Pulsed laser-assisted surface structuring with optical near-field enhanced effects

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(Received 27 December 2001; accepted for publication 25 June 2002)

The effects of optical resonance and near field in the interaction of transparent particles on a substrate with laser light have been examined experimentally and theoretically. It is found that pits can be created at the contacting point between the particle and the metallic surface by laser irradiation (KrF, $\lambda = 248$ nm) with a single pulse. The influence of the particle size and the laser fluence on the structuring of the surface has been investigated. The size of the particle ranges from 1.0 μm to 140 nm in diameter. The morphologies of the holes created have been characterized by an atomic force microscope and a scanning electron microscope. For constant laser fluence, the created hole is sensitive to the particle size. For higher-laser fluence, the corresponding hole becomes larger and deeper. With a low fluence of 300 mJ/cm^2 and for 140 nm particles, the lateral dimensions of created pits can be down to 30 nm. With a high fluence of 750 mJ/cm^2 and 1.0 μm particles, the diameter and the depth of created holes are about 350 and 100 nm, respectively. Theoretical calculations and an accurate solution of a boundary problem indicate that incident light could excite some resonance modes inside the particle and produce enhanced light intensities on the contacting area (substrate surface). The light intensity on the contacting area is nonuniform and sensitive to the particle size parameter. Experimental results are explained and are very consistent with those of theoretical calculations. The experimental results also provide direct evidence of the optical resonance and near-field effects in the interaction of transparent particles on the substrate with laser light. [DOI: 10.1063/1.1501768]

I. INTRODUCTION

The current trend towards submicrometer structures creates the need for methods and technologies of surface structuring and has attracted intense research in recent years. As the traditional masking approach in optical lithography is limited to a minimal resolvable feature size of half wavelength of the light $\lambda/2$ and always requires a complex system and high cost, a lot of alternative techniques have been developed. One approach involves illuminating the tip of a scanning tunneling microscope or an atomic force microscope (AFM) with a pulsed laser. Structures with lateral dimensions below 30 nm and therefore well below $\lambda/2$ could be produced undemeath the tip.[1–5] It was proposed that the strong enhancement of electromagnetic field in the vicinity of the tip is responsible for this nanoprocessing.[4–7] Thus, the setup seemed to be promising for the study of field-enhancement effects at sharp tips, a question of great interest in optics and surface structuring applications.

Another approach involves the illumination of micrometer and submicrometer sized spheres, which should allow the study of field-enhancement effects as well as their application for nanolithography process. Some authors have reported the appearance of particle-induced damage in the irradiated surface area during dry laser cleaning of irregularly shaped Al_2O_3 particles from glass.[8,9] Recent experiments have shown that light enhancement can produce a hot spot, resulting in the formation of a small pit on a silicon substrate using femtosecond or nanosecond pulsed lasers.[10,11] For spherical particles, it is known[12] that they may act as spherical lenses and therefore increase the laser intensity if their diameter is bigger than the laser wavelength. If the diameter of spherical particles is smaller than the wavelength, field enhancement at particles may occur according to the Mie theory.[13–16] A fascinating physical phenomenon can be expected to take place in the effects related to near-field focusing of the irradiation by particles with sizes comparable with laser wavelength. In this study, nanostructures fabricated on metallic surfaces are investigated systematically using particle-enhanced laser irradiation. Pit arrays were created. The dependence of pit diameter and depth on the particle size parameter or laser fluence has been investigated. The morphologies of the features created were characterized by an AFM and a scanning electron microscope (SEM). Theoretical calculations and an accurate solution of a boundary-value problem indicated that incident light could excite some resonance modes inside the particle and produce enhanced light intensities on the contacting area. These calculation results can give a good explanation of many experimental phenomena in laser-assisted structuring of the surface as presented in the following sections.

