Direct femtosecond laser writing of optical nanoresonators

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Abstract. A novel method for single-step, lithography-free, and large-scale laser writing of arrays of metallic (Au) and semiconductor (Si) nanoparticles (nanoresonators) has been developed. Changing energy of femtosecond laser pulses and film thickness it is possible to vary diameter of the nanoparticles, while the distance between them can be varied by laser scanning parameters. This method has an advantage over the most previously demonstrated methods in its simplicity and versatility, while the quality of the structures is good enough for many applications.

1. Introduction

With the advent and rapid progress of fabrication technology in the past few decades, there has been growing interest in the field of plasmonics to explore novel phenomena by manipulating light at nanoscale [1, 2]. Examples of plasmonic devices requiring ordered nanoparticles are plasmonic filters [3, 4], metasurfaces [5], and waveguides [6]. The research area dealing with the interaction of molecules or molecular structures with plasmonic nanostructures is another rapidly growing field, due to potential analytical applications such as surface-enhanced Raman spectroscopy (SERS) and localized surface plasmon resonance spectroscopy [7, 8].

High refractive index dielectric nanoparticles with low dissipative losses provide excitation of strong magnetic optical resonances [9–17] and represent a good alternative to high-loss in visible range plasmonic nanoparticles for such applications as electromagnetic field enhancement and sensing [18–21] and enhancement of nonlinear effects [22, 23]. One of the most popular materials for all-dielectric nanophotonics is crystalline silicon (c-Si), because it is a low-cost CMOS compatible semiconductor with a large real part and a low imaginary part of its refractive index, providing the desirable optical response. Indeed, amorphous silicon has a much larger imaginary part of refractive index (up to two orders of magnitude in visible range) [24] in comparison with the crystalline phase.

To date, the most popular and controllable approaches of nanostructures fabrication are based on direct ion-beam milling or multistage e-beam and nanoimprint lithographies. However, lithography-free and single-step methods are more desirable for large-scale manufacturing. Among single-step techniques, chemical synthesis of monodisperse nanoparticles
colloid is a promising method for high-throughput fabrication, however, it requires additional technological steps to order the nanoparticles into a functional nanostructure [25–28]. An alternative cost-effective and versatile approach is to exploit a self-assembly process via dewetting of heated thin supported films of a wide range of materials [29–31]. Laser radiation [29,32,33], ion-beam [34] or heating on a hotplate [30,31] have been utilized as heat sources for launching the dewetting process. Another way is to employ cost-effective laser technologies in order to controllably create nanoparticles via precise ablation of thin films, exploiting single nanoparticle transfer to a receiver substrate after single-shot femtosecond (fs) laser irradiation of a thin film [35–37] or direct two-shots writing of plasmonic nanoantennas coupled with plasmonic lenses [38].

Although many different approaches have been proposed to fabricate nanoparticles, the successful implementation of nanodevices still requires cost-effective and versatile method of controllable large-scale fabrication of ordered metal or dielectric nanoparticles.

In this work we present a conceptually new, single-step, lithography-free and cost-efficient method for large-scale fabrication of nanoparticle-based structures. The combination of simplicity of thin film dewetting process, along with precision and high-productivity of the laser technology enables extreme simplification of the process of nanoparticles fabrication, while

![Image of single nanoparticle formation under femtosecond laser cutting of patch from a thin film on a glass substrate (a-d). SEM images of a fabricated single gold nanoparticle (e) on a fused silica substrate fabricated by fs-laser irradiation of 30nm Au film at a fluence of 40 mJ/cm². Scale bars correspond to 1 µm.](image-url)

**Figure 1.** A schematic illustration of single nanoparticle formation under femtosecond laser cutting of patch from a thin film on a glass substrate (a-d). SEM images of a fabricated single gold nanoparticle (e) on a fused silica substrate fabricated by fs-laser irradiation of 30nm Au film at a fluence of 40 mJ/cm². Scale bars correspond to 1 µm.
the quality of fabricated structure is well-maintained. In other words, we achieve direct single-step “writing” of nanoparticles by strongly focused femtosecond laser pulses, where the laser irradiation is used to pattern and heat-up the residual film to the dewetting temperatures. We implement this simple method for writing of 0D, 1D, and 2D structures.

