Applied Surface Science 305 (2014) 347–351

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Influence of film thickness on laser ablation threshold of transparent conducting oxide thin-films

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ARTICLE INFO

Article history:
Received 15 November 2013
Received in revised form 21 February 2014
Accepted 14 March 2014
Available online 21 March 2014

Keywords:
Film thickness
TCO
ITO
GZO
Laser ablation threshold
Optical absorption length

ABSTRACT

We report on a comprehensive study of the laser ablation threshold of transparent conductive oxide thin films. The ablation threshold is determined for both indium tin oxide and gallium zinc oxide as a function of film thickness and for different laser wavelengths. By using a pulsed diode pumped solid state laser at 1064 nm, 532 nm, 355 nm and 266 nm, respectively, the relationship between optical absorption length and film thickness is studied. We find that the ablation threshold decreases with increasing film thickness in a regime where the absorption length is larger than the film thickness. In turn, the ablation threshold increases in case the absorption length is smaller than the film thickness. In particular, we observe a minimum of the ablation threshold in a region where the film thickness is comparable to the absorption length. To the best of our knowledge, this behaviour previously predicted for thin metal films, has been unreported for all three regimes in case of transparent conductive oxides, yet. For industrial laser scribing processes, these results imply that the efficiency can be optimized by using a laser where the optical absorption length is close to the film thickness.

Introduction

Laser damage and ablation thresholds of thin metal films play a significant role in, e.g., laser optics and have been intensively studied throughout the last decades [1–5]. In conjunction with applications in the solar cell and display industry, the laser ablation of thin dielectric films has recently attracted additional interest with the focus on process optimization [6–12]. The main underlying physical properties governing the ablation and laser damage of optical materials are the absorption and the heat diffusion within the thin film [13–15]. In addition, the pulse duration of the laser used for the ablation process has to be considered with respect to the relevant energy relaxation times within the electronic system and the lattice. In particular, in case of ultrafast lasers a strong non equilibrium state between the excited electronic system and the lattice may occur [16]. In case of the interaction of ultrafast lasers and metals, this leads to an ablation threshold independent of pulse length in the femtosecond and low picosecond regime (typically about 10 ps). For longer pulses the ablation threshold increases linearly with pulse duration, particularly in the nanosecond regime, in which a complete thermalization of the electronic system and the lattice can be assumed [2,16].

In the nanosecond regime it has been shown by Matthias et al. for thin metal films that for film thicknesses larger than the absorption length ($1/\alpha$), yet smaller than the thermal diffusion length (L_{th}), the ablation threshold increases linearly with film thickness [17]. For a film thickness larger than the thermal diffusion length the ablation threshold remains constant. Furthermore, incubation effects with increasing pulse number have been reported [8,13].

With respect to the technological importance of laser ablation thresholds, these effects have been intensively studied for thin metal, dielectrics, polymers and transparent conductive films as a function of wavelength [18–22], pulse duration [18,22,23], beam radius [24,25], number of pulses [15,18,26], and pulse repetition rate [27].

In optoelectronic devices, such as solar cells or flat panel displays, nanosecond laser ablation is an important industrial process step in structuring thin films of transparent conductive oxides (TCO). Here the film thickness typically exceeds the thermal diffusion length. However, to ensure devise performance in case of organic light emitting diodes the TCO thickness is typically smaller, being comparable to the thermal diffusion length. Moreover, depending on the laser wavelength used for the ablation, the film thickness might be in the range of the optical absorption length. Szörényi et al. [28] investigated laser ablation of indium tin oxide (ITO) with film thicknesses of 70, 160 and 500 nm, respectively, using a KrF Excimer laser at 248 nm. Similar to Matthias et al., the ablation threshold was found to increase with

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http://dx.doi.org/10.1016/j.apsusc.2014.03.082

Table 1
Thermal diffusivity, thermal diffusion length and optical absorption length $1/\alpha$ of ITO and GZO.

	ITO	GZO
$1/\alpha$ at 1064 nm	740 nm	950 nm
$1/\alpha$ at 532 nm	4600 nm	7000 nm
$1/\alpha$ at 355 nm	1500 nm	410 nm
$1/\alpha$ at 266 nm	125 nm	125 nm
Thermal diffusivity	2.3×10^6 m^2/s [28]	8.3×10^6 m^2/s [32]
Thermal diffusion length at the rate of τ_{pulse} 10 ns	152 nm	576 nm

Please note that the values for $1/\alpha$ at 1064 nm, 532 nm and 355 nm are determined by our own measurements, while those for 266 nm are taken from Ref. [31] . of ITO and GZO.

film thickness. However, only in case of the 70 nm ITO, the optical absorption length exceeds the film thickness and a dependence of the ablation threshold on the film thickness in this regime cannot be resolved. In addition, from an industrial point of view nanosecond diode pumped solid state lasers (DPSSL) are the preferred laser source for thin film ablation.

