Nano-processing Utilizing Plasmon on Glass Surface by Femtosecond Laser Pulse with Template of Dielectric Particle Array

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Nanoprocessing using a near-field generated by laser irradiation onto the nano-particle is becoming a new emerging nanofabrication technology, because it can fabricate nano-scale structures even with near-infrared laser. The nano-scale area near the contact point with the dielectric particle on the material surface can be ablated by lens effects and/or Mie scattering depending on the particle size. We report on new phenomena, leading to a new nanoprocessing technique via surface plasmons, even by the use of dielectric particles.

Key Words: Femtosecond laser, Nano-processing, Nano-particle, Plasmonics.

1. Introduction

Nano-processing using a near-field generated by laser irradiation to the nano-particle is becoming a new emerging nanotechnology, because it can fabricate nano-scale structures even with near-infrared laser. The processing technique has been investigated extensively in recent years. This laser processing technique has attracted much attention due to advantages over existing processing techniques. The surface modification can be performed in the atmospheric environment. Furthermore, after deposition of the particles the nanostructuring is realizable in a one step dry process under simple experimental conditions.

In the case of dielectric particles, the electromagnetic field confinement at dimensions smaller than the incident wavelength is related to the microlens effects and Mie scattering depending on the particle size. Using this phenomenon a 2D nano-array was fabricated previously on Si surface using small PS particle irradiated by femtosecond laser pulse. In the case of the metal particle, the near field is generated by collective electrons on the metal surface that oscillate resonantly with the incident electric fields. The electromagnetic field is strongly localized around the metal particle and can result in the surface modification. Using these techniques nanoholes with diameters in the range of tens or hundreds of nanometers can be produced.

Here, we report on new phenomena, leading to a new nanoprocesing technique via surface plasmonics, even by the use of dielectric particles. When the laser pulse irradiates hexagonally arrayed particles at laser fluences below the ablation threshold of the clear glass and silicon substrates, nano-bumps are produced under the particles (positive patterning). However, when higher laser fluences than the ablation threshold are irradiated, nanostructure can be fabricated instead at areas on the surface corresponding to the gap regions between the particles (negative patterning). Thus, the switching of negative and positive nano-pattering by simply controlling the incident laser fluence is experimentally demonstrated for the first time to our knowledge. A simple theoretical explanation for the switching of the positive and negative patterning is presented by Finite Difference Time Domain (FDTD) simulation of the near-field distribution.

2. Experimental procedure

In this experiment, soda lime glass, fused silica and silicon (10 × 30 × 1 mm²) plates were used as a substrate material. Mono-dispersed spherical PS particles (Duke Scientific, n = 1.578 at 800nm) with diameters of 790 nm were deposited and arrayed hexagonally on the soda lime glass and the silicon substrates. PS particle with diameter of 1 μm is also deposited on the fused silica substrate. In the case of silica particle, its specific gravity is larger than that of water. Therefore the mono-dispersed spherical silica particles (Duke Scientific, n = 1.45 at 800 nm) were deposited on fused silica substrate using a suspension method. The experiments were performed using a Ti:sapphire chirped pulse amplification (CPA) laser system. The laser pulses with duration of from 100 fs to 2 ps, center wavelength of 800 nm, and energy of 1 mJ/pulse were delivered at a repetition rate of 1 kHz. The experiments were performed on a single shot basis. The laser polarization was a linear and circular polarization wave acquired by using a quarter wave plate. The laser radiation directed perpendicularly to the substrate surface was focused by a convex lens. The laser fluence Fω was varied from 0.05 to 20 J/cm² by using an adjustable attenuator (in this paper we adopted the average laser fluence $F_{\omega}=E/\pi\omega_0^2$, where E is incident energy and $\omega_0$ is the radius of laser focal spot size). The processed substrate surface was observed by SEM (Sirion, FEI) and AFM (SPM, SII SPI3800).