II. EXPERIMENTAL DETAILS

Monodisperse silica (SiO_2) and polystyrene (PS) spheres with diameters in the range of 140 to 1000 nm were

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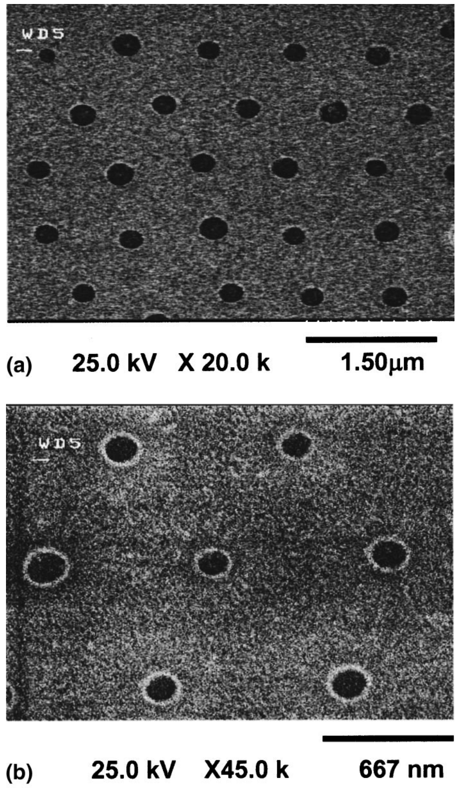

FIG. 1. (a) and (b) SEM image of periodic pit arrays formed after illumination of isolated 0.95 μm SiO_2 particles on an Al surface by a single pulse with a laser fluence of 300 mJ/cm^2.

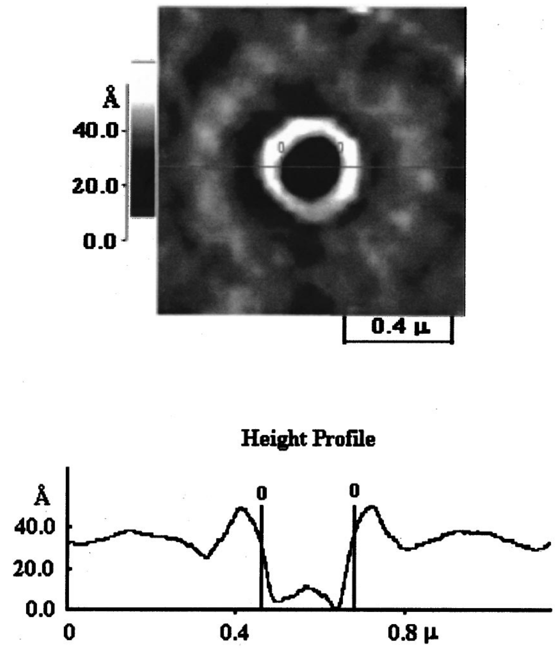

FIG. 2. AFM image and depth profile of a pit formed after illumination of isolated 0.95 μm SiO_2 particles on an Al surface by a single pulse with a laser fluence of 300 mJ/cm^2.

used. These particles are transparent to the ultraviolet light. Colloidal particles can be deposited onto various materials including polymeric, biological, and semiconducting materials. Hexagonally closed-packed colloidal monolayers can be directly prepared on to the surface by a spin-coating or a self-organizing process. The relevant techniques have been described in detail in.[17,18] In this work, we only want to study the mechanism of the formation of nanostructurse on the surface and the relative phenomena. In the preparation of our samples, monodisperse SiO_2 or PS spheres were applied to the sample after the particle suspension had been diluted with deionized water. Isolated spheres at any desired concentration onto the substrate were deposited by controlled application of a colloidal suspension. Aluminum films (35 nm in thickness) on silicon substrates were used as samples and deposited by the sputtering method. The light source was a KrF excimer laser with a wavelength of 248 nm and pulse width of 23 ns. The laser fluence used was in the range of 100 to 800 mJ/cm^2. The $25\,\mathrm{mm}\times5\,\mathrm{mm}$ rectangular laser spot has a uniform light intensity. Compared with the other lasers such as femtosecond lasers, excimer lasers have a larger beam size. The laser beam was incident normally on the sample with particles on the surface. Each sample was treated using a single laser pulse. The surfaces before and after laser treatment were observed with a high-resolution optical microscope. During the laser irradiation, it was found that most of particles were removed from the sample surface. The sample was further ultrasonically cleaned before AFM and SEM measurements were done.

