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Site selective bond breaking in random media

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Abstract

We show that strong light with the frequency slightly less then the 'gap' in electron spectrum of fused quartz cuts off macroscopic balls with fixed diameter 2 ± 0.2 μm and throws them out of the ablation crater. The reason for the phenomenon is the light driven electron bunching and generation of strong static electric field on the bunch boundaries resulting in effective photon absorption and bonds breaking in these regions while the main part of a sample is almost transparent for the photons.

1. Introduction

Electrons in disordered media move in random potential forming the electron energy spectrum quite similar to that of a semiconductor: extended electron and hole bands are separated by the 'gap' filled by localized (trapped) states. If photon energy exceeds the gap then extended electrons and holes are generated as shown in Fig. 1. These states relax rapidly (picosecond time scale) into trapped states where electron (hole) kinetics becomes drastically slower. Electron (hole) relaxation and recombination require shift of the particle from one potential well (trap) to another and small overlap of electron functions in initial and final states makes the rate of the transition small. Life time of long distant electron–hole pair becomes astronomically long.

Photon with the energy less then the gap drives electron transition between trapped states (Fig. 2). An electron absorbing a photon gains energy and transits from one trap to another with higher energy level. Due to the above mentioned small overlap of electron wave functions located in different traps, the absorption is weak as compared to the absorption of high energy photon. Our sample absorbs $\approx 10^{-3}$ fraction of photons 193 nm transmitted. Strong static electric field however changes the situation: electron gains the main part of the energy from the absorbed photon while it gains the lack of the energy from the static electric field during tunneling through some reasonable distance (Franz–Keldysh effect [1,2]). So, photon with the energy slightly less then the gap generates extended electron and hole in the sample regions where static electric field is strong enough.

It was shown recently [3] that light acts in random media like optical piston pushing electrons against the electric force. This response provides positive feedback amplifying the initial perturbation. As a result, homogeneous electron distribution becomes unstable and spatially ordered macroscopic charge bunches are formed [4,5]. This is valid for both laser as well as broad band light [6]. The latter case means that the light driven self-organization might have been in nature under bolt light, for example. Positive feedback may be treated as negative conductivity studied for different conditions in number of papers. We concentrate here on this unusual response caused by light only.

Electron bunch formation results in generation of static electric field. It reaches its maximum on bunch boundary therefore this surface becomes a weak chain in the bonds network of a matter. Our estimates [4,5] have shown that bunch radius in fused quartz is 1 μm and the electric field on bunch boundary may be as high as 10^7 V/cm which is close to the damage threshold 3×10^7 V/cm in our sample.

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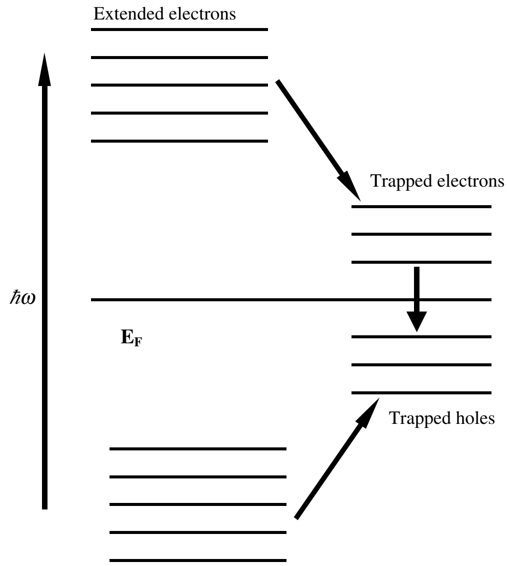

Fig. 1. Extended and trapped electron and hole states in random media.

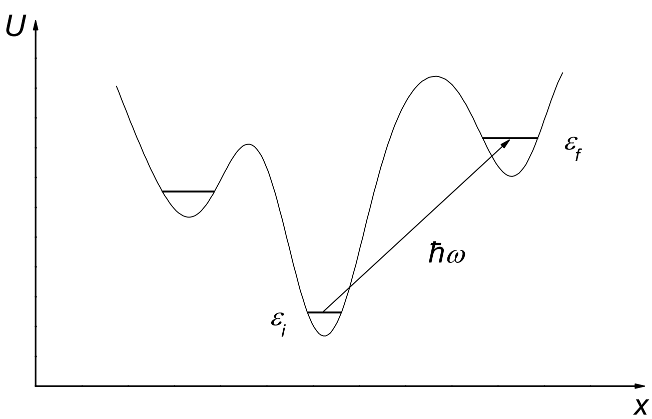

Fig. 2. Light induced electron transition between different potential wells (traps).

