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ScienceDirect
Optics Communications 272 (2007) 221–226
OPTICS COMMUNICATIONS
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Analysis of material modifications induced during laser damage in SiO_2 thin films

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Received 21 August 2006; received in revised form 13 November 2006; accepted 15 November 2006

Abstract

The damage mechanisms in silica thin films exposed to high fluence 1064 nm nano-second laser pulses are investigated. The thin films under study are made with different techniques (evaporation and sputtering, with and without ion assistance) and the results are compared. The material morphological, optical and structural modifications are locally analyzed with optical microscopy and profilometry, photoluminescence and absorption microscopies. These observations are made for fluences near and above the laser damage threshold, and also in the case of multiple pulse irradiations. An increase in absorption in and around the damages is observed, as well as the generation of different defects that we spatially resolve with absorption and luminescence mappings.

Keywords: Laser induced damage; Optical coatings; Silica

1. Introduction

Laser induced damage in optical materials is a key issue for high power laser applications, and a significant number of studies have been published since the advent of lasers. It is widely acknowledged that the damage initiation in the nano-second regime on the surface of wide band-gap materials such as silica, is linked to the presence of nano to micrometer sized defects. These nanometric laser damage precursors may originate from the manufacturing processes (cleaning, polishing, coating) [1–3]. The study of the laser damage initiation mechanisms is difficult, mainly because the identification of nanometric laser damage initiators with low density on silica surfaces is still an issue. To overcome this problem, one solution is to intentionally introduce laser damage initiators and study their behaviour under laser irradiation. Progress has recently been made in the understanding of the laser damage process by studying artificial defects of known size and composition, embedded in silica thin films [4,5]. However the mechanisms could be very different on 'real' samples. Due to the low surface density of the damage precursors, investigations on real samples are usually based on the analysis of already damaged sites [6–9].

For this work we define the 'Damage Threshold' of the sample as the lowest fluence at which we observe mechanical damage of the sample by Normarsky microscopy. We describe here observations of a very early state of laser induced damage, that often is not detected. Using optical profilometry, absorption mappings and luminescence mappings, we also detected laser induced material modifications on 'undamaged' sites (according to the definition above). We will summarize these modifications by the word 'pre-damage'. The study has been carried out on bare fused silica substrates and on silica coatings deposited on these substrates.

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doi:10.1016/j.optcom.2006.11.025

2. Experiment

2.1. Samples

The SiO_2 thin films (200 nm physical thickness) were prepared at the Fresnel Institute by different techniques: electron beam deposition (EBD), reactive low voltage ion plating (IP), dual ion beam sputtering (DIBS) and ion assisted electron beam deposition (IAD). The substrates are Herasil samples especially polished for high power applications, and originating from the same production and polishing batch. Prior to damage testing, all samples have been cleaned with an automatic aqueous cleaning procedure involving ultrasonic immersion and detergents followed by de-ionized water rinsing and drying. Details about the manufacturing of these samples can be found in reference [10].

The *E*-field distribution of the system silica substrate – SiO_2 air is not taken into account in the interpretation of the results since the refractive index of two materials are very closed.

2.2. Laser damage measurements

We irradiated the samples with a Nd:YAG laser (1064 nm, with a pulse duration of 6 ± 1 ns) tightly focused onto the surface (12 μm diameter at $1/e^2$). The test apparatus used for this purpose is described in detail in reference [11]. Laser damage is detected by Nomarski microscopy at 50× magnification. An image of the irradiated zone is acquired by a CCD camera before and after each shot. A simple image processing algorithm then detects changes due to the laser shot. We perform statistical measurements by irradiating 50 sites for each tested fluence and 20 different fluences are tested. Thus we have created on each sample a matrix of 1000 isolated sites irradiated with single shots at different fluences, ranging from fluences that do not result in any modification visible by conventional microscopy, to fluences inducing large damages at the surface of the material. Indeed, laser damage being stochastic by nature due to the initiation by defects of low surface density, we have to test a large number of sites to be able to observe the different steps of damage development. It is then possible to observe the evolution of the irradiated surface under increasing fluences with the different diagnostic tools described below.

