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Proceedings

Crystalline Flat Surface Recovered by High Temperature Annealing after Laser Ablation

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Abstract: Ultra-short laser pulses (1030 nm/230 fs) were used to laser ablate surface of crystalline sapphire. Laser ablated patterns were annealed at high temperature 1500°C. Surface reconstruction took place removing ablation debris field at the edges of ablated pits in oxygen flow. Partial reconstruction of ripples was also observed.

Keywords: ablation; light-matter interaction; femtosecond lasers; nanoscale; high temperature annealing

1. Introduction: high intensity > TW/cm² crystal processing

Matter at extreme conditions of pressures above 1 megabar (10¹¹ Pa) and high temperatures as in the interior of planets - the warm dense matter (WDM) - is one of the active fields of research [1]. High-pressure and high-temperature phases of materials can be created by ultra-fast thermal quenching of a small modified volume inside transparent material, e.g., sapphire [2,3]. Internally confined micro-explosions create WDM conditions similar to the centre of the Earth. For point-like energy deposition, it is informative to present Sedov's solution, where the radius, R , of the shock wave is increasing in time t as [4,5]:

$$R(t) = \left(\frac{E_p}{K(\gamma)\rho_0} \right)^{1/(2+i)} t^{2/(2+i)}, \quad (1)$$

where E_p is the instantaneous (in space and time) release of energy, $K(\gamma) = (0.6 - 0.8)$ is the constant dependent on the adiabatic coefficient $\gamma = C_p/C_v$ ($\gamma = 1.4$ for air), ρ_0 is the mass density in an unperturbed medium, and i is the dimensionality coefficient $i = 3$ for spherical and $i = 2$ for cylindrical explosion; here $C_{p,v}$ is the heat capacities at constant pressure and volume, respectively. Such a shock wave launched from the focal volume creates highly dynamic conditions of high pressures and temperatures, which lead to formation of new materials [2,3]. Also, metastable amorphous phases can be produced as shown for sapphire [6] due to ultra-fast thermal quenching of small volume modified by fs-laser pulse triggered explosion.

The micro-explosion hydrodynamics was shown to follow the established and tested macroscopic versions of strong explosions [7]. The Evolution of micro-explosion is characterized by the independent parameters: energy E (or pressure P), density ρ , and radius r , while the two other parameters required for the full description of the hydrodynamic processes the velocity and time can be expressed as $v = \sqrt{P/\rho} \equiv \sqrt{E/(r^3\rho)}$ and $t = r^{5/2}\sqrt{\rho/E}$, respectively. It is shown that micro-explosions triggered by tightly focused fs-laser pulses are self-similar with macro-explosions made by a 10²¹ large energy deposition when the time t and space r are 10⁷ times larger [7]. All hydro-dynamic phenomena with the same initial pressure and density but differing in space and time scales are described by the same hydrodynamic equations.



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Strong structural modifications induced by high-intensity ultra-short laser pulses could be modified by a post-processing steps of high temperature annealing (HTA) in different gaseous environment, which is a promising direction of research explored in this study.

Here, we show results of laser ablation of sapphire and its high temperature annealing (HTA) for surface roughness reduction and reconstruction of surfaces with ablated ripples. The conditions to recover a crystalline smooth surface up to the rim of the ablated pits were found, which can be useful for applications to 2D materials.

2. Results and Discussion: Laser Ablation of Crystals and High Temperature Annealing

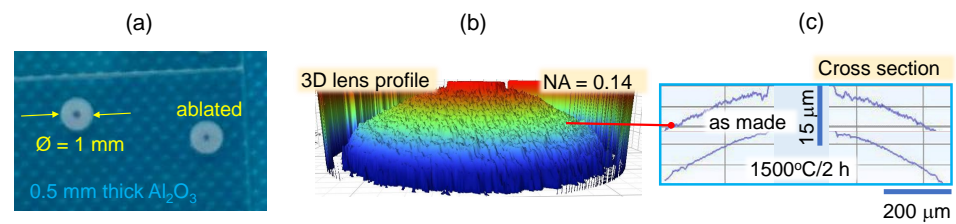


Figure 1. (a) A 1-mm-diameter lens ablated on sapphire Al₂O₃ c-plane with fs-laser pulses 1030 nm / 230 fs. (b) 3D optical profilometer scan. (c) Roughness reduction by a high temperature annealing (HTA) at 1500°C for 2 hours in N₂ flow of 200 ml/hour; same microlens. Ablation was made at a pulse density of 750 pulses/mm; NA = 0.14 (Mitutoyo). Linear polarisation of the E-field of laser pulses was horizontal. Pulse energy was $E_p = 4.375 \mu\text{J}$ (on sample). Fluence was $F_p = 6.91 \text{ J/cm}^2$.