III. RESULTS AND DISCUSSION

A. Influence of particle size parameter on surface structuring features

The first sample reported is a SiO_2 colloidal monolayer on an Al surface. The diameter of the SiO_2 particles is 0.95 μm with a deviation limited to a range of ±5%. Figure 1(a) shows a typical SEM morphology of a periodic pit array, formed after illumination of the colloidal monolayer on the Al surface with a single pulse. The laser fluence was 300 mJ/cm^2. The periodic pit array reflects the previous positions of the colloid spheres on the surface. With higher magnification, SEM analysis shows that the diameter of the created hole is about 190 nm shown in Fig. 1(b). The resultant holes are inhomogeneous in size to some extent. There is small change in the dimensions of the created holes. The depth profile of the hole is shown in Fig. 2. It is revealed that the depth and the diameter of the hole are about 3 and 220 nm, respectively. The second sample consists of a SiO_2 colloidal monolayer with a particle size of (0.47 ± 0.02) μm on an Al surface. Holes were also created on the Al surface after laser treatment by a single pulse with a laser fluence of 300 mJ/cm^2. Figures 3 and 4 show the AFM image and the depth profile of holes formed on the second sample, which display a size of about 86 nm in diameter and about 5 nm in depth. From Fig. 3, the resultant holes also vary in size to a certain extent. Monodisperse PS particles with a size of (140 ± 5) nm in diameter were applied to the third sample. After laser treatment by a single pulse with a laser fluence of 300 mJ/cm^2, holes were created on an Al surface and shown in Figs. 5 and 6. The depth and the diameter of the created holes are about 3 and 30 nm, respectively. Thus, for constant laser fluence, the created hole shows variation with the par-

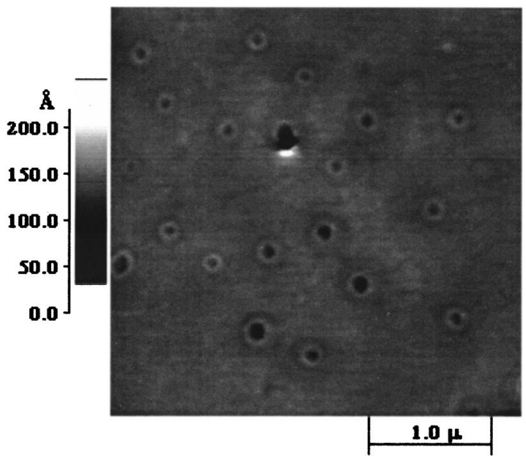

FIG. 3. AFM image of pits formed after illumination of isolated 0.47 μm SiO_2 particles on an Al surface by a single pulse with a laser fluence of 300 mJ/cm^2.

ticle size. When the particle is as small as 140 nm, the created hole becomes as small as 30 nm in lateral dimension.

B. Influence of laser fluence on surface structuring features

When the laser fluence is increased, for each kind of particle mentioned above, the hole becomes bigger and deeper. Figure 7 shows a typical AFM morphology of holes formed after illumination of the colloidal monolayer with a SiO_2 particle size of 0.95 μm on an Al surface by a single laser pulse of 750 mJ/cm^2. The hole thus formed shows a size of about 100 nm in depth and about 350 nm in diameter. For the case of SiO_2 particle size being 0.47 μm on an Al surface, with a high-laser fluence of 750 mJ/cm^2, the created structures are displayed in Fig. 8. The morphology of the features created with this high fluence is very different from those created with low-laser fluence shown in Figs. 3 and 4. From Fig. 8, at the modified points, craters are formed with the dimension close to the particle size. There is a small depressed-center pit at the center of the large crater.

