Surface modification by localized surface plasmon polaritons excited by femtosecond laser pulse

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Nanohole fabrication using near electromagnetic field enhancement in vicinity of gold particles is demonstrated. Gold spherical particles with the diameters of 40, 80 and 200 nm are deposited on substrate surfaces and irradiated by a 100-fs laser pulse at the wavelength of 800 nm. The enhanced near field results in substrate surface modification and nanohole formation under the particle. The applied laser fluence ranges from the values below the ablation threshold of the substrate material without particles to the values slightly above it in order to estimate its influence on the properties of the produced structures. The morphological changes on the surface of soda lime glass, Si, and Au, and the parameters of the produced nanostructures are analyzed by scanning electron microscope and atomic force microscope. The distribution of the near electric field is analyzed by a finite difference time domain simulation code. The produced structures are found to depend strongly on the properties of the substrate and laser parameters. In the case of the metal and semiconductor substrates, the electric field is localized in the vicinity of the contact point. In the case of glass substrate the electric field is spreading in an area larger than the particle size. The enhancement factor is about an order of magnitude lower than the case of using the silicon substrate. The results indicate that this method is capable of producing precise nanostructure of a variety of materials.

OCIS codes: 350.3390, 240.5420, 240.6680, 220.4000.

The research field of precise nanostructuring of different materials attracts a growing interest in recent years[1−4]. This is related to the common tendency of miniaturization of the new optical, electro-optical, electrical, and photonic devices that require a processing with a spatial resolution in a nanometers range. The direct application of lasers as a flexible and capable tool for precise processing faces some restrictions related to the diffraction limit of the focusing optics that limit the spatial resolution of processing by the applied laser wavelength. Although the careful choice of the processing parameters and applied configuration can allow direct nanostructuring[5−7], the method cannot satisfy the requirements of new technologies. Different methods and techniques are developed in order to minimize the spatial dimensions of the affected area based on electron and ion beam lithography[8−10], and laser lithography[11]. A promising technique that has recently been applied is based on the use of low dimensionality of the resonant plasmon field produced from metal nanostructures[12−15]. Due to the effective coupling of the incident electromagnetic radiation with the plasmon oscillation, a significant enhancement of the field in the vicinity of the structure can be produced. The intensity of the enhanced field can exceed melting or ablation threshold of the substrate placed near the metal structure and this can result in permanent modification of the substrate surface. Since the induced near electromagnetic field has properties of an evanescent wave, its amplitude decreases rapidly with the distance from the metal surface. This defines the main advantage of this technique: the size of the field enhanced zone is governed not by the wavelength of the incident radiation, but by the size of the illuminated metal structure.

In this paper we present the specific properties of the near field around gold nanoparticles to produce modification of different materials surfaces. Using a simple method of deposition of gold particles, the method offers a nanostructuring with flexible capabilities and can be realized under simple experimental conditions.

Gold spherical particles with the diameters of 40, 80 and 200 nm, and a standard diameter deviation of less than 8% (BBInternational Corp.) are used for the experiments. The particles are deposited on the substrates of soda lime glass, Si and Au by spin-coating method and colloidal droplet method. The root-mean-square (RMS) roughness of the native substrates is in the order of few nanometers. The experiments are performed with a Ti:sapphire chirped-pulse amplification (CPA) system that produces 1-mJ pulses at a repetition rate of 1 kHz, at a central wavelength of about 800 nm. The laser pulse duration used is 100 fs (full width at half maximum (FWHM)). The laser radiation is directed perpendicularly to the substrate surface and focused by a lens with a focal length of 400 mm. The pulse energy is adjusted by a variable attenuator. The experiment is done in air, on a single-shot basis, as the shot number is controlled by a high-speed mechanical shutter. The outgoing laser radiation is linearly polarized. A quarter-wavelength plate is used for its transformation to circular one. The irradiated samples are analyzed by the atomic force microscope (AFM) (SPA300/SPI3800, Seiko Instruments Inc.) and scanning electron microscope (SEM) (Sirion 400, FEI Company).