2.3. Morphological measurements

The morphological changes have been observed with a surface profiler (Talysurf CCI 3000 Å), with a vertical resolution better than 0.1 nm and horizontal resolution of 0.5 μm in order to measure the dimensional characteristics of the damaged sites. Optical surface profilometry has been associated with Nomarski microscopy (Carl Zeiss Axiotech microscope).

2.4. Absorption and luminescence measurements

Absorption measurements have been performed using a photothermal deflection set-up with high lateral resolution. This 'photothermal microscope' enables the acquisition of absorption mappings at 1064 nm with micronic resolution [12]. Small isolated absorbing defects can be detected with this technique down to a limit of 50 nm diameter gold inclusions in silica [13].

Luminescence mappings have been acquired simultaneously with scattering and lower resolution absorption mappings all excited by a 244 nm pump beam [14]. The luminescence spectrum of isolated (micronic) defects can also be recorded with this apparatus: the minimum excitation spot diameter is 3 μm.

In this paper we report only relative variations of absorption and luminescence. For this reason the calibration procedure of these two apparatus will not be discussed, but more information about calibration and detection limit of the technique can be found in reference [15].

3. Results and discussion

3.1. Laser damage thresholds

The laser induced damage threshold (LIDT) for the coatings are dependent on the fabrication technique: they range from 12 J/cm^2 for EBD to 35 J/cm^2 for DIBS and IAD. For comparison, the front surface LIDT of the uncoated Herasil sample was 70 J/cm^2. The results are summarized in Table 1 and the details of the LIDT measurements can be found in reference [10].

3.2. Laser damage morphology slightly above LIDT

Despite the difference in the LIDT values, the same kind of laser damage morphology is observed on all coated samples at fluences only slightly higher than the LIDT: One or several deep pits in the layer (in most cases one, but in some cases two or three) (Fig. 1, detail A), and a shallow print reproducing the laser spot are observed (Fig. 1, detail B). For fluences 50% higher than the LIDT delamination of the layer occurs.

In case of the uncoated substrate, crater formation has been observed. The crater diameter is about 12 μm corresponding to the laser spot diameter.

Table 1
Comparison of the front face LIDT obtained on coated and uncoated Herasil samples (1064 nm, 6 ns, 1-on-1 mode)

Deposition technology	Substrate	EBD	IP	IAD	DIBS
LIDT at 1064 nm	70 J/cm^2	12 J/cm^2	20 J/cm^2	35 J/cm^2	35 J/cm^2

EBD: electron beam deposition, IP: reactive low voltage ion plating, IAD: ion assisted electron beam deposition, DIBS: dual ion beam sputtering. The coated layer was 200 nm thick SiO_2.

