Deposition of Er:YAG (YAP) layers by subpicosecond and nanosecond KrF excimer laser ablation

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Abstract

Thin films of Er:YAG and Er:YAP were deposited by subpicosecond (450 fs) and nanosecond (20 ns) KrF laser ($\lambda = 248$ nm) on YAG, YAP, fused silica, silicon and sapphire substrates. Laser spot size, energy density, substrate temperature and deposition ambient (vacuum and oxygen) were varied. Comparison of growth rate, morphology, composition, crystallinity and adhesion of the films grown by subpicosecond and nanosecond deposition is presented.

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1. Introduction

Deposition of thin films by laser ablation is a very versatile technique and has enabled the wide scale growth of high quality films. The laser sources that have been mainly used are short wavelength, nanosecond lasers. Recently subpicosecond laser deposition has been an attractive research subject. This stems from the interest to obtain very smooth, particle free films, to improve the properties of the films and to synthesize new or specific materials. During the recent years we have been studying the deposition of smooth, crystalline Nd:YAG ($Y_2AIO_5$) and Nd:YAP ($YAlO_3$) thin films for planar waveguide lasers by the use of KrF excimer laser pulses of 20 ns duration [1–4]. It has been found that in this case a substrate temperature $T_s$ higher than 1200 °C is required in order to obtain crystalline YAG (or YAP) layers.

The goal of this work is to determine the required $T_s$ to obtain smooth and crystalline Er:YAG (YAP) layers by the use of subpicosecond laser and to examine the influence of the pulse duration on the morphology, transparency and stoichiometry of the films.

2. Experimental

The depositions were performed in a vacuum chamber evacuated to a base pressure of $5 \times 10^{-5}$ mbar. Thin films were prepared by laser ablation of crystalline Er:YAG and Er:YAP targets onto YAG, YAP, fused silica (FS), silicon and sapphire substrates.

Two UV KrF ($\lambda = 248$ nm) laser sources were used. One Lambda Physic excimer laser EMG 150 combined...
with a special subpicosecond dye laser generator–amplifier, emitting pulses of $T_{\text{FWHM}} \sim 450$ fs (5 Hz, 5 mJ per pulse) [5]. The second one is a Lumonics PM 842 laser which generated pulses of $T_{\text{FWHM}} \sim 20$ ns (20 Hz, 450 mJ per pulse). The laser beams were focused to yield energy densities from 1.7 to 3 J cm$^{-2}$ (spot size: $\sim 0.1$ cm$^2$) for nanosecond deposition, and from 2 to about 16 J cm$^{-2}$ (spot size: $0.45 \times 10^{-3}$ to $3 \times 10^{3}$ cm$^2$) for subpicosecond deposition.

The target to substrate distance ($d_{T-S}$) was varied from 3.3 to 6.5 cm, while the substrates were heated by resistive or CO$_2$ laser heating [6] in the region from room temperature (RT) to higher than 1000°C. With resistive heating we obtained temperatures up to 750°C. The CO$_2$ laser radiation heated the opposite to the deposition side of the substrate. The change of CO$_2$ power resulted in immediate change of the substrate temperature, even when a BN plate was introduced between the laser beam and the substrate to homogenize the temperature profile. Typical cooling time was about 30 min. The experiments were carried out in vacuum ($5 \times 10^{-5}$ mbar) or in an oxygen ambient pressure of $2 \times 10^{-3}$ mbar.

The films were structurally characterized by XRD. A parallel beam optic geometry with a Huber twocircle diffractometer, powered by a rotating anode generator X-ray source (300 mA, 55 kV), RIGAKU Rotaflex RU 300 was used. Two arrangements were applied: symmetrical ($\omega\sim2\theta$ movement) and detector scan with fixed specimen (20 rotation only).

The morphology was examined by scanning electron microscope (SEM) JOEL 840 and by JEOL JXA 733. The composition of the films was investigated by Rutherford back-scattering (RBS). The 3.5 MeV Van de Graaf generator with a linear electrostatic accelerator provided $\alpha$-particles and beam of protons with ion energy 1–3.5 MeV. For our measurements protons of 1.74 and 2.18 MeV energy were used as projectiles. Barrier detector was collecting protons scattered under scattering angle of 170°. The quantity of the Er, Al, Y contents was evaluated by GISA 3 computer code [7].

3. Results and discussion

3.1. Film thickness and growth rate

Films with thickness of several micrometers were fabricated in nanosecond deposition regime. The growth rate was varied roughly in the region of 0.5–1.5 Å per pulse, and was a little bit higher for the Er:YAG case as compared to the Er:YAP deposition.