Femtosecond laser ablation is the process by which laser pulses with ~ 230 fs pulse duration are focused through an objective lens of different numerical apertures to the surface of materials in order to create high intensity which break down the material and cause its ablation. This is a 2D/3D sculpturing method that can reach sub-micron precision. For the discussed experiment sapphire, Al₂O₃, was the material of choice. Sapphire is a hard and inert material that requires $\sim 10 \text{ TW/cm}^2$ intensities for ablation. Among its virtues is high transparency in UV-to-IR spectral range (200 - 4000 nm) and high heat conductivity. This makes sapphire optics a promising target for industrial and space applications.

Using PHAROS (Light Conversion Ltd.) laser system with $\lambda = 1030 \text{ nm}$ wavelength, $t_p = 230 \text{ fs}$ pulse duration, focusing with objectives lenses with numerical apertures of $NA = 0.26$ and $NA = 0.14$ resulted in focal spots calculated by Airy disk formula ($2r = 1.22\lambda/NA$) of $\approx 4.8 \mu\text{m}$ and $\approx 8.9 \mu\text{m}$. The Rayleigh length is $z_R = \pi r^2/\lambda = 35.62 \mu\text{m}$ and $122.6 \mu\text{m}$, which is half of the depth of focus (in air). For example, for the pulse energy of $E_p = 1 \mu\text{J}$ (on the sample), fluence was $F_p = 5.45 \text{ J/cm}^2$ and average intensity $I_p = 24 \text{ TW/cm}^2$. Laser repetition rate was $f_r = 200 \text{ kHz}$ and linear density of pulses was varied for larger or smaller overlap (typically $10^2 - 10^3 \text{ pulse/mm}$), which affected the material removal rate. Figure 1(a) shows laser ablated 1-mm-diameter lenses imprinted into the surface of sapphire.

HTA was carried out using a horizontal Nabertherm tube furnace. The recipe starts by ramping up to 1500°C at 150°C an hour, holding at 1500°C for 2 hours, ramping down to 1400°C at 200°C per hour and finally, allowing it to cool to 30°C at 100°C and hour. The extra step down to 1400°C was to test how quickly it was possible to ramp down and has been further tested up to 450°C per hour rates.

2.1. Roughness Reduction of Ablated Sapphire Surfaces

Front-side ablation was used with laser pulses traveling from air-into-Al₂O₃; back-side ablation occurs when the focus is placed onto the exit plane (Al₂O₃-to-air). This is usually possible with samples thinner than 0.5 mm and at less tight focusing with $NA < 0.4$. It took $\sim 30 \text{ min}$ to ablate the profile of a 1-mm-diameter lens with a height of $h = 15 \mu\text{m}$.

