Applied Surface Science 256 (2010) 2803–2808

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Application of clean laser transfer for porphyrin micropatterning

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ARTICLE INFO

Article history:
Received 30 October 2009
Accepted 11 November 2009
Available online 6 December 2009

Keywords:
Laser-induced forward transfer
Langmuir film
Porphyrin

ABSTRACT

Blister-based laser-induced forward transfer is proposed as a promising tool for clean, cold and liquid-free local transfer of various organic substances. The feature of the given technique is non-destructive local deformation of an absorbing metal film on a transparent support avoiding the metal sputtering. Application of the blister-based laser transfer of a Langmuir film to fabricate mesotetraphenylporphyrin micropatterns on a silica substrate has been demonstrated. The metal film thickness is found to be a key parameter, which determines the laser fluence range allowing the clean transfer, predominant mechanism of the blister formation and laser-induced heating of the transferred material. According to the numerical modelling confirmed by UV–vis absorption spectroscopy, the target with 1.5 μm thick titanium film provides negligible heating of the porphyrin transferred by 5 ns laser pulses.

1. Introduction

Fabrication of micro-dimensioned patterns of biomaterials on a solid substrate is one of the cornerstones for the development of next-generation biomedical devices including biosensors and biochips. The most extended techniques allowing production of high-density surface microarrays for the current moment are pin microspotting, ink-jet printing and photolithography. An interesting alternative that avoids the use of expensive photolithographic masks and presents higher integration scale than microspotting or ink-jet printing could be the laser-induced forward transfer (LIFT) technique. It consists in the local transfer of material from a thin-film covering a transparent support to a close receiving substrate under the action of a laser pulse. The LIFT has been successfully used to produce patterns of different biomaterials including proteins [1,2], DNA [3,4], living cells [1,2,5] and tissues [1,2].

A few approaches have been proposed to date to minimize heat-induced damage of the transferred biomaterials. First, it has been shown that ultrashort UV laser pulses allow transfer of biomaterials via their direct ablation [3,7]. Thin layer of the material is strongly heated and vaporized, but an essential part of the ejected matter preserves specific functionality. Second, it was proposed to initiate biomaterial transfer by laser ablation of a thin metal film placed between the biomaterial layer and the transparent support [6]. As the transferred layer contacts with a hot metal vapor, partial damage of the biomaterial cannot be avoided. Besides, the ablated metal is deposited in this case on the receiving substrate as numerous micro/nanoparticles. The safest transfer of different organic materials has been demonstrated under usage of a liquid matrix. The matrix provides transportation of the biomaterial due to local laser-induced boiling at relatively low temperature and also operates as a protective environment. The laser radiation is absorbed either directly in the matrix [1,2,8,9] or in a thin metal film [10], which works as a liquid heater. Evidently, life sustaining matrix is natural and indispensable component of any living cell processing including the laser transfer. However, for patterning of most other organic materials, usage of liquids looks rather as technological disadvantage. Indeed, necessary selection of an appropriate liquid matrix essentially complicates adaptation of the transfer procedure to new biomaterials. The resulted spatial resolution is determined not only by the laser spot size; it depends also on many other parameters like liquid viscosity, wettability of the receiving substrate and thickness of the liquid layer at the target. Usage of liquid minimizes the potential ability of the laser transfer to fabricate multilayered and multicomponent structures. Thus, search of clean, safe and liquid-free transfer method remains issue of the day.

Here we report on fabrication of thin surface micropatterns of porphyrin, which is a promising material for optical sensors detecting volatile organic compounds [11]. The patterns were produced via local laser transfer of a liquid-free Langmuir film applying so-called blister-based LIFT (BB-LIFT) technique [12]. The feature of the given technique is non-destructive local deformation of an absorbing metal film instead of its total sputtering. As a result, the BB-LIFT technique excludes contamination of the receiving

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doi:10.1016/j.apsusc.2009.11.031

substrate by the metal particles. This study is the first attempt to prove applicability of the BB-LIFT technique for safe biomaterial patterning and to investigate laser-induced material heating under usage of nanosecond pulses. Principal distinction of the given work from [13], where thin polyimide film was used as an absorbing and blistering layer, is that liquid-free laser transfer has been demonstrated.

2. Experiments

Four targets were prepared depositing titanium films of different thickness (50–1500 nm) on polished silica plates via vacuum evaporation. The Langmuir–Schaefer technique was used to deposit a thin organic layer on the metallized target surface. Mesotetraphenylporphyrin (TPP) and stearic acid (SA) were dissolved in chloroform (both 10^{-3} M) and mixed. Afterwards, the solution was spread onto a pure water sub-phase at 20 °C. After evaporation of the solvent, the monolayer film was compressed up to a surface pressure of 15 mN/m and then five layers were consecutively transferred to the target surface by the horizontal dipping method. It is known that the porphyrin molecules form aggregates in the mono- and multilayer Langmuir films [14]. Comparing AFM and optical microscopy images of a few Langmuir films with different TPP:SA ratio (from 1:0 to 1:10), we have come to conclusion that higher content of stearic acid promotes reduction of the average aggregate size and makes the film more uniform. Finally, the ratio of TPP:SA = 1:1 was found to be a good compromise between improvement of the film morphology and decrease in the optical absorption of the Langmuir films due to lower concentration of the porphyrin molecules. The obtained nanoaggregated TPP:SA layer on the target surface imaged with a scanning probe microscope Solver P47 is shown in Fig. 1.

