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Generation of nanoparticles at a fluence less than the ablation threshold using femtosecond laser pulses

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ABSTRACT

Femtosecond laser machining of crystalline Si in vacuum resulted in the formation of pillars and particles of ~100 nm in size at the wall surfaces and the periphery of the ablated hole. These structures were created at a laser fluence below the ablation threshold. The nanopillars and nanoparticles appear to grow from the target surface. The target surface near the particles showed molten features with descending height, indicating significant mass transport from the surface layer to the particles. The nanopillars and nanoparticles likely formed as a result of successive crystal growth processes including amorphization of the laser-irradiated target surface, followed by crystalline nucleation, melting of the amorphous Si surrounding the crystalline particles, and liquid Si creeping over particle surfaces leading to an increase in particle size. By repeating these processes, the particles grow in cumulative laser shots. These particles are the major debris components distributed near micron-sized holes formed at the ablation threshold fluence in vacuum.

1. Introduction

Femtosecond laser machining of solid state matter is used for ablating holes and grooves tens of microns in size on the surface of semiconductors, metals, and transparent solids. Due to the weak thermal effects and high peak power of femtosecond laser beams, the effects of material removal are limited to the laser-irradiated domain. This technique enables the possibility of machining a solid body with micron to sub-micron dimensions. Recently, the result of machining a groove with sub-micron width using a femtosecond laser was reported [1]. Reducing the machining scale to a micron or below is now within the range of application for sub-micron fabrication. From this point of view, a detailed study of the machining performance, such as the resulting interior structure and peripheral zone of a machined hole, is required.

Our preliminary study suggested that fundamental aspects of laser-matter interaction are reflected in the morphology of machined structures. We pursued laser-machining on the submicron scale in air and vacuum, and showed that machining in air degrades performance by leaving molten features on the laser-irradiated surface and leads to the accumulation of cotton-wool like debris [2,3]. Fine particles are also produced and accumulated as debris in the periphery of the machined hole in vacuum [3]. In the present work, the origin of fine particle debris produced during the ablation of crystalline Si in vacuum is investigated. We found that pillars and particles with sizes of ~100 nm grow during laser irradiation at a fluence below the ablation threshold. These structures represent a major component of debris particles distributed along the hole periphery.

2. Experiment and results

Experimental details can be found in a previous report on the micro-ablation of solid Si [3]. Femtosecond laser pulses were focused on the sample surface with dual axicons and a convex single lens. A Si plate with a (1 0 0) surface orientation was used as a test sample for machining. The sample was placed perpendicularly to the plane of the platform in a vacuum chamber at 0.4 Pa. The femtosecond laser was operated at 500 Hz with wavelength, pulse energy, and duration of 786 nm, 0.67 μJ, and 176 fs, respectively.

Fig. 1(a) shows a micrograph of the ablated hole from 500 cumulative laser pulses, as observed with a field emission scanning electron microscope (FESEM, Hitachi S-4800). The laser fluences at the edge and the center of the hole are ~0.25 μJ/cm^2 and ~0.3 μJ/cm^2, respectively. The opening of the hole is ~1 × 2 μm and is covered with fine particles of dimension <100 nm. On the edge of the hole trenches regularly aligned in perpendicular to the laser polarization with a periodicity of ~660 nm, were formed. The debris is mostly round particles, with some weakly oval-shaped particles. Debris accumulation is found only in the vicinity of the ablated hole.

