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Surface morphology and phase transformations of femtosecond laser-processed sapphire

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ABSTRACT

The morphological and structural modifications induced in sapphire by surface treatment with femtosecond laser radiation were studied. Single-crystal sapphire wafers cut parallel to the (0 1 2) planes were treated with 560 fs, 1030 nm wavelength laser radiation using wide ranges of pulse energy and repetition rate. Self-ordered periodic structures with an average spatial periodicity of ~300 nm were observed for fluences slightly higher than the ablation threshold. For higher fluences the interaction was more disruptive and extensive fracture, exfoliation, and ejection of ablation debris occurred. Four types of particles were found in the ablation debris: (a) spherical nanoparticles about 50 nm in diameter; (b) composite particles between 150 and 400 nm in size; (c) rounded resolidified particles about 100–500 nm in size; and (d) angular particles presenting a lamellar structure and deformation twins. The study of those particles by selected area electron diffraction showed that the spherical nanoparticles and the composite particles are amorphous, while the resolidified droplets and the angular particles, present a crystalline α-alumina structure, the same of the original material. Taking into consideration the existing ablation theories, it is proposed that the spherical nanoparticles are directly emitted from the surface in the ablation plume, while resolidified droplets are emitted as a result of the ablation process, in the liquid phase, in the low intensity regime, and by exfoliation, in the high intensity regime. Nanoparticle clusters are formed by nanoparticle coalescence in the cooling ablation plume.

1. Introduction

The interactions between nanosecond laser pulses and materials are essentially thermal in nature. On the contrary, due to their extremely high peak intensity and short pulse duration, high radiation intensity femtosecond lasers minimize the contribution of thermal phenomena to the ablation process [1]. In fact, due to their ultrahigh intensity, these lasers induce non-linear electron excitation processes such as multiphoton ionization, which promote electrons to the conduction band despite the photon energy being lower than the energy gap. The increase of the electron density in the conduction band leads to an increase of the radiation absorption coefficient and of the reflectivity. On the other hand, electrons in the conduction band absorb very effectively the laser radiation by inverse bremsstrahlung and ionize other atoms by collisional excitation, eventually leading to an avalanche and the formation of a plasma [1]. It is generally assumed that, when the electron density reaches the critical plasma density, i.e. the electron density where the plasma frequency equals the frequency of the laser, ablation occurs [1,2]. Due to the very high values of the radiation absorption coefficient in the plasma the radiation/material energy transfer process is localized within an extremely shallow surface layer and energy absorption by the surrounding material is negligible. For low radiation intensities, in general corresponding to longer laser pulses for similar pulse energy, there is still a large thermal contribution. Energy is transferred from the excited electrons to the lattice within a few picoseconds after the end of the laser pulse, leading to material melting, bubble nucleation and material ejection [1]. For higher values of intensity (larger than about 10^{13} W/cm^2) ablation is essentially athermal [3]. This ablation mechanism, designated by electrostatic ablation, involves photoemission of electrons from the surface followed by electrostatic ejection of the remaining positively charged particles [1,3,4]. Since the excitation process is highly non-linear, the laser effects can be extremely localized and confined to a small focal volume. This localization is further enhanced by the fact that heat transport during the ultra-short laser pulse duration is negligible.

Lasers allow writing periodic or aperiodic surface textures in many materials. Aperiodic micron-sized textures characterized by

