Detection of nano-defects in different glass materials for bulk and surfaces using laser damage investigations.

J. Y. Natoli, L. Gallais and C. Amra
Institut Fresnel (UPRES A CNRS) Ecole National supérieure de Physique de Marseille, Domaine universitaire de St Jérôme 13397 Marseille Cedex 20 France.

In order to study the physical origins of laser damage in optical materials, a specific experimental setup has been developed at the Fresnel Institute. A 7ns pulsed laser focused on a small area of few micrometers, allow accurate and localized investigation of optical substrate for surfaces and bulk. These experimental conditions permit to plot curves of damage probabilities versus the energy density of laser irradiation. From these curves, it is possible to exhibit the densities of invisible defects suspected to be precursor-centers of laser damage. Furthermore, it is possible to discriminate between different kinds of defects in the glasses. To confirm our assumptions, a validation is done on liquids with controlled concentration of impurities.

Results obtained on bulk of different glass materials clearly highlight the presence of sub-micrometric precursor centers. The results obtained on surfaces exhibit the inteface effect, and moreover, allow to have information about the polishing process quality regarding the laser irradition.

On the other hand, an extended study of laser damage morphology on different materials is realized and give usefull informations about the damage process. Two exemples will be shown here.

Intoduction

A topical challenge for most applications linked to the use of high-power lasers, is to improve the quality of optical components. Indeed, a high laser damage threshold is required in these applications. In spite of the huge effort realized by the community, the laser damage process is still not well understand. The assumption of nano-sized site in silica, is today admitted to be at the origin of the damage initiation[1-3]. This assumption permits the calculation of laser damage probability curve[4,5](called also threshold curve) involving parameters such as low and high thresholds, defect densities and spot size.

Firstly we present the conditions of test which allow to record accurate threshold curves and the stochastic phenomenological approach used to determine the defect densities. To make a quantitative validation of our model we present the results obtained in calibrated liquid.

In a second part the procedure is applied to test damage thresholds of glass bulk materials. The densities of defects are extracted and the question of their origin is emphasized. The case of surfaces is then analyzed for silica substrates, and the role of the polishing process is put in evidence.

To go further in the understanding we analyze the laser damage morphology thank to an optical microscope in different operating modes and to an atomic force microscope.

Conditions of test

An accurate description of the test apparatus is still presented[6]. It involves a single mode Yag laser beam with 1.064 μm wavelength and 7 ns pulse duration. A He-Ne probe beam is added to allow location of the region under study. The two beams are aligned and can be focused at the front or back surface of the sample, or in the bulk of substrates. The

size of the beam focused on the sample lies in the range (10μm- 100μm), and the energy density per surface unit (called fluence) lies approximately between 10J/cm2 and 10^4J/cm2. Any modification under irradiation is visualized in real time thank to an in situ optical microscope. An imaging process allow an accurate detection[7].

The laser damage procedure used in this study is 1:1 procedure[8]. This procedure consists of plotting a laser probability threshold curve. For each fluence, a single shot is delivered at N different regions Rn of the sample. The damage probability for one fluence is given by the ratio p= n/N of number (n) of damaged zones over total number (N) of tested zones. As illustrated in figure 1, the result exhibit a great dispersion between the threshold values, inducing the presence of a low (LT) and a high (HT) damage threshold. This result characterize a stochastic process which makes difficult the investigation of damage phenomena. Notice that to have enough accuracy in the probability we chose at least N≥30.