The thickness of the films obtained by subpicosecond deposition was in the range of several hundreds of nanometers, because of lower growth rate ($\sim 0.07–0.17$ Å per pulse). As it was expected a reasonable improvement in the deposition rate was observed with the increase of the spot size and the decrease of the target–substrate distance. Typically we found that the change of the spot size from $6 \times 10^{-4}$ to $3 \times 10^{-3}$ cm$^2$ resulted in about 2.5 times increase in the deposition rate. By changing the distance from 4.2 to 3.3 cm the growth rate increased from 0.07 to 0.17 Å per pulse (for vacuum, 1.73 J cm$^{-2}$).

3.2. Surface morphology

For nanosecond deposition and high $T_s$, it was found that a small amount of oxygen ($\sim 0.2$ Pa) is required to obtain films which are shiny and visibly transparent while in vacuum they were black. The surfaces of the films were covered with small droplets whose concentration was slightly influenced by the ambient atmosphere, $d_{T-S}$ and $T_s$. The layers deposited in oxygen were smoother and the number of droplets was decreasing with increasing $d_{T-S}$. For Er:YAG films the number of droplets was slightly decreasing with the increase in $T_s$, but for Er:YAP films such dependence was not observed.

For subpicosecond deposition, the influence of ambient, $T_s$, $d_{T-S}$, spot size, energy density and targets (Er:YAG, Er:YAP) was studied. All the fabricated films were shiny, except those grown with low energy density but they seem to be less transparent than the films of nanosecond deposition. The surface of the films was always covered with small droplets. We observed only the influence of spot size (energy density) on the number of droplets, while a clear influence of the other deposition parameters was not established. For larger spot size droplets with diameter less than 1 μm were detected, whereas for smaller spots the diameter of the droplets was from 1 to 5 μm. However their density per unit area was roughly the same for both cases. Fig. 1 shows the SEM images of two representative films fabricated by nanosecond deposition (a) and subpicosecond deposition (b).
development of YAP, YAG and Y₃Al₂O₉ phases. The number of diffraction peaks increased with decreasing $d_{T-S}$, probably due to the higher kinetic energy of the ablated species at lower distances from the target.

In subpicosecond regime much more peaks of the above phases were observed at the lower temperature of 805 °C, for deposition performed in vacuum by YAP target, as is depicted in the XRD spectrum of Fig. 2. Even the layers deposited at RT show some diffraction peaks (e.g. (2 0 2) Y₃Al₂O₉ for 3G and 8G layers and (7 2 1) YAG for 8G sample of Table 1) which implies that the crystallization in that deposition regime starts at low temperature.

### 3.4. Stoichiometry

In the Er:YAP target the content 5.5 at.% of Er and 1.8 of Al/Y ratio was measured by RBS. In the Er:YAG target, the Er dopant was 7.5 at.% and Al/Y ratio was 3.3.

The films fabricated in the nanosecond regime from Er:YAP target were found to have lower concentration of the Er dopant (from 4.0 to 4.8) compared to that of the target, whereas the Al/Y ratio varied from 1.33 to 1.46, increasing with $T_s$ (see Table 1a). The Er dopant and Al/Y ratio in the films fabricated from Er:YAG target was also lower than that of the originating target (see Table 1b).

For subpicosecond regime, the transfer of Er dopant and the Al/Y atomic concentration ratio into the layer were very depended on the deposition conditions. The composition of the layers deposited in
oxygen atmosphere and small $d_{T,S}$, is approaching the composition of the target regardless of the $T_s$. The worst transfer was obtained for $d_{T,S}$ higher than 4 cm (see Table 2).

### 3.5. Hardness and adhesion

The hardness and adhesion of the deposited films was roughly checked by mechanically means. Films grown in nanosecond regime, in vacuum or in oxygen atmosphere ($2 \times 10^3$ to $2 \times 10^{-2}$ mbar) were hard, regardless of the $T_s$. Films grown in subpicosecond regime were also hard except from the films grown at low densities ($\sim 2$ J cm$^{-2}$).

### 4. Conclusions

Thin films of Er:YAG (YAP) were grown by nanosecond and subpicosecond KrF excimer laser deposition
from crystalline targets at different deposition conditions. The surface of the films prepared by nanosecond laser was covered with small droplets. The films prepared with subpicosecond laser consisted of small droplets with high density. For less focused laser beam the droplets were smaller. The growth rate for nanosecond deposition was about 10 times higher compared to that of subpicosecond regime. With increasing spot size the increase in growth rate was observed for subpicosecond deposition, but the films were very soft. Films grown in subpicosecond regime were less visibly transparent than those of nanosecond regime. Concerning stoichiometry the Er dopant concentration and Al/Y ratio was always lower than that in source targets, for both deposition regimes. For some experimental conditions the transfer of stoichiometry for subpicosecond regime was similar, or even better, compared to nanosecond regime. The film crystallinity was observed at lower $T_c$ for subpicosecond deposition regime, but the highly textured films were not grown. Optimization of growth parameters in subpicosecond regime is required to obtain crystalline single-phase films. We believe that in our experiments the short deposition pulses, high laser power density and high kinetic energy of particles in the plasma plume influenced positively the formation of crystalline films.

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