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Femtosecond Optical Breakdown as a Source of the Extreme States of Matter

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It is well known that from the two fundamental thermodynamic parameters pressure p is much more efficient in transformation of the matter state than temperature T. Optical breakdown in a form of microexplosion proved to be a simple, cheap, and efficient source of transient extreme pressure and temperature. Our interest is focused on the breakdown performed with femstosecond laser pulses both on a surface and in the bulk of material. The paper delivers some examples of the transformation effects observed mostly in the transparent dielectrics under irradiation with femtosecond laser pulses.

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1. Introduction

Laser ultra-short pulses, even of very limited energy, are able to trigger dramatic changes in the thermodynamics of material by means of optical breakdown [1]. Tight focusing enables deposition of energy in very limited volume. This creates conditions known as a high energy density. Formally, energy density is a measure of pressure and, as a consequence, a very high level of pressure and temperature are achievable. These two parameters determine the thermodynamic state of the matter. It is obvious that extreme thermodynamic conditions can modify dramatically the material structure, frequently giving new exotic states of matter [2, 3]. To achieve this effect, the breakdown should be strong or even have a violent character and exactly the last variant used to be termed a microexplosion [4]. Microexplosion is able, due to its dynamics, to generate shock waves influencing surfaces and the interior of the irradiated transparent dielectrics. The dielectrics need to be transparent to assure occurring the breakdown also in the bulk of material. Independently of that, transparency also facilitates diagnostic of the event with all the optical methods applicable within the visible part of the spectrum. The most of the processes initiated by the breakdown occur on the micrometer- and submicrometer-scales, and diagnostic of the effects requires specific technological equipment as well as versatile and sophisticated measurement techniques. Tight focus of the driving laser beam is the reason for rapid ionization accompanied by strong radiation absorption leading to the aforementioned extreme values of temperature and pressure, achieving tens of eV and hundreds of GPa, respectively. Results of the interaction in a form of phase transitions demand versatile diagnostic techniques to be revealed and quantified. The nanoscale structural changes require standard diagnostic techniques and these include scanning (SEM) and transmission (TEM) electron microscopy, micro-photoluminescence and micro-Raman spectroscopy as well as time-resolved interferometry and shadowgraphy.

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2. Experimental consideration

Our interest was focused on the structural transformations initiated dominantly by fast transient pressure of the generated shock waves. This pressure is, in the case of microexplosions, always accompanied by fast, significant changes in the material temperature. The irradiated materials included silica, soda-lime glass, diamond, sapphire, silicon or SiC to cover both amorphous and crystalline forms of the matter.

High pressure as a thermodynamic variable enforces changes of the interatomic distances in materials and the densities of condensed matter can vary by many orders of magnitude, and thereby impart dramatic changes in physical and chemical properties of materials [5, 6]. Pressure-induced phase transitions in materials are more of a rule than an exception [7] and these can be realised in a dynamic way even by energetically relatively weak irradiation with femtosecond laser pulses assuring ultra-fast energy deposition in a limited space.

Under pressure, most of the observed phase transitions are thought to be diffusionless in nature as pressure tends to suppress the large scale diffusion of atoms in the solid state. This is strengthened by application of the laser

pulse as the driving force. Compression very sharply increases the repulsive forces between neighbouring atoms, with the result that the height of the potential barrier, which must be overcome by the atoms in order to diffuse, increases. As the pressure increases it quickly distorts the structure, shapes, and orientations preparing material for the forthcoming phase transition with very little final displacement of the atoms. These small terminal displacements are source of the symmetry relationships between the parent and the product phases and the phase transitions can be analysed using the Landau theory [7].

Laser pulses deliver extremely short duration of the energy deposition in the material. The first phase transformation effect performed by intense laser pulses of nanosecond duration was pulsed laser annealing and it was, for the sake of clarity, a thermal process. While nanosecond laser pulses depose their energy in the free electrons, these transfer a part of the gained energy to the lattice on the time scale shorter than the excitation duration and the system is essentially in equilibrium achieving, at the sufficient amount of energy, the melting point. For ultrashort laser pulses in the femtosecond regime, however, thermal processes (which take several picoseconds) and equilibrium thermodynamics cannot account for the experimental data. On excitation with femtosecond laser pulses, the electrons and the lattice are driven far out of equilibrium and disordering of the lattice can occur because the interatomic forces are modified due to the promoting a significant (10% or more) fraction of the valence electrons to the conduction band.

