



Femtosecond-laser processing of nitrobiphenylthiol self-assembled monolayers

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ABSTRACT

Single-pulse femtosecond laser patterning of nitrobiphenylthiol monolayers on Au-coated Si substrates at $\lambda = 800$ nm, $\tau < 30$ fs and ambient conditions has been investigated. After laser processing wet etching experiments are performed. Laser irradiation reduces the chemical resistance of the coating. In particular, the monolayer acts as a positive-tone resist. Burr-free pattern transfer is feasible at laser pulse fluences between 1 and 2.7 J/cm². Minimum structure sizes at a 1/e laser spot diameter of about 1 μ m are close to 300 nm, i.e. sub-wavelength processing is demonstrated. Noteworthy, however, no indications for negative-tone resist properties of processed monolayers are evident, that is, cross-linking of the biphenyl moieties, if at all, is marginal. Also, complementary labeling experiments provide no evidence for chemical transformation of the nitro end groups into amine functionalities. Perspectives of resonant fs-laser processing in exploiting the particular prospects of nitrobiphenylthiol monolayers as negative-tone resists and chemically patternable platforms are discussed.

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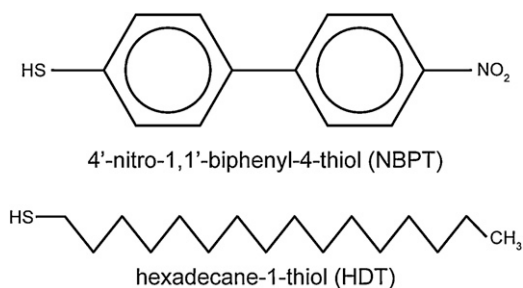
1. Introduction

Self-assembled monolayers (SAMs) are widely used to tailor the surfaces of metals, semiconductors and dielectric materials [1,2]. In recent years, femtosecond (fs) laser processing of self-assembled monolayers has attracted significant interest [3]. Previous studies focused on fs-laser patterning of SAMs on Au-coated substrates [4–7], silicon wafers [8] and quartz glass [9,10]. The ultrathin nature of these coatings allows for single pulse processing and thus ensures short processing times [7–9]. It also allows for well-defined irradiation and burr-free patterning of the coating and avoids bubble and particle formation [3]. Varying the chemical structure of the monolayer, in turn, provides a means to tune cross sections, incubation effects and resist properties [3,10]. In a previous study we investigated single-pulse fs-laser patterning of hexadecanethiol (HDT) monolayers on Au-coated Si substrates at $\lambda = 800$ nm and $\tau < 30$ fs at ambient conditions [7]. Local irradiation results in desorption and decomposition of the monolayer. HDT SAMs act as positive-tone resists. Hence, in conjunction with standard wet etching procedures the patterns can be transferred into the subjacent Au film. Burr-free processing can be carried out

over a wide range of laser pulse fluences from above 2 J/cm² down to 0.5 J/cm². Minimum structure sizes at a 1/e laser spot diameter of about 1 μ m exhibit a diameter of 160 nm, that is, sub-wavelength patterning down to $\lambda/5$ is feasible. Here, we report on a complementary study focusing on fs-laser processing of nitrobiphenylthiol (NBPT) SAMs. For comparison, the chemical structures of HDT and NBPT precursor molecules are shown in Scheme 1. In contrast to HDT SAMs, NBPT SAMs are known to act as negative-resists [11–13]. In particular, upon exposure with electrons dehydrogenation of the molecules is initiated [11,12]. This results in crosslinking of the biphenyl moieties, which increases the chemical resistance of the processed monolayer. Also, chemical transformation of the nitro end groups into amine functionalities takes place along this pathway providing a means for chemical patterning. Generally, these processes are attributed to an indirect mechanism, which involves hot electrons that are generated in the substrate [13]. Excitation energies above 5 eV are required in order to induce dehydrogenation of thiol-based SAMs [14]. Hence, optical processing usually is carried out at short wavelengths, e.g. using extreme ultraviolet (EUV) irradiation [13]. In view of the broad literature in this field, it is, of course, tempting to check whether these processes can also be initiated exploiting the particular prospects of common fs-laser sources in nonlinear processing [15]. In view of the energetic constraints, sub-wavelength patterning appears feasible, e.g. via multiphoton absorption processes or via multiple electronic excitations [3].