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features such as columns, cones, etc. have been studied since many years in surfaces treated with nanosecond pulse duration lasers at fluences slightly higher than the ablation threshold. Their formation mechanisms were the object of intense discussion during more than one decade, radiation shadowing by impurities [5], differential ablation [6,7], hydrodynamic effects [8] or inhomogeneity of the material structure [9] being some of the suggested causes leading to their formation. Surface relief can also appear in thin films deposited by LCVD [10]. When surfaces are submitted to short duration laser pulses parallel ripples with periods in the range 200–800 nm and amplitude 10–100 nm, known as Laser-Induced Periodic Surface Structures (LIPSS), form in a wide range of materials, including semiconductors, metals and dielectrics [11,12]. Their formation was explained by the interference of the incident electromagnetic wave with surface Plasmon polaritons, i.e. electromagnetic modes bound to and propagating along the surface, created by the incident wave coupling with scratches, dust particles and other surface defects [13–15]. A consequence of this mechanism is that LIPSS are perpendicular to the laser beam polarization vector. LIPSS affect important surface properties, such as wetting [16–19], biocompatibility [20], cell adhesion and proliferation behavior [21] and several optical properties [22], and are being actively investigated since several years. A different type of periodic self-organized structures are the parallel nanogratings formed by tightly focusing femtosecond duration laser pulses inside materials such as silica [23,24] or sapphire [25,26]. These nanogratings are perpendicular to the radiation polarization vector as well [27]. Their formation was explained by an inhomogeneity of the plasma distribution within the focal volume created when the incident laser beam interacts with plasmons at the dielectric-plasma interface, leading to periodic field enhancement and further ionization in these periodic nanoplanes. Other types of effects are also observed. When the laser beam is focused within a transparent material, such as silica or sapphire, with intensities near or exceeding 10^{13} W/cm^2, voids typically ~250 nm in diameter are created [28]. These voids are surrounded by a layer of a phase denser than the original material, because the total volume remains constant. Gamaly et al. [29] studied the mechanism of formation of these voids and concluded that the material within the volume affected by the laser radiation (similar to the focal volume ~0.15 μm^3) is ionized and converted into superhot expanding plasma, leading to extremely high temperatures and pressures. Using modeling Glezer and Mazur [28] estimated that if only 30% of the energy of the plasma created by the laser beam is transferred to the surrounding material, the temperature will reach ~10^6 K and the pressure about 3000 GPa. The expansion of this confined plasma leads to the formation of a spherical shockwave that propagates from the focal volume into the material, compressing it. On the other hand, a rarefaction wave propagates to the center originating the void [30–33]. The compression wave may induce the transformation of crystalline sapphire into the amorphous phase, which is 1.14 times denser than the crystalline form. In agreement with the predictions, Juodzakis et al. [32,34] found that a tear-shaped nanovoid surrounded by a shell of amorphous material was created within sapphire for laser beam intensities higher than 10^{14} W/cm^2 as a result of the extremely high temperatures and pressures generated by the focal volume, which the authors estimated at 5×10^5 K and 10 TPa. A value of about 10^{18} K/s was estimated for the cooling rate. For lower intensities no void is formed and a tear shape region of amorphous alumina forms [33]. This amorphous alumina is etched by a HF solution or by the ion milling operation used to prepare transmission electron microscopy thin foils so it appears as nanovoid after etching [34]. The amorphous alumina will crystallize upon irradiation with multiple laser pulses leading to the formation of nanocrystalline material [33]. Nanocracks preferentially oriented along the basal plane of sapphire were observed [31].

The aim of this paper is to study surface topography and phase transformations induced by the ablation of single crystalline sapphire. Sapphire or α-alumina is a crystalline material widely used in the optoelectronic industry. It is brittle and extremely hard and, consequently, difficult to machine using conventional methods, so machining with ultrafast lasers is an interesting alternative to conventional machining processes for the manufacturing of parts such as lenses, high-pressure windows, displays, cutting blades, surgical tips, biomedical equipment, sensors, etc. [35]. However, up to this moment very few studies exist on ultrafast laser processing of sapphire.

2. Experimental methods

2.1. Material processing

The specimens were 10 mm × 5 mm × 1 mm sapphire single crystalline wafers with both faces polished supplied by *CrysTec GmbH, Berlin*. The laser treatments were performed in air using an Yb:KYW chirped-pulse-regenerative amplification laser system (Amplitude Systèmes sPulse HP, Bordeaux) with a radiation wavelength of 1030 nm and a pulse duration of 560 fs. The laser beam was focused perpendicularly to the specimen surface by a 40× high numerical aperture (0.66) microscope objective. The experiments were carried out with stationary sample and laser beam or by translating the sample with respect to the stationary laser beam at constant scanning speed using a computer controlled linear stage. In order to investigate the influence of the processing parameters on the surface topography and material structure, the pulse energy and pulse repetition rate were varied within the ranges 4–100 μJ and 1–100 kHz, respectively. The scanning speed was varied from 0.01 to 2.0 mm/s.

The ablation threshold was calculated on the basis of measurements of the diameter of craters produced with 10, 20 and 40 laser pulses at a repetition rate of 1 Hz and with fluences between 12.5 and 125 J/cm^2. The measurements were carried out on calibrated SEM images using ImageJ software [36]. To compensate for the asymmetry of the craters four diameters were measured in different directions for each crater and an average calculated. Five craters were measured for each set of laser processing parameters. The ablation threshold was calculated using the D^2-method described by Liu [37]. The basis of the method is as follows. Assuming a Gaussian laser beam the maximum fluence (ϕ_0) and the laser pulse energy (E_p) can be related by:

$$\phi_0 = \frac{2E_p}{\pi w_0^2} \quad (1)$$

where w_0 is the laser beam radius at e^{-2} of the maximum intensity. On the other hand, the diameter of an ablation crater (D) is related with the maximum fluence (ϕ_0) by

$$D^2 = 2\,w_0^2\,\ln\left(\frac{\phi_0}{\phi_{th}}\right) \quad (2)$$

where ϕ_{th} is the ablation threshold fluence. As a result, the Gaussian beam radius w_0 can be calculated from a plot of the square of the average crater diameter vs. the logarithm of the pulse energy. The peak fluence can then be calculated from the pulse energy and the laser beam radius at e^{-2}. Knowing this value, the ablation threshold for a given number of laser pulses can be determined by extrapolating to zero a linear plot of the square of the crater diameter (D) as a function of the logarithm of the fluence.

2.2. Specimens characterization

The processed surfaces were observed by scanning electron microscopy using a JEOL JSM-7001F field emission gun scanning

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