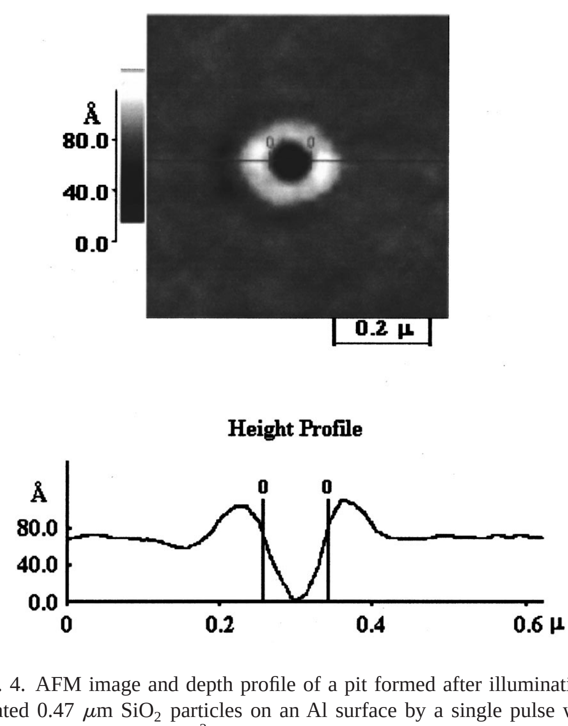

FIG. 4. AFM image and depth profile of a pit formed after illumination of isolated 0.47 μm SiO_2 particles on an Al surface by a single pulse with a laser fluence of 300 mJ/cm^2.

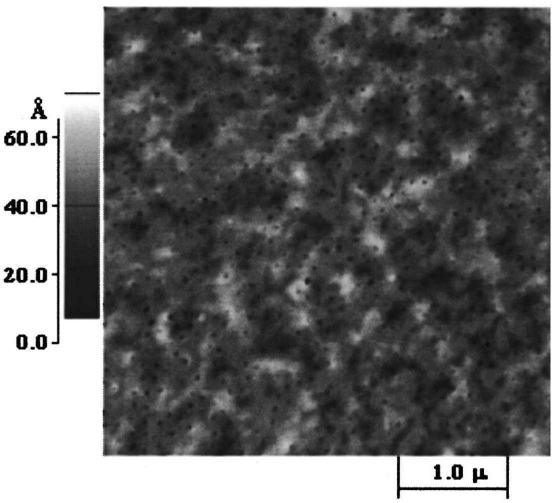

FIG. 5. AFM image of pits formed after illumination of isolated 140 nm PS particles on an Al surface by a single pulse with a laser fluence of 300 mJ/cm^2.

C. Interaction of particle and laser light: optical resonance and near-field effect

The near-field light intensity is based on the solution of a boundary problem: a sphere particle on a flat semi-infinite substrate. Recently, an appropriate method was developed to solve this problem in our previous paper.[19] An accurate solution can be derived using this method. The electromagnetic field is the sum of both the scattered and the incident fields. The calculation shows that the multireflection of the Poynting vector between the particle and the substrate results in

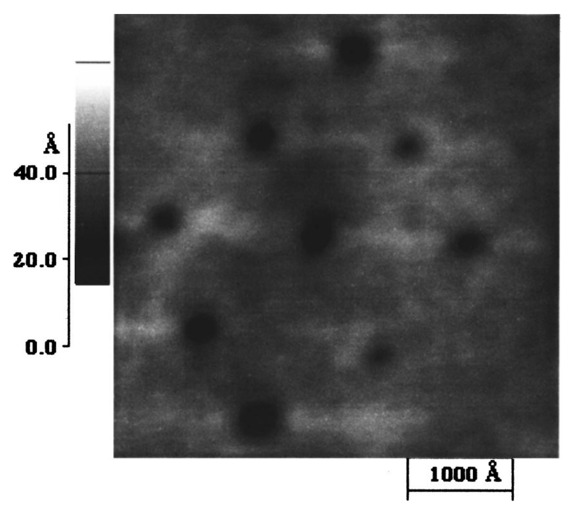

FIG. 6. AFM image of pits formed after illumination of isolated 140 nm PS particles on an Al surface by a single pulse with a laser fluence of 300 mJ/cm^2.

