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Effect of air on debris formation in femtosecond laser ablation of crystalline Si

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ABSTRACT

The ablation products formed by femtosecond laser irradiation of crystalline Si are investigated in detail in air at 1 atm. Ablation products possess a cotton–wool like morphology accumulated on the target surface in the vicinity of the ablated crater. Web-like links of roundish fine particles are also found in more distant regions. The particles are either single or polycrystalline Si linked with finer particulates and amorphous material. The particles are considered to be the result of a fragmentation and coalescence process of molten Si in the air. Electron beam diffraction indicates a small fraction of crystalline quartz among the debris particles. The cotton–wool-like debris are composed of an oxygen-rich Si compound with an atomic concentration ratio resembling that of SiO_2. Ablated matter in vacuum within the peripheral zone of the ablated crater predominantly takes the form of roundish particles with a molten feature. Particles found at a distance of a few millimeters from the crater are nearly spherical and composed of crystalline Si. Particles located far from the crater are likely solidified droplets of liquid Si fragmented from the crater that have cooled at a rate favorable to crystallization during flight.

1. Introduction

Much research effort has been devoted to femtosecond laser ablation of solid matter to understand the dissociation process of the solid and the expansion and coagulation of ablated matter brought about by ultra-short optical pulses. The material decomposition process begins just after an optically excited unstable state is attained in semiconductors or through the heating of the ionic lattice by hot free electrons in metals. Following the rapid expansion of ablated matter, a series of successive events such as material fragmentation, solidification, and deposition on the substrate take place. Ablation products take the form of atoms, atomic clusters, fine particles, and fragments, depending on the fluence at the depth of their origin in the laser excited volume [1–4].

In addition to these fundamental processes associated with ablation phenomena, the formation of fine particles with nanometer dimensions is attracting an increasing interest as shown in a number of previous works [5–8]. The ablation of c-Si in a H_2 gas resulted in larger fraction of crystalline particles at higher gas pressures [9], indicating that the surrounding gas reduces cooling rate of the particles. Even in the gas environment ablation of different materials such as TiO_2 formed amorphous particles [10]. These results indicate that the final format of the fine particles; crystalline or amorphous, depends on the material and laser irradiation condition such as the laser fluence and environmental gas. A complete understanding of the production mechanisms of ultrafine particles in femtosecond laser ablation is still underway.

We recently reported the performance results of micro-drilling in a Si wafer in gas [11,12] and vacuum [13,14]. Our results showed that very sharp hole edges can be obtained in vacuum. However, ablated holes in air degraded through a significant accumulation of debris. This debris consists of particulates in rugged shapes with sizes of tens of nanometers overlaid with thick layers of aggregates resembling cotton–wool [12], which has been shown to be rich in oxygen [14].

In the present paper, we describe the results of our successive work on the ablation of crystalline Si by femtosecond laser pulses in air and vacuum. We identify the effects of air on debris formation by comparing the shapes, structures, and chemical compounds resulting from the ablation products in both environments.

2. Experimental

Fig. 1 presents the experimental setup employed in this work. A femtosecond laser beam, at a 500 Hz repetition rate and wavelength of 786 nm, was focused on a Si plate with a (1 0 0) orientation positioned perpendicularly to the sample platform in vacuum at a residual pressure of 0.4 Pa. A focusing optical system consisted of

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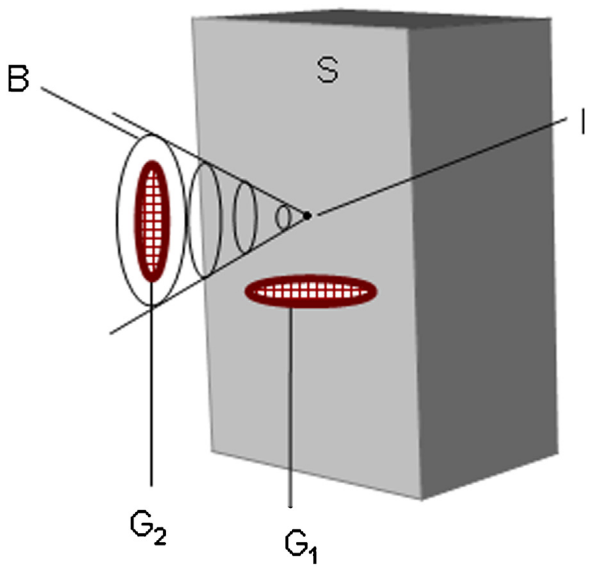

Fig. 1. Experimental setup with micro grids G_1, G_2, Si plate S, Bessel Gaussian laser beam B, and focal point I.

two axicons and a spherical convex lens. This configuration enabled the formation of the focal spot of the laser beam with the diameter of ≤1 μm on the sample surface located ~3 cm from the vacuum chamber window [14] for the sub-micron machining without deteriorating the focusing optics. The ablated crater and fine particles formed on the Si plate were observed with a field emission scanning electron microscope (FESEM, Hitachi S-4800). Micro grids for transmission electron microscopy (TEM) were positioned 3 mm (G_1) below, and 15 mm (G_2) in front of the focal spot on the Si plate [9]. G_2 was attached on the inner surface of the window glass plate of the vacuum chamber, so that it is placed at the center of the donut beam emerging from the second axicon. Ablation products collected on G_1 and G_2 were observed with a TEM and scanning tunneling electron microscope (STEM) (Hitachi HF-2200TU). Elemental compositions were identified using energy dispersion spectroscopy (EDX; NORAN VANTAGE) as furnished with the TEM.