Phenomenological approach of nanocenters

Case of surface precursors

Consider for instance the case of surface defects under a gaussian illumination at normal incidence, the intensity distribution (g) is a function of the radial distance (r) as:
$g(r) = F \exp[-2 (r/L)^2]$ (1), where F is the fluence maximum and L is the radius at e^{-2}. In this first case we assume that all the defects have the same laser damage threshold T. Provided that the interaction between defects can be neglected in our experimental conditions, this analytical formula[9] for the threshold curve can be directly obtained as:
$F < T \Rightarrow p = 0$, $F > T \Rightarrow p = p(F) = 1 - \exp[-d\, S_T(F)]$ (2), where d is the surface density of defects, and S_T is the part of the spot size where the energy density g is greater ($g > T$) than the precursor threshold T. Surface S_T is calculated from equation (1), and is given by **:**
$S_T = 0.5\, S \ln(F/T)$ (3), with $S = \pi L^2$ the spot size defined at e^{-2}. The probability law resulting from equations (2) and (3) can be written as:
$p(F) = 1 - (F/T)^{-(dS/2)}$ (4) → $\ln(1-p) = (dS/2)(\ln T - \ln F)$ (4'), the only unknown parameter is the defect density d. The other parameters are determined by experimental measurements.
We have also to consider the case where several kinds of defects are distributed with densities d_i and thresholds T_i on the surface sample, $T_1 < \ldots < T_i < \ldots < T_M$. In the absence of interaction between defects, we should obtain:
$T_i < F < T_{i+1} \Rightarrow P(F) = 1 - \exp[-\Sigma d_i S_i]$ (5) with $S_i = S_{Ti}(F) = 0.5\, S \ln(F/T_i)$
Thanks to the slope discontinuities, the presence of several kinds of defects can be easily detected on the experimental curves.

The case of bulk precursors

The case of bulk defects is more physical and valid whatever the shot beam is focused at the surface or in the bulk of materials. In this situation, a complete calculation based on the same assumptions leads to: $P(F) = 1 - \exp[-d\, V_T(F)]$ (6), where d is the bulk density of defects, and V_T is the efficient bulk where the energy density is greater than the defect threshold T. The principle is the same as surface case, one kind or several kinds of defect can be detected and the related densities deduced[7].

Validation by using callibrated liquid

In order to test the phenomenological approach, the control of defect densities would be very helpful. For this we chose to use liquids that offer the possibility to mix liquid with different defect densities. In figure 2 the threshold curve measured for non ionized water(NI) exhibits a strong slope change around 300 J/cm^2. To explain this result and to fit the curve with the calculation and with the bulk model, it is necessary to consider the presence of two different kinds of defects with specific densities and low thresholds. As shown in the figure 2, good agreement is obtained for: d_1=3x10^4 defects/mm^3 , T_1=300 J/cm^2, d_2=70 defects/mm^3 , T_2=40 J/cm^2. For the standard water also two kinds of defects are necessary to fit the curve with densities and thresholds given by: d_1=2x10^3 defects/mm^3 , T_1=45 J/cm^2, d_2=8x10^4 defects/mm^3 , T_2=290 J/cm^2. To complete this results, we tested several mixtures of these two liquids, by dropping calibrated wavelets of NI liquid in standard liquid. The curves between NI water and normal water shown in figure 2 reveal an excellent agreement between theory and experiment.

Result obtained on optical substrates

Bulk of substrates

The case of bulks permits to eliminate any cleaning or polishing problem, pits or scratches… In figure 3 several bulks were measured and compared for different substrates. Typically the best threshold value (≈ 200 J/cm^2) of bulk is obtained for Suprasil, while the lowest value (≈ 2 J/cm^2) is obtained for zerodur. All densities are compiled[7]. We notice the very low density of nano-defects (approximately a few tens of defects in a (100μm)^3 volume**,** which explains why these defects are so difficult to detect via powerful non optical techniques such as MEB, TEM…

Surface of substrates

The case of surfaces is more complex to analyze, due to the presence of contaminants originating from cleaning, polishing problems… Figure 4 is given for threshold curves of the two substrate faces of fused silica with two different polishing process. A significant difference appears with the apparition of an other kind of defect in the polishing 2.

Notice the low value of surface threshold (T≈70 J/cm^2) compared to the bulk low threshold (T=200 J/cm^2) given in figure 2 for the same material (fused silica). This result clearly indicates that the nature and number of the defects at the surface (defect density around 10^{10}defects/mm^3) is different from that in the bulk (around 10^4 defects/mm^3).

