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Fabrication of periodic surface topographies via sequential photothermal laser microsintering of silicon nanoparticle films

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ABSTRACT

Photothermal laser microprocessing is exploited in order to induce sintering and compaction of thin silicon nanoparticle (Si NP) films. Ethanolic dispersions of Si NPs with an average diameter of 45 nm are spin-coated on silicon substrates yielding films with a thickness of about 400–500 nm. Scanning electron and atomic force microscopy are used for characterization of the resulting surface morphologies. Sequential processing of the coated layer with a microfocused cw-laser beam at a wavelength of 532 nm generates periodic surface structures. The periodicity of these structures is determined by the distance between adjacent laser-written lines. Despite a $1/e$ laser spot size of 1.4 μm, fabrication of topographic surface structures with submicrometer periodicities is feasible. In particular, surface topographies with periodicities of 600 nm and a topographic amplitude of 80 nm are fabricated. These results point to a high nonlinearity, which is attributed to the strongly activated, temperature-dependent laser sintering process. These experimental observations are reproduced qualitatively considering a simple photothermal model and an activated sintering process. Prospects of photothermal laser microsintering of nanoparticle films to fabricate biomimetic surface structures are discussed.

1. Introduction

Nature in many respects sets incredible benchmarks in the fabrication of functional micro- and nanostructured surface architectures [1]. Prominent examples include the surface of the lotus leaf, the skin of the sandfish and the corneal structure of the moth eye, which show extraordinarily superhydrophobic, self-cleaning, low-stiction and antireflective performance, respectively [1–4]. Generally, the particular functions of these surfaces originate from a unique combination of hierarchical micro-/nanotopographic architectures – often in combination with an optimized surface chemical composition [2–4]. Inspired by such examples, there is an ongoing effort in science and engineering in order to build up coatings and structures, which mimic these and other functions. Applications range from the fabrication of antifouling and drag-reducing surfaces for marine purposes to the design of antireflective textures for photovoltaic cells [5–7].

Laser processing has evolved as a fast and facile technique for the fabrication of micro- and nanostructured surface topographies [8]. Commonly, these studies follow a top-down approach, that is, bulk material is machined, e.g. via laser ablation and chemical laser texturing [9–12]. In addition, laser techniques also have been exploited in order to build up micro- and nanostructures via photothermal sintering of nanoparticulate materials following a combined top-down/bottom-up approach, e.g. for the fabrication of conductive patterns or mesoporous electrodes [13,14]. Recently, we investigated the impact of oxide formation on the morphology of laser-sintered silicon nanoparticle (Si NP) films [15]. Laser processing of thin silicon nanoparticle films in air results in the formation of strongly oxidized granular films while oxide formation is largely suppressed in vacuum. Varying the laser parameters at these conditions allows one to tune the film morphology, e.g. in order to fabricate either mesoporous or compact films. Sequential laser scanning results in periodic surface structures. In this study, we investigate the dependence of such surface structures on the distance between adjacent laser-written lines during sequential processing. Noteworthy, the fabrication of periodic surface structures with periodicities well below the laser spot size is feasible. In particular, the fabrication of surface structures with sub-micron periodicities is demonstrated. In conjunction with common silanization routines this provides promising perspectives in the fabrication of biomimetic surface structures.

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2. Materials and methods

Phosphorous-doped Si NPs with an average size of 45 nm are synthesized via gas phase pyrolysis of silane and phosphine in a microwave plasma reactor following an established method described in detail elsewhere [16]. The material used here exhibits an average size of 45 nm with a standard deviation of about 20–30 nm and the phosphorous concentration is about 250 ppm (1.2×10^{19} cm^{-3}). Coating and laser processing are carried out as detailed in Ref. [15]. For spin-coating, 5 wt% ethanolic dispersions of Si NPs are prepared. 1 cm × 1 cm pieces of commercially available Si(1 0 0) wafers (p-type, 1–20 Ωcm) are used as substrates to produce Si NP thin films by spin-coating. Prior to film formation, the substrates are dipped into a 6% HF solution in water for 5 min in order to remove the native surface oxide layer [17]. Spin coating is carried out at 5000 rpm. In order to remove residual ethanol after drying, the samples are mildly heated at 60 °C for 5 min. The coated samples are then again dipped for 20 s into a 10% HF solution in order to remove the surface oxide layer from the NPs [15]. After oxide striping, the resulting H-termination protects the Si substrate and the Si NPs against oxidation for some hours.