An example of the tight focusing a femtosecond laser pulse with a microscope objective and consequences of this fact for the material are sketched in Fig. 1.

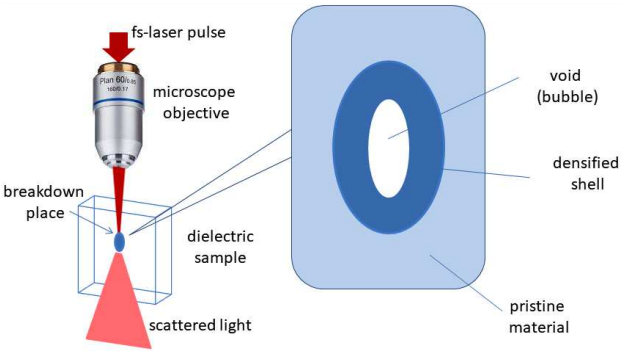

Fig. 1. Scheme of the irradiation geometry and morphology of the breakdown site after irradiation with a femtosecond laser pulse [2, 3].

3. Results and discussion

The data regarding non-linear absorption in the transparent dielectrics irradiated at high intensities/fluences is limited and focused rather on the statistically determined damage threshold. We have proposed physically justified determination of the laser induced breakdown threshold and delivered the relevant values for some selected transparent dielectrics (see Table I). The method based on the analysis of the Hill function gave results surprisingly deviating not so much from the non-physical definition based on the critical electron density ($n_e = n_{cr}$), critically reviewed, for example, in [8]. The stationary points of the absorption curve deliver, in our opinion, more unambiguous and practice-oriented definition of the laser-induced breakdown threshold (LIBT).

The Hill function has been defined as:

$$A(F) = A_{\max} F^q / (K^q + F^q), \tag{1}$$

where $A_(F)$ refers to absorption, F is the incident fluence and K^q is a material constant determining the photon concentration (fluence) needed to bind half of the available photon population. The Hill function as that in Eq. (1) describes fractional changes in the number of photons available for absorption during the laser pulse as a function of the total photon concentration and strength of cooperativity. We found that the stationary points of the function (q is the Hill coefficient) describe the absorption process in a more reasonable, i.e. physical way. The fluence corresponding to the stationary point of the 2nd order in the absorption curve we have used as LIBT in Table I.

TABLE I

LIBT measured for the selected materials under femtosecond irradiation. Lower raws show values of the Hill function fit parameters after the breakdown.

Material	Band gap [eV]	LIBT [J/cm^2]	$A_{\max}$	K	q
sapphire	9.7	0.92	0.85	1.11	9.0
			0.85	1.35	2.2
fused silica	7.5	0.7	0.88	0.95	6.0
			0.88	1.45	1.05
BK7	4.28	0.33	0.88	0.74	2.9
			0.88	0.72	1.2
soda-lime	3.9	0.19	0.87	0.62	2.68
			0.88	0.43	1.1

The data regarding the real amount of the absorbed energy is limited and frequently based on rough estimates. More accurate measurements including the Ulbricht sphere for determining the level of scattering (easily emulating absorption losses) revealed limited amount of the scattered radiation, generally not surpassing 11%.

The example of the morphological and phase transformations during irradiation of a sample surface was given applying tight focused femtosecond laser pulses to a monocrystalline diamond (type-IIa) and n-type 4H-SiC. Investigation of the surface effects was strengthened by analysis of irradiation influence on the subsurface area, especially by the hydrodynamic effects [9, 10]. Under our irradiation conditions the estimated value of the pressure exerted by laser radiation was about 2 TPa. Even if overestimated due to uncertainty in the validity range of the applied formula [11], the pressure was higher than

any of the parameters determining materials rigidity (e.g. Young's modulus). Compositional analysis performed to evaluate the structural properties of the irradiated region of diamond showed existence of graphite and amorphous carbon. The cross-sectional analysis of the area with the use of a TEM revealed a thin layer of amorphous carbon with a thickness of a few tens of nanometers, capping the monocrystalline diamond. A more detailed inspection of the internal structure within the layer with a high-resolution TEM (HRTEM) highlighted presence of different nanographitic structures, immersed in the amorphous carbon and giving in this way diamond-like carbon (DLC) [10].

