Nanoparticle formation by the debris produced by femtosecond laser ablation of silicon in ambient air

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Abstract

The debris produced by femtosecond laser ablation (180 fs, 775 nm, 1 kHz) of Si in ambient air is deposited around the ablated craters in a circular zone with diameters between ~40 and 300 μm for laser fluences (F) in the region F=0.2–8 J/cm². The debris consists of nanoparticles. The mean height of the nanoparticles increases with laser fluence (from ~70 to 500 nm for fluences in the range F=0.25–4.38 J/cm²) but at high fluences (F=8 J/cm²) becomes equal to ~170 nm. The average horizontal dimension of the nanoparticles increases with laser fluence. Their average vertical dimension increases in proportion to their average horizontal dimension, but at high fluences becomes much smaller than their corresponding average horizontal dimension. The nanoparticles were found to be single crystals with d spacing of 1.71±0.08 Å (corresponding to {311}).

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1. Introduction

Laser ablation of materials results inevitably in the formation of debris due to the volume of the material which is removed by the laser beam. A number of studies of the morphological, structural and optical properties of the debris which is formed following long (ns) or short (fs) pulse laser ablation of a number of different materials ranging from metals, dielectrics and semiconductors, has been reported [1–7]. In particular the debris which was accumulated around the ablated areas as a backward-deposited layer in the case of single pulse ns or fs laser ablation (248 nm/30 ns or 248 nm/500 fs) of steel in air using a beam with rectangular profile (spot size of 2×1 mm²) at atmospheric pressure, was shown to consist of nanoparticles with an average size of 4.5 nm and 2.92 nm respectively [2,3]. Silicon nanoclusters with sizes ranging from 1 to 5 nm were produced by ns laser ablation (193 nm/15 ns) of the silicon target in a He atmosphere and the mean size of the clusters was found to increase from 1.3 to approximately 2.7 nm with laser fluence in the interval from 1 to 3 J/cm² [4]. The nanoclusters were shown to have size dependent photoluminescence properties. Nanoparticles with a shape and size widely distributed ranging from tens of nanometers to as high as approximately 500 nm were found in the case of femtosecond laser (800 nm/50 fs) ablation of aluminium in vacuum (10⁻⁴ Torr) [5]. The debris deposition profile characteristics around the ablated craters, in the case of ablation of zinc borosilicate glass (266 nm/6 ns) [6] or polyimide (248 nm/15 ns) [7] under air or inert gas atmospheres with different pressures, respectively, was found to follow the predictions from the classical shock-wave expansion theory.

In this letter we investigate the deposition characteristics and morphological features of the debris which is accumulated around craters ablated by using femtosecond laser irradiation (180 fs, 775 nm, 1 kHz, fluences (F)=0.2–8 J/cm²), onto a silicon substrate surface in ambient air. In particular, we demonstrate that the debris consists of single crystal Si nanoparticles with mean height ranging from ~70 to 500 nm for fluences in the range F=0.25–4.38 J/cm² and ~170 nm at high fluences (F=8 J/cm²). We have also observed
previously by TEM, nanoparticles with diameters ranging from ~20 nm to ~1 µm and with an average diameter of ~300 nm, produced by the debris which was generated during femtosecond laser microstructuring of alumina ceramic in ambient air [8].

2. Experimental details

A Clarke-MXR 2010 femtosecond laser system was used for the ablation, which delivers ~1 mJ per pulse at 1 kHz rep. rate and λ = 775 nm, 180 fs pulse length and observed bandwidth Δλ ~5.5 nm. The output is attenuated before being directed to the input aperture of a scanning galvanometer with 100 mm focal length fθ lens. The spot diameter 2W0 (1/e2) at the focal plane was measured to be ~30 µm by plotting the squared diameter of craters ablated with different laser energies versus the logarithm of energy. The substrates were mounted horizontally and the substrate surface could be brought to the focal plane using a precision vertical lab jack with 10 µm resolution. The target substrate was irradiated with the laser beam at normal incidence with N=100 pulses and with pulse energies from ~1 to ~25 µJ (F=0.25–8 J/cm²). Optical microscope images were taken of the ablated regions on the sample surface by using white light side illumination. Atomic Force Microscopy (AFM) imaging was performed on the debris produced around the ablated region with a Veeco CP-II instrument in non-contact mode using Si cantilevers with a given radius of curvature less than 10 nm (Tap300). The AFM images where the debris is in the form of a continuous deposit (agglomeration of nanoparticles) were analysed by using the software ImageJ with the module for watershed segmentation [9] to find the boundaries between touching particles and reveal particles inside agglomerates. For