To study near-field properties around the irradiated nanoparticles, the finite difference time domain (FDTD) simulation model is applied. This computational technique based on the numerical solution of the Maxwell's equations[16] is proven to give an adequate picture of the electromagnetic field distribution in the near and far fields around structures with arbitrary shapes[17]. In all the simulations a plane wave irradiates gold particles placed on various substrates. Electric-field strength of

1671-7694/2007/S1S122-04

the incident irradiation is set at 1 V/m. The optical properties (i.e. dielectric function) of the investigated substrate materials are introduced in the model by using data taken from Refs. [18] and [19].

Figure 1 shows a SEM image of nanoholes fabricated on Si substrate when 200-nm gold particles are deposited on the surface and it is irradiated by laser pulse at fluence of 0.21 J/cm^2. The measured maximal depth under these conditions is about 33 nm and the hole diameter is about 200 nm. As it can be seen, the formed nanoholes have a symmetrical shape. This is connected to the use of circular polarization light, which ensures a symmetrical distribution of the near electromagnetic field in vicinity of the contact point between the particle and substrate[20]. It should be noted that the used laser fluence is about 40% lower than the fluence where surface modification is observed when a single laser shot irradiates clear Si surface.

In order to estimate the ability of the presented method of nanostructuring of different materials, experiments are performed using with dielectric and metal substrates. Figure 2 represents the SEM images of nanoholes fabricated on soda lime glass, silicon, and gold substrates, when particles with a diameter of 200 nm are used. The laser fluence in all cases is about 40% lower than the single-shot ablation threshold of the different substrates.

The parameters of the produced holes are also found to depend on the gold-particle size. This dependence is investigated for Si substrate. Figure 3 shows SEM images of holes produced when a 0.185-J/cm^2 laser pulse irradiates silicon surface with gold particles with diameters of 200, 80, and 40 nm. The maximal depths of the produced holes are 30, 15, and 7 nm, respectively. The results clearly indicate that the decrease of the particle size results in the decrease of the hole dimensions.

In order to clarify experimentally the observed such dependences, FDTD model is applied to describe the near-field distribution properties. Figure 4 represents the calculated distributions of the electric-field intensity (ratio between the obtained electric-field intensity and the incident one, i.e., $|E/E_0|^2$) around the gold particle with a diameter of 200 nm placed on Si surface. The incident laser radiation is circularly polarized. The electric-field intensity distribution is shown in a cross-sectional plane of the system, through the center of the sphere and the point of contact with the substrate. When the particle is placed on the substrate surface the field is localized in the vicinity of the contact point on the Si surface.

The strong field on the gold-particle surface induces image charges in the substrate material. The electric field in the region of the contact point between the particle and substrate is strongly enhanced and the electric-field intensity is about 10^3 times higher than the

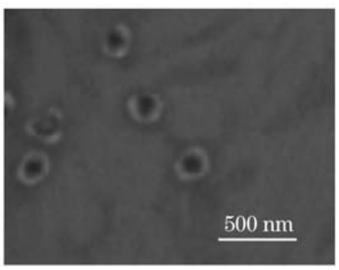

Fig. 1. SEM image of nanoholes produced on Si surface using gold particles with diameter of 200 nm. Laser fluence is 0.21 J/cm^2. The polarization of the incident radiation is circular.

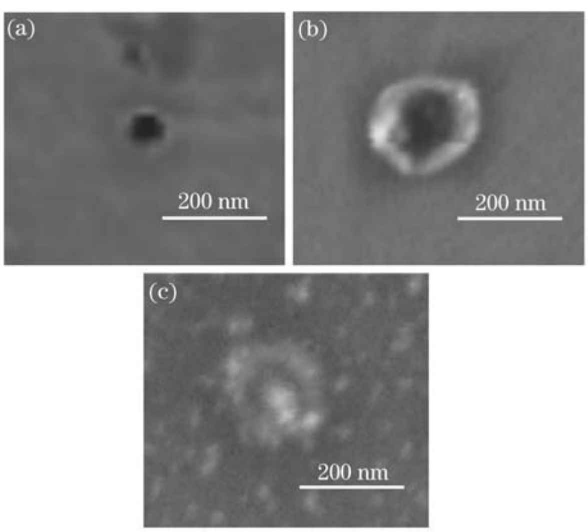

Fig. 2. SEM images of nanoholes produced on different substrates when gold particles with a diameter of 200 nm are deposited and irradiated by a 100-fs laser pulse. (a) Soda lime glass substrate, laser fluence $F = 4.2$ J/cm^2; (b) silicon substrate, $F = 0.21$ J/cm^2; (c) gold substrate, $F = 0.1$ J/cm^2. Circular polarization light is used in all cases.