3. Results

3.1 Nano-hole fabrication on the silicon substrate

The 790-nm-diam. PS particles arrays are on the silicon substrate, as shown in Fig. 1 (a). Figure 1 (b) shows an SEM image of the Si surface after the laser irradiation, which is irradiated by 120 fs laser pulse duration with a fluence of 240 mJ/cm². In this case, the silicon under the PS particle (positive pattern processing), in the vicinity of the contact point with the Si substrate, is ablated and nanoholes are formed. This principle of the ablation can be explained by the fact that PS
particles act as microlens and the Mie scattering \(^5,\ 6\). The diameter of the ablated hole is about 200 nm. This processing size is smaller than that of diffraction limit.

The shape of these nano-holes collapses with the increase of laser fluences. Figure 1 (c) shows the silicon surface after laser irradiation (450 mJ/cm\(^2\)). The nano-hole diameter becomes larger, and then neighboring outer circumferential nano-holes intervene in each other. The pitch of nano-holes is limited, because the PS particles are arrayed in a hexagonal reticular pattern (see Fig. 1 (a)). Hence, the extension of the size of nano-holes above 800 nm is impossible as shown in Figs. 1 (b) and (c). The results show that the incident energy is focused on the surface by PS particles. In case of the small dielectric particle on the Si substrate, the experimental result coincides with Mie scattering theory and FDTD calculation results. However, in the case that the substrate ablation threshold is higher than or equal to the threshold of PS particle, the phenomenon disaccord with the theory is found.

3.2 Nano-hole fabrication on the soda lime glass

Figure 2 (a) shows a SEM image of the soda lime glass surface after the laser irradiation with circularly polarized laser. Figure 2 (b) shows the result of linear polarization beam. The laser pulse duration is 120 fs and the incident fluence \(F_{av}\) is 8.5 J/cm\(^2\). White dashed line in Fig. 2 (a) shows the PS particle position before laser irradiation. The fabricated nano-hole position is obviously different compared to the Si surface. The holes shown in Figs. 1 (b) and (c) are fabricated at the position under the contact point of the particle. The nano-holes shown in Fig. 2 (a) are formed at the areas corresponding to the gaps between the particles, and the holes fabricated under the particles disappear completely. The experimental results as shown in Figs.1 (b) and (c) cannot be observed in the experimental conditions of Fig. 2. This difference is explained by the multiphoton absorption process of the silicon and the soda lime glass. The Si ablation takes place mainly via single- and two-photon processes, while the soda lime glass is ablated via four-photon process. Actually the ablation threshold of silicon substrate is about 0.2 J/cm\(^2\) at 120 fs pulse duration \(^5\), while the experimentally determined ablation threshold of the soda lime glass without particles is 5.9 J/cm\(^2\) at 120 fs laser pulse duration. Consequently, it is assumed that the PS particles are ablated before the soda lime glass is ablated, therefore the incident energy cannot propagate to the substrate surface. The ablation threshold for bulk PS is 4.9 J/cm\(^2\), which is smaller than that of soda lime glass.

4. Discussion

4.1 Nano-processing using silica particle

For confirmation of this assumption, we used the silica particle with diameter of 1 \(\mu\)m. Silica particles were deposited on fused silica substrate. The ablation threshold of bulk fused silica is 8.0 J/cm\(^2\), which is higher than that of soda lime glass substrate. The relative order among ablation thresholds of material can be described as

\[
F_{\text{Silica}} > F_{\text{Sodalime}} > F_{\text{Polyystyrene}} >> F_{\text{Silicon}}.
\]

In case of silica particle, we obtained nano-holes under the silica particle as shown in Fig. 3. The position of fabricated nano-holes is corresponding to that of silica substrate. When the ablation threshold of utilized dielectric particle is greater than or equal to the threshold of substrate, the phenomenon according with theory is generated. This result shows that in the case of \(F_{\text{PS}}\) is lower than \(F_{\text{substrate}}\) PS particles may be ablated, before the incident energy reaches the substrate surface. It is because the free electrons inside the PS particle are generated by multiphoton absorption. However, the reason why nanoholes appear at the gaps between particles cannot be explained from this point of view.