![Fig. 1. Optical microscopy images of the debris deposited around craters ablated onto the Si substrate surface with 100 pulses and different fluences of: (a) 0.51, (b) 1.32, (c) 2.33, (d) 3.78, (e) 5.56, and (f) 7.96 J/cm², respectively. (g) diameter of the total circular zone of the debris deposition (circle points) (extracted from the images in (a)–(f)) and of the corresponding ablated craters (square points), versus peak laser fluence (bottom scale) or peak laser power density (top scale).](image)
TEM measurements, the debris was collected on a carbon coated grid whose edge was placed at a distance of ~30 µm from the centre of the ablated hole. TEM was performed with a JEOL JEM-2000FXII instrument equipped with EDS Genesis 4000 system to enable also acquisition of EDX spectra. Field Emission Scanning Electron Microscopy (FESEM) was done with a Zeiss Supra 40VP instrument. Undoped (001) Si wafers were used with resistivity $>8000 \Omega$ cm and thickness of ~250 µm. The substrates were cleaned by sonicating them for 15 min each time on acetone, isopropanol and methanol.

3. Results and discussion

3.1. Formation and deposition of the debris around the ablated region

Fig. 1 (a)–(f) shows typical optical microscope images of the craters and surrounding areas, on the ablated target surface, obtained at laser fluences in the range 0.51–7.96 J/cm², as indicated.

The debris which accumulates in the regions of the sample surface around the craters is shown. It is readily seen that the debris in the form of a continuous deposit of matter onto the substrate, is deposited to a good approximation (error $\leq 5\%$) in a circular area (zone) around the ablated craters. A small amount of debris, in the form of a non-continuous deposit onto the substrate surface, is deposited beyond that area even for the lowest fluences used. In the optical microscopy images of the area around the craters, this non-continuous deposit is seen more easily in the images (e) and (f) corresponding to craters ablated using fluences $F > 5$ J/cm².

Deposition of debris around the ablated craters following laser irradiation of the target can be described on the basis of the shock wave theory [10]. The plasma plume which is created following laser irradiation of the target, consisting of a high density of energetic species (neutral Si atomic clusters and their cations [11]), is accelerated outward from the sample surface compressing the surrounding air molecules. A shock wave is created which exists as a high pressure front (shell) of heated and compressed air molecules between the plume and the surrounding air. At a critical radius $R_B$ where the pressure in the blast wave equals the equilibrium ambient air pressure $P_0$ the expansion of the blast wave ceases, degenerating into a sound wave [10,6] (at $t \sim 100$ ns [12]). During its expansion, the pressure in the plume drops and as a result the plume front slows down and separates from the faster moving shock wave front. Eventually, the plume front reaches a radius $R_P$ where the expansion stops. When the shock weakens and the inner gas cools by conduction and radiation, the ambient gas flows back into the inner region. This inward flow effectively drags and re-deposits the debris particles of the plume onto the substrate surface. From the images in Fig. 1 one can see that for low fluences ($F < 5$ J/cm²), around the perimeter of the circular debris zone, a ring of debris with thickness of ~9–10 µm is observed (“outer ring”), which is separated by the inner circular zone with a ring of thickness ~6–7 µm (Fig. 1 (b), (c) and (d)) where almost no debris is observed. Singh et al. found previously that the plume radius $R_P$ was a fraction of the shock front radius $R_B$ [6], the debris field in the present case corresponds to the perimeter of the inner circular zone. The formation of the outer ring of debris may be explained by the presence of some ablated species within the shock wave shell [13]. The outer ring of debris is hardly distinguished in the images for very low fluences ($F < 1$ J/cm², Fig. 1(a)) due to the fact that the plume pressure reaches atmospheric pressure in a very short time before any separation of the shock wave from the ablation plume takes place and for very high fluences ($F > 5$ J/cm²) due to the non-uniformity in the energy distribution of the ablated species within the ablation plume.

In Fig. 1 (g) the diameter of the total zone where debris is observed to be deposited (including the “outer” ring distinguished in the images in Fig. 1 (b), (c) and (d)) (circle points) as well as the diameter of the
corresponding ablated crater (square points) for comparison, is plotted versus laser fluence (bottom scale) or laser power density (top scale). Each point is a statistical average of ten measurements. The total diameter of the zone where debris is deposited varies from ~40 µm to ~300 µm for laser fluences in the region $F = 0.3\text{–}8 \text{ J/cm}^2$.

3.2. Microscopic properties of the debris: size and shape of nanoparticles

In order to obtain information about microscopic properties of the debris such as shape and size of microparticulates, regions around the ablated craters where the debris is formed have been scanned. We have followed the methodology of ref. [4] where the dependence of mean cluster size versus laser fluence was determined by positioning the AFM tip at the same distance (5 mm) from the laser spot for the different fluences used. Fig. 2 shows typical AFM images of the debris formed around craters ablated onto the sample surface by using fluences: 0.25 (a) (5×5 µm$^2$ image), 0.64 (b), 0.90 (c), 4.38 (d) (10×10 µm$^2$ images) and 8 J/cm$^2$ (e) (20×20 µm$^2$ image), (g) (50×50 µm$^2$ image) and (h) (30×30 µm$^2$ image). (f) shows watershed segmentation of image (e).