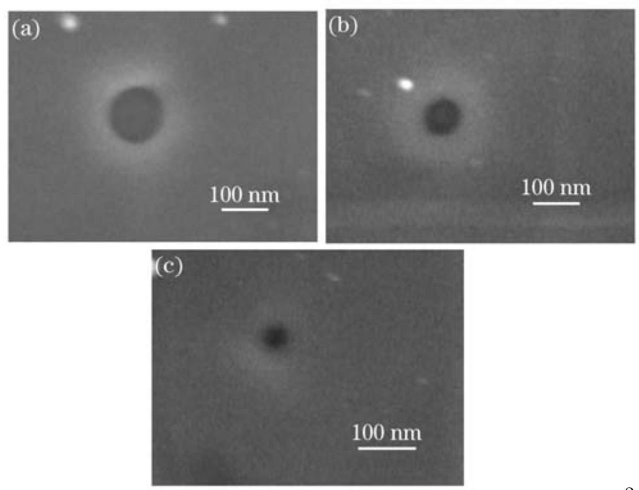

Fig. 3. SEM images of holes produced when a 0.185 J/cm^2 laser pulse irradiates Si surface with gold particles with diameters of (a) 200, (b) 80, and (c) 40 nm deposited on it.

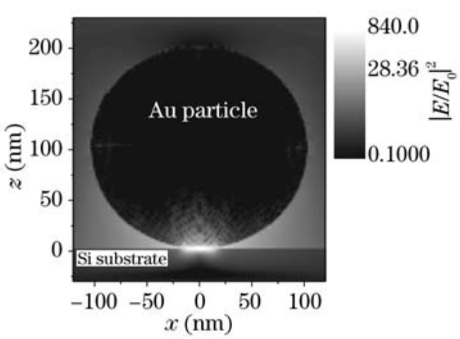

Fig. 4. Distribution of the electric-field intensity around Au particle with a diameter of 200 nm placed on Si surface.

incident one. The value of the charge density induced on the substrate surface depends on the dielectric properties of the substrate material. Thus, one can expect that changing the substrate will affect the properties of the near field. Figure 5 represents the electric-field distribution on the substrate surface ($z = 0$) where the calculations are performed for soda lime glass, silicon, and gold. The results clearly indicate that the substrate material strongly influences the near-field properties. The changes are related both to the spatial distribution and magnitude of the field. In all cases the area of the strongest field enhancement is symmetrical with the diameter several times smaller than the particle's one. In the case of glass and metal substrates, the strongest field has a ring shape on the surface which can be explained by some geometrical considerations. In the presented simulations the incident radiation is perpendicularly directed to the substrate surface. In this case, the polarization of the metal particle follows the direction of the incident electric field. The highest displacement of the electrons with respect to the ions is realized around the equator of the particle. The magnitude of polarization decreases in direction to the poles where it approaches zero. Furthermore, the magnitude of the near electromagnetic field rapidly decreases with the increase of the distance. Thus, when a substrate is present, the induced charge density on its surface will increase in direction to the contact point between the particle and substrate. As a result of these effects, the enhanced field will form an area with a ring shape. In the case of silicon substrate, the observed distribution has different features. A possible explanation could be related to the high refractive index of Si (high polarization) and the low absorption at this wavelength. This can result in a redistribution of the near field in the small spatial region around the contact point.

The field enhancement dependence on the substrate material can be explained by the interaction between the charges on the particle surface and image charges induced into the substrate. The density of the induced charges is governed by the values of dielectric function of the substrate material. In the case of gold substrate, electromagnetic coupling between plasmon modes in the particle and the substrate may also play an important role, leading to the strong enhancement of the electric field.