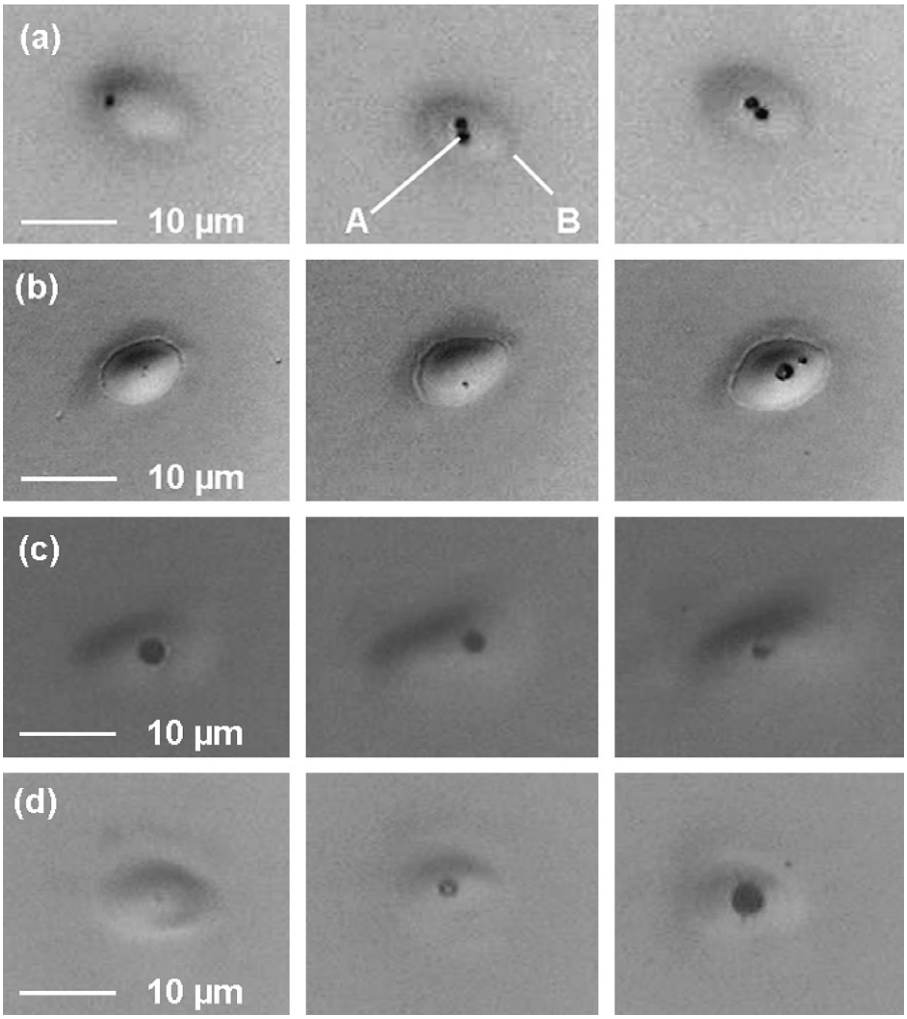

Fig. 1. 1064 nm laser damage morphologies observed by Nomarski microscopy. The images correspond to damages at the LIDT (see Table 1) for EBD (a), DIBS (b), IP (c) and IAD (d) SiO_2 thin films.

From these observations, it comes out that the laser damage mechanism on the coated samples is most probably the result of initiation by 'nanometric' precursors, and the observed pits could correspond to their localization before irradiation. Ablation of a small volume around the precursor or its ejection could cause the observed pit. Plasma formation after damage initiation by the precursor could cause the shallow ablation under the laser spot (plasma formation is visually observed). We can note that the dimension of the pit diameter depends on the fabrication technique: we have measured pit diameters of 1–2 μm for the IAD and IP techniques, less than 1 μm for EBD samples and less than few hundreds nanometers for the DIBS samples. The size of the pits is linked in a complex way to the size of the laser damage precursor, and also depends strongly on the thermal and mechanical properties, residual stress and adhesion of the different thin films. For instance, Papernov and Schmid [4] state that the pit diameter in silica thin films can reach ten times the initiator diameter. In the case of laser damage initiated by an absorbing inclusion, it has been shown that the possible size of laser damage precursors for silica thin films ranges from some tens of nanometers for metallic inclusions up to some hundred nanometers for dielectric inclusions [16,17]. The nature of these defects is linked to the coating deposition process and not to residuals from the polishing process since the LIDT of the coated samples varies with deposition technique and is lower than the LIDT of the bare substrate (70 J/cm^2). Impurities in the coating chamber or non-stoichiometric defects (Si or SiO nanoclusters for instance) linked to the oxide deposition process are possible absorbing laser damage initiators. However, no evidence for damage presursors was detectable when inspecting the layer before irradiation with the used characterization techniques (photothermal microscopy especially).

3.3. Material modifications slightly below LIDT

On these samples we have studied the different sites irradiated with fluences corresponding to the LIDT. At this fluence, one or two damages (Fig. 1) occur when 100 sites are irradiaded. In order to obtain information about the material just before damage occurs, we observed the