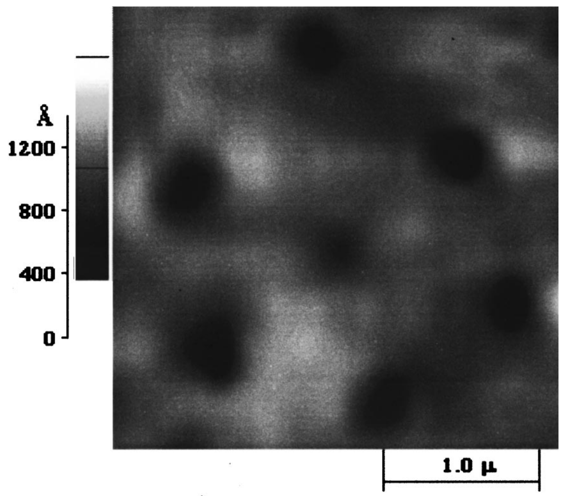

FIG. 7. AFM image of pits formed after illumination of isolated 0.95 μm SiO_2 particles on an Al surface by a single pulse with a laser fluence of 750 mJ/cm^2.

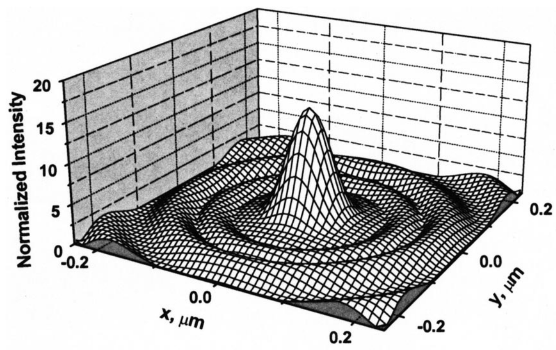

FIG. 9. Calculated field intensity near the contacting point between a 0.95 μm particle and Al surface.

higher intensity in the contacting area, and the full width at half maximum for the intensity distribution is even smaller than that from the Mie solution. For a nonabsorptive spherical particle, incident light could excite some resonance modes inside the particle as well as produce enhanced light intensities in the contacting area. In this case, the particle acts like a lens, as was shown in Refs. 12 and 19. Normalizing the incident plane wave to unity, and assuming that the wave propagates along the z coordinate, the electric vector is along the x coordinate, and magnetic vector along the y coordinate. The contacting point is set to be $(0,0,a)$, where a is the radius of the nonabsorptive sphere. Figure 9 shows the calculated field intensity on the Al surface and near the contacting point between the particle and the surface. The particle size is 0.95 μm in diameter. The relative field intensity in the area (substrate surface) of $-0.24\ \mu\text{m} \leqslant x \leqslant 0.24\ \mu\text{m}$, $-0.24\ \mu\text{m} \leqslant y \leqslant 0.24\ \mu\text{m}$ is clearly shown in Fig. 9. It is shown that when the laser normally irradiates the substrate, the laser fluence on the contacting area is greatly enhanced.

To elaborate the characteristic of the "point heating" of the substrate, we assume the near-field light intensity as the simplest Gaussian distribution of laser intensity.[20]

$$I(r,t)=I(t)e^{-r^2/r_0^2}, \tag{1}$$

where r_0 is the radius of Gaussian beam, and $I(t)$ is the pulse shape. A typical excimer laser pulse can be approximated by a smooth function:[21]

$$I(t)=I_0\frac{t}{\tau}\exp\left[-\frac{t}{\tau}\right]. \tag{2}$$

The total laser energy is given by $E=\pi r_0^2 I_0 \tau$, laser fluence in the center is given by $\Phi=I_0\tau$, and pulse duration at full width at half maximum $t_{\mathrm{FWHM}}\approx 2.446\tau$.

