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Ultrashort-laser-pulse damage threshold of transparent materials and the role of incubation

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Abstract. We present investigations of the surface damage threshold for transparent materials, e.g. a-SiO$_2$, CaF$_2$ and LiF, after single- and multiple-laser-pulse irradiation at 800 nm in the picosecond and sub-picosecond duration range. Our study shows clearly that the surface damage threshold drops dramatically during multiple-laser-shot irradiation, due to material-dependent incubation effects. This has important consequences for applications such as laser machining and for the lifetime of optical components. Different processes that can reduce the surface damage threshold with increasing laser shots are evaluated, such as subsurface damage and defect formation. The mechanism of laser-induced defect formation, e.g. color centers, is believed to be mainly responsible for the observed reduction in the threshold for surface damage with increasing laser-shot numbers.

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Surface damage threshold under laser irradiation has been the subject of numerous studies over many years. The pulse-duration dependence of laser-induced damage on dielectrics for infrared laser pulses in the nanosecond to the sub-picosecond range have been outlined in several recent publications [1–5]. For wide-band-gap materials at a laser-pulse duration τ_P above approx. 10 ps, the generally accepted picture of damage involves conventional heat conduction by thermal diffusion, leading to an approx. $\tau_P^{1/2}$ dependence of the threshold. For a shorter pulse duration the threshold is expected to follow a different dependency owing to the material-specific time interval necessary to complete the energy transfer from the electronic system into the lattice. For dielectrics there is a continued decrease in the threshold for laser pulses approaching the 100-fs and 10-fs pulse-duration range that is, however, less significant than that in the range between 10 ps and several ns.

Generally, several important aspects have to be carefully evaluated when comparing the experimental threshold levels from different groups. (1) What is the definition of damage? It seems obvious that (surface) damage can be characterized as a sudden observation of some sort of irreversible modification. However, the means of observation, e.g. optical or electron microscopy, differ strongly in sensitivity for different types of modification. In addition, the damage threshold can depend on the experimental standards set during the investigations and may rely strongly on the subjective impression of the individual studying the target. (2) How many laser shots were used to determine a (more or less) rigorously defined damage threshold? In addition, the type of modification generated at a laser fluence near damage threshold can differ significantly depending on the number of laser shots. (3) How strong is the pulse pedestal or a possible pre-pulse from the amplifier system compared to the ultra-short laser pulse? Pre-excitation of the surface or plasma-laser interaction may have a strong effect on the damage threshold under investigation.

A deeper understanding of the effects of incubation at laser fluences below the single-shot fluence is, however, very important for applications, i.e. for estimating the lifetime of optical components and for laser processing. Obviously, for most applications the laser structuring of micro-pockets and grooves will make multiple-shot processing on the same area of the surface necessary. Our interest is in applying laser pulses of picosecond and sub-picosecond pulse duration for machining and to investigate material and pulse-duration dependencies in the surface-damage threshold for a different number of laser shots N. Based on a comparative study on the pulse-duration-dependent threshold of multiple-shot surface damage we can estimate the minimum fluence level necessary to activate prevailing incubation effects in different transparent dielectrics.

1 Experiment

The experimental setup is described in detail in [6]. To determine the surface damage threshold at a given pulse duration and number of laser shots we used the following three-step method. (1) Surface damage was detected in situ by the detection of scattered light. To monitor the changes in the light scattering, the investigated spots were additionally il-

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luminated by a 1 mW continuous-wave He-Ne laser beam. The surface was observed by using a combination of a long-distance microscope objective and a CCD camera positioned at a viewing angle of approximately 30° with respect to the surface normal [7]. With this arrangement even very slight surface modifications could be detected by the increase in intensity of the scattered He-Ne laser light or a significant change in the speckle pattern. This way we obtained the first uncertainty interval in the damage threshold during the experiment. (2) We viewed the surface via an optical Normarski and scanning electron microscopy (SEM) to determine the difference between the fluence when no modification was observable and when there was a (sudden) on-set of visible damage. Visible damage at a laser fluence close to the threshold level was usually accompanied by an increase in the surface roughness, verified by atomic force microscopy (AFM). These visible modifications regularly originate in that part of the illuminated region which corresponds to the peak fluence of the Gaussian laser spot. Basically, we verified the results by monitoring the scattered light, reducing the error slightly. However, the uncertainty interval remained greatest for the single-shot threshold, where an unambiguous observation of a sudden change is more difficult than for higher shot numbers. (3) For several laser fluence levels above the obvious damage threshold we determined the ablated area. A semi-logarithmic plot of the ablated area versus the fluence leads to the expected linear dependency [6, 8], from which the ablation threshold can be estimated. This analysis for each individual region and pulse duration yields a "zero modification" threshold defined as the intersection of the linear fit with the horizontal fluence axis. In all cases these values were inside the uncertainty intervals determined in the first two steps, where the definition of damage relied on the subjective impression of a sudden visible on-set of change between two experimental fluence levels. This last step reduced the error considerably, especially for the values determined at a single and limited number of laser shots.

