Excimer laser ablation and film deposition of Ti:sapphire

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Abstract

ArF laser ablation of Ti:sapphire (Ti:Al₂O₃) has been investigated as a potential means for micromachining this laser crystal and depositing thin layers for use as active waveguides. Plume spectra recorded for ablation in low pressure oxygen and a preliminary assessment of layers grown by this method are reported.

1. Introduction

The UV excimer laser ablation of inorganic crystals and glasses may find potential use as a technique for micromachining fine-scale structures such as waveguides and gratings in these materials and for forming thin layers by ablation-deposition. There has been a recent growth of activity on the fabrication of laser-active waveguides by a variety of methods [1-4], and the exploration of laser-ablation-deposition as an alternative approach is of interest because of its versatility, particularly with regard to materials having complex stoichiometry [5].

In this paper we describe studies of the UV laser ablation and ablation deposition of titanium sapphire (Ti:Al₂O₃), a crystal system which is widely used as a broadly tunable (~ 0.66-0.98 μm) laser [6]. The ability to ablate this material in a controlled way might prove useful for fabricating microlasers operating in optical waveguide configurations. Previous work has reported the UV laser ablation characteristics of undoped sapphire [7] and there has been a growing interest in laser ablation-deposition [8] and surface modification [9] of the related ceramic form – alumina. Our investigations show that Ti:sapphire can be etched at the rate of ~ 10’s nm per pulse using the ArF laser even though, like the undoped crystal, it is only relatively weakly absorbing in the deep UV. Spectroscopic studies of the plume produced by ablation in low pressure oxygen and a preliminary assessment of thin layer growth on glass and crystal substrates are also reported.

2. Experimental

The experiments made use of a Questek Series 2000 excimer laser operating on the 193 nm ArF transition. In order to obtain a well defined fluence distribution at the target, the output beam from the laser was passed through a rectangular aperture to select the central quasi-uniform section of the beam. A fused silica lens was then used to form a demagnified image of this aperture at the target plane. The
Etch-rate of Ti:Al₂O₃ at 193 nm was measured in air using an optical microscope to measure the depth of the ablation crater with a resolution of ±2 µm following exposure to a known number of pulses. The craters were also examined by scanning electron microscopy.

Ablation–deposition experiments were carried out in a vacuum chamber (base pressure 10⁻⁵ mb) into which slow flowing oxygen was admitted at a pressure of ~0.2 mb. Emission spectra were recorded by forming an image of the plume external to the chamber using a fused silica lens and sampling the image using a 0.5 mm fibre connected to the entrance slit of a monochromator (Bentham Instruments, 300 mm with S20 photomultiplier) or Si-CCD array spectrograph (Oriel, InstaSpec IV).

Deposited layers were formed on soda lime glass and Yttrium Aluminium Garnet (YAG) substrates heated using an RF excited CO₂ laser to temperatures in the range ~600–750 K. Soda lime glass was chosen as a low cost substrate having a reasonably close thermal expansivity (~9 × 10⁻⁶ °C⁻¹) with sapphire (α = 8.4 × 10⁻⁶ °C⁻¹). Its refractive index (~1.5) is also significantly lower than sapphire (nₐ = 1.76) making it a suitable substrate for assessing layer waveguiding properties. Soda lime glass was found, however, to fluoresce under 590 nm dye laser pumping, masking any component from the Ti:Al₂O₃ layer. For this reason high quality YAG substrates were also investigated as these were essentially non-fluorescent at this pump wavelength.

The ablation targets were 0.23 at% Ti doped sapphire polished to optical finish (supplied by the Optical Materials Research Centre, University of Strathclyde) and had a measured fluorescence lifetime of 2.6 µs under 590 nm dye pump excitation at room temperature.

3. Results

ArF ablation of Ti sapphire was investigated to ascertain the ablation thresholds, etch-rates and quality of the irradiated surface. Fig. 1 shows the etch-depth per pulse, x, versus fluence, F, for exposure using the 193 nm ArF laser. Above about F = 1.5 J cm⁻² the data could be reasonably well described by a Beers law type dependence of the form \( x = \alpha \ln \frac{F}{F_{TS}} \) where \( \alpha \approx 3.6 \times 10^5 \) cm⁻¹ is the effective absorption coefficient and \( F_{TS} \approx 1.5 \) J cm⁻² is the threshold for significant etching. Weak etching at the level of ≤5 nm per pulse was, however, evident at fluences down to as low as 0.5–0.6 J cm⁻² (figure 1) which is similar to the etching threshold at 193 nm for undoped sapphire [7]. It is notable that the effective absorption coefficient deduced from the etch-rate data greatly exceeds the corresponding small-signal value measured for Ti:sapphire in the deep UV. At 190 nm, for example, Moulton [6] reports that a sapphire sample containing 0.05 wt% Ti₂O₃ (corresponding to 0.035 at% Ti doped sapphire) had a measured small-signal absorption coefficient of ~27 cm⁻¹ which, assuming absorption scales directly as the Ti concentration, would translate to ~177 cm⁻¹ for our material. As with undoped sapphire, which exhibits very weak bulk absorption even at 193 nm, the ability to etch Ti doped sapphire in a highly controllable way using the 193 nm laser would appear to be a result of surface mediated absorption [7].