2. Methods
A commercial femtosecond laser system (Femtosecond Oscillator TiF-100F, Avesta Project) was used, providing laser pulses at 800 nm central wavelength, with a maximum pulse energy of 5 nJ, and a pulse duration of 100 fs at a repetition rate of 80 MHz. The laser energy was varied and controlled by an acousto-optical modulator (R23080-3-LTD, Gooch and Housego) and a power meter (FielfMax II, Coherent), respectively, while the pulse duration was measured by an autocorrelator (Avesta Project).

Laser pulses were tightly focused by an oil immersion microscope objective (Carl Zeiss 100×) with a numerical aperture (NA) of 1.4. According to the relation $d \approx \frac{1.22 \lambda}{NA}$, the estimated full-width at a half-maximum diameter of the beam focal spot size is $d = 0.68 \mu m$, which is close to the value measured by the standard method (0.64 µm) based on the dependence of laser-damaged area on incident laser energy [39].

The laser beam was focused on supported Au or Si films with thicknesses in the range of $h = 10 – 100$ nm, thermally evaporated (Bock Edwards Auto 500) on the back side of a 140 µm-thick silica glass without any additional adhesion-improving layers. The samples were then placed on a three-dimensional air-bearing translating stage driven by brushless servomotors (ABL1000, Aerotech), allowing sample translation with various scan speeds up to 300 mm/s. In all experiments, film surface scanning by the laser beam was carried out with velocity of 1 mm/s, providing the number of laser pulses per each point of approximately $N \sim 10^4$.

In order to characterize the crystalline structure of the initial film and the fabricated nanoparticles, we provided Raman scattering measurements. The Raman spectra were recorded by a micro-Raman apparatus (Raman spectrometer HORIBA LabRam HR, AIST-NT SmartSPM system) under excitation by a 632.8 nm HeNe laser through a 100× microscope objective (NA = 0.9) and projected onto a thermoelectrically cooled charge-coupled device (Andor DU 420A-OE 325) with a 600 g/mm diffraction grating.

3. Results and discussion
In order to make the method of nanoparticles array fabrication as simple as possible, we replace all lithographical stages of film patterning [40–43] by their direct fs-laser cutting with simultaneous heating of the remain patches up to the dewetting temperatures (figure 1). Although the proposed method is single-step, it is divided into several physical stages.

First, a strongly focused fs-laser beam irradiates a thin film at a fluence slightly higher than the thin film ablation threshold, which increases with growth of the film thickness. Since the scanning conditions correspond to the number of pulses $N \sim 10^4$ and the time delay between the fs-laser pulses in train is 12.5 ns, the temperature in the vicinity of the irradiated area is gradually accumulated pulse-by-pulse and achieves the level of film ablation in a certain region. Importantly, there is almost no ablation debris nearby each groove, being a result of the evaporative mechanism of ablation, rather than the spallative one followed by random dissemination of sub-100 nm nanoparticles in the vicinity of the heated area [44]. In this regime, rather clean and narrow (width of $\Delta \approx 400$ nm $\leq \lambda$) grooves can be written directly on the surface (figure 1).

Second, a single patch can be easily cut (figure 1(b)) with any size larger than the uncertainty of the grooves edges ($\pm 50$ nm, figure 1(d),(e)). The cut patch is thermally isolated since the thermal conductivities of the silica substrate and air are two and four orders of magnitude smaller than that of gold, respectively. Therefore, the isolated patch can be easier heated up to
the temperatures where the film undergoes dewetting process. The dewetting temperature of
the films could be much lower than the melting point of bulk material. For instance, a 10 nm
Au film on fused silica is dewetted even at 430 K, while 60 nm Au film undergoes dewetting at
temperatures lower than 870 K [45]. Moreover, the smaller the patches (with a smaller total
volume), the higher the temperatures that can be achieved at a fixed fluence. As a result, the
heated cut Au patch transforms into a nanoparticle of the same volume during the dewetting
process (figure 1).

