Applied Surface Science 255 (2009) 9745–9749

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Formation of amorphous sapphire by a femtosecond laser pulse induced micro-explosion

Vygantas Mizeikis [a], Shigeru Kimura [b,c], Nikolay V. Surovtsev [d], Vygandas Jarutis [e], Akira Saito [f], Hiroaki Misawa [a], Saulius Juodkazis [a,*]

[a] Research Institute for Electronic Science, Hokkaido University, N21W10 CRIS Bldg., Sapporo 001-0021, Japan
[b] Research and Utilization Group, Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Sayo-Cho, Sayo-Gun, Hyogo 679-5198, Japan
[c] Japan Science and Technology Agency, CREST, 5, Sanbancho, Chiyoda-ku, Tokyo 102-0075, Japan
[d] Institute of automation and electrometry, Novosibirsk 630090, Russia
[e] Laser Research Center, Department of Quantum Electronics, Vilnius University, Sauletekio 9, 2040 Vilnius, Lithuania
[f] Division of Precision Science & Technology and Applied Physics, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, 565-0871 Osaka, Japan

ARTICLE INFO

Article history:
Available online 22 April 2009

PACS:
81.07.−b
91.60.Gf
91.60.Hg
61.46.−w

Keywords:
Phase-transitions
Laser nano-fabrication
Shock waves
Sapphire
Synchrotron X-rays

ABSTRACT

We report on structural characterization of void-structures created by a micro-explosion at the locus of a tightly focused femtosecond laser pulse inside the crystalline phase of Al_2O_3 (*R*3*c* space group). The transmission electron microscopy (TEM), micro-X-ray diffraction (XRD) analysis, and Raman scattering revealed a presence of strongly structurally modified amorphous regions around the void-structures. We discuss issues of achieving the required resolution for structural characterization and assignment of newly formed phases of nano-crystallites by TEM, XRD, and Raman scattering from micro-volumes of modified materials enclosed inside the bulk of the host phase.

1. Introduction

Modification of materials are expected at high pressures and temperatures which applied statically [1,2] or dynamically by shock waves [3–6]. Recently graphite-to-diamond transient transition was observed on the surface of a highly oriented pyrolytic graphite after irradiation by a femtosecond laser pulse [7]. However, the sp^3 bonding lasted only for tens-of-picoseconds due to a pressure relaxation in this non-constricted on-the-surface geometry. A three-dimensional (3D) enclosure could be used to sustain a high pressure much longer [8]. Such 3D enclosure should help to retrieve meta-stable phases of shock transformed materials formed by amorphisation and shock-compression at the micro-explosion sites triggered by single tightly focused femtosecond pulses inside glasses and crystals [9]. The presence of amorphous region at the focal volume *without central void* has been recently observed by a high-resolution transmission electron microscopy (HRTEM) [10]. When the void is formed, a surrounding amorphous phase is expected to have a larger density. Also, a micro-/nano-crystallites were observed inside the amorphised volumes in sapphire at multi-pulse exposure [11]. However, there are difficulties in a post-fabrication determination of structural properties of those minute volumes due to standard grinding and polishing procedures of sample preparation for TEM observation. When void is present it becomes unreliable to obtain thin enough (~10 nm) slices of the irradiated regions in hard and brittle materials. Moreover, the sample preparation procedures can alter the interior of the sample, especially, when meta-stable forms of materials are formed inside the laser affected zone. Hence, an application of other high-resolution methods avoiding cutting and polishing is required for characterization.

Here we report on characterization of amorphous sapphire formed by fs-pulse-triggered micro-explosions inside crystalline sapphire. Structural analysis was carried out by three different techniques: transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman scattering. The merits and shortcomings of these techniques for detection of structurally modified nano-/micro-volumes of materials are revealed and discussed. The

* Corresponding author.
E-mail address: saulius@es.hokudai.ac.jp (S. Juodkazis).

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doi:10.1016/j.apsusc.2009.04.063

volume fraction of the photo-modified regions was maximized by recording extended areas (with cross sections of tens-of-micrometers) of closely-packed void-structures inside a slab of single crystal of sapphire avoiding crack formation.

2. Experimental

The voids were recorded using a standard direct laser writing (DLW) setup consisting of fs-laser and a microscope equipped with a computer controlled PZT-stage [12]. The numerical aperture of the objective lens was NA = 1.35. Three-dimensional (3D) regions of voids were formed inside the 80-μm-thick sapphire (along *c*-axis, ⟨0 0 1⟩ direction). Samples of a *z*-cut α-Al_2O_3 sapphire ($R\bar{3}c$ space group; from Shinkosha Co., Ltd.) were thinned and polished at Tecdia Co., Ltd. The irradiated volumes were separated by several micrometers from the front and back surfaces of the sample. An estimate of the volume fraction of photomodified material for a 1-μm-thick spherical shell inside the volume of a $2 \times 2 \times 2.5\ \mu m^3$ unit cell is about 43%. This was enough to avoid crack formation. The presence of voids was also confirmed by direct optical and scanning electron microscopy (SEM) observation after cleaving the sample along the void-structures. The 3D matrix of sub-micrometer sized voids was stable against formation of cracks (Fig. 1). The samples with voids recorded at 210 nJ/pulse (at the entrance of the microscope; an overall transmission of the microscope was $T \simeq 0.5$ at 800 nm wavelength) were used for X-ray diffraction experiments without any further preparation.

