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Abstract. We applied a 0.3 mJ, 1.7 ns, 46.9 nm soft X-ray Argon laser to ablate the surface of large band gap dielectrics: CaF_2 and LiF crystals. The ablation versus the fluence of the soft X-ray beam has been studied varying the fluence in the range of 0.05-3 J/cm^2. An ablation threshold of 0.06 and 0.1 J/cm^2 and an ablation depth of 14 and 20 nm have been found for CaF_2 and LiF, respectively. These results define new ablation conditions for these large band gap dielectrics, which can be of interest for the fine processing of these materials.

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Recently, a lot of experimental work (see, for example, Ref. [1-7]) has been devoted to the laser ablation of hard dielectrics for their crucial role in the field of photonics and the fabrication of micro-optical devices. Most of these dielectrics, such as CaF_2, LiF, BaF_2 and SiO_2 is characterized by ultra large band gaps (E_g ≈12.0, 13.6-14.5 or 9.1 eV for CaF_2, LiF and BaF_2 respectively[8,9]), so that they are highly transparent to the optical radiation up to the vacuum ultraviolet (where $h\nu < E_g$). A large number of investigations have been performed on these materials using different laser wavelengths and laser pulse durations. Mostly, they have concerned two different regimes: irradiation by ns vacuum ultraviolet excimer lasers[1-3,6,7] and irradiation by ultra-intense optical picosecond- and femtosecond-laser pulses[1,4,5,7]. A more efficient mode of ablation of these dielectrics should be expected using extreme ultraviolet (EUV) and soft X-rays ($h\nu >> E_g$), due to the large linear absorption of this radiation by these crystals. However, only very recently, great advances have been made in developing reliable

EUV and soft X-ray sources with a sufficiently large power content[10-12]. In this Letter we have studied the laser ablation of CaF_2 and LiF crystals by focusing a 46.9 nm, 1.7 ns soft X-ray Ar laser and analyzed the ablated surfaces using scanning electron microscopy (SEM) and a vertical profilometer. The etch rates of these crystals have shown a well-defined threshold behavior with ablation thresholds at 0.06 for the CaF_2 and 0.11 J/cm^2 for LiF. These values are about two orders of magnitude lower than those typical of the conventional ns-UV laser light and determine new ablation conditions for the studied dielectrics characterized by a large linear absorption of the laser radiation.

The measurements were performed using the strongly saturated 46.9 nm, 0.3 mJ, 1.7 ns soft X-ray laser source pumped by a fast capillary discharge in a pure Ar gas[11,13]. The laser beam had annular structure with divergence of 5 mrad and was focused on the samples by a 12 cm-focal-length spherical Ir mirror, located at 200 cm from the capillary output with the mirror plane forming an angle of 85° with the beam axis (reflectivity ~15%). The laser energy was monitored shot by shot with a calibrated vacuum photodiode[11] collecting a small fraction of the laser beam by a Lloyd-mirror beam slitter located along the beam axis. The fluence was varied by changing the position of the sample along the optical axis of the mirror. Unfortunately, the great simplicity of this system is paid at the cost of several limitations. Firstly, the focused beam is strongly dominated by the optical aberrations that produce an elongated shape of the beam and limit the focusing resolution to only a few tens of micrometers. In this concern, using a corrected optical system one could expect an ablation resolution well below 1 μm[14]. Secondly, the optical aberrations of the optical system can produce an irregular illumination of the sample and a non-planar wavefront of the beam. Thirdly, it should be noticed that by moving the sample along the optical axis of the mirror, we have changed not only the fluence but also the curvature of the wavefront and this, in principle, can affect the results of the measurements. Regarding the fluence, for each exposure, we assessed an average fluence on the sample by measuring the area of ablated craters and the energy of the beam. The effect of the shape of the beam wavefront and its variation with the sample position was difficult to evaluate[14] and, presently, was not taken into consideration. Despite the poor focusing resolution, we reached the maximum laser fluence of 3 J/cm^2, which is well above the ablation thresholds (see data below). In these measurements, we operated in a multi-shot irradiation mode using 25 shots for each ablation. The CaF_2 samples consisted of 2-mm thick plates optically polished on both sides, while the LiF samples consisted of 1-mm thick plates polished on one side. The samples were placed in an evacuated environment at the pressure of 10^{-4} Torr. The ablation was studied analyzing the craters produced on the surfaces through a vertical profilometer (TENCOR) and an atomic force microscope (AFM). Scanning Electron Microscopy (SEM), employed in back scattered electron mode, was used as a complementary experimental technique, for the visual inspection of the damage topography.

