Single-stage fabrication of low-loss dielectric nanoresonators from high-loss material

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Abstract. High refractive index subwavelength dielectric nanoresonators, which support both electric and magnetic optical resonances, are a promising platform for many nanophotonic applications. However, the resonant properties of the nanoresonators are highly sensitive to defect concentrations. Therefore, to maintain low defect concentrations, it has generally thought inevitable to use crystalline precursor materials for nanoresonator fabrication. Here, we show that it is possible to fabricate crystalline (low-loss) resonant silicon nanoparticles by femtosecond laser ablation from amorphous (high-loss) silicon thin films. The crystallinity of the fabricated nanoparticles is proven by means of Raman spectroscopy and electron transmission microscopy, and their optical resonant properties are studied by means of dark-field optical spectroscopy and discrete-dipole simulations.

1. Introduction

Dielectric nanoparticles with high refractive indexes and low losses provide excitation of strong magnetic optical resonances [1–9], making them a viable alternative to plasmonic nanoparticles, which have high losses in the visible range, for such applications as electromagnetic field enhancement and sensing [10–13], antireflection [14], perfect reflection [3, 15], light wavefront manipulation [16,17], superdirective scattering [18] and enhancement of nonlinear effects [19,20].

Crystalline silicon (c-Si), being a low-cost CMOS compatible semiconductor and providing the desired optical response because of its large real and low imaginary parts of its refractive index in the visible range, is one of the most popular materials for all-dielectric nanophotonics. The most controllable method of c-Si film structuring — reactive ion etching combined with electron-beam lithography — is appropriated only for microscale structuring. Therefore, various methods of resonant silicon nanoparticle fabrication have been developed during last years, including colloidal chemistry [21], thin film dewetting [22] and laser ablation [6,23]. To achieve the crystalline state of nanoparticles, it was necessary to use initially bulk crystalline samples because amorphous silicon has an up to two orders of magnitude larger imaginary part of its refractive index as compared to crystalline silicon in the visible range [24], diminishing the resonant properties of nanoparticles.
Amorphous thin films are known to crystallize when heated [25], so laser annealing has been used for nanoscale amorphous surface [26] and nanoparticle [23] crystallization. In this paper, we study the fabrication of crystalline nanoparticles from amorphous hydrogenized silicon films, with magnetic Mie-type resonances, by means of an improved method of laser-induced transfer. The technique, so-called laser printing of nanoparticles [23] is shown in figure 1. The main advantage of this method over those reported previously, is that it allows single-stage low cost non-lithographic fabrication of crystalline optical nanoresonators on both transparent and opaque materials.

2. c-Si nanoparticle printing
The silicon nanoparticles were printed by a femtosecond laser system (Femtosecond Oscillator TiF-100F, Avesta Poject), which emits laser pulses at a central wavelength of 800 nm, with pulse duration of 100 fs and repetition rate of 80 MHz. Laser pulses selected by a Pockels cell-based pulse picker (Avesta Poject) were tightly focused by an oil immersion microscope objective (Olympus 100×) with a numerical aperture of $NA = 1.4$. According to the relation $d \approx 1.22\lambda/NA$, the estimated diameter of the beam’s focal spot size is $d = 0.7 \mu m$ which is close to the value measured by a method based on the dependence of the laser-damaged area on incident laser energy (0.68 μm) [27].

The nanoparticles were fabricated from an 80 nm thick a-Si:H film, which was deposited on a substrate of fused silica by plasma enhanced chemical vapor deposition from a SiH₃ precursor gas. The samples were placed on a three-dimensional air-bearing translating stage driven by brushless servomotors (ABL1000, Aerotech) with sample translation accuracy being at least 100 nm.

The nanoparticles were fabricated by single laser pulses (from a previously undamaged surface) in the forward-transfer geometry, in which the receiving substrate is placed under the film with a spacing of $\sim 50 \mu m$ (figure 1). This geometry has an advantage over the back-transfer geometry owing to the possibility of nanoparticle printing onto a wide variety of substrates including opaque and structured samples. The silicon nanoparticles were printed at laser energies in the range of $0.5 – 1.2$ nJ providing fluences in the range of $0.12 – 0.16$ J/cm². The nanoparticles are almost spherical in shape (figure 2(b)) and their diameters lie in the range of $50 – 200$ nm depending on the fluence.
Figure 2. (a) Experimental Raman spectra from an individual nanoparticle with a diameter of about 170 nm (red), initial, donor, film (purple), and reference bulk crystalline silicon (blue). (b) Ellipticity distribution of Si nanoparticles; insets: SEM and TEM images of typical Si nanoparticles (c). Electron diffraction picture from the crystalline nanoparticles.

3. Nanoparticle Characterization

3.1. Crystallinity

The crystalline structure of the initial film and the produced individual nanoparticles were characterized by Raman scattering measurements by a micro-Raman setup (Raman spectrometer HORIBA LabRam HR, AIST SmartSPM system). The Raman spectra were recorded under excitation by a 2 mW, 632.8 nm HeNe laser through a 100× microscope objective (NA = 0.9) and projected onto a thermoelectrically cooled charge-coupled device (CCD, Andor DU 420A-OE 325) array with a 150 g/mm diffraction grating. Spectra of individual nanoparticles were recorded by precisely positioning the nanoparticle (accuracy down to 100 nm) in the center of the laser beam (1.8 µm in diameter) focused on the substrate.