Laser damage morphology study

The damage morphology can be observed for bulk and surfaces in real time thank to an optical microscope in different operating mode. For surfaces an ex situ atomic force microscope allow a quantitative study. Lot of examples can be given to proof the damage morphology study interest. We chose here to show two specific examples:

In figure 5 we can see scratches revealed after laser irradiation. Figure 6 is an AFM picture of this scratches, in fact the revelation consist of aligned little particles (nano-scale). The origin of this effect could be attribute to the polishing process, because of the constant direction and the sub surface location of the particles.

In figure 7(a-b-c-d) the damage was created at large fluences (F>HT) in the bulk of amorphous and crystalline materials. For crystalline materials (here Kbr and NaCl) the damage pattern reveals the crystalline structure while for amorphous materials (fused silica and zerodur) the damage morphology is random. Notice the difference of signature between the two amorphous materials, due to the weak thermal expansion coefficient of Zerodur. From these observations it is clear that thermo-mechanical effects should be involved in the damage process.

Conclusion

We have shown that with a destructive tool consisting to plot a laser damage probability curve it will be possible to proof the existence of nano-centers in silica and to determine their density. Different materials had been tested and had revealed as expected different results.

The examples on morphology study show that precious information about the damage mechanism and also on the nature of the material under irradiation could be obtained .

In addition to this destructive approach, non destructive tools as photothermal measurement, plasma spectroscopy are developed to exhibit the nano-defect and the related process of damage. By changing wavelength we can also expect to reveal different kind of defects.

