the deposition process, it is reasonably to note that the grown structure may exhibit some misorientation around its epitaxial [1 1 1] direction. Such a disorder may also give its own contribution into the observed differences in the YAG lattice constant resulting in a poorer quality of the deposit compared to other grown YAG samples.

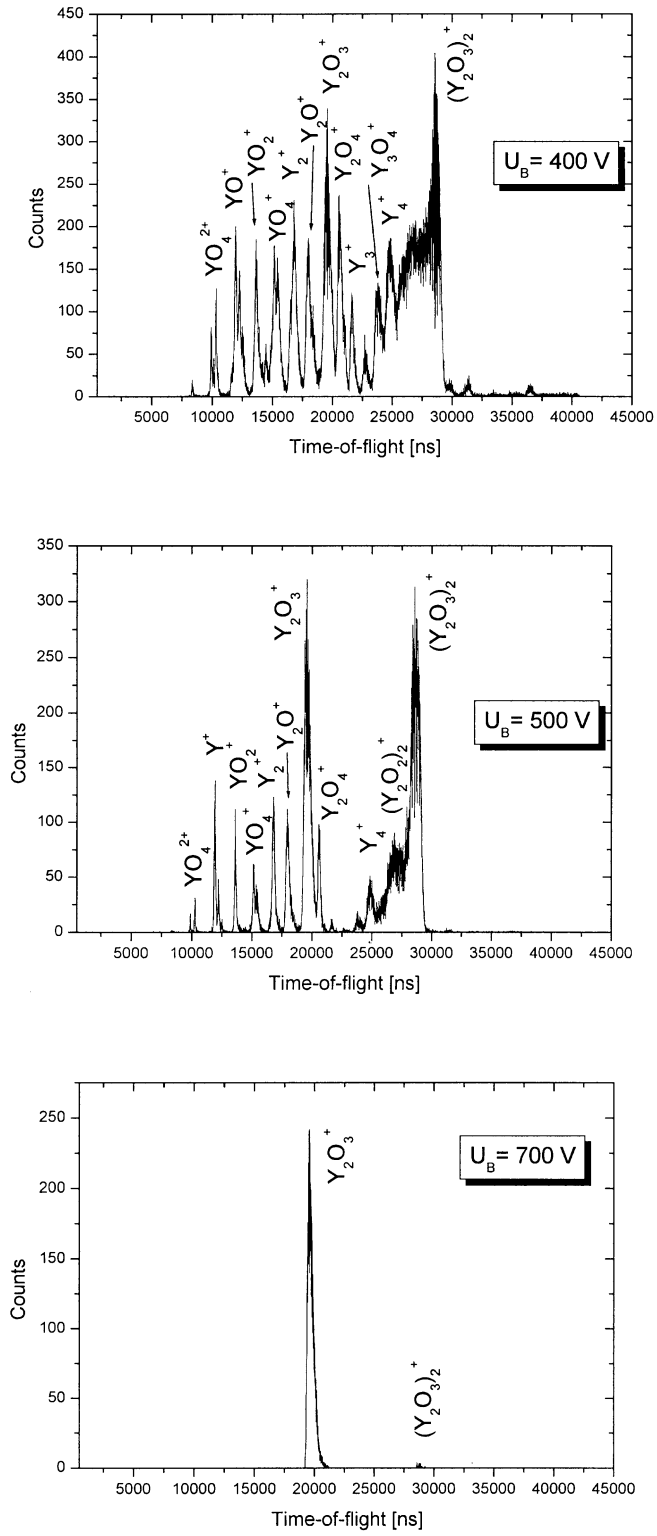

Fig. 1. TOF spectra of Y_2O_3 for different potential barriers U_B.

Another point is that the YAG which does not grow exactly along with [1 1 1] axis may come from non-epitaxial growth mode.

