Microablation of gold nanolayers by direct write lithography

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Abstract. The laser ablation is widely used for the formation of metal nanoparticles, nanorods, nanodisks, nano-networks and polymeric microchannels. This paper reviews the results obtained when using of the microablation of the gold layers that are tens of nanometer think deposited on various transparent surfaces, such as Poly(tert-butyl methacrylate), Poly(methyl methacrylate) -PMMA, Polydioxymethyl siloxane, PDMS, and glass, with a low power laser (low fluences of 4-500 μJ/cm², 337nm wavelength and 4ns pulses). The microablation results in the preferential formation of gold wire-like nanostructures at the edges and across the ablated channels on PMMA and PTBMA; and of gold nanoparticles on glass and PDMS. This contrasting behavior is explained by the presence of gas-generating pyrolysis on PMMA or PTBMA as opposed to lack of it on glass and PDMS.

1. Introduction

The laser ablation is widely used for the formation of metal nanoparticles, nanorods, nanodisks, nano-networks and polymeric microchannels. The ablation can be carried out either from the top, where the laser beam impinges directly on the machined material; or from the bottom of the surface, where the laser beam passes through a transparent medium, e.g., glass or fluid, before impinging the material on the top surface.

It has been found that the ablation from the top of the sample leads to poor edge quality and creates plumes, whereas in the bottom side irradiation the forward transfer of the ablated material is in the direction of the laser beam, which leads to better definition and clean-ness of the microfabricated structures.

It is possible to carry out layer-by-layer micromachining of a multilayer film using successive laser pulses. A combination of the laser parameters, e.g., tunable laser energy, frequency of pulses, spot diameter and material parameters, e.g., material absorbance, as well as film thickness, influence the quality of the formed micro-structure. In addition to these, several parameters such as glass transition temperature (Tg, related to the state of the polymer, i.e., glassy below; or elastomeric state above Tg) and physical or chemical processes induced by radiation, should be taking in to account while creating microstructures in polymers.

Recently Sawant et al. have demonstrated the formation of gold nano-wire like structures by UV laser micro-ablation in addition to formation of micro-channels in certain polymers. These nanosize metallic wire-like structures can be useful for the detection of probe biomolecules (e.g., proteins, oligonucleotides, etc.) in microassays or could be of interest to nanoelectronics.
The present paper reviewed the effect of substrate and fluence on the formation of gold structures and micro-channels by the bottom-side energy-tuned microablation of a gold layer that has a thickness of few tens of nm.

2. Materials and Methods

2.1. Materials

All chemicals are purchased from Sigma-Aldrich and used as it is without purification.

2.2. Sample Preparation

The procedure have been reported previously.4,5 4 \% w/v solutions of Poly(methyl methacrylate) (PMMA, Mol wt: 101,000) and 1 \% w/v solutions of Poly(tert-butyl methacrylate), PtBMA, were made in 99\% propylene glycol methyl ether acetate solvent. Using a Specialty Coating Systems spin coater (model P6708), above PMMA and PtBMA solutions were spin-coated on hexamethyldisilazane-primed glass slides at the speed of 3000 rpm for 45 seconds, and baked in the oven at 85°C for thirty minutes, to produce a 1 μm polymeric layer on glass.

Planar PDMS sheets12 were formed by thoroughly mixing the silicone elastomer curing agent and silicone elastomer at 1:10 ratio (Sylgard 184 silicone elastomer kit, Dow Corning Corporation, USA), followed by vacuuming the mixture for an hour to remove the trapped air-bubbles, followed by spreading the mixture carefully in a plastic dish, and cured at 65°C for an hour to harden the PDMS films. Finally PDMS films were peeled off.

2.3. Instrumental Methods

We used previously optimized conditions for gold coating5,12 which are as follows: 25 mA for 90 s at 0.1 Torr using a gold sputtering coating unit E5100 (Polaron Equipment Ltd.). These conditions resulted in the formation of 50 nm gold on bare glass slide, PDMS surface, PTBMA and PMMA-coated glass slides. Gold sputtering of 180 s produced 100nm of gold layer.

Back scattered imaging of all samples was performed on JEOL JSM840 microscope along with elemental identification using energy dispersive X-ray (EDX) analysis. A sessile drop method was used to determine the contact angle of water on different surfaces. An average of five readings was considered as contact angle of the surface under study.

2.4. Microablation Methods

The laser scissors system (module 337/120, Cell Robotics, Inc, USA) mounted on a Nikon Eclipse TE300 inverted microscope and coupled with a computer controlled, pulsed nitrogen was used for the direct write laser micro-ablation. The wavelength of laser was 337 nm, and maximum intensity obtained by laser was 120 μJ/pulse. The single pulse duration of laser was 3-4 ns. The beam-spot size before entering the optical system was 3mm x 8mm. Therefore the fluence of 120 μJ/pulse was estimated as 500 μJ/cm² before entering the optical system of the laser scissors.

The laser beam was focused directly on to the gold layer through the microscope objectives. The quasi-continuous ablation of the gold film was achieved using a pulse rate of 20 pulse/s at 22°C and a relative humidity of 45% and at different microscope stage speeds.
3. Results and Discussion

Sessile drop method calculated contact angles of water on PDMS, PMMA, and PtBMA, as $95^\circ$, $75^\circ$, and $78^\circ$, respectively, indicating the hydrophobic nature of these surfaces.