2 Results

The SEM studies were performed without coating the surfaces and at a fairly low acceleration voltage of 1.2 keV to avoid an increasing load on the dielectric surface with increasing exposure time. The SEM pictures in Fig. 1 of CaF_2 surfaces after (multiple) laser illumination at a fluence near threshold illustrate the differences in the modification (or in the on-set of damage) depending on the method of detection. The laser-induced modifications in Fig. 1a (at a fluence of $2.5\,J/cm^2$ and with $N = 10$ laser shots) lead to unambiguous observation of an increase in the scattered light from the surface. The roughened surface is only a few µm in diameter and is located at the point of peak intensity of the focused laser beam. For $N = 5$ and identical fluence the changes in the scattered light signal were too vague to secure confidence in the presence of damage (hence the question mark). However, by means of Normarski microscopy slight changes in color or contrast (alteration in dispersion?) can be seen in a small region, which correspond to the topography of minor modifications visible in the SEM picture in Fig. 1b. After lowering the fluence down to $2.2\,J/cm^2$ we observe from the scattered-light monitoring and optical microscopy that there is "damage" after about 20 laser shots. The SEM image in Fig. 1c, however, depicts sub-µm cracks after 10 laser shots, which are not revealed by the Normarski microscope at its highest resolution. The SEM picture Fig. 1d depicts the surface after 100 shots at a fluence of $1.7\,J/cm^2$. There are no cracks, voids or other micro-structures visible; these are all modifications that would otherwise increase the mean roughness of the CaF_2 surface. Also, there are no changes in dispersion seen in the optical microscope that would attest sub-surface modification. However, the material must have undergone some laser-induced alteration. The image of this "white cloud" in Fig. 1d is almost identical in size with that of the focused laser beam on the CaF_2 surface prior to SEM analysis. This modification is not considered to be surface damage in our work. No ablation has taken place and the mean roughness remained unchanged. However, similar images of this kind have been reported elsewhere [9]. This effect could be considered as a pre-cursor to the surface damage. Actually, only very few additional laser shots at a slightly higher fluence (+5%) yielded a very sudden on-set of massive ablation, leading to a hole several µm in depth. Similar results were obtained with LiF. Our investigations into laser-induced surface damage of a-SiO_2 with ultra-short laser pulses match the results obtained for the fluorides with one important exception: the white cloud in the SEM image was not observed for fused silica (or other oxides, e.g. corundum).

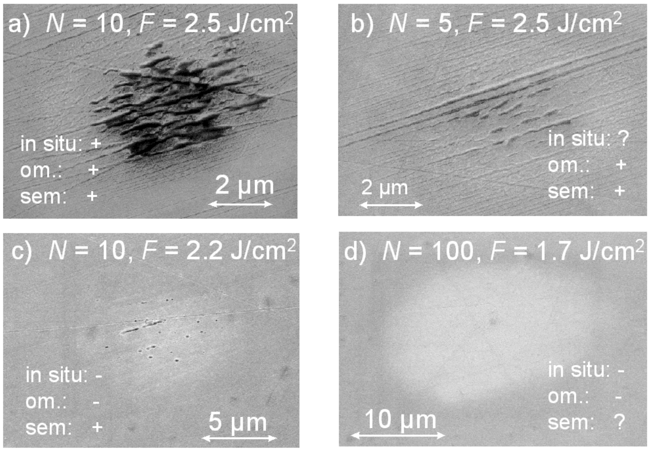

Fig. 1a–d. SEM pictures of laser-induced modifications at **a** fluence of $2.5\,J/cm^2$ and $N = 10$ laser shots lead to unambiguous observation of an increase in the scattered light from the surface. **b** modification at a fluence of $2.5\,J/cm^2$ and $N = 5$ laser shots, **c** image in this fig. however, depicts $sub - \mu m$ cracks after 10 laser shots, not revealed using the Normarski microscope at highest resolution, **d** surface after 100 shots at a fluence of $1.7\,J/cm^2$