Presented analysis strongly suggests that the growth of thin YAG films gives the best results when carried out either at approximately 540 °C (where the measured

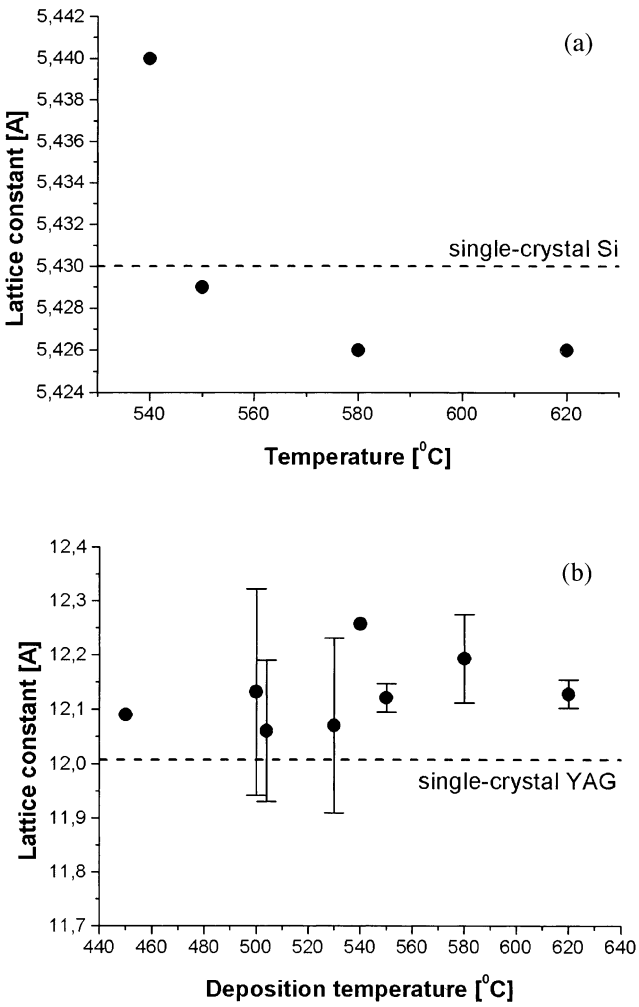

Fig. 2. Changes in lattice constants both of (A) substrate a_{Si} and (B) YAG a_{YAG} dependent on the substrate temperature T_{sub}.

and the referenced YAG lattice constant intersect) or above 600 °C. The latter result, in general, agrees with results reported by other authors [4,5].

External DC polarization, when applied between target and substrate, may also exert reasonable influence on the structural properties of the deposit on account of induced ion bombardment. The positive substrate biasing in the course of ablation of Al_2O_3 and Y_2O_3 results in the plasma plume reduction, suggesting that the ablated particles are charged positively. Fig. 3a shows a two-dimensional plot of a XRD pattern taken from the sample deposited with accompanying bias voltage of 500 V (T_{sub} = 500 °C). It was found, in general, that all the YAG-related peaks were broadened along the χ-axis, while for the Si(1 1 1) peak this feature was not found (Fig. 3a). For a given sample orientation, the χ co-ordinate is defined by an angle between the surface normal and the incidence plane in this way that results from Fig. 3a suggesting a high volume of polycrystalline material for investigated structure. As shown in Fig. 3b, the sample deposited without any external polarization does not exhibit similar features. Furthermore, in this case the recorded peak is evidently sharper and more intense, which attests to a improved YAG quality, even if the same deposition temperature was employed. In such a way, external polarization is responsible for the observed deterioration in the crystal quality.

Additionally, as shown in Fig. 4, the applied bias of the order of 500 V was also found to affect the structure of a single-crystal substrate maintained at 540 °C. The recorded shape of the Si(1 1 1) line exhibits two distinct maxima connected with the following d_{111} interlayer distances: 3.099 (left peak) and 3.141 Å (the right one). Both peaks possess equal intensity. In order to clarify the observation simple calculations of a penetration depth of X-rays into silicon were carried out [7]. The