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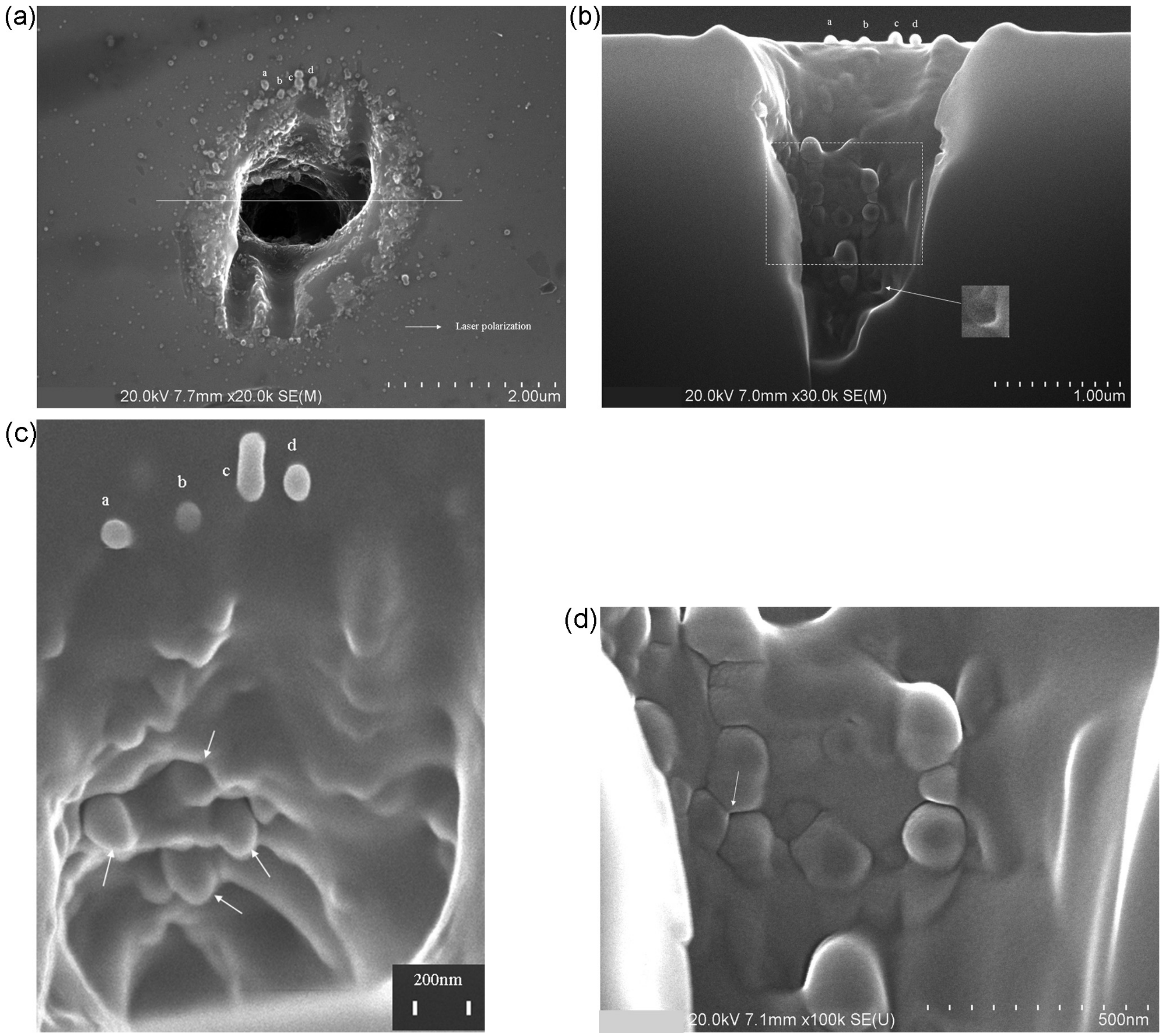

Fig. 1. (a) Ablated pattern formed in vacuum by 500 laser pulses with a wavelength, pulse energy, and duration of 786 nm, 0.67 μJ and 176 fs, respectively. (b) Vertical section of the hole milled along the line shown in (a). The particles labeled a, b, c, and d are the same particles in (a). The inset is a brightness enhanced view of the dent after the departure of a particle. (c) The ablated hole viewed from 45° above. The arrows indicate pillars formed perpendicular to the wall of the hole. (d) Magnified view of the area encircled by the square in (c). The arrow indicates grain boundaries intersecting at an angle of ∼120°.

A vertical section of the ablated hole was obtained by milling the Si plate with a focused ion beam (FIB; Hitachi FB-2000A) along the line shown in Fig. 1(a). Fig. 1(b) presents a cross-sectional view of the hole observed with the FESEM. The particles labeled a, b, c, and d in Fig. 1(b) correspond to the same particles in Fig. 1(a). The cross-sectional view shows that the fine particles a–d on the edge of the hole opening are partially molten, and that round particles with sizes of ∼150 nm have nearly been formed in the squared area on the wall of the hole. The particles are preferentially formed on the wall where the incoming laser light is in an s-polarization state. A vacant hole left by ejecting a particle is indicated by the arrow and the inset with increased brightness and contrast. Fig. 1(c) is a 45° view of the hole, showing protrusions of pillars, with some nearly detached from the wall, as indicated by arrows. A magnified view of the area enclosed by the square in Fig. 1(b) is presented in Fig. 1(d). This picture clearly shows that the wall surface is filled with humps and swells, and that grains with sizes of ∼100 nm are growing. The arrow indicates that the grains have boundaries intersecting at an angle of ∼120°.

Fine particles formed from a laser irradiation fluence below the ablation threshold are observed in a separate experiment. Fig. 2(a) is a view of the ablated hole after 500 shots of irradiation on c-Si with a pulse energy and duration of 0.45 μJ and 220 fs, respectively. The laser fluences at the edge and the center of the hole are ∼0.25 μJ/cm^2 and ∼0.27 μJ/cm^2, respectively. This result shows that humps and pillars are growing from the wall of the hole, and the edge and the darker peripheral zone of the hole, often referred to as the heat affected zone, are covered with fine particles. The particulates resemble the remnants of ablated droplets. The circled region shows grains separated by 90° boundaries. Round white patches with sizes similar to the fine particles are distributed outside of the heat affected zone as well, for example as shown by the arrow. Periodically aligned faint stripe patterns also appear at the upper and under sides of the hole periphery. The fine structure of