The simulations performed with particles with different diameters predict a decrease of the enhanced field area with decrease of the gold particle diameter. This effect is related to the strong confinement of near field in the vicinity of the particle surface. The estimated enhanced field area is several times smaller than the particle diameter. This result is in agreement with the experimental results (see Fig. 3) and it indicates that both the size of the enhanced field and the produced structures are precisely controllable by the particle size.

The nanohole formation is also investigated for laser radiation at the wavelength of the second harmonic of Ti:sapphire laser ($\lambda \approx 400$ nm). The pulse width of the second harmonic is 300 fs, approximately. At this wavelength the plasmon resonance is significantly damped because this wavelength falls into the interband transition of gold. The FDTD results clearly indicate a decrease of the near-field amplitude compared with the case of 800 nm. For the case of 200-nm gold particle on Si substrate the simulation results predict an about 4 times decrease in the amplitude of the electric field. The experiments confirm these predictions. When the wavelength of 400 nm is used, the nanoholes are only observed at fluences near to the surface modification threshold. Due to the absence of ablation the gold particles are not removed from the substrate after laser irradiation at low fluences. Their presence is confirmed even after tens of laser shots. In these cases clear traces of particle melting and decomposition are observed which are related to the strong absorption of gold at this wavelength.

An interesting phenomenon is observed when experiments are done at the wavelength of 400 nm. Figure 6(a) represents the SEM images of Si surface after 20 consecutive laser pulses at fluence of 0.05 J/cm^2. As is clearly

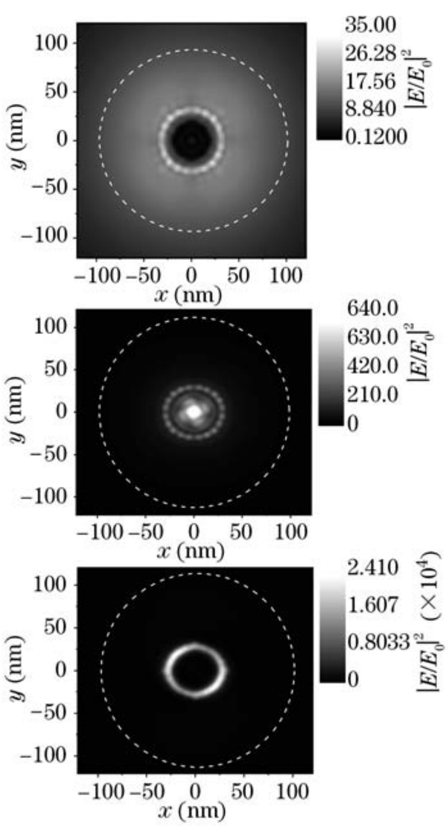

Fig. 5. Distribution of the electric-field intensity on the substrate surface ($z = 0$, see Fig. 4) when Au particle with a diameter of 200 nm is used. (a) Soda lime glass substrate; (b) silicon substrate; (c) gold substrate.

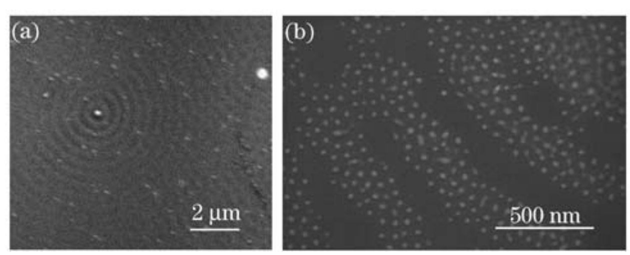

Fig. 6. SEM images of Si surface with deposited 200-nm gold particles on it after irradiation with 20 laser pulses at wavelength of 400 nm. (a) The laser fluence is 0.05 J/cm^2; (b) the laser fluence is estimated to be 0.008 J/cm^2. Circular polarization light is used.

seen, a large-scale surface modification is produced. This modification consists of concentric rings centered at the gold particle's position. They are spaced to a distance equal to the laser wavelength. We attribute the formation of this structure presumably to the mechanism of ripple formation, often observed in laser material processing[21]. At the edge of the laser spot, where the laser fluence is significantly low (the spatial intensity distribution is Gaussian) the modification of the surface contains sub-wavelength structure (Fig. 6(b)). The mechanism of this structure formation is still unclear, but it may be attributed to the presence of non-thermal effects that can dominate the energy dissipation into the material at low laser fluences and structure changes related to them.

