Three-dimensional fabrication of metallic nanostructures over large areas by two-photon polymerization

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Abstract: An experimental protocol for the realization of three-dimensional periodic metallic micro/nanostructures over large areas is presented. Simultaneous fabrication of hundreds of three-dimensional complex polymer structures is achieved using a two-photon photopolymerization (TPP) technique combined with a microlens array. Metallization of the structures is performed through the deposition of thin and highly conductive films by electroless plating. A chemical modification of the photopolymerizable resin and the production of a hydrophobic coating on the glass surface supporting the structures are realized. This process prevents metal deposition on the substrate and restricts adhesion on polymer. Our technique can produce periodic and/or isolated metallic structures with arbitrary shape, created by more than 700 individual objects written in parallel.

OCIS codes: (160.5470) Polymers; (190.4180) Multiphoton processes; (220.4000) Microstructure fabrication; (310.1620) Coatings.

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1. Introduction

Two-photon photopolymerization (TPP) technique has been intensively used in the past few years to realize three-dimensional (3D) patterning [1-4]. TPP enables to draw complex objects [5-7] with sub-diffraction resolutions [8] since the absorption of light in the material occurs only at the focal region of a tightly focused laser beam, via a nonlinear multiphoton process. While most studies on TPP have focused on the realization of polymeric micro/nanostructures, it is of great interest to consider this technique also for the fabrication of metallic 3D patterns for future nanotechnological applications. Recent studies on the reduction or induced growth of metallic nanoparticles in a polymer resin by femtosecond laser irradiation have led to the production of two-dimensional (2D) metallic structures [9-10]. To our knowledge only two groups have reported on the realization of 3D metal patterning. Wu et al. achieved the formation of discrete

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silver particles inside a remaining matrix [11], and Stellaci et al. fabricated self-supporting 3D structures made of different metals, with a method using a non-commercially available polymer nanocomposite material [12]. Yet, these techniques employing direct single-beam laser writing into a polymer matrix are time-consuming and thus unlikely to be adopted for mass manufacturing. The fabrication of numerous metallic 3D structures for micro/nanoelectromechanical systems or for nanophotonic optoelectronic devices would require a parallel approach. As a first step towards this goal, we have recently proposed an experimental setup based on multiple beam two-photon photopolymerization technology [13-14]. 3D periodic polymer structures were created with a two-order increase in the fabrication yield compared to single-beam TPP by means of a microlens array. A natural form of microlens array can be found in nature in the compound eyes of certain arthropods. These eyes are composed of up to thousands of small lenses acting as individual receptors to form a large mosaic image covering the entire field of view [15]. Our technique employs a similar approach to extend the fabrication area to a large scale.

In this paper, we report on an experimental protocol for the realization of 3D periodic metallic micro/nanostructures over large areas, through a TPP technique combined with a microlens array. The central part of this work is the chemical modification of the photopolymerizable resin properties before TPP fabrication, as well as the realization of a hydrophobic coating on the glass substrate supporting the resin matrix before making an uniform metal coating by electroless plating. This preparation enables a selective deposition of thin and highly conductive metal films only on the polymer surface all over the sample, and to avoid metal deposition on the substrate. By taking advantage of the high-accuracy and arbitrary shape modeling of TPP fabrication, we can realized complex periodic metallic micro/nanostructures which were so far out of reach. The processing efficiency of our technique is demonstrated with the fabrication of several large samples created by more than 700 objects written in parallel.

2. Experimental method

Different methods can be employed to metalize the surface of a sample. However, the most commonly used like vacuum evaporation, sputtering or chemical vapor deposition, require heavy and expensive equipments. In order to deposit thin metal films over polymer structures, we employ a chemical technique called electroless plating, which can be effectively realized at ambient conditions. Electroless plating is suitable for metal deposition onto insulating samples since it does not demand the use of an external electric field [16]. It allows uniform coating over large areas and even structures with complex shapes and occluded parts can be metal coated [17-18]. However, polymers are naturally hydrophobic materials and they do not adhere well to metal films due to differences in surface energies [19]. For this reason, we first chemically modified the photopolymerizable resin before the fabrication of the 3D polymer structures. Then, a pre-treatment is applied before metal deposition to improve silver nucleation and adhesion on the polymer surface [20]. Another issue is that untreated glass surfaces are well-known hydrophilic surfaces and can easily adsorb a large variety of compounds due to the presence of silanol groups (Si-OH). To minimize silver deposition during the electroless plating, a hydrophobic coating on the glass slides used as substrate for TPP fabrication has to be realized to modify their surface properties.