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Scheme 1. Chemical structure of 4'-nitro-1,1'-biphenyl-4-thiol (NBPT) and hexadecane-1-thiol (HDT).

2. Materials and methods

Commercial Si(1 0 0) wafers coated with a 5 nm Ti adhesion layer and a 40 nm Au layer (MaTeck) are cut into small pieces, about 10 mm × 10 mm in size, and used as substrates. For coating, all samples, at first, are cleaned with piranha solution (3:1 mixture of 96% sulfuric acid and 30% hydrogen peroxide) for 5 min, thoroughly rinsed in ultrapure water and dried in a stream of high-purity argon. Subsequently, these samples are immersed into a 2 mM solution of 4'-nitro-1,1'-biphenyl-4-thiol (NBPT, synthesized as detailed in Ref. [11], cf. Scheme 1) in degassed N,N-Dimethylformamide (DMF) for 72 h in a light-tight container in a glove box, followed by rinsing in DMF and ethanol and drying with argon. For characterization of the SAMs infrared reflection-absorption spectroscopy (IRRAS) is used. Infrared spectra are collected with a Bruker spectrometer (Vertex 70) equipped with a variable-angle reflection accessory (A513). A polarizer is placed in front of the sample in order to measure spectra with p-polarized light. The angle of the incident light is set to 85° with respect to the surface normal. The spectra are taken at a resolution of 4 cm⁻¹ by using 1024 scans and referenced to a clean gold sample without any further data manipulation. In agreement with the literature [11], peaks for the ν(C–N) scissoring mode at 856 cm⁻¹, the symmetric and asymmetric stretching modes ν_s (NO₂) and ν_{as} (NO₂) at 1348 cm⁻¹ and 1549 cm⁻¹ and the aromatic stretching modes at 1470 cm⁻¹, 1530 cm⁻¹ and 1597 cm⁻¹ are observed in the fingerprint region.

Laser processing in air is carried out within one day after coating using a commercial Ti:Sapphire oscillator-amplifier system (Femtopower compact Pro, Femtolasers Produktions GmbH) operated at a constant repetition rate of 1 kHz. The laser system provides Gaussian laser pulses with a wavelength and a pulse length of λ = 800 nm and τ < 30 fs, respectively. A 36× Schwarzschild microscope objective with a numerical aperture NA = 0.5 is used to focus the laser pulses onto the substrates. Taking data from patterning experiments a 1/e laser spot diameter d_{1/e} of about 1 μm is determined as outlined below. Further details of the experimental setup can be found elsewhere [16].

For etching, the patterned samples are immersed into a solution of K₂S₂O₃ (0.1 M), KOH (1.0 M), K₃Fe(CN)₆ (0.01 M), and K₄Fe(CN)₆ (0.001 M) at room temperature for 15–20 min [7]. Subsequently, the samples are rinsed with ultrapure water and blown dry with argon.

For characterization of the patterned samples atomic force microscopy (AFM, Autoprobe CP from Veeco) is used. AFM images are recorded in contact mode with standard cantilevers. Only fully etched structures with depth equal to the Au film thickness are considered for analysis. Width measurements are not corrected for tip size effects and refer to values measured at half-depth.

Complementary labeling experiments are carried out using dispersions of citrate-stabilized Au nanoparticles (NPs) with an average size of 16 nm [17]. Laser-processed samples are immersed into such dispersions in order to test for amine functionalities.

