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Laser processing of metal thin films using transparent microsphere arrays

C. Constantinescu*, L.N.D. Kallepalli, P. Delaporte, O. Utéza, D. Grojo**

Aix-Marseille Université/CNRS, Laboratoire LP3 (UMR 7341), F-13288 Marseille, France

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ABSTRACT

We present results on a microsphere-assisted laser processing method that allows the parallel ablation and printing of metal, leading to the formation of negative patterning (nanopinholes) and positive patterning (nanodroplets). High density packed monolayers of transparent microspheres on quartz substrates are covered with thermally evaporated silver films of controlled thickness. When back-illuminated using picosecond laser pulses, the laser interaction with the microsphere near-field mask produces periodic local detachments of the films that can be collected on a receiving substrate. We report on the resulting metal nanostructures, as our experiments lead to well-defined nanohole arrays with characteristics that can be controlled with the type of spheres and the laser energy. We characterize the ablated narrow-size-distribution nanodroplets that are randomly distributed on a receiving surface, as these aspects reveal some of the challenges associated to downscaling to the nanometer scale of laser printing techniques.

1. Introduction

Colloidal lithography is a simple, versatile, and cost-effective fabrication technique for researchers in the field of micro/nanofabrication and photonics, based on suspensions of particles [1,2]. Usually, the colloidal particles are monodispersed spheres, with diameters in the micro- and nanometre range, that may be made of organic or inorganic materials (*e.g.* polystyrene/PS, polymethylmethacrylate/PMMA, fused silica, *etc.*), and with plain or functionalized surface [2–9]. Solvent evaporation-induced self-assembly is the most common method for producing close-packed two-dimensional masks, composed of closed-packed spheres on hydrophilic surface substrates [4], a spontaneous attachment process triggered by appropriate hydrodynamic flow conditions and favorable particle-surface interactions [9]. However, this is not efficient and more advanced methods to generate and/or deposit self-assembled monolayers of hexagonally close-packed (HCP) micro-/nano-spheres include spin coating, dip coating, drop casting, thermoelectrically cooled angle coating, electrophoretic deposition [10–19], convective assembly [20], assembly at air/liquid and liquid/liquid interface [13,21,22], and even laser-induced forward transfer (LIFT) [23,24]. Such methods can be applied to substrates that are organic (*e.g.* various plastics) or inorganic (*e.g.* silicon wafers, glass or quartz slides, metal sheets, *etc.*), planar or curved, or may be particles much larger in size than the depositing ones [17]. The obtained monolayers of spheres find applications in surface chemistry [25], for the fabrication of biologically inspired structures [26], and in photonics including micro-/nano-structuring of surfaces by photonic nanojets [6–8,27–32].

In this paper, we have investigated the focusing effect of polystyrene spheres over light, and used them as an array of microlenses. Transparent microsphere monolayers, grown on transparent substrates by Langmuir–Blodgett (LB) technique [28,32], are covered with a thermally evaporated silver (Ag) film of controlled thickness. When back-illuminated using a single laser pulse, the laser interaction with the microsphere near-field mask produces periodic local detachments of the film that can be collected (or not) on a receiving substrate, leading to the printing of nanodroplets and/or the formation of controlled size nanopinholes on the spheres.

2. Experimental

2.1. Langmuir–Blodgett technique and formation of the microsphere monolayers

Langmuir–Blodgett films are formed on solid substrates by transferring the Langmuir film spread onto an aqueous subphase.

* Corresponding author. Tel.: +33 4 91 82 92 92/95 12; fax: +33 4 91 82 92 89.
** Corresponding author.
E-mail addresses: constantinescu@lp3.univ-mrs.fr (C. Constantinescu), grojo@lp3.univ-mrs.fr (D. Grojo).

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Such a deposition method requires that the spheres are able to freely diffuse across the substrates, seeking their lowest energy configuration. This is often achieved by chemically modifying the surface of spheres with a negatively charged functional group, *i.e.* carboxylate (R-COO$^-$) or sulfate (SO_4^{2-}), thus making them electrostatically repelled by the negatively charged surface of a substrate such as quartz, glass or silicon. Capillary forces draw the spheres together, packing them in a close hexagonally pattern on the substrates, as the solvent (water or alcohol) evaporates. The structure of the film can be controlled at the molecules/particles level, by controlling the surface tension of the liquid [18,22,32,33]. The LB technique requires water insoluble particles, but soluble in volatile organic solvents (*e.g.* ethanol, isopropanol, *etc.*).

For this work, we decided to use particles that are functionalized with long aliphatic chains, so that the heads are hydrophilic while the tails are hydrophobic; such structures are referred to as amphiphiles [32–34]. LB film depositions were carried out using a commercial deposition trough system (KSV-Nima "Mini" machine), placed on a table isolated from mechanical vibrations during the preparation of monolayer. The monodisperse polystyrene (PS) spheres were commercially purchased (micromod Partikeltechnologie GmbH) in the size range of 1–5 μm, covered by a hydrophobic octadecyl (C18) surface, and supplied in water without any surfactants (concentration: 50 mg/ml) [35]. In previous work, we determined that the mean and standard deviation of the 5 μm PS are 5.13 and 0.22 μm respectively [28]. 2 ml of ethanol mixed with 0.5–1 ml of dispersed particles were spread with a syringe in the LB trough.