The micro-X-ray diffraction analysis was carried out on the beamline BL40XU at the SPring-8 synchrotron radiation facility. X-ray beam was collimated to a 5 μm diameter and illuminated onto the sample. The very same setup has a technical ability to achieve a collimated beam of a 100 nm diameter. It can technically resolve a single void, however, in this first study we aimed at maximizing the volume fraction of shock-affected regions by registering an average signal of diffraction from the 3D-matrix of void-structures in sapphire. Such XRD measurement can be compared with a structural characterization by Raman scattering in terms of detection sensitivity to any structural changes (new lines/peaks, spectral broadening, intensity change) between optically modified and undamaged regions of sapphire. In both methods, the volume is probed and signals from the modified and unmodified regions are superimposed.

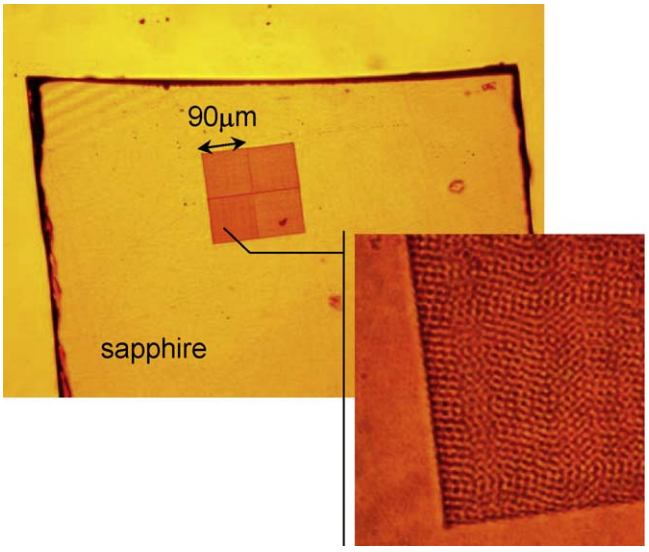

Fig. 1. An optical image of the sample with 20 layers of void planes recorded in a logpile mode. The in-plane separation of the voids was 2 μm with 1.5 μm between planes. Pulse energy was 180 nJ; focusing with NA = 1.35 lens.

The Raman scattering was measured by focusing Ar-laser (514 nm, 0.5 W) or solid-state laser (532 nm, 0.4 W) emission onto a 30 μm spot on the modified regions of sapphire. The entire volume of the void-structures (along the propagation of laser beam) was placed inside the focal region at a constant irradiance. The spectra were recorded by imaging on a triple-grating TriVista 777 spectrometer equipped with multi-channel CCD camera with a 2.5 cm^{-1} resolution.

3. Results and discussion

Fig. 2 shows a representative HRTEM image of a sharp crystalline-to-amorphous transition and its Fourier analysis. The amorphous phase was formed by a single 60 nJ/pulse. In this case, all focal volume was amorphous without presence of the central void. Very sharp transition from crystalline to amorphous was observed [13]. In order to check for the presence of new crystalline phases around the amorphous core, which exerts compressive stress to its surroundings, a Fourier analysis of the HRTEM image was carried out. The spatial frequency of 1.6 Å, which does not correspond to the known low Miller index planes defining the facets of crystalline sapphire (Table 1), was selected (a circle on FFT map). It was used for filtering the image by the following procedure. The selected region was moved numerically to the origin point of FFT map (0,0). Then the inverse Fourier transform was carried out and the resultant phase is plotted. This procedure allows to visualize the locations where there are regions of the particular selected spatial frequency. Since the selected region on FFT map was moved to the origin ($k_x = 0$; $k_y = 0$) the filtered image has no high spatial frequency. This facilitates to qualitatively visualize the amorphous and crystalline locations in the filtered image. The only phase of the particular 1.6 Å period is present in the filtered image. One can see that there was no particular localization of this phase at the edge of crystal-amorphous transition; it was present in all crystalline region (a 2π folding of the phase is a result of FFT). Most probably this phase corresponds to the high-index plane of sapphire rather to a new phase, e.g., the period of ⟨1 1 6⟩ planes is close to 1.6 Å. The precision necessary to quantitatively assign the measured period to the known crystalline periodicity was more than by a magnitude lower even for the HRTEM (Table 1). It is noteworthy, an aliasing can occur in FFT treated images and the most out-off-center diffraction peaks can be mistakenly assigned as discussed earlier [14]. This highlights limitations of TEM image analysis by FFT in identification of new phases.

It was found, that sample preparation for HRTEM alters the sample. Usually a central amorphous part surrounding the void drops out upon sample thinning, which was done by a standard grinding step of sample preparation for TEM analysis. In order to avoid artifacts in numerical analysis of TEM data as well as due to uncertainties introduced by sample preparation, an in-bulk measurements by micro-X-ray diffraction and Raman scattering were carried out.

Fig. 3 shows a typical rocking curve of a XRD pattern collected from a region with void-structures. The XRD pattern was measured by rotating the sample from 0° to 5° (see, inset of Fig. 3). Such diffraction patterns measured from the void-structures inside the bulk of crystalline phase without any specific sample preparation were obtained for the first time. The diffraction from the known sapphire planes is discernable on the image as well-defined spots. The halo regions, most probably, indicates presence of an amorphous phase, which is known to be present only around the voids [16,17].

The angular integration around the center of the XRD image was carried out to obtain the rocking curve (Fig. 3). The center of