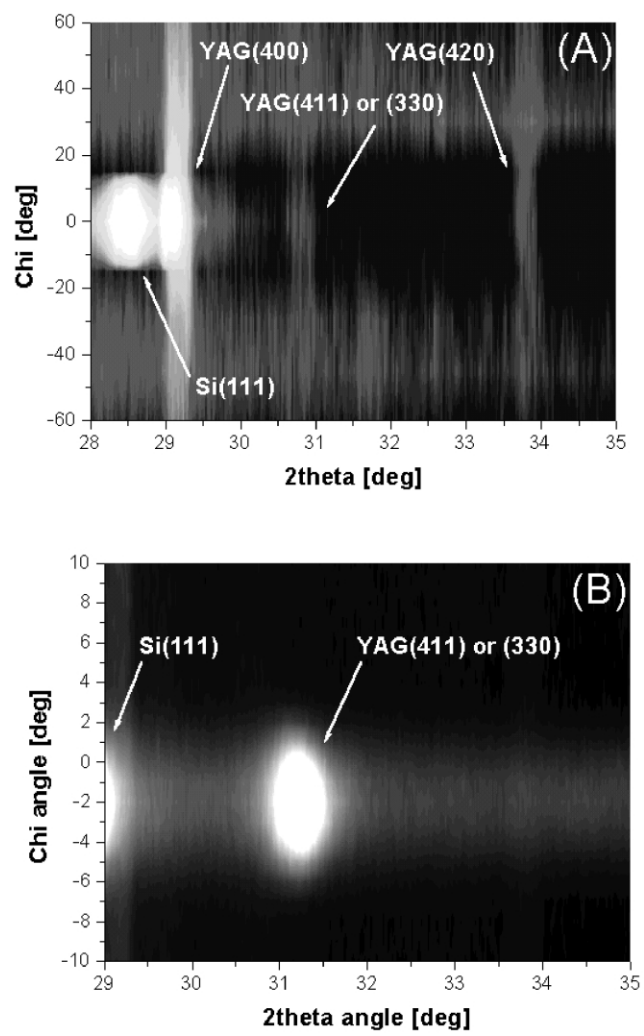

Fig. 3. Two-dimensional XRD patterns of samples deposited (A) with bias voltage of 500 V and (B) without any external polarization. The former reflects a polycrystalline structure of the deposit while the latter clearly proves a high ordered film with predominant orientation YAG(4 1 1) or YAG(3 3 0) parallel to Si(1 1 1).

obtained results indicate that nearly 95% of the beam intensity detected is scattered in the 30 μm thick subsurface silicon layer. In turn, the substrate used is as thick as 250 μm, and, therefore, the XRD pattern (Fig. 3) corresponds to the Si region adjacent to the substrate–deposit interface. According to that, it is reasonable to consider the transformation of cubic silicon from its original diamond-type fcc structure into a hexagonal one on account of ion bombardment (one can compare transition between the two similar structures of diamond: cubic and hexagonal (lonsdaleite) [8]). The obtained results clearly attest to the detrimental influence of an external polarization on the quality of the samples.

Apart from point defects, extended defects are also observed in the films. Fig. 5 shows an XRD pattern taken from the sample deposited at $T_{sub} = 500$ °C (without any bias voltage) exhibiting obvious splitting of the peak along the χ-axis. The angle between twin-planes is approximately 4°, but the peak does not seem to be YAG-related. This is because of its unusual intensity compared with those previously measured for other samples. Unfortunately, we are not able to state on the nature of the twinning simply because of its irreproducibility (i.e. dependence on deposition conditions). In that manner one can speculate mainly about incorporation of some chemical impurities. XRD spectra reported by other authors [9] further support such a conclusion especially with respect to the contamination with Y_2O_3, suggesting at the same time that growth of $YAlO_3$ cannot be concerned. Fig. 5 also exhibits another XRD feature in the region studied presumably indexed as YAG(4 0 0). The recorded peak is centred at $2\theta = 29.14°$ resulting in a lattice constant $a_{YAG} = 12.25$ Å. Generally, pattern presented in Fig. 5 reflects the rather complicated structure of YAG grown by the PLD method on account of the introduced defects and the impurities.