Electron bunch contains 10^6 extra electrons which is 10^{-5} part of the valence electrons inside. We used 7 eV photons while the gap is 8 eV. Electron gains 7 eV absorbing photon and lack of the energy 1 eV it receives from the electric field 10^7 V/cm during tunneling through the distance 10^{-7} cm. The tunneling distance is quite reasonable providing high efficiency of the process. The excited electron transits to an extended state breaking the bond on the bunch surface. That is why light cut off micron radius balls from the fused quartz and throws them out the ablation crater.

There are numerous investigations of the light driven structuring of a fused quartz by femtosecond laser pulses [7,8,9]. Short pulses due to high peak power generate plasma in species. We used 20 ns pulses providing much more soft condition of the excitation. Light power in our experiments was $\approx 10^9$ W/cm^2 which is five orders of magnitude less than 2×10^{14} W/cm^2 used in [7]. Despite the fact that a light induced bond breaking was achieved and ablation was observed in our experiments we can suggest that relatively weak excitation of the sample was performed. Bonds were broken on the spheres of micron radius but much more bonds inside the balls were not touched. Only 10^{-5} part of the valence electrons were excited in our experiments which is very far from plasma generation regime.

The electron bunching discussed belongs to the class of self-organization phenomena in open dissipative systems. The most famous examples of this class are the Benard convection [10], Belousov–Zhabotinsky reactions [11] and the Turing instability [12]. All self-organization phenomena are driven by some external flow through the system: heat in Benard convection, chemical reagents in Belousov–Zhabotinsky reactions, etc. The optical analogue of Turing instability was presented by Arecchi [13]. In this case light amplitude has been modulated in time and space, which was crucial for the organization to occur. Our investigations [14,15] have shown that steady light flow through a system can provide ordering either. Such steady light is a driving force which bunches the electrons in the case in hand.

We observed structuring of fused quartz by light and period of the newly formed structure had nothing in common with the light scales (light wavelength, coherent length, beam size, etc.) that is a peculiar feature of the self-organized systems. We performed about ten preparations of the new structure using light beams with different coherent lengths, beam diameters and different beam power and found the same period 2 ± 0.2 μm in fused quartz which, according the theory, is determined by material characteristics the main being the density of the trapped electrons.

2. Electron bunching and bond breaking on bunch boundary

Normally electrons move in the direction of electric force e**E** (here e is electron charge and **E** is local electric field). The force points the direction of potential energy drop and according to the thermodynamic laws electron tends to lower energy. This is not always valid for open systems where this law is not applicable. Electrons may choose higher energy levels for light induced transition if they are closer to resonance condition. Detailed study of electron kinetics in disordered media under light pumping [14,15] have shown that due to long life time low energy excitation dominate. Their energy ε_f–ε_i (Fig. 2) is less than laser photon energy $\hbar\omega$ therefore electrons prefer to move against the acting force in order to increase this energy and reduce mismatch. Electron motion against the force e**E** prevails if light power is high enough and light induced transitions win competition with ordinary dark mobility aligned with the force.

Electron is transported by light towards another electron (or group of electrons) and coagulation process starts. So, light forms bunch structure in random media. Due to repulsion between bunches caused by their charges, we should expect that they will form spatially ordered structure analogous to Wigner crystal. This ordering was observed in the experiment presented bellow: after laser treatment of the sample the ordered bubble surface corresponding to maximum of static electric field was observed in ablation crater bottom.

Light action looks like omnidirectional light ‘pressure’ acting upon the electrons. This ‘pressure’ is different from Lebedev’s light pressure which acts in the direction of the light beam and is proportional to the photon impulse $\hbar\mathbf{k}$. Our ‘pressure’ acts in all directions (to the center of the electron bunch) and does not depend on $\hbar\mathbf{k}$. Electron bunching results in the generation of static electric field. The growing field $\mathbf{E}$ stops electron bunching when it reaches some threshold level in the domain 10^7 V/cm and dark electron mobility compensates the light induced transitions [4,5]. Obviously, sample regions with so high electric field close to damage threshold 3×10^7 V/cm are very stressed therefore bond breaking may be achieved here easily. Light induced bond breaking due to Franz–Keldysh effect becomes so far site selective. It takes place on the bunch boundaries where the electric field gains maximum. We observed this site selective bond breaking in ablation process: 2 μm size balls are cut by light and thrown out of the ablation crater. Probably due to electric charge of the balls opposite to charge of the sample remained they return to the surface and cover area near the ablation crater. Here we see again spherical balls with diameter 2 ± 0.2 μm.