3 Discussion

Figure 2a illustrates the dependence on the shot number of the surface damage threshold for a-SiO_2. During the first 20 laser pulses we obtained a 70% decrease in the damage threshold: $F_{th}(1, 0.1\,ps) = 3.7\,J/cm^2$ reduces to $F_{th}(20, 0.1\,ps) = 1.2\,J/cm^2$. The damage threshold for $N > 100$ $F_{th}(N > 100, 0.1\,ps)$ occurs in a smaller range of fluence, which is similar to observations made by Stuart et al. [3] for $F_{th}(N = 600$ to $10\,000,\ 0.4\,ps)$. However, it is import-

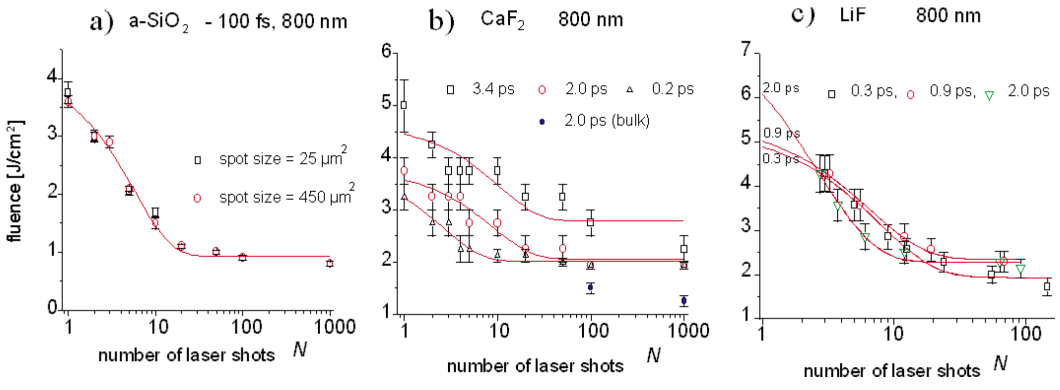

Fig. 2a–c. Semi-logarithmic plot of the surface threshold versus shot numbers in **a** fused silica determined at a laser wavelength of 800 nm and at a pulse duration of 0.1 ps. Solid line from fit following (1), **b** CaF_2 for three different pulse durations and **c** LiF for three different pulse durations.

ant to note that the dramatic change in threshold during the first 20 laser shots has the most crucial implications for laser machining.

Incubation effects in dielectric materials can be greatly influenced by the excitation and generation of conduction-band electrons, which will eventually lead to an accumulation of defect sites. The primary (resonantly enhanced) multi-photon excitation will lead to a production of electron-hole pairs on a sub-100-fs time scale. These states have a lifetime between 150 fs and several ps [10] before forming self-trapped excitons and Frenkel pairs. A small fraction of these Frenkel pairs may not recombine and stabilize to F centers [11], introducing additional energy levels and excitation routes for the next laser shot. The relative change in the laser-induced defect concentration will decrease with increasing shot numbers until finally reaching a point of saturation in the dielectric. The reduction in damage threshold is therefore less pronounced at higher shot numbers. In such a case, irradiation at a fluence below a minimum level would require an infinite number of pulses to initiate the defect accumulation and, hence, activate macroscopic damage. In other words, irradiation at a fluence below a minimum level would require an infinite number of pulses to initiate macroscopic damage. Before discussing the mechanism of the most likely process responsible for incubation in dielectrics, let us assume that the relative change in damage threshold at the N_{th} shot, $\Delta F_{th} = F_{th}(N, \tau_p) - F_{th}(N-1, \tau_p)$, is proportional to the damage threshold a laser shot earlier, $F_{th}(N-1, \tau_p)$. This would imply that the effect of incubation (and therefore the relative impact it will have on the absorption cross section) is strongest for the initial laser shots and then trends to be less significant for additional shots until finally the damage threshold reaches a constant level at high shot numbers. We can then describe how the surface damage threshold, $F_{th}(N, \tau_p)$, depends on the laser shot number for a given pulse duration τ_p by the following simple exponential decay formula [12]:

$$\begin{aligned} F_{th}(N, \tau_p) = {} & F_{th}(\infty, \tau_p) \\ & + \left(F_{th}(1, \tau_p) - F_{th}(\infty, \tau_p)\right) \exp[-k(N-1)] . \end{aligned} \tag{1}$$

Here, $F_{th}(1, \tau_p)$ is the single shot threshold and the empirical parameter k describes the strength the incubation effect has on the relative change in the absorption cross section (in this model independent of N). The larger k is, the fewer laser shots are necessary to obtain the constant damage threshold $F_{th}(\infty, \tau_p)$, below which an infinite number of laser shots would not reduce the lifetime of the sample optics, theoretically. The threshold data are plotted semi-logarithmically in Fig. 2a, where the solid line is the calculated curve obtained from the fit of the threshold behavior based on (1). Also included in Fig. 2a is the damage threshold $F_{th}(N, 0.1\ \text{ps})$ for $N = 1$, 2, 5 and 10 determined at a focal spot size of 25 μm^2 at the surface by using the 25-mm lens. Within the experimental uncertainty the fluence threshold levels are identical with those determined at a larger spot size. The quality of the fit is quite satisfactory.