The whole fabrication process is described in Fig. 1. Prior to the polymer structure realization, a hydrophobic coated glass surface is prepared (1) and the photopolymerizable resin is chemically modified. This modified resin is deposited on the hydrophobic substrate and used for TPP fabrication (2). Then a surface pre-treatment with $SnCl_2$ is applied to improve metal deposition and adhesion onto the polymer (3). Finally, silver coating is realized by electroless plating (4).

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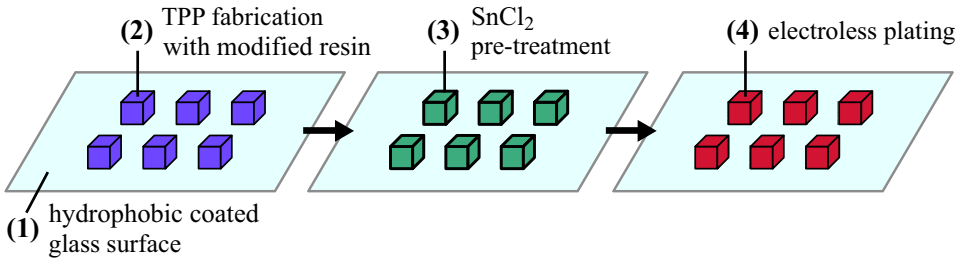

Fig. 1. Fabrication process: (1) Hydrophobic coating of the glass slides to avoid metal deposition, (2) TPP fabrication with chemically modified photopolymerizable resin, (3) $SnCl_2$ surface pre-treatment to improve metal deposition and adhesion, (4) Silver coating by electroless plating.

2.1. *Hydrophobic coating*

To achieve selective metal deposition between the substrate and the polymer structures, the glass surfaces have to be deactivated before the fabrication of the samples [21]. The glass slides are cleaned in a 0.1 mol/l sodium hydroxide solution for 15 minutes, rinsed with water and dried. They are then soaked into a 5 wt.% solution of dimethyldichlorosilane (DMDCS, $(CH_3)_2SiCl_2$) in toluene ($C_6H_5CH_3$) for 1 minute, washed thoroughly with methanol and dried. After this treatment, the chemical on the glass substrate behaves as a hydrophobic coating since two methyl (-CH_3) groups coming from the DMDCS now align at the surface [22] instead of the hydroxyl (-OH) groups. This hydrophobic coating will prevent the adhesion of silver particles during the electroless plating and thus its quality is of critical importance in the experiments.

2.2. *Resin modification*

The material used for TPP fabrication consists of a commercially available photopolymerizable resin (Z7012C, JSR) mixed with styrene ($C_6H_5C_2H_3$) in a 1:1 volume ratio. This resin as a two-photon absorption cross-section of about 1×10^{-50} cm^{4}s/photon at 780 nm. In the case of two-photon absorption, the chemical reaction progresses by radical attacking [1] and thus is very effective for styrene which has a vinyl group with a double bond. We noticed empirically that compounds containing benzene groups such as polycarbonate, polystyrene or polyethylene terephthalate (PET) show a better affinity towards silver adhesion compared to other compounds like polyethylene or polymethyl methacrylate (PMMA). The addition of styrene also slightly reduces the minimum voxel size that can be produced via TPP [8].