3. Experimental

High quality fused quartz samples were used in our experiments. Before the experiment the samples had been subjected to ultrasonic cleaning in acetone and ethanol followed by washing in de-ionized water. The experimental setup scheme for fused quartz ablation is shown in Fig. 3. The ArF excimer laser (193 nm, CL-7000, PIC GPI) was used. It generated 20 ns FWHM pulses with energies up to 350 mJ and pulse repetition rate up to 100 Hz. Laser beam was focused on the rear side of the sample by the lens made of MgF_2. Ablation has been performed in ambient air. Surface morphology and etched structures depth have been analyzed with an optical microscope on further recording with OLYMPUS C-4000 ZOOM digital camera. Normally the stable resonator for ArF laser has been used together with a homogenizer that enabled to minimize energy density distribution fluctuations (deviation from Gauss form is less than 2×10^{-2}) and also minimize spatial coherence of the beam.

It is convenient to study output surface of the sample in convergent beam. In this case maximum of the light intensity in the sample is located at the studied surface and it is easy to provide soft condition of the ablation. The study of the input surface is more difficult because bellow the treated surface light power is higher therefore optical damage takes place prior to ablation.

As a precursor of the ablation we observed red fluorescence reported in numerous papers (see for example [16,17]). It starts inside the beam channel after UV treatment and gains maximum near the surface just before ablation. Fig. 4 shows the beam channel radiating strong red light and ablation plume.

The material sputtering (ablation) occurs on the rear side of sample with no stimulation of the process (such as plasma generation in the vicinity of a sample or specific UV absorbing medium used in [18]). The process triggers itself at the upper threshold laser fluence level ≈5.5–6 J/cm^2. If the ablation threshold is passed and the polished surface is broken the process may be proceeded at lower laser fluences down to 1.5 J/cm^2.

Fig. 5 shows microscopic photographs of ablated crater bottom and surrounding area. One can see bubble structure produced by light on the crater bottom. The profile of the bottom consists of the packed system of identical half-spheres. Diameters of the spheres and period of the prepared structure were measured by microscope and turned to be 2 ± 0.2 μm. The order observed by eye is confirmed by corresponding diffracted signal of probe HeNe beam. We believe that light drives this process according to the following scenario: light drives electron bunching and subsequent local bond breaking on the boundary of the bunches where the static electric field is maximal. Light structures the matter and ablation reveals this structure (see for details [4,5]).

The period of the self-organized structure is a characteristic of the matter but not the light. We found that it does not depend on light wavelength, beam size, coherence length, etc. To the contrary, period of the structure

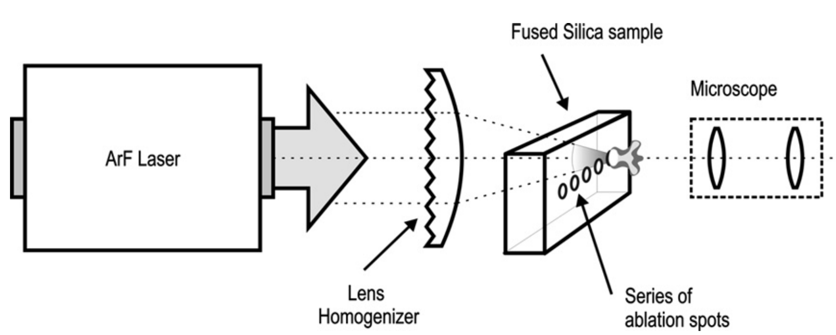

Fig. 3. Optical scheme of experimental setup.

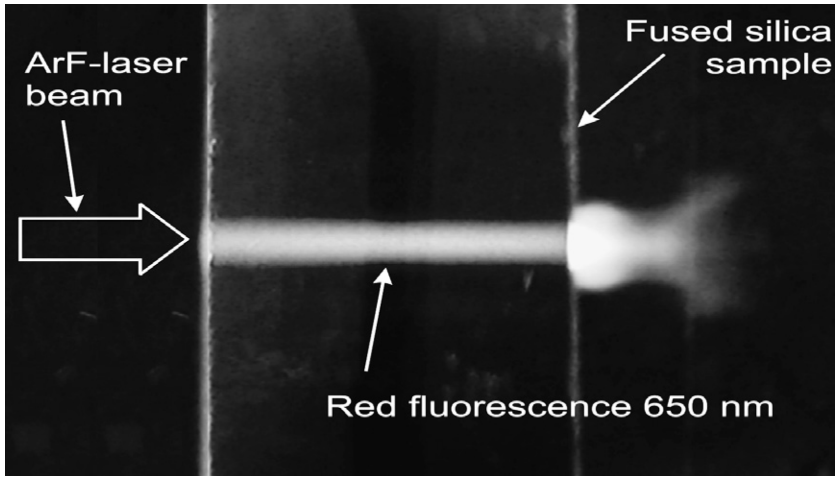

Fig. 4. Fluorescence trace and ablation plume in a fused silica samples under ArF-laser irradiation.