The comparison of the calculated near-field light intensity (after light scattering by 0.95 μm silica particle) with the Gaussian spatial profile is shown in Fig. 10. It is found that the main lobe of the calculated field fits the Gaussian beam well. The main lobe is confined to an area less than 200 nm. Since the magnitude of the side lobes is an order less than the main lobe, their contribution to the sample heating can be ignored.

The numerical calculation for the nonlinear case was carried out to investigate the thermal conduction in the

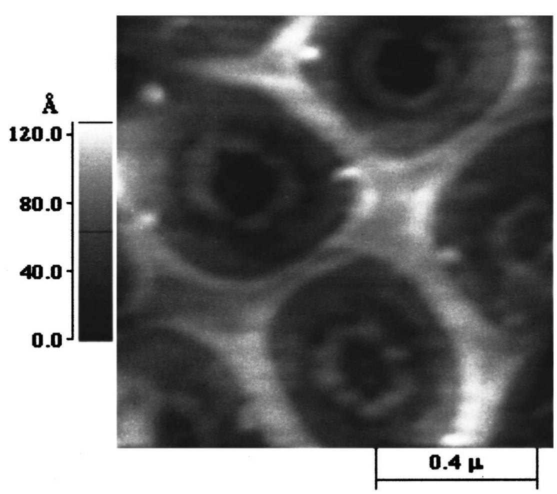

FIG. 8. AFM image of pits formed after illumination of isolated 0.47 μm SiO_2 particles on an Al surface by a single pulse with a laser fluence of 750 mJ/cm^2.

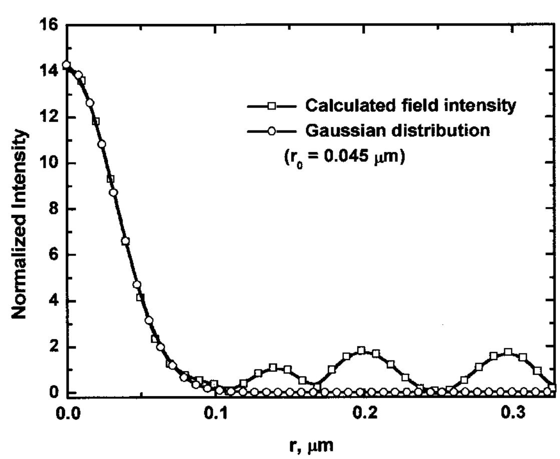

FIG. 10. Light intensity profile of the calculated field (after light scattering by 0.95 μm SiO_2 particle) and Gaussian beam.

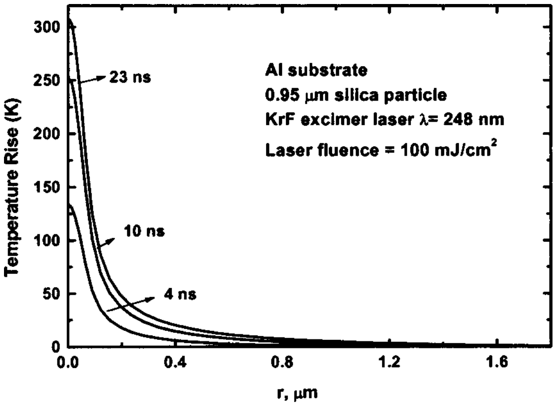

FIG. 11. Surface temperature rise at different times due to "the point" heating.

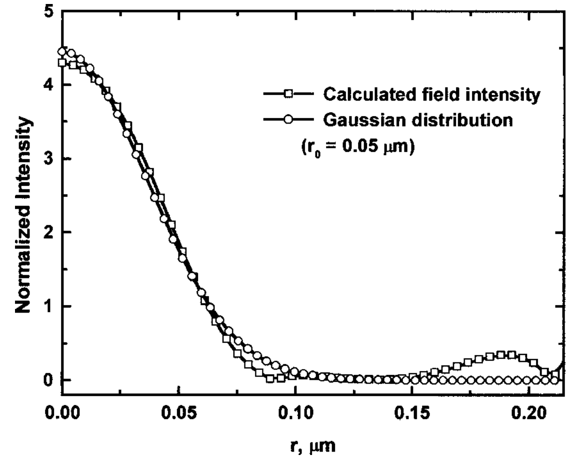

FIG. 12. Light intensity profile of the calculated field (after light scattering by 0.47 μm SiO_2 particle) and Gaussian beam.