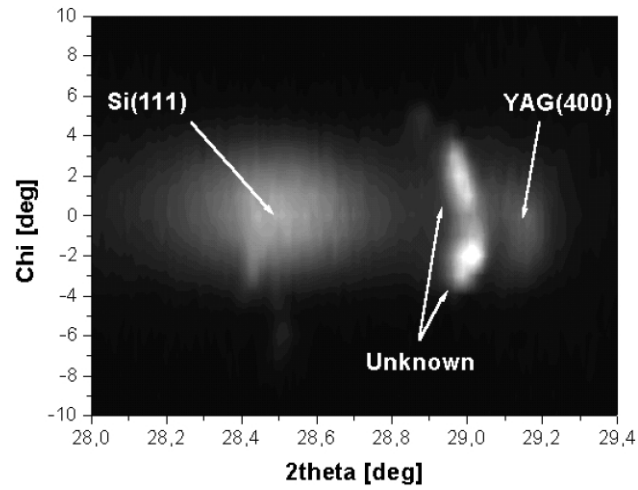

Fig. 5. Two-dimensional XRD pattern with observed twinning presumably due to introduced chemical impurities. The twin peak is labeled as 'Unknown'.

4. Conclusions

Thin Nd:YAG films were grown by the PLD method on Si(1 1 1) substrates. The method employed enables producing both single-crystal as well as polycrystalline

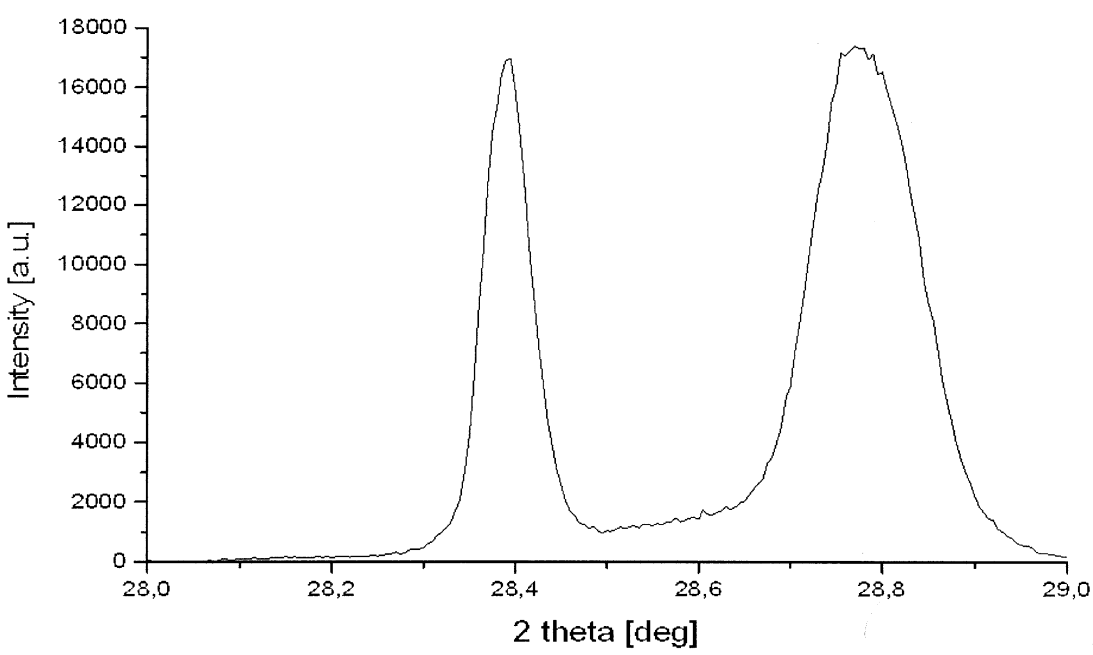

Fig. 4. Splitting of the substrate Si(1 1 1) XRD peak under bias conditions (500 V) probably due to disorder of the lattice induced by the ion bombardment.

films of different structural properties as seen in their XRD spectra. The substrate temperature is found to surpass 450 °C so that a sufficiently high growth rate is attainable. In turn, an applied bias is found to exert a strongly detrimental influence on the quality of the deposits, which follows from their enhanced polycrystallinity. The analyses performed for calculating the YAG lattice constant point out as optimal substrate temperature for the growth process at 540 °C. The further investigations of the plasma plume and the energy distribution of particles are required for improving the quality of the PLD layers.

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