Figure 1 (a) shows two vertical profiles of the craters obtained in CaF_2 at 0.36 J/cm^2 and 3 J/cm^2. The topography of the ablated areas depends strongly on the laser fluence. At the lower fluence the inhomogeneous distribution of the laser intensity produces an irregular profile of the crater (see dotted line). This effect can be attributed to an inhomogeneous heating of the surface. By contrast, at values >1 J/cm^2, the fluence is sufficiently high to produce evaporation of material over the whole beam cross section. The ablated crater has, in this case, a conical shape with regular vertical profile and deepness >1-1.5 μm (see solid line). The analysis performed at the AFM (Fig. 1 (b)) for the case of Fig. 1 (a) (solid line) confirms the regularity and the deepness of the ablated region. Similar behavior in the vertical profile of the craters is found in the case of

LiF. The behavior of the ablation rates/pulse versus the fluence is shown in Fig. 2. The experimental points manifest a clear threshold behavior for both materials, which can be well fitted by the standard expression[15]: $L = d \cdot \ln(F/F_{th})$, where L is the ablation rate, F and F_{th} are the irradiation fluence and the fluence threshold respectively, and d is a characteristic ablation depth, related to the effective absorption length of the radiation in the material. The results of Fig. 2 represent, to our knowledge, the first experimental data reported on these materials by a soft X-ray radiation and show several interesting aspects. Firstly, we find very low ablation thresholds: 0.11 J/cm^2 for LiF and 0.06 J/cm^2 for CaF_2, while with the nanosecond 248 nm laser beam the typical values are in the range of 20-40 J/cm^2 [16]. Secondly, the best fit of the experimental data provides for d the values of 20 and 14 nm for LiF and CaF_2, respectively. These values are in agreement with the optical penetration depths (α^{-1} ~14 nm and ~10 nm) assessed for λ = 46.9 nm from Ref. [17] and are about five orders of magnitude smaller than in the deep UV. This is due to the large photon energy ($h\nu$ = 26.4 eV) of the radiation, which induces efficient excitations of electrons from the valence band into the vacuum level of the crystal. This strong interaction introduces new ablation conditions for these large band gap dielectrics. Such a small value of d could be of significant interest for the fine processing of these materials.

It is generally recognized that a better energy coupling of the laser energy with the material should lead also to an improved morphology of the ablated region. Figures 3 (a) – (d) show the SEM images of LiF and CaF_2 irradiated with the fluence of 0.8 J/cm^2 ((a)-(b)) and 3 J/ cm^2 ((c)-(d)). Irregular reliefs on the ablated region can be reasonably attributed to the irregular distribution of laser fluence due to the diffraction of the beam and not to liquid waves formed by the melting of the surface. An improved optical system should easily avoid these effects. This analysis shows also that the ablation processes at 46.9 nm is accompanied by the formation of micro-sized cracks inside the irradiated area. These cracks are due to the strong thermoelastic stress on the surface and to the brittleness of the materials. An interesting behavior is that the cracks are observed already very close to the ablation threshold at very low irradiation fluences and increase with the number of pulses. In the case of LiF (see Fig. 3) cracks stand along preferential directions, which should correspond to the cleavage planes of the crystal. The higher density of short microcracks at the periphery (see Fig. 3 (a)-(c)) of the craters can be attributed to the different thermoelastic forces acting inside and at the edge of the laser spot. As the fluence is increased from the threshold, the evaporation of material is more efficient, cracks become less evident and a cleaner condition of ablation is found. Fractures on CaF_2 samples are typically less evident and of smaller dimensions. They present irregular shape homogeneously distributed through the irradiated area. Approaching 3 J/cm^2 (Fig. 3 (d)), the mechanical stress of the surface becomes so large to detach away from the surface macroscopic pieces of material and the quality of ablation is lost. The presence of cracks even close to the ablation threshold is in contrast to what is generally expected by the shortening of the laser wavelength and suggests the necessity for the modeling and a better understanding of the ablation processes induced by EUV and soft X-rays.

