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# Silicon bump arrays by near-field enhanced femtosecond laser irradiation in fluorine liquid precursors

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ABSTRACT

A simple approach to fabricate periodic arrays of conical bumps on silicon (Si) substrate is reported. In the process, a single pulse from a 200 fs laser at 387 nm wavelength was applied on a self-assembled monolayer of 700 nm and 390 nm diameter silica spheres on a n-doped Si (1 0 0) wafer. The surface was irradiated at normal incidence by immersing the silicon substrates in a glass container filled with 1, 1, 2 trichlor-trifluorethan liquid precursors. After laser irradiation, at laser fluences in the range from 1 to 40 J/cm$^2$, a regular array of conical Si bumps was fabricated. The density of the Si bumps can be varied by varying the particle size diameter. The influence of the medium on the near-field interactions for both sizes silica particles layer is investigated.

## 1. Introduction

Nanoprocessing technology plays an important role for emerging nanotechnology. Most widely used industrial technology for ultralarge scale integration is photolithography using vacuum-UV ArF (193 nm) and F2 (157 nm) excimer lasers, which requires highly precise mask, expensive advanced dispersion-free optical system, complex multilayer resists, and accurate optical alignment system. Many research groups have demonstrated patterning of surfaces at resolution below the diffraction limit using optical near-field effects through the use of light-coupling masks [1], an evanescent near-field optical lithography method [2], or embedded-amplitude mask [3]. A nanofabrication method induced by the optical near-field around transparent particles, without using a scanning probe, enables to realize high throughput nanohole patterning with a simple apparatus [4]. Since the localized spot is governed mainly by the particle size, the method permits the fabrication of nanoscale pits or dents on a solid surface [5–9]. Theoretical and experimental results on the tuning effect of a liquid (water) media on the focusing properties of self-assembled particle-lens array and a single particle on a glass substrate were also presented in the literature [10]. Due to the presence of water medium, the multiple focusing spots of the microsphere array illuminated by femtosecond (fs) laser were tuned to positions beneath the surface, and focal length is greatly extended. Depending on the laser fluence, it has been demonstrated that different micro/nano-structures such as nano-height ring-bumps and convex bumps can be fabricated on glass surface in large area without cracks and debris. In this article, we report on the fabrication of silicon conical shape bumps on an n-doped Si (1 0 0) wafer (Crystal GmbH). The method employs a regular two-dimensional (2D) lattice of 700 nm and 390 nm silica microspheres (Bangs Laboratories, Inc). Such lattices were formed by well known self-assembly processes from colloidal suspensions [11]. In contrast to previous reports published in the literature, we have placed the lattice of silica microspheres (deposited on the Si wafer) at the bottom of a glass container filled with liquid precursors, such as 1,1,2 trichlor-trifluorethan ($C_2Cl_3F_3$). This liquid precursor with refractive index of $nC_2Cl_3F_3 = 1.43$ has been chosen due to the silicon etching activity of the molecules containing chlorine and fluorine [12]. The effects of femtosecond laser processing of Si in a fluorine liquid precursor have been investigated by our group in the far field. In this paper, the ablation and photochemical/photothermal processes induced by the optical near-field around the particles are investigated. The created nanofeatures under the particles and its morphology, both on 700 nm and 390 nm layered system, are studied.

## 2. Materials and methods

In the experiments, silica colloidal particles with diameter of 700 nm and 390 nm were used. The monodisperse silica spheres

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were applied to an n-doped Si (1 0 0) substrate after the suspension had been diluted with deionized water. The Si substrate, previously kept for some minutes in an oxygen plasma environment in order to transform them from hydrophobic to hydrophilic behavior, was kept still until all of the water had been evaporated. As a result, a silica bead, mono layer array, within a large area (tens of square micrometers) was obtained on the surfaces. We placed the Si (1 0 0) substrate, with the silica colloidal particles on top, at the bottom of a glass container filled with liquid precursor $C_2Cl_3F_3$ (purchased from Merck). The glass container was mounted on a three-axis translation stage, and the sample with the silica particle array was irradiated at normal incidence. A similar setup was described in our previous work where we have described the silicon wafer structuring with liquid precursors using the femtosecond laser [12]. The sample was irradiated with single pulses 200 fs duration at 387 nm wavelength and with horizontal polarization from a double frequency amplified Ti:sapphire laser (Clark-MRX 2101). The laser pulses were focused by a 75 mm focal length lens and travelled through 5 mm of liquid before striking the surface at normal incidence. The laser fluence is in the range from 1 J/cm$^2$ to 40 J/cm$^2$. The fabricated nanofeatures were analysed using a Carl Zeiss EVO 50 XVP Scanning Electron Microscope (SEM) equipped with LaB6 cathode and Atomic Force Microscope (AFM) XE100 model from Park System.