Figure 2b illustrates the surface damage threshold in CaF_2 for $N = 1$ to 1000 shots for three different pulse duration, 0.2, 2.3 and 3.3 ps, in a semi-logarithmic plot. The focal spot size on the surface in this case was 700 μm^2. Note that the dependence of the surface damage threshold on the shot number differs for each individual pulse duration. Here again, the solid lines illustrate the calculated $F_{th}(N, \tau_p)$ based on the fit using (1) for each τ_P. Also included in Fig. 2b is the bulk damage threshold obtained at $N = 100$ and 1000 shots for $\tau_P = 2.0$ ps. In events in which the first damage point is generated 100–200 µm below the surface, only very few laser shots are necessary to obtain a violent ablation feature at the surface. This effect makes the determination of $F(N > 100, \tau_p)$ sometimes difficult and can lead to unexpectedly low surface damage threshold levels. This may be the case for the surface damage threshold determined at 3.3 ps and $N = 1000$ laser shots in CaF_2. For picosecond pulses this sub-surface damage effect is more likely than for sub-picosecond pulses, since in the latter case self-focusing requires a higher laser power [13]. The results for the damage threshold we obtained for LiF by using 0.3-ps, 0.9-ps and 2-ps near-infrared laser pulses, depicted in Fig. 2c, are very similar.

4 Conclusion

We have demonstrated that for transparent materials the number of laser shots with picosecond and sub-picosecond pulses plays a key role in the surface damage threshold with near-infra-red ultra-short laser pulses. This has important implications for the lifetime of optical components for such lasers and for controllable and precise laser machining at low fluence. The most dramatic change in the damage threshold is observed typically during the first 20 laser shots and is related to defect accumulation, e.g. F-center formation. This is most evident for the strong ablation phase in sapphire. Sub-surface damage related to self-focusing of the laser beam and bulk defect accumulation can lead to surface ablation at a high number of laser shots and at a fluence below the estimated surface damage threshold for an infinite number of laser shots.

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References

1. A.-C. Tien, S. Backus, H. Kapteyn, M. Murname, G. Mourou: Appl. Phys. Lett. **82**,(19), 3883 (1999)
2. B.C. Stuart, M.D. Feit, S. Herman, A.M. Rubenchik, B.W. Shore, M.D. Perry: J. Opt. Soc. Am. B **13**, 459 (1996)
3. B.C. Stuart, M.D. Feit, S. Herman, A.M. Rubenchik, B.W. Shore, M.D. Perry: Phys. Rev. B **53**, 1749 (1995)
4. H. Varel, D. Ashkenasi, A. Rosenfeld, R. Herrmann, F. Noack, E.E.B. Campbell: Appl. Phys. A **62**, 293 (1996)
5. M. Lenzner, J. Krüger,, S. Satania, Z. Cheng, C. Spielmann, G. Mourou, W. Kautek, F. Krauz: Phys. Rev. Lett. **80**, 4076 (1998)
6. D. Ashkenasi, A. Rosenfeld: SPIE Proc. **3618**, 102 (1999)
7. D. Ashkenasi, H. Varel, A. Rosenfeld, F. Noack, E.E.B. Campbell: Nucl. Instrum. Methods Phys. Res., Sect. B **122**, 359 (1997)
8. J. Liu: Opt. Lett. **7**, 196 (1982)
9. S. Gogoll, E. Stenzel, H. Johansen, M. Reichling, E. Matthias: Nucl. Instrum. Methods Phys. Res., Sect. B **116**, 279 (1996)
10. G. Petite, P. Daguzan, S. Guizard. P. Martin: Nucl. Instrum. Methods Phys. Res., Sect. B **107**, 97 (1996)
11. N. Itoh, K. Tanimuara: Opt. Eng. **28**, 1034 (1989)
12. D. Ashkenasi, R. Stoian, A. Rosenfeld: Appl. Surf. Sci. 1999
13. D. Ashkenasi, H. Varel, A. Rosenfeld, S. Henz, J. Herrmann, E.E.B. Campbell: Appl. Phys. Lett. **72**, 1442 (1998)