2.3. *Multiple two-photon fabrication with microlens array*

To produce multiple focus spots for parallel fabrication, we use a 50×50 microlens array [23-24] covering a total range of 15×15 mm^2 (Ricoh Optical Industries). The lenses are 300 μm in diameter and are arranged in a square lattice with a lattice constant of 300 μm. Their focal length and numerical aperture (NA) are respectively 1.5 mm and 0.07. TPP is initiated inside the resin using a pulsed Ti:sapphire laser (Coherent Mira 900) operating at 76 MHz (100 fs pulse width, 799 nm wavelength). In order to provide enough energy per pulse at each focalization spot, the laser is amplified by a regenerative amplifier (Titan 527DP, Quantronics). This results in 138 fs pulses at a 1 kHz repetition rate. The beam is focused into the resin matrix, through a microscope glass slide, via an inverted oil-immersion objective (Olympus, 60X, NA = 1.4).

At this point, it is important to reduce as much as possible the inhomogeneities in the laser beam intensity distribution, to provide the same amount of energy for each lens and to fabricate

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structures with uniform sizes. For this reason, the laser beam is expanded to cover the entire surface of the microlens array, and only the central part of the beam is effectively used. We have checked the intensity distribution of the laser beam before the microlens array by directly inserting a large-area, high dynamic range CMOS camera ($7.68\times5.76\,mm^2$, pixel size 12 μm) into the beam. Figure 2(a) shows a profile of the beam intensity (in arbitrary units) recorded along the horizontal direction. Instead of its initial gaussian profile at the laser exit, the laser beam now shows a flattop profile suitable for parallel fabrication.

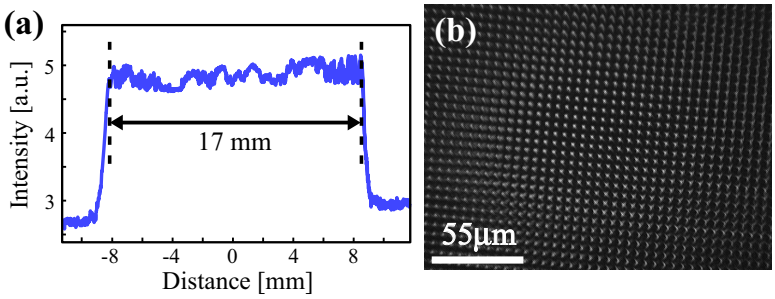

Fig. 2. (a) Intensity profile of the expanded beam measured before the microlens array along the horizontal direction. (b) Optical image of the fluorescence emitted from a PMMA film mixed with coumarin 314 dyes, due to the excitation by the multiple spots after the microlens array.

A serious issue with parallel fabrication is the perpendicular alignment of the laser beam propagation direction with respect to the glass surface. A small tilt will result in the formation of structures above the substrate (and therefore not fixed) or no photopolymerization if the focal spots are found below the surface. To adjust the alignment, we monitored the fluorescence emitted from a PMMA film mixed with coumarin 314 dyes, due to the excitation by the multiple spots after the microlens array. Figure 2(b) shows an optical image of the fluorescence pattern recorded with a CCD camera after optimization of the alignment. Around 1100 spots are visible, which represents about 44% of the total number of lenses, but the ones on the outmost parts of the image are not perfectly focalized. Consequently, the number of structures which can be simultaneously fabricated will be smaller in practical.

At the focal region, TPP occurs for each individual spot like in single-beam TPP process [1]. Under these conditions, the threshold power required to trigger the resin polymerization for an irradiation time of 200 ms is about 210 mW (measured before the microlens array). From this, we estimate the threshold energy and intensity per lens to be respectively around 21 nJ and 4×10^{13} Wcm^{-2} during each pulse, higher than in our previous experiments [14] due to the addition of chemical. Adding radical quenchers in the resin could reduce this threshold level [8]. By translating the microlens array in the XY-directions and the sample holder in the Z-direction with a computer program, solidified polymer patterns with arbitrary shapes can be drawn in parallel inside the matrix. The lateral separation of the spots at focus can be tuned by changing the focal length (currently 150 mm) of the relay lens between the microlens array and the objective. For all the structures presented in this paper, the separation between two spots is about 5.5 μm. After the TPP fabrication, the sample is washed thoroughly with acetone to remove the remaining unsolidified resin, then washed with water and methanol to remove any styrene trace from the substrate.