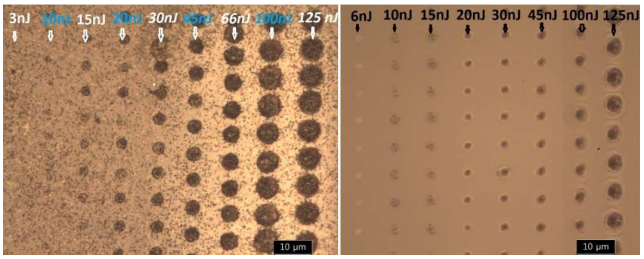

Fig. 2. Voids at the irradiation site as a function of the incident energy for doped interface SiO_2/Si (left part) and the undoped interface (right part).

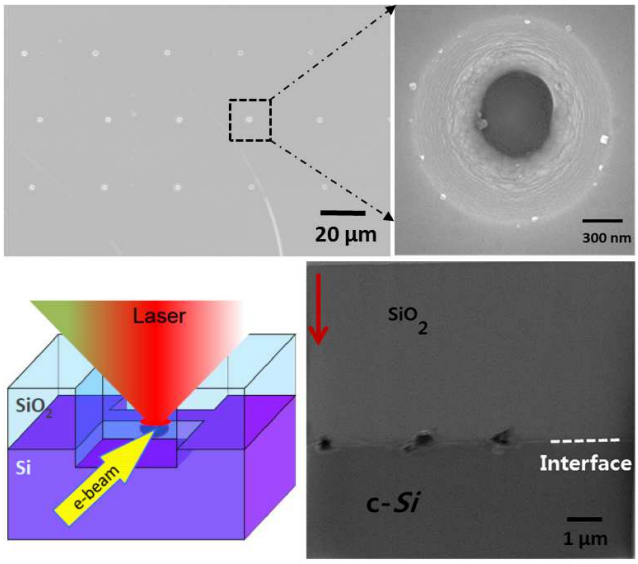

Fig. 3. Voids seen through the silica surface and a single, magnified element in the case of doped interface; geometry of the interface irradiation (lower left part) and the cross-sectional look at the interface after the breakdown.

Spectroscopic investigation of the local electronic and structural transformations on the irradiated SiC surface suggested bond breaking i.e. transformation of crystalline SiC to amorphous silicon a-Si and amorphous carbon a-C [9]. These observations were augmented by investigations applying atomic force microscopy (AFM), micro-photoluminescence (PL) spectroscopy, and high resolution X-ray diffraction (HRXRD). A high-resolution cross-sectional study of laser-modified region with TEM showed a thin amorphous layer in the vicinity of the geometrical focus with deformations and stacking faults in the sub-surface area [9]. Having considered the existing ablation theories, a complex interplay of fast laser heating followed by melting and rapid re-solidification as well as dynamic relaxation of the laser-induced stresses seems to be responsible for formation of the observed structural changes. The natural questions regarding the control over the interaction process arises in this context. The control by the laser pulse parameters is the obvious solution. However, there exists also the possibility to control irradiation geometry and the material features.

The solution proposed by us in this case is combination of an interface and material doping with nanoelements. Intense light-matter interactions at the SiO_2/Si interface during femtosecond-laser irradiation constitute a confined ablation and produce pressure waves sufficient to induce phase transformations in monocrystalline silicon used as a substrate. The induced phase transitions cover the major structural transformation, from amorphisation to different polymorphs of silicon. The mechanisms of the transformation processes are still not fully revealed, even for the cases as doping Si by femtosecond laser irradiation of its surface [12]. Ablation is a result of the laser interaction with a surface but its advanced form is confined ablation. This is in fact a breakdown in an inhomogeneous (by the presence of interface) bulk and can deliver a new look at the ways towards structural transformations. The confined regime strengthens the backward (towards the sub-surface) effects by the ablation occurring into a dense medium (solid SiO_2). The next strengthening happened by application of nanoplasmonic effects to enhance the interacting optical field but still keeping moderate laser pulse fluence. The irradiation effects in a form of craters are shown in Fig. 2 for the doped and undoped interface. Figure 3 shows the craters, irradiation geometry and cross-section of the irradiated interface with visible morphological changes.

4. Conclusion

We have sketched some of the interaction results coming out from interaction of the femtosecond laser pulses with a solid matter (transparent dielectrics). It was demonstrated that using the femtosecond laser-induced optical breakdown one can obtain extreme thermodynamical conditions with (p, T) and these could be a source of extreme matter states. It was also explained what type of transformation one can expect by this type of irradiation applied to either surface or bulk of the material. It has been pointed out that typical plasmonic effects, e.g. by doping material with metallic nanoparticles, and capping an interface with a transparent solid thin layer can markedly strengthen the interaction effect.

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