It has been demonstrated before that laser microablation of gold on PMMA can be used to create microchannels. Recently we found that besides the formation of microchannels, the ablation of gold produces polydispersed gold nanoparticles and nanowire like structures on PMMA irrespective of the fluence. We found that the gradual reduction in the laser fluence from 500 μJ/cm$^2$ to 3.8 μJ/cm$^2$ results in the gradual decreases of the channel width from 10μm to 1μm when 40X optical objective and 20μm/sec microscope stage speed is used. The stage speed of 20μm/sec is critical to obtain the smooth channel; otherwise at low speeds, e.g., 5 μm/sec, the dotted structures form instead of the formation of quasi-continuous microchannels. We also found that different laser fluences control only the width of ablated microchannels, and do not have a significant impact, for the range of fluences mentioned here, on the lateral dimensions of the gold nano-wires and particles. Therefore the distance between the nano-wire-like structures without varying the size of wires and particles can be easily controlled by simply varying the laser fluences. Also, bridging nanowire-like structures across the ablated microchannel are also formed when using 100X optical objective, at stage speeds of 10μm/sec and 125 μJ/cm$^2$ of fluence. These interconnecting nanowire-like structures could be of interest for nanoelectronics. These nano-structures described above are resilient and do not wash water, even under harsh conditions.

Figure 1: A typical 4X optical view of the laser ablation of 50nm gold on PMMA at 40x optical objective and at fluences of (a) 375 μJ/cm$^2$ and (b) 187.5 μJ/cm$^2$.

Figure 1 depicts a typical example of 4X optical view of the laser ablation of 50nm gold on PMMA using 40x optical objective and at fluences of (a) 375 μJ/cm$^2$ and (b) 187.5 μJ/cm$^2$. The light line at the centre of channel is the subchannel formed in the microchannel, which is confirmed by atomic force microscopy studies. This subchannel is created due to the Gaussian distribution of energy imparted across the channel. The formation of the subchannel is sensitive to the alignment of the laser.

Figure 2a depicts a typical scanning electron microscopy (SEM) example of a micrograph of gold nanoparticles and a channel of PTBMA. Since the ablation is carried out from the bottom-up position, the gold nanoparticles and polymeric by-products are dispersed in and around the microchannel. The average diameter of gold particles is found to be 150nm ± 50nm.
In PtBMA and PMMA, at the beginning of the pulse, the laser energy is concentrated in the gold film and on the top of the polymer. The heat transfer is limited laterally and in depth due to the low thermal conductivity and low mobility of the polymer chains (which results in a high Tg). In the middle stages of the ablation pulse, the polymer start to depolymerise (starting around 200°C) and then to pyrolise, followed by melting and ablation of the metal. In the last stages of the ablation pulse the gases generated by PMMA and PtBMA pyrolysis push the residual gold that was not ablated towards the edges of the ablated area.\footnote{12}
The formation of nanoparticles and microchannel did not occur on PDMS surface, because the rubbery state of the PDMS allows the propagation of the heat transfer deep inside the polymer and decrease the concentration of the energy in the gold layer; hence delaying the ablation. The large variations of polymer specific volume lead to an uneven surface beneath the gold, which could lead to pockets of gold islands\textsuperscript{15}, possibly melted. The high heat transfer coefficient due to PDMS elastomeric state results in quick cooling of the gold islands and small gold nanodroplets would evaporate\textsuperscript{16}.

Unlike PMMA (or PtBMA) and PDMS, on glass, the build-up of the thermal energy is confined in, and just beneath the gold layer due to the high rigidity of the material (glass does not pass through a rubbery state and melts at high temperatures). This limits the heat transfer vertically but allows its spread laterally due to higher conductivity at the glass-metal boundary, leading in turn to a “frying pan” effect. Eventually, in the last stages of the ablation pulse, the melted gold boils and gold islands are formed on the glass surface\textsuperscript{12}. Also, the high conductivity of glass permits a quick cooling of the unablated gold islands. Therefore only small gold particles can detach from the surface, as suggested\textsuperscript{15}, but large droplets remain on the surface. Moreover, it was demonstrated\textsuperscript{16} that smaller gold nanoclusters can melt, and therefore ablate, about 200°C before the bulk melting temperature.

Figure 2b depicts a typical example of the elemental identification of gold nanoparticles by EDX. Peaks of gold are identified along with peaks of Si, Zn, Al, K, etc. which originated from the substrate.

In conclusion, one can fabricate gold wire-like nanostructures, nanoparticles and microchannels by direct-write laser microablation of gold nanolayer deposited on transparent materials, through careful selection of base materials, thickness of the metal film and laser parameters. The microablation results in the preferential formation of gold wire-like nanostructures at the edges and across the ablated channels on PMMA and PtBMA; and of gold nanoparticles on glass and PDMS. This contrasting behavior of gold ablation is explained by the presence of gas-generating pyrolysis on PMMA or PtBMA as opposed to lack of it on glass and PDMS.

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