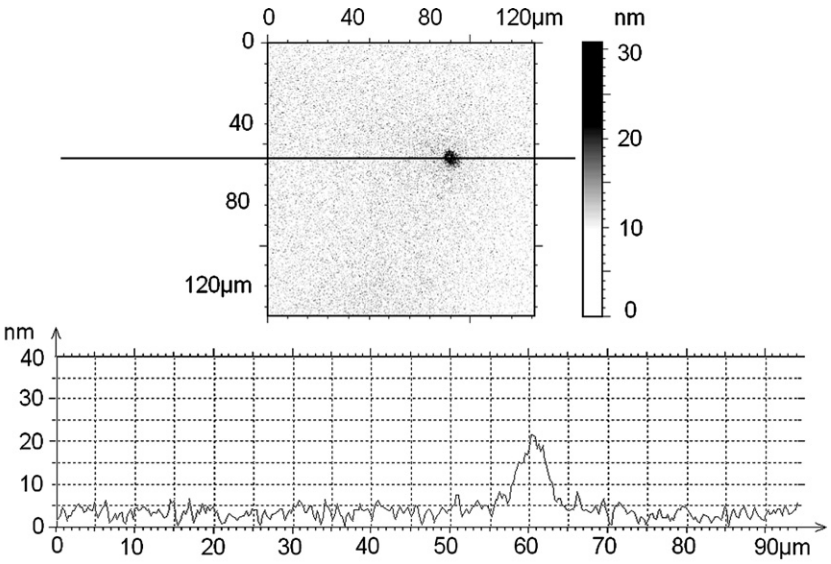

Fig. 2. Observation by optical surface profilometry of a modified area on an EBD sample irradiated at 12 J/cm^2, 1064 nm.

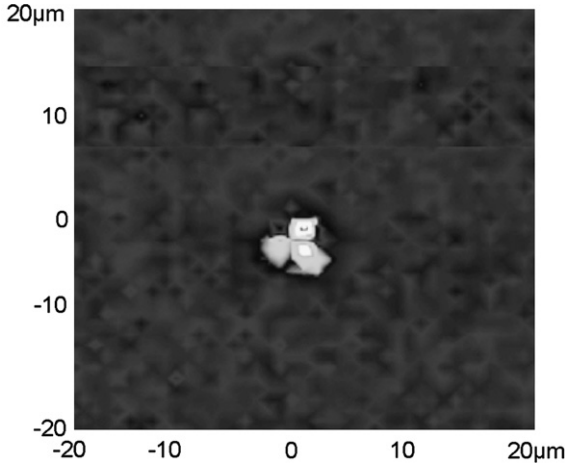

Fig. 3. Absorption mapping at 1064 nm of the same area (Fig. 2). The pump beam has a 1 μm diameter (the signal to noise ratio on the mapping is 5).

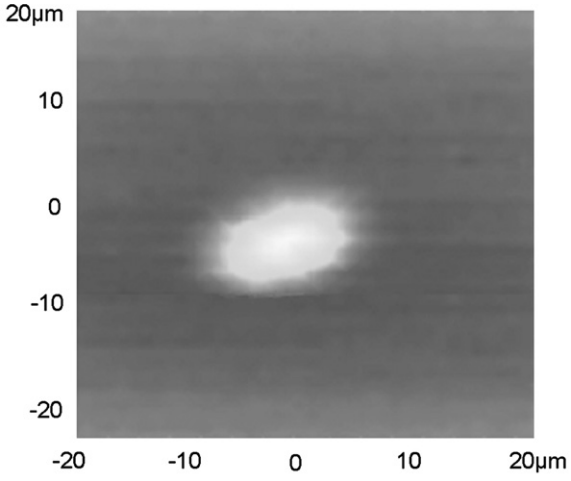

Fig. 4. Luminescence mapping of the same area (Figs. 2, 3). Excitation at 244 nm with a 3 μm diameter pump beam, signal integrated in the wavelength range 400–1000 nm.

remaining 99–98 sites where no modification was visible by Normarski microscopy. On the EBD and DIBS samples it was possible to detect on some sites a slight modification of the material by optical profilometry (Fig. 2). Only one or two sites of this kind have been observed on each sample, and none were detected on the IP and IAD samples. Figs. 3 and 4 show the mappings of such a site with photothermal microscopy at 1064 nm and integrated luminescence excited by 244 nm light respectively.

In case of the uncoated substrate, none the above techniques revealed modifications below the LIDT.

On these pre-damaged sites, the surface has been modified on a 5 μm diameter area under the irradiation spot. We have measured with the profilometer (Fig. 2) a bump height of 15 nm, indicating that the layer may have peeled off the substrate. The material itself has been strongly modified as evidenced by absorption and luminescence measurements: the film has become absorbing at 1064 nm (Fig. 3) and a strong signal of luminescence is recorded (Fig. 4) indicating an enhanced concentration of structural defects in this area. In this stage of damage, the material has changed but there is no apparent surface damage. To explain these modifications, we can refer to the models suggested to explain laser damage by nanoabsorbers: a nanoabsorber is strongly heated and energy is transferred to the surrounding matrix that is converted into an absorptive material [18–20]. Due to the lack of laser pulse energy in the case of sub-threshold irradiation, the process could have been stopped before macroscopic damage, making it accessible for observation. For higher pulse energy, further energy deposition in the absorbing matrix, plasma and crater formation occurs [4].