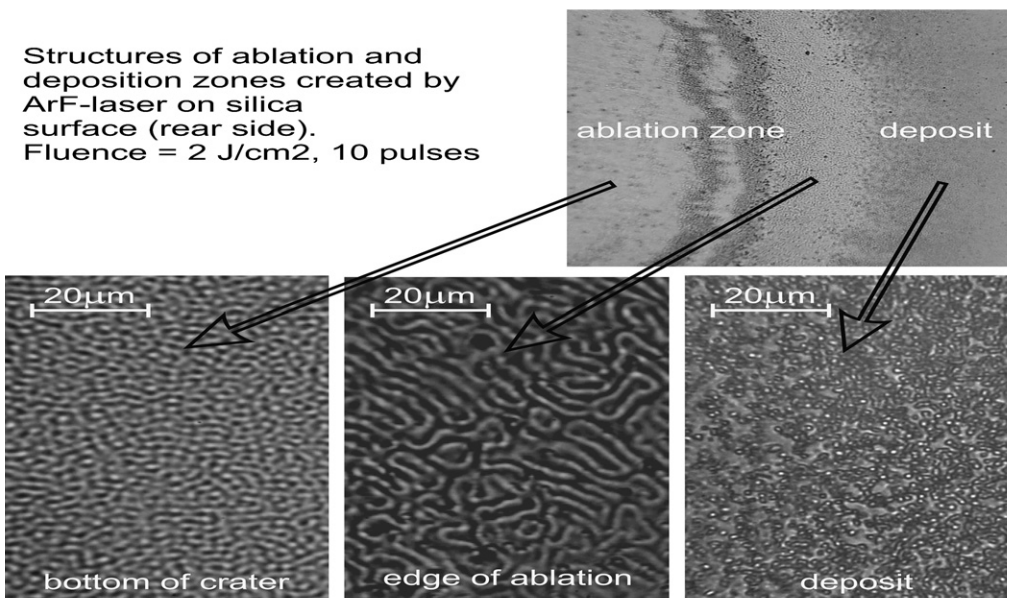

Fig. 5. Structures of ablation and deposition zones.

prepared in femtosecond experiments [7,8,9] is determined by light wavelength λ: structure spaced at $\sim\lambda/2$ was observed. Authors interpreted this structuring by the interference of the input beam with generated plasmon. Analogous behavior was observed in [19] where surface structuring took place at the SiO_2–Si interface and was explained in another way as interface property.

It is worth mentioning that the area near the crater is filled by the same spheres (Fig. 5). Long distant single balls are randomly distributed in the region far from the ablation crater. Their diameters were measured by microscope. It was found that all of them have the same diameter 2 ± 0.2 μm that coincides with the half sphere size on the crater bottom. This high accuracy of the ball calibration allows us to conclude that they are the same (unchanged) balls which left the ablation crater. These cannot be the result of particle aggregation since in this case different sizes would be observed.

Balls return to the fused quartz surface probably due to their charge opposite to the charge of the remained sample. They loose charge contacting with the surface and may aggregate after that into ball blobs if their concentration is high enough. The most intriguing fact is that there are no balls with other diameters; only elementary balls 2 ± 0.2 μm and their couplings are observed. Probably invisible microscopic dust cover the surface but one can not find ball with diameter 1 or 3 μm, for example. Only 2 μm balls are present. Wavelength used is one order of magnitude less and special attention was paid to receive spatially homogeneous light field. Hence we can conclude that the ball size is not related to external conditions but represents internal property of the matter studied. Varia-

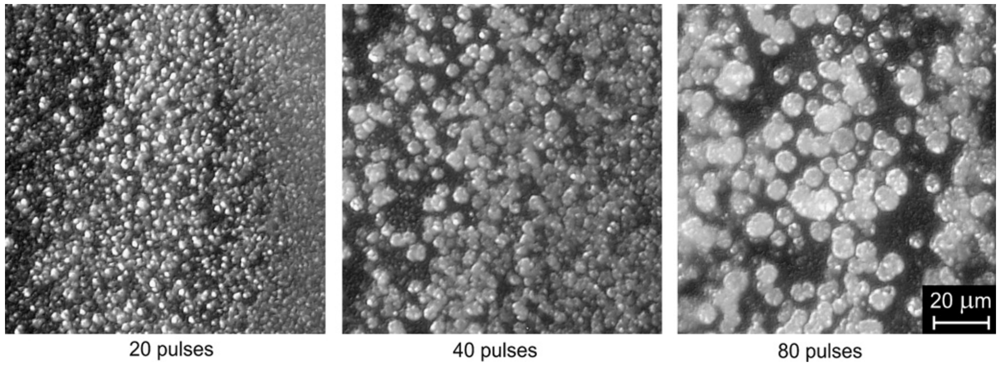

Fig. 6. Microscope pictures of deposition grains after 20, 40 and 80 laser pulses. Fluence = 2 J/cm^2. Blobs are result of coagulation of 2 μm size balls.