4.2 Intensity distribution calculated by FDTD

In order to understand the intensity distribution in the vicinity of the PS particles, we calculated it by an FDTD simulation method. The simulated system consists of hexagonally arrayed 790-nm-in-diam. particles placed on the
soda lime glass surface and the incident laser beam is irradiated normally to the surface. Figure 4 shows the cross-sectional image of the PS particle (x-z plane). As it can be seen in Fig. 4, the intensity distribution inside the PS particle is significantly focused, where an almost 7 times increase in the optical intensity is achieved. It is high enough to induce self focusing and multiphoton absorption process. The laser intensity at this position over 10^{12} W/cm^2, resulting in the optical breakdown is induced. At an early stage of the excitation the high peak intensity will lead to the optical breakdown in the PS. A large number of electrons are generated by multiphoton ionization or avalanche ionization process. The characteristic time for this process is several tens of femtoseconds at intense femtosecond laser irradiation, i.e. at the leading edge of the laser pulse used in our experiment. The free electron density at breakdown conditions in the dielectric particles increases to the order of 10^{21}/cm^3, corresponding to the free electron density of metal. Hence, this is the reason why the incident laser cannot propagate inside the dielectric particle and then nanoholes disappear just under the particles. Because the enhanced position inside the PS particle becomes metal-like condition. The shape of enhanced areas corresponding to the position of centre and bottom inside the PS particle is similar to the form of hemisphere. The high peak intensity produces a large number of electrons in the hemispherical area where enhanced field is seen. In Fig. 4, the intensity distribution inside the PS particle is similar to the form of hemisphere. The free electron density of 10^{21}/cm^3 at 800 nm, the incident energy cannot penetrate into the dielectric particle. In the case of low peak intensity, the incident laser energy is expected to propagate to the substrate through inside the PS particle, because the optical breakdown does not occur by multiphoton and avalanche ionization process. It is given as follows

$$\frac{dn(t)}{dt} = \alpha I(t)n(t) + \sigma_k I(t)^k,$$  \hspace{1cm} (2)$$

where \(k=\nu_0 \exp[-4\ln2(t/\tau_p)^2]\) is a peak intensity with respect to time, \(\alpha\) is an avalanche coefficient and \(\sigma_k\) is a k-photon absorption cross-section \textsuperscript{12}. The smallest value of \(k\) satisfies \(k \nu > E_g\), where \(\nu\) is a laser frequency and \(E_g\) is a material bandgap. The first term in right-hand side represents the avalanche ionization and the second term represents the multiphoton ionization. The bandgap of PS is about 4.6 eV, therefore the value of \(k\) becomes three. As shown in Eq. (2), the number of free electron is strongly affected by the time-dependent laser peak intensity. Especially, the peak intensity in the term of multiphoton ionization is to be third power. It gives the influence strongly to the free electron density. The free electron density reaches critical electron density of 10^{21}/cm^3 at 800 nm, the incident energy cannot penetrate into the dielectric particle. The shape of enhanced areas corresponding to the position of centre and bottom inside the PS particle is similar to the form of hemisphere. The high peak intensity produces a large number of electrons in the hemispherical area where enhanced field is seen. In Fig. 4, the intensity distribution inside the PS particle is similar to the form of hemisphere. The free electron density of 10^{21}/cm^3 at 800 nm, the incident energy cannot penetrate into the dielectric particle. In the case of low peak intensity, the incident laser energy is expected to propagate to the substrate through inside the PS particle, because the optical breakdown does not occur by multiphoton and avalanche ionization process. Figure 5 shows the dependence of the ablation threshold on laser pulse duration. The ablation threshold means the smallest incident energy of fabricating nano-holes on glass surface (positive-pattering). The pulse durations for the observed ablation threshold are 120, 225, 408, 650, 803, 1010, 1540 and 2022 fs. At 120 fs the nanoholes under the particle are not observed.