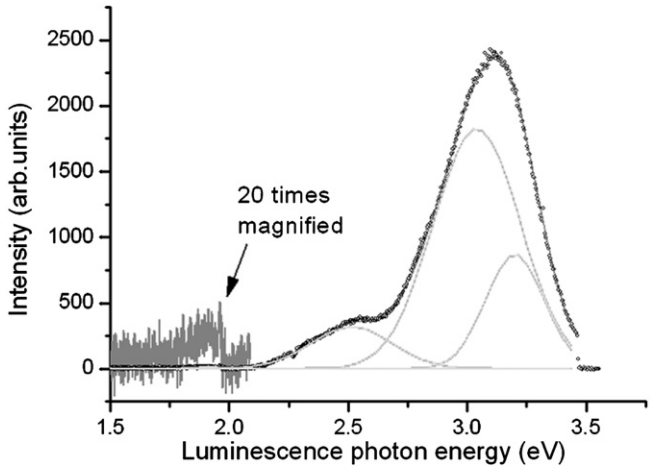

Fig. 5. Recorded luminescence spectrum in the center of the modified silica (Fig. 4). Points: measurement of the spectrum. In grey: result of the deconvolution of the spectrum with Gaussian components. Black solid curve: fit of the spectrum.

To go further in the understanding of this 'pre-damage' step, we have analyzed the luminescence spectrum of the modified material. For this, the 244 nm–3 μm diameter pump beam is localized at the centre of the luminescent area (Fig. 4) and a spectrometer is used to record the signal (Fig. 5).

On this spectrum, photoluminescence bands corresponding to different defects in silica can be identified. The band centered on 3.1 eV might be explained by oxygen deficiency centers (ODC) [21]. However it has been shown that this band has a double nature, consisting of 3.04 eV and 3.15 eV bands (same defect but in different environments) [21]. On our measurement, we obtain a better fit of the recorded spectrum with two bands rather than one band. A photoluminescence band at 2.5 eV is also observed, but to our knowledge cannot be attributed to identified defects. Another band, but with a very low intensity can be detected around 1.9 eV and is associated to Non-Bridging Oxygen Hole Centers (NBOHC) [22].

The physical process associated to the modification of the material and the generation of defects involves strong material heating and deformation, as suggested by the bump observed at the material surface. which can lead to thermal and photoionization [23]. The rapid heating and subsequent thermal expansion also induce a high stress field around the precursor. In this case the formation of ODC observed could be the result of oxygen losses due to material heating, and NBOHC could be linked to plastic deformation and stress leading to dangling bonds (as suggested by Kucheyev and Demos in the case of fused silica [24]).

3.4. Observations at higher fluences

When more energy (above the LIDT) is deposited on the sample, delamination of the coating occurs, as shown on Fig. 6 and cracking when further energy is deposited (Fig. 7). We have observed several modifications of the material in the crater and its surrounding: an increase of absorption and luminescence. A spectral analysis of the luminescence signal reveals that the generated defects are identical as the ones observed on what we have defined as a 'pre-damage' previously (ODC and NBOHC). But in this case we have noticed a higher level of NBOHC (1.9 eV) compared to ODC (3.1 eV), as shown on Fig. 8 (the ratio is 1–160 on the 'pre-damage' and 1–4 on the damage of Fig. 8). Indeed in this case the stronger deformation, cracking and the occurrence of a plasma can lead to more NBOHC.

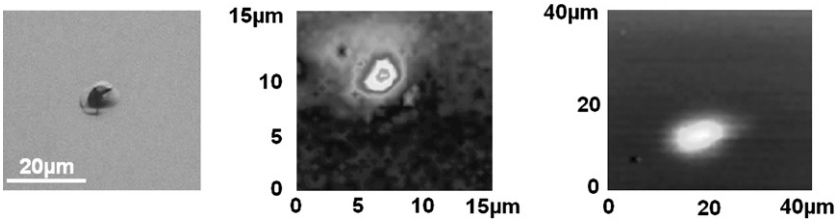

Fig. 6. Nomarski image (left), absorption at 1064 nm (middle) and luminescence mapping (right) of a damage site in a silica coating (Deposited by Ion Plating) irradiated at 30 J/cm^2.