Figure 3(a) is a scanning electron microscopic (SEM) image showing an example of large periodic structure which can be designed by making the fabrication areas for every spots overlapping each other. The sample consists of long empty channels, 1.8 μm wide, separated by

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polymer walls (2.7 μm in height). The walls were written in parallel with about 2000 exposures pulses (200 ms, laser power ∼280 mW) for a fabrication time of 150 minutes. Employing a single beam TPP setup to realize such a structure would definitively be time consuming. Figure 3(b) shows a SEM image of more complex structures. The sample, written with about 400 exposure pulses (200 ms, laser power ∼390 mW), is composed of self-standing empty cubic structures connected by pairs (see magnified view). Each structure is about 2.5 μm large and 4.6 μm high.

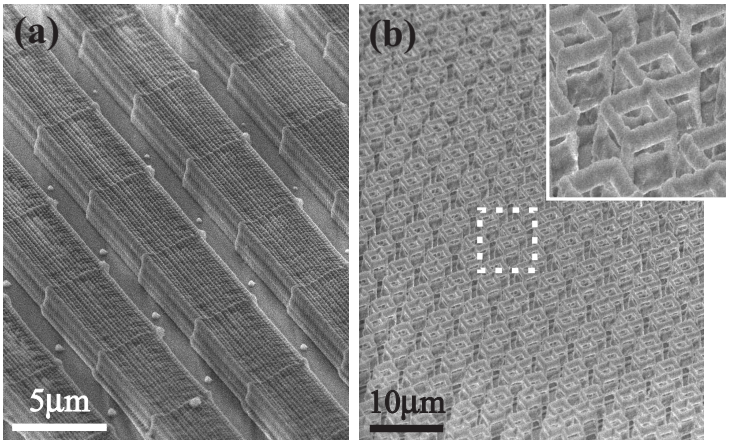

Fig. 3. (a) SEM image of polymer channels (height ∼2.7 μm) written in parallel using the microlens array. (b) SEM image of self-standing empty cubic structures (height ∼4.6 μm) connected by pairs.

2.4. $SnCl_2$ pre-treatment

As mentioned earlier, the adhesion between a metal film and the surface of a polymer is very weak. To improve the deposition of silver particles onto the polymer structure, a pre-treatment involving tin ions is realized over the entire sample surface. We prepared a sensitizing solution [25], made of 1.5 g of stannous chloride ($SnCl_2$) dissolved in 84 ml of water and 6 ml of hydrochloric acid (HCl). The sample is dipped into the solution for 1-2 minutes, then washed thoroughly with water to remove any $SnCl_2$ trace from the glass surface. During the process, Sn^{2+} ions are adsorbed by the polymer surface which will act as a preferential catalyst site for the reduction of the silver ions. This treatment ensures that silver particles remain strongly attached to the structure after the plating.

2.5. Electroless plating

An uniform metallic coating of the sample is realized through an electroless plating method, also known as mirror reaction, which involves the reduction of silver nitrate [16]. The solution used for silver deposition is made as follows: we prepared 0.1 mol/l silver nitrate ($AgNO_3$) in water as the silver ion solution, in which a 0.2 mol/l activating ammonia (NH_3) solution was added in drops until a brown Ag_2O precipitate is formed and then dissolved into $[Ag(NH_3)_2]^+$ ions. The reductant is made of 1 mol/l glucose ($C_6H_{12}O_6$) in a solution of 30 vol.% methanol (CH_4O) and 70 vol.% water, mixed with the silver nitrate solution to trigger the reduction of silver ions and the nucleation of metallic particles. The polymer structure is dipped into the plating solution and the reaction is stopped by washing the sample with acetone. The Sn^{2+} ions introduced by the pre-treatment also work as reducing agents for the metal ions [25]. If

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the reaction is realized over non-modified polymer, the main metal deposition originates from silver particles formed inside the solution and falling on the structure. This leads to a weak adhesion of the metal particles and to a poor coating of the surface. The diameter of the silver particles can be tuned easily from 10 nm to more than 100 nm by changing the $AgNO_3$ and glucose concentrations [26, 18], while the duration of the reaction controls the total coating thickness.