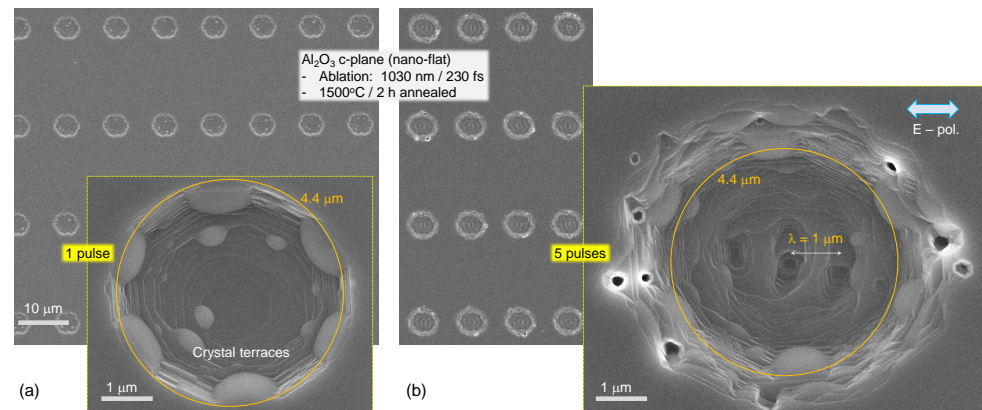


Figure 2. Sapphire Al_2O_3 c-plane after fs-laser ablation and high temperature annealing (HTA) at 1500°C for 2 hours in O_2 flow. Ablation was made by: (a) one pulse and (b) five pulses per ablation site. Focusing of 1030 nm/230 fs pulses was carried out with an objective lens of numerical aperture $NA = 0.26$ (Mitutoyo). Linear polarisation of the E-field of laser pulses was horizontal; shown by marker. Pulse energy was $E_p = 10 \mu\text{J}$ (on sample). Fluence was $F_p = 54.5 \text{ J/cm}^2$.

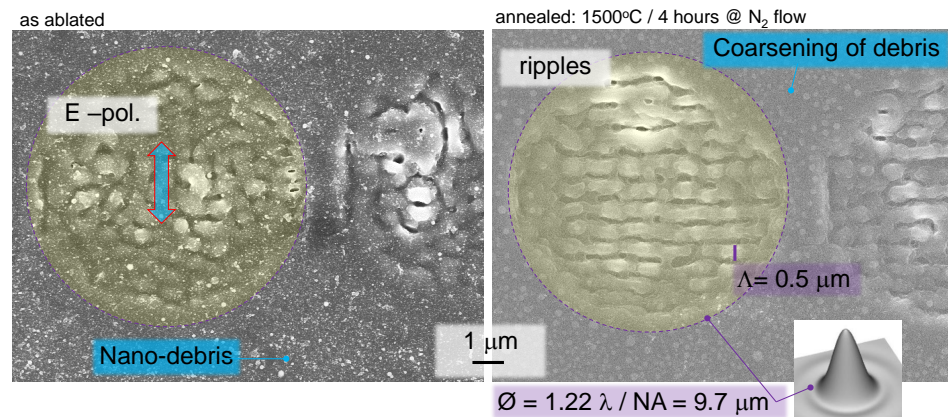


Figure 3. Single pulse ablation and HTA of Sapphire Al_2O_3 c-plane. HTA at 1500°C for 2 hours in N_2 flow. Ablation was made by one pulse per ablation site. Focusing of 1030 nm/230 fs pulses was carried out with an objective lens of numerical aperture $NA = 0.14$ (Mitutoyo). Linear polarisation of the E-field of laser pulses is shown by arrow marker. Pulse energy was $E_p = 6.25 \mu\text{J}$ (on sample). Fluence was $F_p = 9.87 \text{ J/cm}^2$.

Surface roughness of as-ablated surface was $\sim 200 \pm 50 \text{ nm}$ and was reduced to $70 \pm 30 \text{ nm}$ after 2 hr annealing (Fig. 1(c)). However, light scattering was still strong and the surface remained visibly white. Initial roughness was also dependent on the focusing conditions and pulse overlap during ablation. Other smoothing strategies need to be tested, e.g., ablation with more focused pulses. When ablation takes place at the very top of lens profile (surface of sapphire) there was a strong change in ablation conditions, which resulted in non-ablated plateau, which is $\approx 150 \mu\text{m}$ in diameter (Fig. 1). This is a known issue and can be circumvented by placing a micro-layer of a matching refractive index material, e.g., asilica film, that allows to ablate sapphire [8]; the added layer is later washed out in solvent/acid.

The effect of HTA was examined through the ablation of crystalline flat c-plane Al_2O_3 which lead to better understanding of surface changes. Since the maximum temperature used was 1500°C , which is much lower than the melting point of $\text{Al}_2\text{O}_3 \sim 2050^\circ\text{C}$, surface restructuring by surface tension driven flow of the molten phase was absent and other contributions from surface diffusion at atomic level, coarsening of debris nanoparticles, as well as sublimation took place. Sapphire has a melting point of 2053°C and boiling