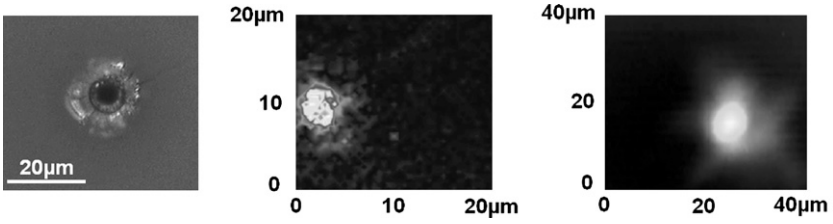

Fig. 7. Nomarski image (left), absorption at 1064 nm (middle) and luminescence mapping (right) of a damage site in a silica coating (Deposited by Dual Ion Beam Sputtering) irradiated at 100 J/cm^2.

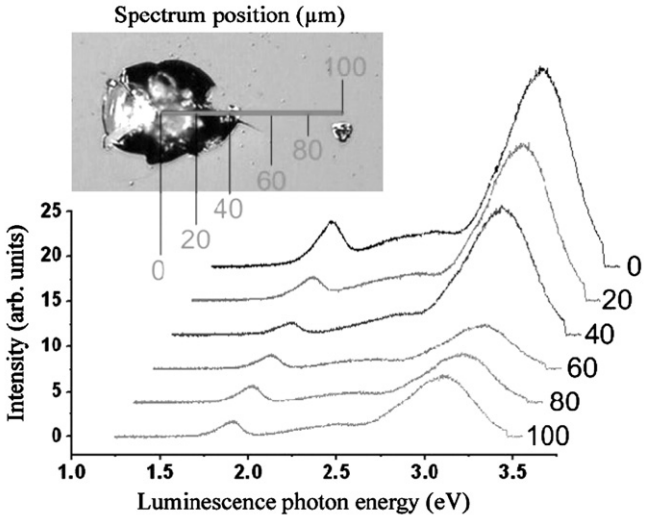

Fig. 8. Microscope image of a damage site obtained after repetitive shots (thirty shots) and luminescence spectra recorded at different locations of the damage site (Note that the shift between the different spectra is a perspective effect).

3.5. Damage growth

For applications, it is interesting to know the behaviour of a damage site under multiple pulses. Indeed the damage can be stable or leading to a catastrophic destruction of the component. The strong modifications that we have observed on our samples, in particular the increase in absorption on and around the damage can induce growth of damage after subsequent shots. For instance, we present on Fig. 8, a damage site that has been grown with thirty shots at 30 J/cm^2 on the EBD sample: the laser spot size was 12 μm (1064 nm) and centered in the middle of the resulting damage, which has a 100 μm size (see figure). As shown on the figure, we recorded the luminescence spectrum in the center, where the laser was pointing, in the edge, and far from the damage. We can see an increase in the intensity of all peaks when going from the edge to the middle of the damage site. A combination of plasma, thermal and mechanical effects have lead to a catastrophic damage.

4. Conclusion

We have studied laser damage of silica thin films deposited with different techniques on Herasil substrates. Normarski microscopy was used to define the LIDT. By this means, we described an early damage morphology appearing for all deposition techniques. The similarity of this morphology with artificial defect studies further supports that ns-laser damage is initiated by nanometric absorbing precursors.

A 'pre-damage' modification of the material was observed for EBD and DIBS layers on sites where no modification was visible with Normarski microscopy. These sites exhibit a characteristic 15 nm high and 5 μm diameter bump on our samples. Pre-damage gives also rise to enhanced absorption at 1064 nm and enhanced luminescence with only a very small NBOHC-component.

These new observations are compared to characterization of the usual single shot damage morphologies in layers by the same tools and an example of a multi-shot damage is given. Our experimental investigations provide mew information on early states of laser induced damage in silica thin films and support the nano-precursor model for ns-laser damage initiation.

Acknowledgements

We thanks Michel Cathelinaud, Luc Roussel and Michel Lequime for the manufacturing of coatings.

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