Buzás et al. [29] studied the laser ablation of aluminium doped zinc oxide (AZO) for photovoltaic applications having film thicknesses of 100 nm and 1000 nm using frequency doubled and quadrupled DPSSL at 532 nm and 266 nm, respectively. Different ablation behaviour was found, yet ablation thresholds are not determined.

Here, we report a systematic study of the ablation threshold of both, thin indium tin oxide (ITO) and gallium doped zinc oxide (GZO) films using a DPSSL with emission wavelengths of 1064 nm, 532 nm, 355 nm, and 266 nm, respectively. GZO is used alternatively to AZO, as gallium has a greater electronegativity as compared to aluminium leading to an increased resistance against oxidation [30]. Film thicknesses are varied in the range between 90 nm and 150 nm in case of ITO and 180 nm to 750 nm in case of GZO, respectively. Depending on the specific wavelength used for the laser ablation, these values correspond to different regimes in the relation of the film thickness, the absorption length and the thermal diffusion length. The parameters for ITO and GZO are summarized in Table 1.

Experimental details

For our study we used commercial ITO on a 0.7 mm glass substrate with film thicknesses of 90 nm, 110 nm, 130 nm, and 150 nm, respectively. Commercial GZO on a comparable glass substrate had film thicknesses of 180 nm, 340 nm, and 750 nm, respectively. In both cases, a 15 nm SiO_2 layer is deposited between the glass substrate and the TCO to prevent diffusion of metal components from the substrate into the above lying active layers of the OLED. The samples were processed without further pre-treatments of the surfaces. The relevant parameters as film thickness, absorption length and thermal diffusion length, respectively, for both ITO and GZO are summarized in Table 1.

A $Nd{:}YVO_4$ (EKSPLA Techno35C) laser was used in these experiments operating in TEM_{00} mode with the fundamental wavelength of 1064 nm and its harmonics at 532 nm, 355 nm, and 266 nm and a M^2 of 1.4. For all experiments the pulse duration was nominal 10 ns and the pulse repetition rate was 20 kHz. The laser beam was focused onto the sample using a lens system with a focal length of 50 mm. The laser energy impinging the sample was adjusted through an external beam attenuator. The samples were placed onto a motorized stage for scanning with velocities of up to 500 mm/s to achieve single shots. The patterning processes for these experiments were carried out from the TCO-side.

The area of single laser pulse ablated spots was analyzed with a confocal microscope (FRT CFM) with a nominal vertical resolution of 1 nm and a lateral resolution of 0.37 μm.

Determination of ablation thresholds

A well established method to determine the ablation threshold is based on the destructive interaction between the laser beam and the sample [21,23,33,34]. This method was first published by Liu [35]. For a Gaussian beam the spatial fluence profile $\Phi(r)$ is

$$\Phi(r) = \Phi_0 \times \exp\left(-2 \times \frac{r^2}{\omega_0^2}\right) \tag{1}$$

with the distance from the beam centre r, the beam radius ω_0, and the maximum fluence Φ_0. The fluence and the pulse energy, E are directly related by [24]

$$\Phi = \frac{(2 \times E)}{(\pi \times \omega_0^2)} \tag{2}$$

By the ablation of single pulses with different pulse energy the resulting diameter of the generated area is an indicator for the required fluence to ablate the thin film. According to Liu this fluence can be interpreted as ablation threshold. Using the ablated diameter D and the related pulse energy Φ_{th} instead of r and $\Phi(r)$, Eq. (1) can be converted to [36]

$$D^2 = 2\omega_0^2 \times \ln\left(\frac{\Phi_0}{\Phi_{\text{th}}}\right) \tag{3}$$

or with respect to Eq. (2)

$$D^2 = 2\omega_0^2 \times \ln\left(\frac{E_0}{E_{\text{th}}}\right) \tag{4}$$

This relationship can be illustrated by plotting the ablated diameter against the logarithmic of the used pulse energy. By interpolation the beam radius can be estimated through the slope of this plot. The estimated beam radius can then be used to calculate the employed fluences which in turn can be used to plot the ablated diameter against the logarithmic of the used fluence. The intercept of this diagram is finally used to calculate the specific ablation threshold Φ_{th}.

Linear regression was calculated using the least-squares-fit approach. Additionally, the standard deviation from a triple experimental procedure was calculated using statistic program *R* for each wavelength tested.

Based on the logarithmic interpolation and the standard deviation the ablation thresholds with its errors are calculated using uncertainty propagation.

Results and discussion

The ablation thresholds have been determined as a function of irradiation wavelength in regimes where either the film thickness is lower or larger than the absorption length. To the best of our knowledge, the later regime has previously not been systematically studied.

Thin film ablation for film thicknesses smaller than the optical absorption length

In previous studies, the laser ablation of transparent conductive oxides has commonly been investigated in a regime where the film thickness is smaller than the optical absorption length ($d \leq 1/\alpha$) [11,27,37,38]. In our study, this regime can be examined in case of GZO for film thicknesses in the range between 180 nm and 750 nm for wavelengths 532 nm and 1064 nm, respectively. In case of ITO,