In summary, we have used 46.9 nm, 1.7 ns soft X-ray laser pulses to ablate the surface of dielectrics with ultra large band gaps. Our results present two interesting aspects. Firstly, we can reach a different ablation mode of these dielectrics characterized by large linear absorption coefficient (with α^{-1} of ~15 -20 nm) and very low ablation thresholds: 0.1 J/cm^2 for LiF and 0.06 J/cm^2 for CaF_2. These very short ablation lengths can be of interest for the fine processing of these materials. Secondly, our measurements have shown that even in these new ablation conditions, fractures and cracks are produced in the irradiated region. This second aspect suggests the necessity for a better understanding of the physical mechanisms leading to the ablation of hard dielectrics by EUV and soft X-rays.

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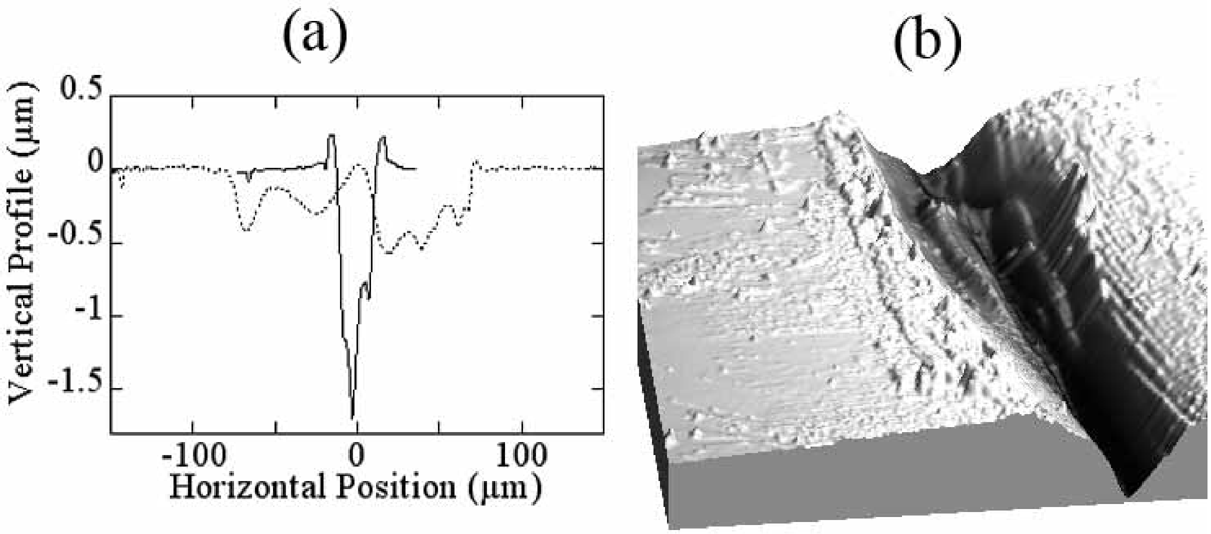

Fig. 1. (a) Experimental vertical profiles of craters produced on CaF_2 by the 46.9 nm laser at the fluences of 0.36 (dotted line) and 3 J/cm^2 (solid line) using 25 laser shots. (b) AFM image of the crater produced on CaF_2 with the f luence of 3 J/cm^2.