3. Results

Laser pulses with pulse energy and duration of 0.67 μJ and 172 fs, respectively, irradiated the Si substrate in the vacuum, forming a crater with a diameter of ~1 μm after accumulating 500 shots. The estimated laser fluences at the edge and the center of the crater were ~0.25 J/cm^2 and ~0.5 J/cm^2, respectively. Fig. 2(a) shows the debris distribution ~1 μm from the right edge of the crater. This figure indicates that the debris is composed of mostly roundish nanoparticles that are deformed more prominently with increasing size. The vacuum chamber was then moved horizontally with the same vacuum level, forming an array of craters on the sample, to ablate a sufficient amount of material to ensure debris was collected on the TEM grid. Fig. 2(b) presents a particle trapped on the TEM grid G_1, showing the appearance of a nearly perfect sphere. Fig. 2(c) provides a magnified view of the squared area, predominantly revealing crystalline features with (1 1 1) Si lattice planes.

Laser irradiation of the sample was performed by introducing air to the vacuum chamber at 1 atm. Fig. 3(a) presents the ablated pattern formed from a pulse energy and pulse duration of 1.0 μJ and 172 fs, respectively. The ablated pattern shows a dense

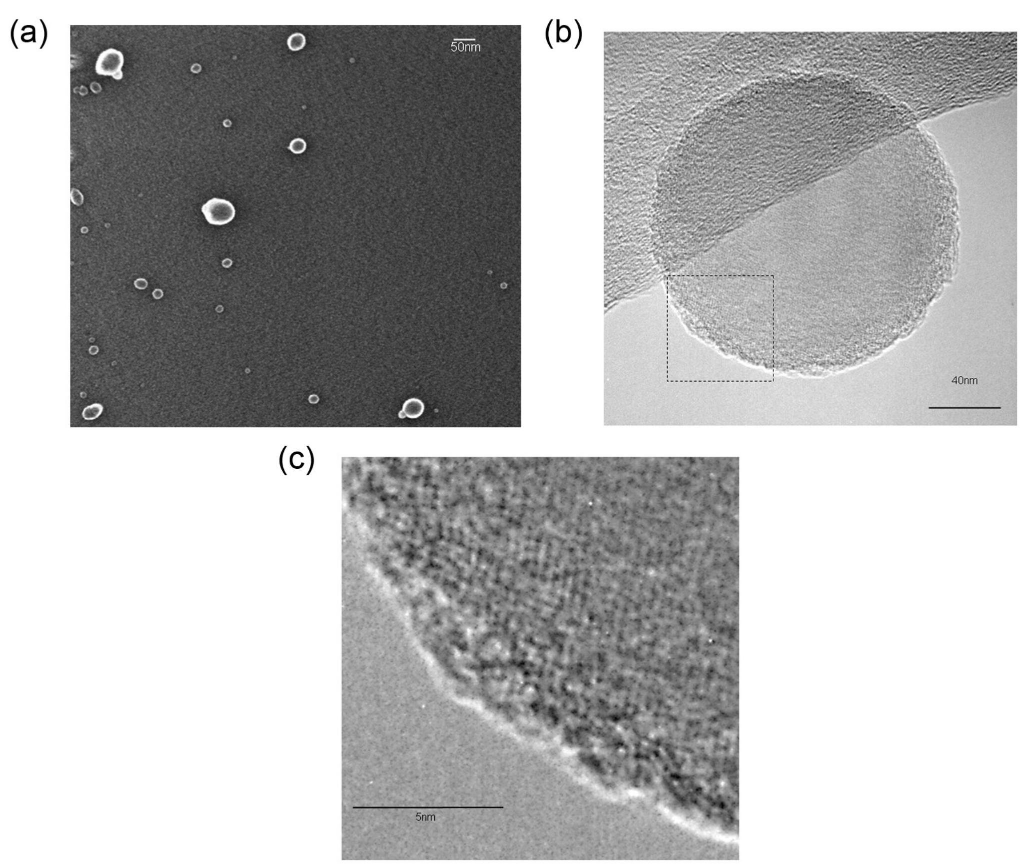

Fig. 2. Nanoparticles (a) distributing at ~1 μm from the crater edge produced by 500 pulses of 0.67 μJ with a 172 fs duration in vacuum with the residual pressure of 0.4 Pa, (b) captured on G_1 by forming arrays of craters, (c) further magnified view of the square area of (b).