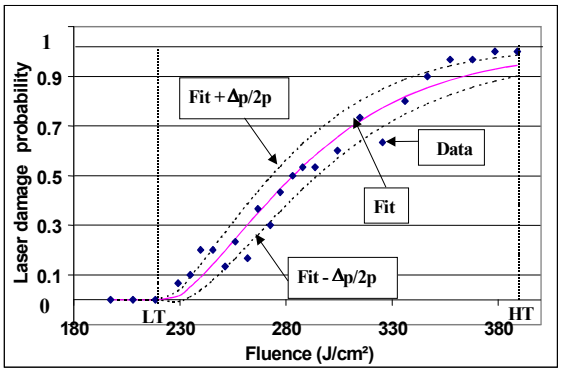

Fig.1: distribution of damage threshold in bulk of silica

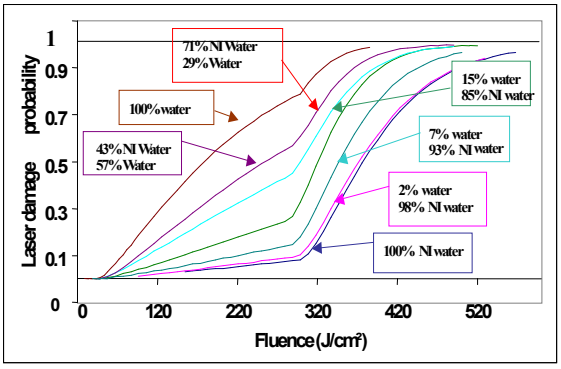

Fig.2: Threshold curves obtained by mixture of DI water and normal Water

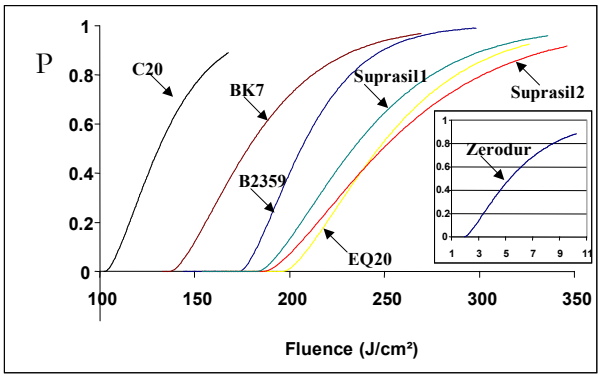

Fig 3: Threshold curves measured in bulk of different substrates

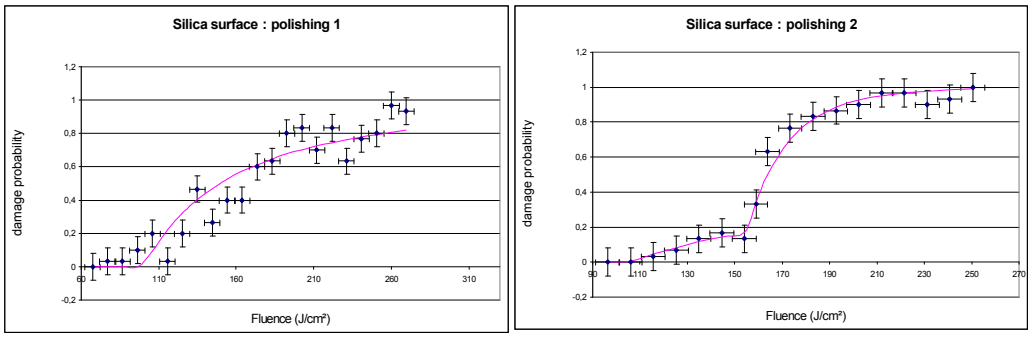

Fig 4: Threshold curves measured for two surfaces with different polishing process

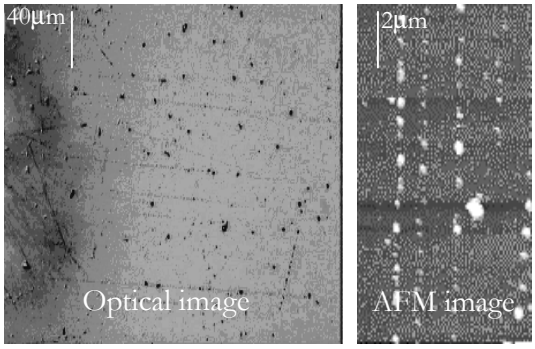

Fig.5: Silica surface observed after laser irradiation

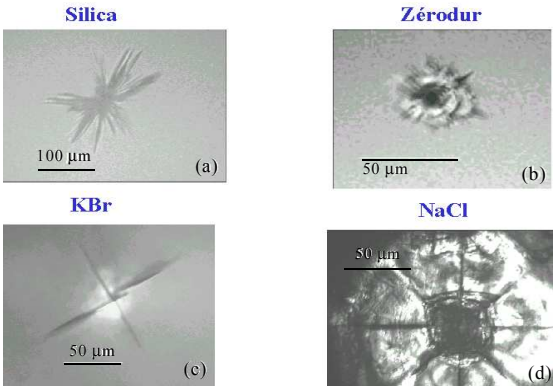

Fig.6: Damage morphologies observed on different bulk materials

---

[1] J. Dijon, T. Poiroux, and C. Desrumaux, in *Laser-Induced damage in Optical Materials*, **1997**, edited by H. Bennett, A. Guenther, M. Kozlowski, B. Newnam, and M. Soileau, 2966,p.315–325.

[2] S. Papernov, A . Schmid,; R.Krishnan and L. Tsybeskov, in *Laser-Induced damage in Optical Materials*, **2001**, edited by G. Exarhos, A. Guenther, M. Kozlowski, K. Lewis, and M. Soileau, 4347, p.146-154.

[3] J. Y. Natoli, L. Gallais, H. Akhouayri and C. Amra in *Laser-Induced damage in Optical Materials*, **2001**, edited by G. Exarhos, A. Guenther, M. Kozlowski, K. Lewis, and M. Soileau, 4347, 295-305 .

[4] J.O. Porteus and S.C. Seitel, Applied Optics. **23**, p.3796-3805 (1984).

[5] R.M. O'Connell, Applied Optics. **31**, p.4143-4153 (1992).

[6] J. Y. Natoli, L. Gallais, and C. Amra, Applied Optics (in press) issue juin2002.

[7] L. Gallais and J. Y. Natoli, , Applied Optics (submited March 2002).

[8] NF EN ISO 11254-1, S10-112-1, octobre 2000 ,**1:1 test.**

[9] R. Picard, D. Milam, and R. Bradbury, Applied. Optics. **16**, 1563-1571 (1977).