Although dewetting is a spontaneous process for homogeneous films [29,32], the reproducible
formation of a certain number of nanoparticles has been demonstrated by heating of
lithographically cut microscale patches of thin film [31, 34, 40, 41, 46]. Moreover, a single
nanoparticle formation from each patch is possible, when the patch width-to-height ratio
(\(\xi = w/h\), where \(w\) is the lateral size of the square patch and \(h\) is the film thickness) is smaller
than a certain value [40].

3.1. Gold nanoparticle writing

In the case of Au film on SiO\(_2\), this value must fulfill the condition \(\xi < 40\), to provide an almost
one hundred percent probability of single particle formation with a certain diameter [40]. In our
experiments we achieve the most controllable formation of nanoparticles at \(\xi \approx 15 \sim 30\).

This technique enables direct writing of 0D (a single nanoparticle, figure 1(d)), 1D (a line
of nanoparticles, figure 1(e)) and 2D (an array of nanoparticles, figure 1(f)) nanoparticle-based
structures. The 2D structures are produced by laser beam scanning of the film surface in
two orthogonal directions, allowing extremely high production rate of \(\sim 1 \text{ mm}^2/\text{min}\) at the
available speed of laser scanning of \(\sim 0.3 \text{ m/s}\). All types of the structures have been successfully
fabricated on 20 and 30 nm Au films, while the other thicknesses (10 and 60 nm) provide much
less controllable film patterning. Beside the film thickness, another parameter that affects the
diameter and quality of the nanoparticles is the width \(w\) of the cut patch.

In figure 2, SEM images of the fabricated 2D structures on a 30 nm Au film are shown as
a sequence of reduced period between 90°-crossed laser scans at a fluence of 40 mJ/cm\(^2\). The
laser fluence is chosen to provide as narrow and reproducible grooves as possible. Evidently,
there are four main regimes: (i) square micro-patches formation (figure 2(a)); (ii) unstable
transition from square micro-patches to nanoparticles; (iii) formation of ordered and almost
identical nanoparticles (figure 2(b),(d)); (iv) formation of disordered different-size nanoparticles
(figure 2(c)). The fabricated particles have an almost spherical shape and are partly embedded
into the substrate (figure 2(d)), owing to dewetting on a molten substrate.

For the film thickness \(h = 30\) nm, we observe reproducible formation of sub-100 nm
nanoparticles conglomerates nearby each ordered nanoparticle when periods of scan are smaller
than 0.9 \(\mu\)m (see inset of figure 2(c)). Similar behaviour has been observed when some parts of
a molten film are not absorbed by larger particles during dewetting process, and interpreted in
terms of the multimodal Rayleigh-Plateau instability [43]. Indeed, the conglomerates are formed
preferably from the side of last cutting of each patch (see left side in inset of figure 2(c)).

Similar to the scan period (the patch width) dependencies, there are also some ranges of
thicknesses where the quality of the 2D nanoparticles array is the most optimal. Non-monotonic
behaviour of the size dispersion dependence on the scan period and film thickness can be
attributed to two main reasons: (i) the conditions \(w/\lambda_m > 1\) and \(\xi < 40\) are not fulfilled
for very small thicknesses and (ii) the dewetting temperature is much higher for thicker films.
Therefore, too thin films can not provide ordered nanoparticles formation, while too thick and
large patches can be hardly heated homogeneously during laser cutting to achieve controllable
dewetting.
Figure 2. SEM images of the Au nanoparticles arrays fabricated at a fluence of 40 mJ/cm² and a periodicity of crossed laser scan of 2.0 (a), 1.0 (b), and 0.8 µm (c). Scale bars are 2.0 µm. The upper-right insets: Fourier spectra of the SEM images. The lower-left insets: enlarged SEM images of typical nanoparticles from the arrays with scale bars of 100 nm. (d) AFM image of the nanoparticles array, corresponding to the picture (b).