## 3. Results and discussion

It is known that there is an optical field enhancement by micro/nanospheres in the near-field region, which can be explained by the Rayleigh and Mie scattering [13]. Rayleigh scattering takes place when the diameter of the sphere is less than the wavelength of the light. In this case, the sphere is treated as dipole radiator. When the diameter of the sphere is larger than the wavelength, light is scattered elastically according to the Mie scattering law. For the sphere diameter larger than the laser wavelength as in the present work, according to the Mie theory, the electric field is enhanced by several times toward the forward area of the sphere. To estimate the field enhancement at the surface of the silica spheres, in air and liquid environment [10], we performed calculations using the finite-difference time-domain (FDTD) method using simulation software (RSFOT purchased from the RSoft Design Group). The refractive index of the silica particles was considered to be $n_{\text{silica}} = 1.47$. A two-dimensional (2D) simulation was performed in which four Maxwell's equations were solved. The total simulation area had a width equals to 5 μm and a length equals to 2.2 μm. The grid discretization size of 50 nm is small enough to resolve the smallest feature in the structure. Fig. 1 shows the distribution of the total energy density for an incident Gaussian wave of unit amplitude $\lambda = 387$ nm, for a Si substrate covered with colloidal particles of 700 nm and 390 nm. The complex refractive index of the Si substrate is $n_s + ik_s$, where $n_s = 6.548$ and $k_s = 0.885$ at 387 nm [14]. The numerical simulation indicates different intensification factors (about 9 in air and about 5 for the immersion of the 700 nm silica particle in $C_2Cl_3F_3$) depending on the size of the particle and medium environment, e.g. air ($n_{\text{air}} = 1$) or $C_2Cl_3F_3$ ($n_{\text{liquid}} = 1.43$) liquid precursor. The obtained intensification factors are an interplay between the refractive indexes of the substrate, environment medium, colloidal particle and the wavelength of the laser. The simulations indicate that by going to UV laser wavelength, even at nearly negligible differences in the refractive index of the medium ($n_{\text{liquid}} = 1.43$) and the colloidal particle ($n_{\text{silica}} = 1.47$), it is possible to obtain an enhancement factor of the electromagnetic field underneath the colloidal particle sitting on a Si substrate ($n_s = 6.548$). The field strength enhancement does not take into account that the ablation mechanism is also triggered by possible photochemical reactions leading to radical generation in the liquid precursor. Fig. 2 shows a scanning electron microscopy (SEM) image of a small part of the Si substrate, covered with a monolayer of 390 nm silica particles, irradiated in air (Fig. 2a) and the one irradiated by immersion in $C_2Cl_3F_3$ (Fig. 2b) that has been patterned by a single Ti:sapphire laser shot at 387 nm wavelength. The focused beam on the sample had a Gaussian spatial beam profile with a negligible energy density fluctuation. A 1/e$^2$ focal spot diameter size of 10 μm was used to calculate the laser fluence on the sample surface. Due to the Gaussian shape of the laser pulse, the colloidal particles at the edge of the irradiated area were exposed to less energy than those near the center. The arrangements of features generated on the sample reveal the hexagonal lattice structure of the silica microspheres. The area irradiated in air indicates the nanoscale pit array which were similar as reported in the literature [15]. By varying the laser fluence in the range 1–40 J/cm$^2$, we did not observe any formation of nanoscale bumps on silicon when irradiating in air. Below 1 J/cm$^2$ there is no effect observed underneath the colloidal particles, while 40 J/cm$^2$ is our maximum laser fluence that we could use with our laser system. When the laser irradiates through the liquid environment (laser fluence in the range 10–40 J/cm$^2$), an uniformly distributed bump array was fabricated (Fig. 2b). The effective transmission of the light into the sample at normal incidence is $T_m = (4n_{\text{liquid}}n_s)/(n_{\text{liquid}} + n_s)^2 + k_s^2$, where $n_{\text{liquid}}$ is the refractive index in liquid, $n_s$ and $k_s$ are the real and imaginary parts of the complex refractive index $n_s + ik_s$ of the Si substrate. If we make the assumption that the threshold fluences are the same in liquid and in air, i.e. $F_{\text{th}}(\text{liquid})T_{\text{liquid}} = F_{\text{th}}(\text{air})T_{\text{air}}$, the ratio of the measured $F_{\text{th}}$(liquid) to measured $F_{\text{th}}$(air) will be a ratio of $T_{\text{air}}/T_{\text{liquid}}$ [16]. In consequence, the fluence threshold decreases in liquid with a calculated factor of approximately 0.6. The atomic force microscopy (AFM) images represented in Fig. 3a and b clearly show that the created features have a density that is dependent on the silica particle diameter size. Fig. 3a evidences a regular array pattern of bumps with a conical shape with a pronounced ring-shape trenches, the center to center distance for the Si bumps being about 700 nm (the size of the colloidal particle). Fig. 3b evidences the same hexagonal arrangements of the Si bumps, the distance in between them being about 390 nm (the size of the colloidal particle). In the case of Fig. 3b the ring shape trench is not so pronounced. According to our numerical simulations, the field enhancement factor is higher for the 700 nm. We assume that the ring-shape trench

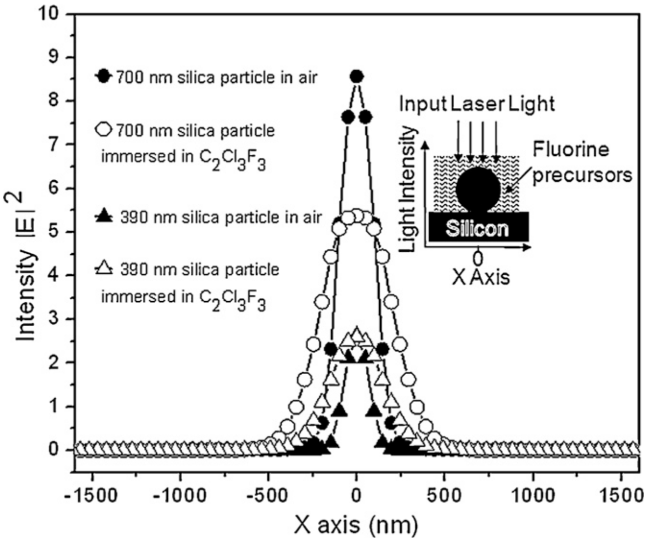

**Fig. 1.** Distribution of the total energy density for an incident Gaussian wave of unit amplitude, $\lambda = 387$ nm, for a Si substrate covered with colloidal particles of 700 nm and 390 nm, obtained after FTDT simulations in air and in $C_2Cl_3F_3$ liquid.