In this work we presented the experimental and theoretical results on nanostructuring of different surfaces using the enhanced near field in vicinity of gold nanoparticles irradiated by the femtosecond laser pulse. The results clearly indicate that this technique is capable in the nano-sized surface modification of different materials such as dielectrics, semiconductors, and metals. The parameters of the produced holes strongly depend on the substrate material properties. Furthermore, the dimensions of the produced structures are found to be governed by the nanoparticle size. This result indicates that the size of the applied particles can be used to effectively control the parameters of the produced structures. The results of the numerical model are in good agreement with the experimental data, which confirms its validity.

This work was partially supported by a Grant-in-Aid for the 21st Century COE for Optical and Electronic Device Technology for Access Network from MEXT in Japan. N. N. Nedyalkov is grateful to a JSPS Fellowship under Grant No. P 05334. N. N. Nedyalkov's e-mail address is niki@obara.elec.keio.ac.jp.

References

1. N. Yasumaru, K. Miyazaki, and J. Kiuchi, Appl. Phys. A **81,** 933 (2005).
2. F. Korte, J. Koch, J. Serbin, A. Ovsianikov, and B. N. Chichkov, IEEE Trans. Nanotechnol. **3,** 468 (2004).
3. Z. B. Wang, M. H. Hong, B. S. Lukyanchuk, Y. Lin, Q. F. Wang, and T. C. Chong, J. Appl. Phys. **96,** 6845 (2004).
4. H. J. Munzer, M. Mosbacher, M. Bertsch, J. Zimmermann, P. Leidere, and J. Boneberg, J. Microscopy **202,** 129 (2001).
5. J. Koch, F. Korte, C. Fallnich, A. Ostendorf, and B.N. Chichkov, Opt. Eng. **44,** 051103 (2005).
6. Pereira, A. Cros, P. Delaporte, S. Georgiou, A. Manousaki, W. Marine, and M. Sentis, Appl. Phys. A **79,** 1433 (2004).
7. N. Yasumaru, K. Miyazaki, and J. Kiuchi, Appl. Phys. A **76,** 983 (2003).
8. P. Ghenuche, R. Quidant, and G. Badenes, Opt. Lett. **30,** 1882 (2005).
9. G. S. Chen, C. B. Boothroyd, and C. J. Humphreys, Appl. Phys. Lett. **62,** 1949 (1993).
10. Y. E. Guan and A. J. Pedraza, Nanotech. **16,** 1612 (2005).
11. A. B. Poghossian, J. Platen, and M. J. Schoning, Electrochem. Acta **51,** 838 (2005).
12. S. Kawata, *Near-Field Optics and Surface Plasmon Polaritons* (Springer, Berlin, 2001).
13. P. Leiderer, C. Bartels, J. König-Birk, M. Mosbacher, and J. Boneberg, Appl. Phys. Lett. **85,** 5370 (2004).
14. N. Nedyalkov, H. Takada, and M. Obara, Appl. Phys. A **85,** 163 (2006).
15. J. Jersch and K. Dickmann, Appl. Phys. Lett. **68,** 868 (1996).
16. A. Taflove and S. C. Hagness, *Computational Electrodynamics: the Finite-Difference Time-Domain Method* (Artech House, Boston, 2000).
17. K. Sendur, W. Challener, and C. Peng, J. Appl. Phys. **96,** 2743 (2004).
18. P. B. Johnson and R. W. Christy, Phys. Rev. B **6,** 4370 (1972).
19. E. D. Palik, *Handbook of Optical Constants of Solids* (Acad. Press, San Diego, 1998).
20. N. Nedyalkov, T. Miyanishi, and M. Obara, J. Phys. D **39,** 5037 (2006).
21. M. von Allmen, *Laser-Beam Interactions with Materials* (Springer, Berlin, 1987).