The initial silicon film was shown to be completely amorphous because of its broad Raman peak centered around 480 cm$^{-1}$. The Raman spectra of the individual nanoparticles have narrow peaks at 521.5 cm$^{-1}$ indicating a crystalline cubic diamond structure in all the nanoparticles with diameters in the range of 120–200 nm. The reference Raman signal from a bulk crystalline silicon wafer and the literature data suggest that the Raman peak of a pure crystal corresponds to 520 cm$^{-1}$. The slight positive shift of the peak of nanoparticles $\Delta \nu = 1.5$ cm$^{-1}$ is explained by residual compressive stress [28]. Another important characteristic extracted from the Raman spectra is the size of the nanocrystallite, which is larger than $\sim 20$ nm because the Raman peaks of the nanoparticles have almost the same halfwidth ($4 - 5$ cm$^{-1}$) as the peak from a bulk crystalline silicon wafer ($4.5$ cm$^{-1}$) [29].
The Raman measurements agree with the characterization of the printed nanoparticles by means of transmission electron microscopy (TEM). We used specimen grids (3 mm-diameter 200-mesh copper grids coated on one side with a 20 nm-thick film of amorphous carbon) to collect nanoparticles ablated from the a-Si film. The size, structure, and composition of the collected nanoparticles were determined using bright and dark field TEM imaging. In our experiments, we observed mainly single-crystal nanoparticles with the mean size in the range of 100 − 200 nm (figure 2(b)). The analysis of the electron diffraction pattern from several nanoparticles shows clear maxima, corresponding to certain crystalline planes (figure 2(c)). TEM imaging also provides information on the oblateness of the particles along the orientation perpendicular to the collecting surface, giving the average ellipticity of about $a_{||}/a_{\perp} \approx 1.12$, where $a_{||}$ ($a_{\perp}$) is the particle semi-axis oriented perpendicular (parallel) to the surface of the substrate. Indeed, scanning electron microscopy (SEM, Carl Zeiss, Neon 40) shows that values of $a_{||}$ are almost the same in all directions (figure 2(b)). These results correlate with previously observed oblateness of the printed silicon nanoparticles [8].

As in previous studies [23,30], in our experiments the average size of the printed nanoparticles strongly depends on laser fluence. We observed two different regimes of nanoparticle generation. In the first regime, average nanoparticle sizes grow with an increase of fluence up to 150 mJ/cm² manifesting in the change of their colors from blue to red (figure 3(a)-(c)). This growth can be described in terms of the spallation mechanism of laser ablation, where a thin molten layer is spalled due to laser-induced tensile pressure waves [31, 32], breaking into a number of liquid droplets via the Rayleigh-Plateau instability [33]. The photomechanically spalled volume increases as $V \sim \ln(E)$ under the action of a Gaussian beam, owing to the logarithmic dependence of the spalled surface layer area $s_s^2 \sim \ln(E)$ [34], whereas the thickness of the layer remains almost constant [31] or even decreases [32]. In previous studies of nanoparticle printing from crystalline silicon, such an increase of molten volume led to an increase in the number of nanoparticles [30] and their size [23], which agrees with our results (figure 3(a)-(c)). However, using amorphous silicon films it is not possible to reproducibly print one nanoparticle per laser shot, unlike when printing from crystalline films.

The second regime of nanoparticle fabrication corresponds to $F > 150$ mJ/cm²,
Figure 4. Experimental (a) and simulated (b) spectra for scattered p-polarized incident light (angle of incidence is $70^\circ$) from individual nanoparticles with semi-axis parallel to the substrate surface $a_\perp = 85$ nm.

where large (red) nanoparticles are followed by small nanoparticles with a much broader size distribution (figure 3(d)). This regime is related to the regime of unstable boiling of superheated silicon [31, 32, 35]. In this regime nanoparticle formation occurs through the explosive decomposition of the material into vapor and small clusters/droplets [32, 36] yielding nanoparticles with average sizes smaller than 100 nm [37].

The almost perfect crystalline phase of the printed silicon nanoparticles (proved by Raman, TEM and SEM characterization) means that it is possible to fabricate crystalline silicon nanoresonators from amorphous films, which is very useful for low-loss all-dielectric nanophotonics.

3.2. Optical properties

The excellent resonant properties of the particles were demonstrated using polarization-resolved scattering spectra measurements in a dark-field scheme, with the nanoparticles illuminated by p-polarized light from a halogen lamp (HL-2000-FHSA) at an angle of $70^\circ$ to the surface normal and scattered signal collection performed by means of an Mitutoyo M Plan APO NIR 50× objective ($NA = 0.45$) [38]. The scattered light was registered by the same spectrometer as in the Raman measurements.

The excitation of electric dipole (ED) and magnetic dipole (MD) resonances is proven by simulations using the discrete dipole approximation [39, 40]. The scattering geometry is modeled as a c-Si sphere of a given radius $R$, consisting of 3069 dipoles, on a a-SiO$_2$ substrate. The sphere is irradiated by a plane wave at an angle of $70^\circ$ in vacuum. Modeling of scattering spectra (figure 4(b)) shows good agreement with the corresponding experimental ones (figure 4(a)). Some differences between the shapes of theoretical and experimental spectra arise from the ellipticity of nanoparticles and the presence of a thin natural oxide layer on the surface of nanoparticles [41]. Such optical and TEM/SEM analysis of average ellipticity and crystallinity of nanoparticles will be useful for further applications of the laser printing method.

4. Conclusions

We have experimentally proven that laser fabrication of crystalline (low-loss) silicon nanoparticles, supporting magnetic Mie-type resonance, can be performed from amorphous (high-loss) a-Si:H films, making it unnecessary to use initially crystalline material or any additional annealing. Analysis of the printed nanoparticles shows that they are monocrystalline with similar dimensions at certain fluences. Our method of nanoparticle printing does not limit
us to using transparent substrates, meaning that nanoparticles can be printed onto a wide variety of substrates/devices.

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