3.2. c-Si nanoparticle writing

The novel method of direct laser writing is also applicable for c-Si nanoparticles fabrication from initially amorphous a-Si:H film. Under the optimal conditions of fabrication, the resulting array of nanoparticles has a period of about 0.9 µm, exhibiting bright colors owing to resonant scattering (figure 3(a)) [17].

Although the cutting should produce a rectangular grating, our SEM images show the spherical shape of the nanoparticle. Indeed, the laser fluence $F \approx 100$ mJ/cm² provides film heating close to the melting point even in a single shot regime, whereas a 12.5 ns delay between pulses leads to the temperature accumulation and exceeding the ablation threshold. The heat transferring from the ablated area to the surrounding film is accumulated much more efficiently in the cut patches, which are thermally isolated from the rest of the film. These micro-patches are unstable at high temperatures and undergo dewetting to a certain number of similar nanoparticles [47]. In order to provide deeper insight, we model the time dynamics of the cut liquid Si patch with a height of 80 nm and similar widths of 300 nm (Figs. 3B) on a fused silica substrate in the COMSOL software, solving the incompressible Navier-Stokes equations and taking into account the parameters of the used materials. The modeling shows that after ten nanoseconds the patch is transformed into a semisphere with a height of about 130 nm and a width of about 310 nm (Figs. 3B-E), giving qualitative agreement with the experimentally observed shapes.

The corresponding Raman signals from these nanoparticles reveal the crystalline state of the nanoparticles written by the laser, demonstrating a narrow peak at 520 cm⁻¹, with the halfwidth of about 10 cm⁻¹ (figure 3), which is larger than the halfwidth of the printed nanoparticles being
Figure 3. (a) Optical image in the dark-field scheme and array of the silicon nanoparticles fabricated by direct laser writing at a fluence of 100 mJ/cm², a repetition rate of 80 MHz and a scan period of 0.9 μm. The inset displays the SEM image of the written nanoparticles covered by a few nm thick gold layer with scale bars of 700 nm. Modelled evolution of the liquid silicon patch with a height of 80 nm and equal sides of 300 nm on the solid fused silica at different time-steps: about 0 ns (b), 1 ns (c), 4 ns (d), and 10 ns (e).

of about $4 \rightarrow 5$ cm$^{-1}$. The larger halfwidth corresponds to the smaller mean crystalline size, i.e. less than 10 nm according to the previous studies [48]. The origin of this difference is related to the faster cooling rate for the written nanoparticles on the fused silica substrate as compared with nanoparticles flying in air before deposition in the printing mode, owing to the 20-fold larger value of the glass thermal conductivity in comparison with that for air.

4. Conclusions
In conclusion, the developed novel single-step and lithography-free method of direct nanoparticles fabrication opens new opportunities to fabricate plasmonic and all-dielectric nanoresonator based structures on a large scale. To the best of our knowledge, it is the first demonstration of simultaneous cutting and dewetting of thin film processes that paves the way to extremely simplify the technology of monodisperse and ordered nanoparticles fabrication.

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References
[1] Maier S A 2007 Plasmonics: fundamentals and applications (New York: Springer)
[2] Luk'yanchuk B, Zheludev N I, Maier S A, Halas N J, Nordlander P, Giessen H and Chong C T 2010 Nature materials 9 707–715
[3] Kravets V, Schedin F and Grigorenko A 2008 Phys. Rev. Lett. 101 087403
[48] Campbell I and Fauchet P M 1986 *Solid State Communications* **58** 739–741