We considered that the multiphoton ionization process dominates in this discussion. The simple rate equation to calculate the free electron density \(n(t)\) was derived from Stuart et al. \textsuperscript{12}. This equation considers the multiphoton ionization and avalanche ionization process. It is given as follows

$$\frac{dn(t)}{dt} = \alpha I(t)n(t) + \sigma_k I(t)^k,$$  \hspace{1cm} (2)$$

where \(k(t)=\nu_0 \exp[-4\ln2(t/\tau_p)^2]\) is a peak intensity with respect to time, \(\alpha\) is an avalanche coefficient and \(\sigma_k\) is a k-photon absorption cross-section \textsuperscript{12}. The smallest value of \(k\) satisfies \(k \nu > E_g\), where \(\nu\) is a laser frequency and \(E_g\) is a material bandgap. The first term in right-hand side represents the avalanche ionization and the second term represents the multiphoton ionization. The bandgap of PS is about 4.6 eV, therefore the value of \(k\) becomes three. As shown in Eq. (2), the number of free electron is strongly affected by the time-dependent laser peak intensity. Especially, the peak intensity in the term of multiphoton ionization is to be third power. It gives the influence strongly to the free electron density. The free electron density reaches critical electron density of 10^{21}/cm^3 at 800 nm, the incident energy cannot penetrate into the dielectric particle. In the case of low peak intensity, the incident laser energy is expected to propagate to the substrate through inside the PS particle, because the optical breakdown does not occur by multiphoton and avalanche ionization process. Figure 5 shows the dependence of the ablation threshold on laser pulse duration \(\tau\) (FWHM). The ablation threshold means the smallest incident energy of fabricating nano-hole on the soda lime glass surface just under the particle as nano-holes on silicon surface (positive-pattering). At around \(\tau=100\) fs the nano-holes cannot be fabricated under the PS particle, only negative-pattering appeared in the high energy region. From around \(\tau=200\) fs the nano-hole can be fabricated under the particle. At pulse duration of 800 fs ablation efficiency becomes optimum value. In the region of below 800 fs, the ablation threshold energy becomes higher.
with shortening pulse durations, because the high peak intensity generates free electrons. Therefore the incident laser energy is hard to propagate to the substrate. Consequently, the ablation threshold is higher than the optimum pulse duration point. While in the region of above 800 fs, the ablation threshold becomes higher with expanding pulse duration. This result corresponds to the recent ablation theory, in which the avalanche ionization process becomes dominant effect. Assuming this transition, we simulate the interaction of the laser irradiation with the PS particle (Au) as an interaction with a metal particle in excessive laser fluence domain. With the assumption that the metal transition will be clearly seen in Fig. 6 where the enhanced field generates at the edge of the hemispheres. The strong field is additionally affected by a plasmon coupling between the neighboring particles. This coupling is related to the opposite charge accumulation in the vicinity of the contact point which results in strong electric field. The use of circular polarization ensures a symmetrical distribution of the near filed in all directions. The obtained field distribution is consistent with the experimentally observed ablated areas, as shown in Fig. 2 (a). In Fig. 6, the value of intensity at the area between particles is low. However, this assumed hemisphere shape will expand to outside with time. Therefore, the diameter of this hemisphere becomes big, and then the area between particles becomes narrow. This condition results in the fabrication of nanoholes between particles by the increasing the intensity of near-field. Note that simulation with other metals i.e. Al show similar results. This means that the value of free electron density is important.

5. Conclusion

We demonstrated a new nanoprocessing technique using the near electromagnetic field around small transparent particle irradiated by an 800 nm femtosecond laser pulse. A 2D nanohole array with negative pattern was fabricated on soda lime glass by irradiating 790 nm diameter polystyrene (PS) particles monolayer arranged in close-packed hexagonal lattice with a femtosecond laser pulse. In the case of the glass substrate, the incident energy is hard to propagate to the substrate surface by the absorption and scattering due to free electrons inside the particle. The material properties are changed by free electrons, and negative patterning is induced. We assumed that a position of generated free-electron becomes metal-like condition and explained this ablation phenomenon by using FDTD method. In the case of an ablation threshold of substrate is higher than that of small dielectric particle, we can obtain the new nano-processing technique via nano-plasmonics, even by the use of dielectric particles.

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References


Fig. 6 Electric field intensity distribution at the contact plane between gold hemispheres and glass surface (z = 0 nm) calculated by FDTD. The diameter of hemisphere is 790 nm, and height is 395 nm. The incident polarization is circular.