The images in Fig. 2 (a)–(e) were taken at a distance of ~5 µm from the edge of the ablated crater, on an area where the debris is in the form of a dense deposit covering completely the substrate. However, the images in Fig. 2 (g) and (h) were taken on an area outside of the optically visible debris zone on the high fluence ablated crater (distance ~150 µm) where, due to scattering of ablated matter the debris is in the form of isolated deposits onto the substrate. The image in Fig. 2 (h) was taken at a distance from the border of the debris zone further away than the distance at which the image in Fig. 2 (g) was taken (where the density of deposits becomes lower). It is readily seen that the debris in fact consists of nanoparticles which appear on the 2-D images as circles.

Height distribution histograms of the AFM images were found to follow a normal Gaussian distribution consistent with the fact that many independent effects additively contribute to each measurement of height. In Table 1 results are summarized for the mean height value ($h_0$), standard deviation ($\sigma$) and FWHM ($\Gamma$) of the distribution versus laser fluence. It is seen that for low fluences ($F = 0.25, 0.65$ and 0.90 J/cm$^2$), $h_0$ takes the values of 74, 221 and

<table>
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<th>Image (Fig. 2)</th>
<th>$F$(J/cm$^2$)</th>
<th>$I$(W/cm$^2$)</th>
<th>$h_0$(nm) ± $\sigma$(nm)</th>
<th>$\langle \Delta x \rangle$ (nm)</th>
<th>$\langle \Delta y \rangle$ (nm)</th>
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<td>(a)</td>
<td>0.25</td>
<td>1.38×10$^{12}$</td>
<td>74 ± 20</td>
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<tr>
<td>(b)</td>
<td>0.65</td>
<td>3.61×10$^{12}$</td>
<td>221 ± 67</td>
<td>342 ± 127</td>
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<tr>
<td>(c)</td>
<td>0.90</td>
<td>5.00×10$^{12}$</td>
<td>305 ± 84</td>
<td>391 ± 145</td>
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<tr>
<td>(d)</td>
<td>4.38</td>
<td>2.43×10$^{13}$</td>
<td>478 ± 103</td>
<td>413 ± 152</td>
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<tr>
<td>(e)</td>
<td>8(agg)</td>
<td>4.44×10$^{13}$</td>
<td>175 ± 47</td>
<td>549 ± 92</td>
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</tr>
<tr>
<td>(f)</td>
<td>8(isol)</td>
<td>4.44×10$^{13}$</td>
<td>37 ± 1.3</td>
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Fig. 3. TEM images (a), EDAX spectrum (b), X-ray diffraction pattern (c) and SEM images (d), (e) of the nanoparticles. (d) corresponds to a top view of the substrate while (e) corresponds to the substrate tilted by 50°.
305 nm and 478 nm for intermediate fluence \((F = 4.38 \text{ J/cm}^2)\) increasing with fluence (as well as the distribution width), while at a high fluence \(F = 8 \text{ J/cm}^2\) \(h_0\) takes the value of 175 nm. For a high fluence \(F = 8 \text{ J/cm}^2\), for the isolated nanoparticles deposit, \(h_0\) has the value of 37 nm. In Table 1 results are also reported of the average horizontal \((\langle \Delta x \rangle)\) and vertical \((\langle \Delta y \rangle)\) size of the particles. It is observed that the horizontal size of the nanoparticles is determined to be larger than their vertical size. Thus we conclude that in the case of femtosecond laser ablation of Si, in ambient air, it is possible to obtain nanoparticle debris of oblate disk shape (platelets) (with horizontal diameters larger than their vertical sizes). For the isolated particles deposits (AFM images shown in Fig. 2 (g) and (h)) the dimensions of the nanoparticles were determined by following a simple tip deconvolution geometrical formula (to account for the “tip effect” in AFM images consisting of isolated particles) which predicts that when a spherical object with height \(\Delta y_m\) is imaged with a spherical tip with diameter \(d\), the object will always appear to have an apparent width \(w = \sqrt{4(\Delta y_m) d}\) [14].