temperature of 2980°C. It has recently been shown that lower temperatures with larger times can also yield surface re-flow, which can be understood from length of diffusion scaling $\propto \sqrt{D_s \times t}$, where D_s [cm²/s] is the surface diffusion coefficient and t is time. Temperatures of 1100°C and 1200°C at 3, 6, 9, 18, and 30 hours (in air ambience) have been tested and showed smoothing of c-plane sapphire terraces in step configurations [9]. Laser modified regions under high intensity irradiated in air also might have surface formation of ceramic ALON phase (AlN)_x·(Al₂O₃)_{1-x} with $x = 0.30 - 0.37$. Generation of defects, vacancies, and interstitials under high intensity fs-pulses is taking place, e.g., F⁺ color center of the oxygen vacancy with a trapped electron created by fs-laser machining of sapphire is fully annealed at 1100° [10]. Frenkel pair defects - interstitial-vacancy - observed earlier by MeV-electron irradiated high-pressure cubic-BN was induced by fs-laser pulses [11] at similar conditions used in this study. Chemical bond breaking by high intensity laser pulses can create metal enriched regions on the surface of oxides and nitrides due to formation of volatile O₂ and N₂. Such laser ablated surfaces of oxides rich with defects, debris, and depleted of oxygen are expected to be restructured by HTA. We chose O₂ flow in order to facilitate surface migration of Al-atoms to form terraces of Al₂O₃ under oxygen supply. This is one probable contribution to formation of smooth crystalline surface.

2.2. Recovery of crystalline smooth surface on ablated sapphire

Figure 2 shows scanning electron microscopy (SEM) images of single and five-pulse ablated sites after HTA in O₂ flow. A single pulse of $E_p = 11.25 \mu\text{J}$ which corresponds to a fluence of $F_p = 61.32 \text{ J/cm}^2$ and an average intensity of $I_p = 266 \text{ TW/cm}^2$ ablated a hole of 300 nm depth and a re-healed 4.4 μm diameter, which almost perfectly matching the focal diameter of 4.8 μm . After annealing, a perfectly smooth surface was observed near the rim of the ablated pit. When the number of pulses was two or more, formation of ripples [12] was observed (see structure of period $\Lambda \approx 1 \mu\text{m}$ at the bottom (Fig. 2(b))). Recovering smooth surface during HTA in O₂ flow is a promising outcome for opto-electronic applications of 2D materials.

When focusing using less tight objective lens $NA < 0.14$, where the focal spot is twice that shown in Fig. 2 and single pulse ablation with HTA in N₂ flow, the results are different in terms of more debris left after annealing (Fig. 3). Nitrogen rich atmosphere was not favorable to recovery of crystalline surface as compared with oxygen flow (see discussion above). Also, a pattern of single pulse ablation showed non-periodic structure with close-to-wavelength feature length. Also, there was no typical ablation crater, rather a nano-textured surface resembling thermally quenched molten phase. The pulse fluence used was $F_p \approx 10 \text{ J/cm}^2$ or average intensity of $I_p \approx 43 \text{ TW/cm}^2$, which is smaller by more

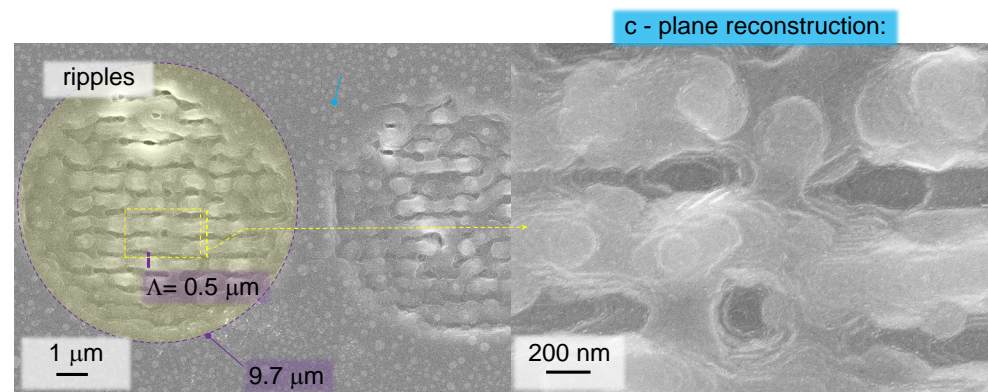


Figure 4. Single pulse ablated Sapphire Al₂O₃ c-plane (Fig. 3) after HTA at 1500°C for 4 hours in N₂ flow at different magnifications. Focusing of 1030 nm/230 fs pulses was carried out with an objective lens of numerical aperture $NA = 0.14$ (Mitutoyo). Linear polarisation of the E-field of laser pulses is shown by arrow marker. Pulse energy was $E_p = 6.25 \mu\text{J}$ (on sample). Fluence was $F_p = 9.87 \text{ J/cm}^2$.