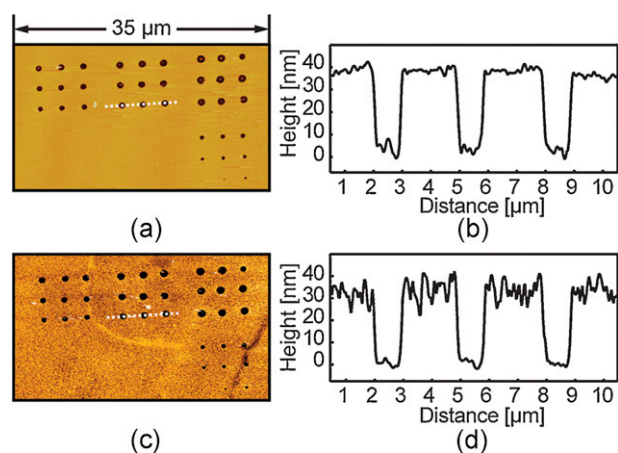


Fig. 1. AFM data from patterning experiments of NBPT SAMs on Au-coated silicon samples with single laser pulses at λ = 800 nm, τ < 30 fs, d_{1/e} = 0.96 μm and distinct pulse fluences between 0.1 and 3.2 J/cm². Starting at 3.2 J/cm², the pulse fluence has been decreased by 0.064 J/cm² from one position to the next. Processing is carried out in 3 × 3 sub-patterns from the top right to the bottom left of the image. The pulse fluence within one 3 × 3 sub-pattern is changed row by row going from the top right to the bottom left. The data displays patterns after wet-chemical etching for: (a) and (b) 15 min and (c) and (d) 20 min. Height profiles in (b) and (d) are taken at the position marked by dashed white lines in (a) and (c).

3. Results and discussion

In order to explore the resist properties of NBPT SAMs, fs-laser processing has been carried out over a wide range of laser pulse fluences between 0.1 and 3.2 J/cm². In addition, the etching time has been varied. Typical AFM data after laser patterning and wet-chemical etching are shown in Fig. 1. Evidently, at short etching times the NBPT SAMs act as positive-tone resists (Fig. 1a and b). In particular during etching the 40 nm thick Au film in the center of the irradiated surface areas is completely dissolved, whereas the SAM in the surrounding areas hinders removal of the underlying Au layer. Apparently, laser processing results in a decomposition and/or desorption of the thiol molecules. This is in agreement with results reported in a previous contribution focusing on fs-laser patterning of hexadecanethiol (HDT) monolayers [7]. Note, upon irradiation ionization in air might be initiated. Hence, reactive species could interact with the organic monolayer [4–6]. From our data, however, no effect of such processes is evident. Upon increasing the etching time significant pitting in the surrounding areas takes place resulting in increased height variations (Fig. 1c and d). Note, this affects those areas, which have not been irradiated, and those areas in direct proximity of the hole structures. Pitting is also observed in those areas, which have been processed at low fluences. Hence, cross-linking between the biphenyl moieties, if at all, is marginal. In particular, irrespective of the laser parameters and the etching time processed NBPT SAMs do not act as negative-tone resists.

Experimental data at short etching times are analyzed in more detail (Figs. 2 and 3). Considering the 1/e penetration depths at λ = 800 nm of 14 nm, laser light absorption essentially takes place in the Au film [7]. Electronic excitations and phonons, of course, can reach deeper levels. Hence, at high fluences also the Si substrate is affected. After removal of the Au layer, this damage at the Au/Ti/Si-interface is clearly visible as bumps in the center of the structures (Fig. 2a and b). In contrast, at low fluences the Si substrate remains unaffected (Fig. 2c and d). In agreement with the thickness of the Au layer, height profiles show depths of 40 nm. In addition, a rather smooth surface of the Si substrate is evident. Fabrication of such well-defined patterns is feasible between about 1 and 2.7 J/cm².

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