Even assuming that the tip maintains its minimum given diameter of 20 nm (no wearing of the tip) and after deconvolution of the measured horizontal dimensions of the particles on the images in Fig. 2 (g) and (h), the horizontal dimensions of the nanoparticles are still determined to be larger than their vertical sizes. By further assuming that the real half horizontal size of a nanoparticle in the case that the nanoparticle is not spherical, is no less than 2/3 of its apparent size, the real horizontal diameter of the nanoparticle (deconvoluted horizontal size) is estimated to be: \(\langle \Delta x \rangle \approx \frac{w + 2 \langle \Delta y_m \rangle}{3}\), where \(\Delta y_m\) is its measured horizontal diameter. By assuming a given tip diameter \(d = 20\) nm, the ratio of horizontal to vertical sizes of the nanoparticles are estimated equal to \(\sim 3.4\) and \(\sim 2.3\) for the low fluences region and \(\sim 4.5\) and \(\sim 8.9\) for the high fluence, for continuous and isolated particles deposits respectively. Larger ratios of horizontal over vertical sizes are expected by assuming larger tip diameter.

The Si nanoparticles produced here by femtosecond laser ablation of the target in ambient air have in general sizes larger than the nanoparticles produced in pulsed laser deposition (PLD) ablation of Si in high vacuum of the order of \(\sim 10^{-7}\) mbar [15,16]. This may be due to the compression of the plume of the ablated species because of the expansion in ambient air which results in a decrease of the plume density dilution rate according to the model of formation of nanoparticles by rapid expansion, quenching and subsequent fragmentation of the supercritical fluid which is created onto the target surface by the intense femtosecond laser beam [17]. Their determined ratios of long to short axis of \(\sim 2.4\) in the low fluences region of \((0.25–0.90 \text{ J/cm}^2);\) intensities of \(1.38–5 \times 10^{12} \text{ W/cm}^2)\) agrees well with the eccentricities of 1.4–6.6 determined for nanoparticles produced in PLD ablation with laser intensities in the region of \(2.9 \times 10^{17}–3.7 \times 10^{12} \text{ W/cm}^2\) \((0.30 \text{ ps}/527\) nm or 0.85 ps/1055 nm laser pulses) [18]. Observation of nanoparticles with oblate shape is consistent with the mechanism of formation of nanoparticles by direct ejection from the target (fragmentation of supercritical fluid upon expansion), deposition of the liquid droplets onto the substrate and subsequent solidification. The large values of the horizontal to vertical size ratios of the particles which are obtained at high fluences \((8 \text{ J/cm}^2,\) intensity \(4.44 \times 10^{13} \text{ W/cm}^2)\) can be understood by the fact that the average size of the particles at this high fluence is also very large and thus it takes longer time for the larger mass to cool down to room temperature rather than for particles with smaller mass which are observed at the low fluences region, thus larger deformation of a particle is expected at high fluences. Also the intensity of \(4.44 \times 10^{13} \text{ W/cm}^2\) which we use here is very close to the intensity of \(\sim 5 \times 10^{13} \text{ W/cm}^2\) at which the most effective nanoparticle production was predicted to occur [5].

3.3. TEM and FESEM imaging of the observed nanoparticles

To get information about the structure and elemental composition of the observed nanoparticles the debris was deposited onto a carbon coated TEM grid which was placed near the ablated region. In TEM images shown in Fig. 3 (a) (corresponding to the high fluence crater) the nanoparticles appear as circles with diameters in the region of \(\sim 400\) to 600 nm. EDAX analysis (typical spectrum shown in Fig. 3 (b)) shows that the nanoparticles are composed of Si with a small percentage of oxygen (SiOx). The electron diffraction pattern (shown in Fig. 3 (c)) also confirms that the nanoparticles are single crystals with d spacing of 1.71±0.08 Å (corresponding to \{311\}).

Finally, FESEM images of the debris on the substrate, ablated with high fluence where the debris appears as isolated nanoparticles (corresponding AFM images shown in Fig. 2 (g), (h)), are shown in Fig. 3 (d) and (e). In the image of Fig. 3 (d) corresponding to a normal view of the substrate, the nanoparticles appear circular. The oblate shape of the nanoparticles however, is revealed in the image of Fig. 3 (e) which was taken with the substrate tilted by 50°, supporting AFM measurements of the lack of sphericity.

4. Conclusions

The debris following femtosecond laser ablation of Si in ambient air is deposited into circular patterns around the ablated crater, consisting of a circular zone and a thin circular ring in its perimeter for fluences in the range of 1.32 to 3.78 J/cm². The debris consists of nanoparticles. The mean height of the nanoparticles increases with laser fluence (from \(\sim 70\) to 500 nm for fluences in the range \(F=0.25–4.38 \text{ J/cm}^2)\) but at high fluences \((F=8 \text{ J/cm}^2)\) becomes equal to \(\sim 170\) nm. We have demonstrated that also in this case of femtosecond ablation of silicon in ambient air, it is possible to obtain nanoparticles of oblate shape similar to the case of nanoparticle thin films deposited by the technique of pulsed laser deposition. The size and shape of the nanoparticles can be tuned and controlled also by adjusting appropriately the laser ablation energy.

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