The monolayers were prepared on two types of substrates. Slides made of quartz (1 mm thick, *Heraeus SUPRASIL 3*) and optical quality borosilicate glass (BK7) (1 mm thick, *Thermo Scientific/Gerhard Menzel GmbH*) were cut into pieces of 2 cm × 4 cm to fit exactly into the LB tank. Finally, after pulling the samples, the monolayer coating reaches ~98% coverage ratio of the 2 cm × 4 cm slides, as we have previously demonstrated elsewhere [32].

2.2. Laser processing of metallic micro-/nano-arrays

Similarly to colloidal lithography, a noble metal is deposited over the monolayer. This plays a role of deposition mask to generate arrays of a micro-/nano triangular prisms, but here we use the monolayer as an array of microlenses. In the 1980s, Fischer et al. reported on using such periodic arrays of microspheres as shadow masks for the deposition of nanomaterials [3], while two-dimensional (2D) colloid crystals have been already reported as early as 1950s [2]. Ag thin films have been grown by thermal evaporation (BOC Edwards Auto306) on samples covered with monolayers of PS spheres. After reaching the desired pressure inside the evaporator (~7×10^{-7} mbar), the films were grown at a deposition rate of 0.1–5 nm/s and the substrates were kept at room temperature throughout the procedure to avoid melting of the spheres. The film thickness, controlled by an *in situ* quartz crystal microbalance (QCM), was set to 10, 20 or 30 nm. Finally, the samples have been used in irradiation and/or printing experiments. A neodymium doped yttrium aluminium garnet (Nd:YAG) picosecond laser (Continuum "Leopard S10/20", 355 nm wavelength, 50 ps pulse duration) is used to irradiate the samples from behind in terms of monolayer position (*i.e.* back-side irradiation), as presented in the schematic from Fig. 1a. A mask is used to select a homogeneous part of the laser beam, and a lens projects it at the surface of the donor sample. Fig. 1b shows the beam profile revealing that we irradiate the target with (quasi) top hat energy distribution over an area of ~380 μm × 380 μm. As previously mentioned, the microspheres act as an array of microlenses, focusing the laser light on the films grown on them. We have characterized the focusing effect of the spheres, by using the experimental arrangement described in Ref. [30], and in Fig. 1c we show the array of hot spots produced by the 5 μm PS microsphere monolayers. This shows that with single pulse irradiation we are processing the film with a large number of beams with size <500 nm (resolution limit of our measurement) and a periodic arrangement imposed by the microsphere self-assembly (hexagonal structure).

When placing a receiver substrate on front of the back-side irradiated transparent substrate supporting the films, as presented in Fig. 1a, the technique is called laser-induced forwards transfer (LIFT), performed here at nanometer scale, as it will be shown. The LIFT technique is a cost-efficient and fast process allowing the deposition of a wide variety of materials without damaging their structures or their properties on different kind of substrates, and previously demonstrated as a high-accuracy spatially resolved laser deposition method. Further details are given elsewhere [36–39].

2.3. Optical and morphological analysis of structures

Optical microscopy images of the samples have been assessed with a 3D optical surface metrology system (Leica "DCM 3D"). The morphology and roughness have been analyzed by atomic force microscopy (AFM) (Park Systems "XE-100"), in non-contact mode, using a tip with 10 nm radius of curvature. The thickness of the films and prismatic structures has also been verified by AFM, as step measurement. Scanning electron microscopy (SEM) investigations (JEOL "JSM-6390") have been performed with the electron acceleration voltage set at 5 kV.

3. Results and discussion

In LIFT, the pixel size can be varied with the laser spot size as needed, in the range of a few micrometer to a few mm [37], to control the lateral resolution of the formed structures. In this work, taking benefit of microsphere focusing, we aim at LIFT at the nanometer scale. The donor substrate supporting the monolayer of spheres and covered with a thin metallic film is either in contact with the receiver substrate, or they can be separated by a distance (d) when using spacers at two opposite edges (*i.e.* 2 pieces of 25 μm titanium foil), as presented in Fig. 1a. After accurately shaping the laser beam (Fig. 1b and c), tests have been made using Ag covered (30 nm thick) monolayer of spheres (PS, 5 μm in diameter). Fig. 2 reveals the accuracy of energy delivery at the monolayer level, as the nanopinholes are visible over the irradiated area when using the projected mask image laser spot. The spheres act as lenses and thus the laser energy is focused at the exit interface of the sphere, leading to the local melting of the metallic layer and its subsequent ablation. Due to (quasi) top hat beam shape (Fig. 1b), one can observe that the laser exposed zone exhibits high intensity gradients at the edges, separating abruptly spheres with nanopinholes and spheres that are undamaged. Further on, in order to determine the adequate fluence range needed to control the ablation, transfer and printing processes, a series of experiments have been made by irradiating the samples using various laser energies, as presented in Fig. 3. The range between the threshold (700 μJ/cm^2) and the maximum (>50 mJ/cm^2) usable fluences reveal that the pinholes can be as small as a few hundred nanometers and up to the micrometer level, respectively. The green lines on the sides of Fig. 3 indicate increasing energy. At energies above 50 mJ/cm^2, the monolayer itself is destroyed (upper right side image), while further increasing of the fluence leads to complete removal of spheres.

Previous studies have shown that using the spheres as a mask, covering them with a thin metallic film and after subsequent removal of the spheres, leads to a remaining array of triangular prismatic particles. Such particles can also be further laser processed, transformed into spherical droplets by strong surface tension forces