The transfer process was initiated by single 5 ns (FWHM) laser pulses at 1078 nm wavelength generated by a Nd:YAP laser in the Q-switch mode. The upward directed laser beam was focused at the metal–silica interface of the horizontal target forming a Gaussian spot. A receiving substrate made of polished silica was placed above the target at the distance of about 10 μm. The target and the receiving substrate were installed on a computer controlled motorized XY stage to fabricate patterns of arbitrary shape in multishot regime. Fluorescent images of the generated patterns were obtained with a Nikon E600 epifluorescence microscope.

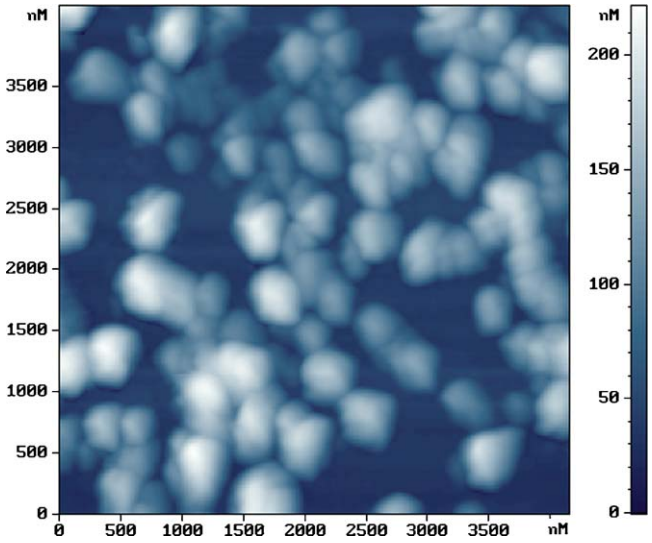

Fig. 1. SPM image of aggregated TPP:SA layer.

Absorption spectra of the original and transferred porphyrin in a UV–vis spectral range were recorded with a spectrophotometer Shimadzu UV-250. Large-area surface patterns (8 mm × 8 mm) consisting of many round microspots were deposited from the targets with different metal thickness for the spectroscopic measurements. The spots on the target were not overlapped and the porphyrin filling space between the irradiated spots remained at the target. Efficiency of the material transfer under the large-area patterning was estimated as $f \approx 50\%$. To examine sensitivity of the absorption spectra to the thermal effect, few TPP:SA films deposited on silica plates and annealed in an oven (in air) during 1 min at the temperatures of 60–500 °C. The TPP melting point was determined on a Boecius apparatus.

3. Temperature profile calculations

Since the lateral dimensions of the irradiated areas are much larger than the thermal diffusion length in both the support and the metal film, laser-induced temperature changes are described by the one dimensional heat conduction equation:

$$\frac{\partial T}{\partial t} = \frac{1}{\rho \cdot C(T)} \frac{\partial}{\partial z}\left[K(T)\frac{\partial T}{\partial z}\right] + \frac{\alpha I(z,t)}{\rho \cdot C(T)} \quad (1)$$

where T, ρ, α, $C(T)$ and $K(T)$ denote temperature, material density, optical absorption coefficient, specific heat and thermal conductivity of the metal film or the silica support. The heat flow into the porphyrin layer was neglected due to lack of corresponding thermophysical data. This unlikely can lead to noticeable error in the temperature calculations taking into account typically low thermal conductivity of organic material and high porosity of the Langmuir film due to porphyrin aggregation. The spatial and temporal dependence of the intensity is given as:

$$I(z,t) = I_o(t)(1-R)\exp(-\alpha z) \quad (2)$$

where z is the distance from the metal–silica interface, $I_o(t)$ is the intensity of the laser beam and R is the reflectance of the metal–silica interface at 1.08 μm. The temporal intensity dependence $I_o(t)$ was approximated by a Gaussian profile.

The heat conduction equation has been solved using the method of finite differences taking into account the temperature dependence of specific heat and thermal conductivity and incorporating metal melting and vaporization. The thermal and optical data used are compiled in Table 1.

4. Results and discussion

4.1. Laser transfer process

Each of the examined targets was irradiated varying energy of the laser pulses. Local removal of the TPP:SA layer from the undamaged metal film (Fig. 2a), as well as sputtering of the titanium film within the laser spot (Fig. 2b) could be easily detected with optical microscopy. The local fluence relating to the edge of the transfer region was found to decrease slightly with rise of the transfer region at the target. Extrapolation of the calculated local fluences to the vanishing size of the transfer region has yielded us the porphyrin transfer threshold—F_{tr}. Applying similar procedure to the zone of the metal sputtering, we have evaluated another important parameter defined as the ablation threshold of the titanium layer—F_{ab}. Thus, the condition ensuring ejection of the porphyrin without the metal sputtering is given by the following inequality: $F_{tr} < F_{max} < F_{ab}$, where F_{max} is the maximum fluence in the laser spot. The porphyrin ejected from the target formed detectable patterns at the receiving substrate. Titanium removed from the target at $F_{max} > F_{ab}$ also transferred onto the receiving