tion of the coherence length and beam diameter performed does not influence the ball size.

High concentration of the balls is observed close to the crater. They are packed in this region analogously to the structure on the crater bottom (Fig. 5). Ball bonding and bulk sample restoration take place in the near vicinity of the crater. Structure here looks like worms consisting of the coupled spherical species. We see again that balls packed and bonded near the crater have the same diameter as that scattered in far region – 2 ± 0.2 μm. Kinetics of the ball coagulation is shown in Fig. 6. Averaged blob size grows with number of the laser pulses as presented in Fig. 7.

Light driven self-organization is very similar to second order phase transition. The last is known to be independent on numerous details of an experiment. This fact allows us to introduce order parameter and write down universal Landau equation valid for different transitions – magnetic, ferroelectric, structure transitions, transitions to superconducting state, etc. Light driven self-organization and the following after that site selective bond breaking reveal the same independence. Period of the light induced structure observed on the crater bottom and the diameter of the fused quartz balls thrown out of the crater was the same for different light characteristics. Normally, temperature is governed parameter in phase transitions while light intensity plays this role in light induced self-organization. Other light parameters (coherence length, light band width, beam diameter, etc.) are not important.

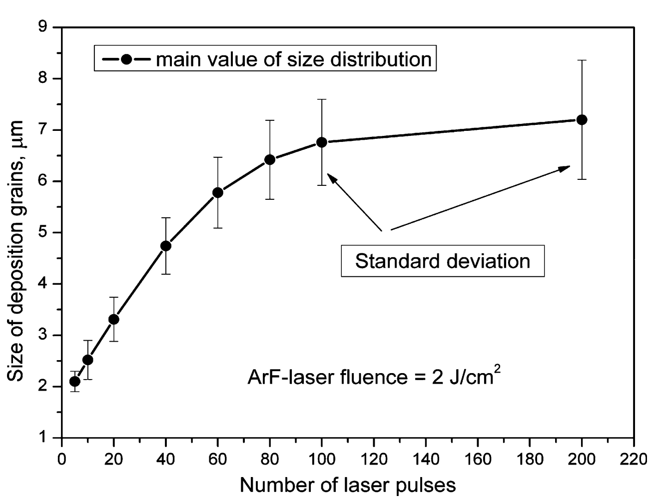

Fig. 7. Grain size vs. number of laser pulses.

Special attention was paid in order to obtain homogeneous irradiation and be sure that structure observed is not connected with light intensity profile. We checked that our light field is homogeneous nevertheless we fulfilled simple experiment which shows directly that indeed homogeneous irradiation forms the observed structures. During experiment the sample was moved back and forth in the direction perpendicular to the beam axes. It was found that the motion does not influence the experimental results and this fact confirms our statement. If light intensity profile provides corresponding structure in a sample it obviously would be smoothed by the sample motion during the structure preparation.

An interesting question is how the electron bunching has manifest itself in the surface structuring. Bunch formation is accompanied by strong electric field generation. It gains maximum on the bunch boundary. An electron bunch grows up to the state when the field reaches its threshold 10^7 V/cm and local kinetic equilibrium is established: dark electron mobility driven by this field is compensated by the light induced electron transfer. This condition determines bunch size, therefore it is fixed with high accuracy. The field generated is close to the damage field 3×10^7 V/cm in our sample. This means that bunch boundaries are in very stressed state and the material bonds are broken easily namely on the bunch boundaries. The main part of the material is almost transparent for the photons used but on the bunch boundaries they are absorbed effectively breaking the material bonds and revealing the bunch structure.

4. Conclusion

Experimental evidence of light driven self-structuring followed by site selective bonds breaking is presented. ArF laser beam pushes electrons in fused quartz into macroscopic bunches generating static electric field at the bunch boundaries. In the areas of high electric field photon absorption rate increases drastically leading to breakdown of the bonds. As a result, the ablated crater bottom is packed by ordered structure of 2 μm half-spheres and surrounding area is filled by balls of the same size and their coupling.

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