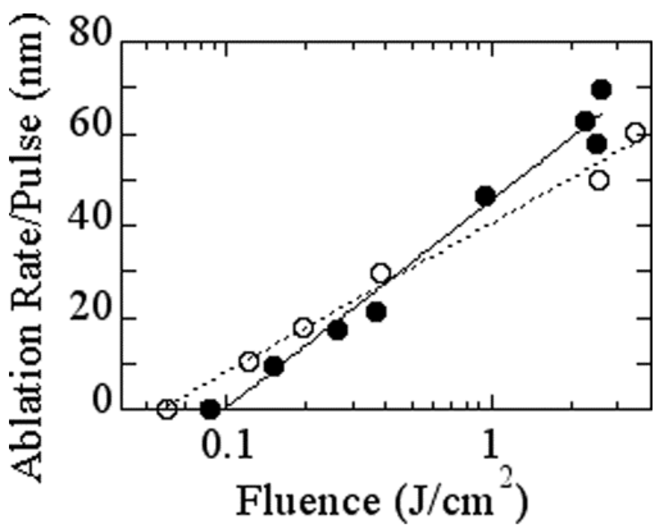

Fig. 2. Experimental ablation rates/pulse versus the fluence of the 46.9 nm laser for LiF (full circles) and CaF_2 (empty circles). The solid and the dot ted lines are the results of the theoretical fittings obtained using the logarithmic curve (see formula within the text) for the two materials, respectively.

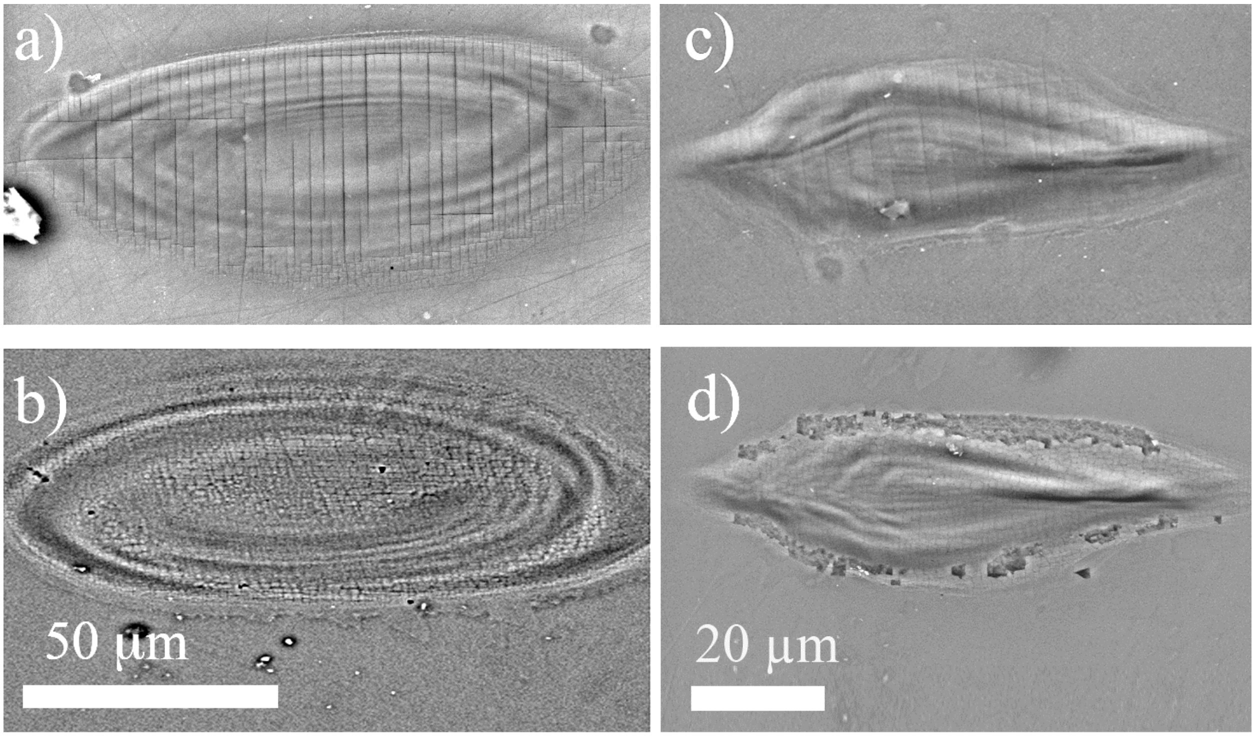

Fig. 3. SEM images of the ablated spots. The pictures a) and c) are obtained on LiF with 25 shots at the fluence of 0.8 and 3 J/cm^2. Pictures b) and d) are obtained at the same fluences as a) and c) respectively, on CaF_2 crystals.

Figure captions

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