In Fig. 2(a) and (b) the ablation crater produced in Ti sapphire using the ArF laser is seen to have well defined edges and smooth walls and floor. There is some evidence for localised melting having occurred suggesting that the surface temperature reaches at least 2300 K. The absence of surface cracking under these relatively severe conditions is attributed to the shallow extent of any melt layer produced. Assuming purely surface heating the depth of significant heat flow during a laser pulse of duration \( \tau \) can be
gauged using the heat diffusion length \( l \equiv \sqrt{D \tau} \) where \( D \equiv 0.13 \text{ cm}^2 \text{ s}^{-1} \) is the thermal diffusivity for sapphire. With \( \tau \approx 20 \mu\text{s} \), \( l \approx 0.5 \mu\text{m} \) and the likelihood of crack propagation resulting from tensile stress in the rapidly cooled surface is much reduced because of the small layer thickness.

When ablation was carried out in low pressure oxygen (\( \sim 0.2 \text{ mb} \)) using the ArF laser, an intensely luminous plume with a diffuse boundary extending out to \( \sim 20 \text{ mm} \) from the target was produced. Fig. 3(a) and (b) show spectra of the plume recorded over the wavelength interval of 250–725 nm at a distance of 5 mm from the target using the Si–CCD spectograph. Dominant emission lines arise at 396 nm and 310 nm originating from Al. Weaker lines attributable to neutral and ionized Ti and Al are evi-

![Image of ablation crater](image)

**Fig. 2.** (a) Ablation crater produced in titanium sapphire using 900 ArF laser pulses at a fluence of \( \sim 6 \text{ J cm}^{-2} \). The crater is approximately 30 \( \mu\text{m} \) deep. Redeposited material is evident surrounding the crater when ablation takes place in air. (b) As (a) but at higher magnification to show detail of the walls and floor.
dent as well, and a number of bands corresponding to the diatomic oxides of Ti and Al also appear in the visible and near infrared. It is evident that titanium features strongly in the emission spectra even though it is only present as a minority in species in the target.

Layers were grown on substrates located at a distance of 15 mm from the target so as to place them near the tip of the plume that formed in oxygen [10]. These layers were found to be robust and strongly adherent to the glass and YAG substrates and under visual and optical microscope examination.

Fig. 3. Emission spectra of titanium sapphire ablation plume recorded at a distance of 5 mm from the target surface. Oxygen pressure 0.2 mb, ArF laser fluence 1.5 J cm$^{-2}$. (a) 240–350 nm spectral interval (below ~ 240 nm the fibre used to transmit radiation to the spectrograph becomes strongly absorbing). (b) ~ 335–725 nm (the inset shows detail of Al emission at ~ 394 and 396 nm).
they appeared to be transparent and smooth. A scanning electron micrograph of the surface of a 1 μm thick layer produced on a glass substrate at 700 K using 5.4 × 10^4 laser pulses at a fluence of 1.2 J cm^{-2} is shown in Fig. 4(a). It is evident that although most of the surface is relatively smooth, the residual roughness being at the sub 100 nm level, some circular protuberances with diameters in the range ~ 250–500 nm are present possibly as a result of droplet incorporation. From Fig. 4(b), which shows a fracture surface through the film-substrate system, it can be seen that the upper surface is very smooth, suggesting that these ‘droplets’ do not extend significantly above the mean surface level. The average growth rate of layers was approximately 1.9 × 10^{-2} nm per pulse.

Normal incidence reflectance measurements over the spectral interval 600–800 nm yielded a mean refractive index for the layers of 1.74. This is ~ 98.7% of the sapphire value and similar to that obtained for e-beam evaporated ion assisted Al₂O₃ films deposited on heated substrates [11]. An attempt was made to observe fluorescence centred at ~ 700 nm from the 2E→2T₂ transition in Ti³⁺ using 590 nm dye laser excitation of layers grown on glass and YAG. Emission was detected for layers on YAG (lifetime ~ few μs) but this was very weak, possibly indicating that the relevant α-Al₂O₃ phase incorporating Ti³⁺ was not formed in significant quantities. The small volume (~ 10^{-6} cm³) probed in the fluorescence experiment was also a limiting factor and an improvement in detection sensitivity should help provide more detailed information.

4. Conclusions

ArF laser ablation of Ti:sapphire can produce good quality etched features in this material even though it has a relatively low small-signal absorption in the deep UV. Removal rates at the level of a few 10’s of nm per pulse are attainable through what is thought to be a surface absorption mediated ablation process [7], pointing to the possibility of using the ArF laser to micromachine fine scale features in this material.

A preliminary assessment of layers grown on glass and crystalline substrates using ArF laser ablation deposition in a low pressure oxygen atmosphere shows that surface quality and thicknesses appropriate for use as optical waveguides can be achieved. Additional work is currently underway to determine the phase of the deposited layers using X-ray diffraction techniques and to explore their optical characteristics for growth on glass and crystalline substrates.

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