than an order of magnitude than the the self-clamping intensity of fs-pulse $\sim 10^{14}$ W/cm², when multi-filaments are formed in air [13] and could cause a random pattern of dot-like modifications similar to those in SEM image (Fig. 3(a)). Formation and quenching of a molten phase is more probable. Under such high intensity 43 TW/cm²/pulse exceeding the ablation threshold of sapphire by ~ 5 times, formation of a highly excited plasma skin layer of tens of nanometers was expected during the laser pulse [14]. Light-matter interaction takes place as if there is a nano-film of different optical permittivity $\epsilon \equiv \tilde{n}$ placed on dielectric sapphire; $\tilde{n} = n + i\kappa$ is the complex refractive index. Such transient material state described by changing permittivity $\epsilon(t)$ is called Die-Met (from dielectric and metal-like plasma) [14]. It has strong absorption due to reduced n and increased κ due to electron generation and is also referred to as epsilon-near-zero (ENZ) state $\epsilon = (n - \kappa)^2 + i2n\kappa$ [15].

The ablation of thin films, which proceeds after the end of laser pulse, follows an imprint of a fs-laser pulse intensity. Such modulation has $(\lambda/n)/2$ period and, under multi-pulse exposure, reveals itself as ripples [12]. After HTA, a more orderly ripple pattern emerged with period smaller than $\Lambda < \lambda$. The period of ripple-like pattern which evolved after HTA (Fig. 3(b)) resembles ripples ablated under multi-pulse exposure. We put forward here a conjecture (for future validation) that light intensity modulation $\sim \lambda/2$ occurred due to presence of highly excited plasma nano-layer. Such modification of sub-surface region at the sapphire-plasma interface is hidden from SEM observation in Fig. 3(a), which shows surface of a quenched molten phase. HTA was responsible to restructure surface and the imprinted modification was revealed. Figure 4 shows closeup SEM views of the ripples with evident re-crystallisation following c-plane of Al₂O₃ (hexagonal pits). Even HTA temperature protocol was the same, the surface quality of HTA treated ablated surface had more debris as compared with that made under O₂ flow (Fig. 2).

3. Conclusions and Outlook

Sapphire ablation with different numerical apertures ($NA = 0.26$ and 0.14) and similar pulse energies ($10 \mu\text{J}$ and $6.25 \mu\text{J}$) are compared. SEM images showed the formation of ripples with period close to the wavelength of the laser irradiation for the $NA = 0.26$ and, interestingly, it was half of the wavelength of the laser for $NA = 0.14$. After the samples had undergone high temperature annealing at 1500°C for 2 to 4 hours in either an O₂ or N₂ environment these ripples underwent restructuring and a crystalline step-like structures become apparent. It was also shown that annealing in an O₂ environment reduced the amount of debris and the surface become smooth. In the case of HTA in N₂, however, debris were still present and their coarsening took place. Detailed X-ray Photoelectron Spectroscopy (XPS) experiments are planned for detailed understanding of material modification on the surface during HTA in O₂ and N₂ flow. Apparently, the O₂ flow was important factor for restoration of a smooth c-plane surface by HTA.

We show that the restructuring of laser ablated crystalline surfaces can be applied to the fabrication of micro-optical elements in reducing the surface roughness and allowing for tighter control over the surface profile while maintaining the precision of a shape definition. Differently from glasses [16], where HTA cause a surface tension driven reflow and formation of spherical surfaces which might be different from the required shape for a defined optical function. However, the true extent of the control over surface roughness is yet to be fully explored using this technique. The optimal time of annealing and the optimal temperature to achieve the most restructuring without sacrificing the surface profile will be determined in future studies. Sublimation via solid-to-gas occurring along with solid-fusion-vaporisation stages during HTA need better understanding and can be different in other crystals.

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