sample. First, the near-field light intensity is assumed as the Gaussian distribution shown in Eq. (1), and the sample as a bulk Al. The results at different times t after the laser pulse begins are shown in Fig. 11. With a laser fluence of 100 mJ/cm^2, the maximal surface temperature rise is 307 K. Then, if it is considered that the sample is made of a thin metallic sheet placed on a semi-infinite Si support, one can expect a different result. A laser beam is normally incident on the smooth multilayer sample surface without particles. SLIM (simulation of laser interactions with materials)[22] of multilayer structures can be employed to calculate the thermal effects of this problem. Using the SLIM model, the calculated maximal surface temperature exceeds the equilibrium melting point of Al for a laser fluence of 300 mJ/cm^2. In our experiment, the laser beam normally irradiates the multilayer sample with particles on the surface. Incident light could excite some resonance modes inside the particle as well as produce enhanced light intensities in the contacting area. Our problem is much more complicated than that of the SLIM model. However, that model can be used to estimate the thermal effects in our system. Considering the optical enhancement = 14 (for 0.95 μm silica particles) at the contact point between the particle and the substrate, an extremely high-temperature rise can be obtained at the modified point on the sample surface.

Based on the above estimation of temperature rise in the sample surface and configurations of the pits presented in previous Secs. III A and III B, we would attribute the formation of these pits to the occurrence of rapid melting or evaporation in nanosized domains of the sample during laser irradiation. From Fig. 11, it is clearly seen that in the pulse duration, the temperature rise is localized in a small region less than 200 nm, the same size where the main resonance occurs. As is shown in Figs. 1–3, the hole created with the SiO_2 particle (0.95 μm) also has the same size as that of the region where the main resonance or heating occurs. Therefore, the main resonance mode excited by the SiO_2 particle (0.95 μm) contributes to rapid melting or evaporation in a small domain, resulting in the formation of the hole at this hot spot.

The light enhancement is due to the excitation of optical resonance modes in the particles.[23–25] The light enhancement is very sensitive to particle size. Figure 12 displays the calculated field intensity for a particle size of 0.47 μm. Comparing both cases of particle sizes (0.95 and 0.47 μm), shown in Figs. 10 and 12, respectively, both main resonance modes are confined to regions with almost the same size. However, for the latter, the light enhancement is much smaller. With a low-laser fluence, only a part of the main resonance light intensity near its center contributed to the creation of holes with a size of about 86 nm in diameter shown in Figs. 3 and 4. With a high-laser fluence of 750 mJ/cm^2, the side lobe shown in Fig. 12 could also play a role in the formation of holes. Both contributions from the main and side resonance modes resulted in the formation of holes with the morphology shown in Fig. 8. Figure 13 displays the calculated field intensity for a particle size of 140 nm according to the Mie theory. The light enhancement is about 2.5 at the contact point between the particle and the surface. A part of the main resonance light intensity near the contact point may be responsible for the formation of holes with a size of about 30 nm shown in Figs. 5 and 6. Although it is expected that field enhancement at particles may occur according to the Mie theory if the diameter of particles is smaller than the

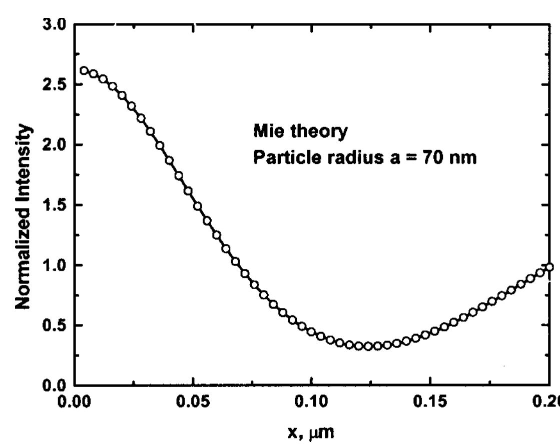

FIG. 13. Calculated field intensity near the contacting point between 140 nm particle and an Al surface based on the Mie theory.