Photothermal laser processing is carried out in a vacuum reaction cell ($p < 1$ mbar) using a microfocused scanning cw-laser setup with a Gaussian beam profile operating at a wavelength of 532 nm [15]. Briefly, the laser beam of a diode-pumped solid state laser (Laser Quantum, Ventus) is focused onto the sample surface using an optical microscope objective (Olympus, LM Plan FI 20x) with a numerical aperture (NA) of 0.4. For focusing, the objective is mounted on a stepper motor stage (Micos, PLS-85). For positioning in the focal plane, the sample can be moved within an area of 26 mm × 26 mm at speeds of up to 15 mm s^{-1} using two additional stepper motor stages (Micos, PLS-85). Laser beam profiling with a knife-edge system (Beam Master BM-3 UV-VIS, Coherent) reveals a $1/e$ focal spot diameter of $d_{1/e} = 1.4$ μm. For comparison, a value of 1 μm is calculated considering ideal abberation-free optical alignment, NA = 0.4, a truncation ratio $T_r = 0.9$ and a diffraction index $M^2 = 1.1$, cf. Refs. [8,18]. An acousto-optical modulator (A.A. Opto-Electronic, A.A.MTS.110/AS.VIS) allows one to adjust the laser power and to switch the laser beam on and off. A rotary vane pump is used in order to evacuate the reaction cell down to a base pressure p below 1 mbar. Typically, photothermal laser processing at a given set of laser parameters is carried out via laser beam scanning along a line pattern yielding a sintered square of 100 μm × 100 μm. Subsequent processing at distinct parameters is performed in adjacent areas on the same sample. In conjunction with microscopic techniques, this provides a very convenient and reproducible procedure to study the dependence of resulting film structures on the experimental parameters.

Sample characterization is carried out using scanning electron microscopy (SEM, FEI Company, ESEM Quanta 400), atomic force microscopy (AFM, Bruker AXS, Autoprobe CP and Nanoscope IIIa) and reflection optical microscopy (Olympus).

3. Results and discussion

For fabrication of periodic surface topographies sequential photothermal processing of thin Si NP films is carried out with a microfocused laser spot as described in the experimental section. Scanning electron micrographs of structures obtained from patterning experiments carried out at constant laser power ($P = 200$ mW) and writing speed ($v = 0.4$ mm s^{-1}) but different scanning distances s of 0.6 and 2 μm are shown in Fig. 1. For comparison, Fig. 1a and b displays scanning electron micrographs of the as-deposited Si NP film. Irradiation of Si NP films with the microfocused laser beam induces a local temperature rise. As a result, sintering of the NPs takes place and local compaction of the film is initiated [15]. AFM measurements reveal a thickness of the as-deposited Si NP films of $h_0 \approx 400$–500 nm, cf. Fig. 2. For these measurements the as-deposited film (right side of Fig. 2a and b) is gently removed via scratching along a thin line. This exposes the bare substrate surface (left side of Fig. 2a and b). Maximum compaction during sintering leads to films with thicknesses of $h_{min} \approx 200$ nm (cf. data below). This provides a means to build up periodic surface topographies. At large scanning distances, i.e. at $s = 2$ μm, voids in the overlapping region of the adjacent laser scans remain visible (Fig. 1c and d). Evidently in these areas sintering is largely incomplete. Such structures disappear at distances of $s = 1.4$ μm. As displayed in Fig. 1e and f, periodic surface structures are visible down to a distance of 0.6 μm. Further results show that periodic structures are no longer discernible at $s < 0.4$ μm. Considering a $1/e$ laser spot diameter of 1.4 μm, these results point to a highly nonlinear process, i.e. an overall process, which is not linear in applied laser power density [8]. We detail this issue further below.

Additional characterization of the laser-fabricated surface structures is carried out using AFM. Fig. 3 displays AFM measurements of surface structures as obtained after laser processing at $P = 200$ mW, $v = 0.4$ mm s^{-1} and $s = 0.6$ μm. These data show the particular micro- and nanostructure of the laser-processed films. Firstly, striped structures with periods of 600 nm and topographic amplitudes of about 80 nm are evident. Secondly, the grain boundaries between individual particles are clearly visible in the derivative image of the topographic data. The average particle size at the conditions considered here is about 70 nm.

Further AFM data are shown in Fig. 4. Laser processing again is carried out at $P = 200$ mW, $v = 0.4$ mm s^{-1} and $s = 0.6$ μm generating periodic surface topographies. These structures are shown on the left in the topographic image in Fig. 4a. On the right, the unprocessed surface area exposing the as-deposited NP film is shown. The height profile across the processed and unprocessed areas allows one to determine a height difference of 220 nm between the as-deposited film and the sintered film. In view of the initial film thickness of $h_0 \approx 430$ nm, this yields $h_{min} \approx 210$ nm.

As discussed above, the experimental data in Figs. 1, 3 and 4 point to a high nonlinearity of the overall laser process. Commonly, in photothermal laser processing, a strong nonlinearity is introduced via the temperature dependence of the initiated process [8,19]. In the following a simple model is considered in order to illustrate this interplay. At first, intensity profiles I_n during sequential laser processing along adjacent laser scans n at a distance s are calculated considering a Gaussian beam profile:

$$I_n = I_{max} \exp\left(-\frac{4 \cdot (x - n \cdot s)^2}{d_{1/e}^2}\right), \quad (1)$$

where I_{max} corresponds to the maximum laser intensity, calculated via $I_{max} = 4P/\pi d_{1/e}^2$, and x depicts the lateral position. Intensity profiles of eight successive laser scans and the corresponding total intensity profile of all laser scans are shown in Fig. 4c. Clearly, the intensity profiles of the successive laser scans strongly overlap. Hence no periodic structure is discernible in the total intensity profile. For this reason, a linear process, that is, a process, which is linear in the applied laser intensity, fails to reproduce the experimental data. Instead the experimental data point to a strongly nonlinear process. We emphasize, that nonlinearities are quite common in laser processing and may have different causes [8,19].

Of particular importance in photothermal laser processing, of course, is the generated spatial temperature profile. Quantitative modeling necessitates a detailed knowledge of the