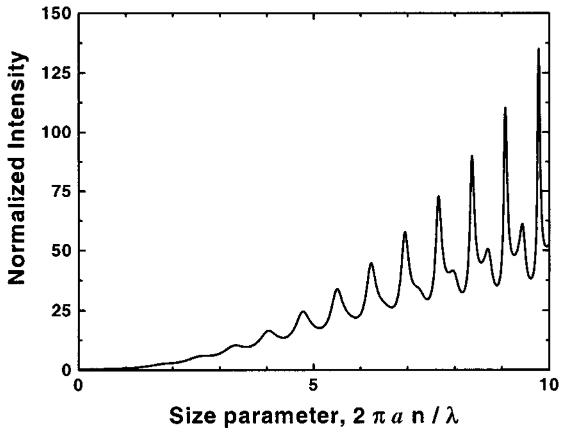

FIG. 14. The intensity distribution under a particle with refractive index $n = 1.6$ calculated according to the Mie theory.

wavelength of the light, our results provide important data and a direct evidence for this prediction.

The resultant structured surface showed inhomogeneity to some extent as described in the previous Sec. III A. The small transparent particle can work as a focusing lens. As particle size (radius) a is very small and comparable with radiation wavelength λ, particle extinction and other scattering characteristics shows oscillations with the change of the particle size. These oscillations are caused by optical resonance.[25] If one considers the particle as a perfect sphere with a refractive index of n, then a common size parameter $q = 2\pi an/\lambda$ arises within the Mie theory. Figure 14 shows the laser radiation intensity versus the size parameter under a transparent particle with refractive index $n = 1.6$. The calculation is performed on the basis of the Mie theory. This intensity is a clearly near-field characteristic and in resonance with the size parameter. It is shown that a major effect on the intensity distribution can be seen within the range of size parameter variation between the two near-optical resonances (maximal intensity varies twice). The concept of this optical resonance suggests variations in surface structuring assisted by a pulsed laser with small changes in the size parameter. For a constant laser wavelength, small variations and deviations in sizes of particles can result in varying laser intensity under particles. Therefore, inhomogeneity in pit patterns shown in Figs. 1, 3, and 5 can be explained by the optical resonance and be attributed to small variations and deviations in particle size. Combined with self-organization techniques, e.g., utilizing two-dimensional colloidal monolayers,[17,18] the laser-assisted surface structuring method will have important and exciting consequences for the structuring process, which allows the structuring of large substrate areas and can result in a million or more holes for a single pulse.

IV. CONCLUSION

Optical resonance and near-field effects in the interaction of particles on a substrate with laser light have been studied both experimentally and theoretically. Pits have been created at the contacting points between the transparent particles and the metallic surface by a single pulse. The influence of particle size and laser fluence on the structuring of the surface has been investigated. The morphologies of created holes are characterized by AFM and SEM. For a constant laser fluence, the created holes show variation with the particle size. With higher-laser fluence, the relevant holes become larger and deeper. For 140 nm particles, with a fluence of 300 mJ/cm^2, the diameter and the depth of created holes are about 30 and 3 nm, respectively. With a high fluence of 750 mJ/cm^2 and for 1.0 μm particles, the diameter and the depth of created holes are about 350 and 100 nm, respectively. Theoretical calculations of intensity distribution versus the particle size on the contacting area (substrate surface) were carried out. The calculation shows that for a nonabsorptive spherical particle, incident light could excite some resonance modes inside the particle and produce enhanced light intensities on the contacting area. It is also showed that the light intensity is nonuniform and sensitive to the particle size parameter. Experimental results are explained and coincide well with those of theoretical calculation. The experimental results also provide direct evidence of the optical resonance and near-field effects in the interaction of the transparent particles on the substrate with laser light.

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