3. Results

To emphasize on the necessity of the different chemical modifications, polymer structures were fabricated on a regular glass slide by using the non-modified Z7012C resin. 'N' structures were written in parallel with 23 exposure pulses (200 ms, laser power ∼400 mW) for a fabrication time of about 2 minutes. Then, a short electroless plating was realized during 4 minutes. Figure 4(a) shows two SEM images of a large view (left) and a magnified view (right) of the sample. The polymer objects remained uncoated but a thin silver film composed of particles about 60 nm in diameter was deposited all over the glass substrate. This result confirms that the usual resin used in TPP cannot be metal coated by direct electroless plating. Although the procedure followed to obtain the sample visible on Fig. 4(a) is not applicable to the fabrication of "direct" metallic structures, it could be used to realize "inverse" or "negative" 2D and 3D templates, i.e. polymer structures embedded in a metallic matrix.

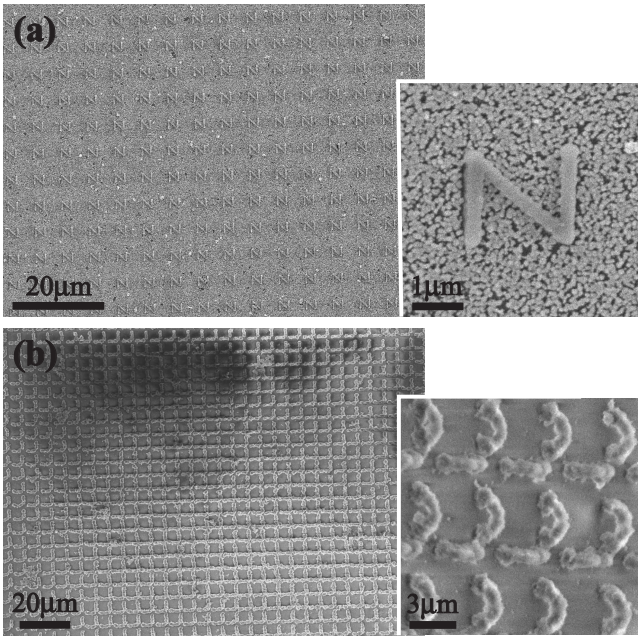

Fig. 4. (a) SEM image of polymer structures fabricated with non-modified resin on a regular glass slide. Uncoated 'N' objets surrounded by a thin silver film after electroless plating. (b) Left: $170\times125\ \mu m^2$ SEM image of a large 3D metallic periodic structure fabricated by multiple-beam TPP process and selective silver overcoating. Right: tilted magnified view.

Figure 4(b) shows a SEM image of a large ($170\times125\ \mu m^2$) fabricated area (left) of 3D silver coated polymer structures on a modified glass substrate, and a tilted magnified view (right). The sample was realized after a careful optimization of the illumination conditions. Over 720 self-standing half-rings were simultaneously produced with 160 exposure pulses (200 ms, laser

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power ∼240 mW) for a total fabrication time of about 10 minutes. More structures were actually fabricated (around 850) but the ones at the outer parts of the fabrication area, which are not visible on Fig. 4(b), appear smaller due to inhomogeneities in the beam intensity distribution. Despite this drawback, a three-times factor increase of yield efficiency is achieved compared to our previous results [14]. The plating reaction time was about 15 minutes, leading to a thick and continuous silver coating on the polymer surface. As expected with the hydrophobic coating, almost no metal deposition is visible on the glass surface. One could find surprising that the polymer structures still adhere well to a surface that has been modified with methyl groups. Yet, we reproducibility observed that the structures strongly adhere to the substrates even after even after thorough washing by acetone and ethanol. A possible explanation could be that the hydrophobic coating is locally altered by the high energy pulse used to produce a solidified voxel because the laser beam is exactly focused on the glass surface to fabricate the first polymer layer. Thus, it is likely that the hydrophobic coating only remains on the unfabricated areas of the sample. Figure 4(b) confirms that large areas can be selectively overcoated at once, but it reveals that the homogeneity of the metal film is difficult to control. To solve this problem we have modified the resin used so far to improve the adhesion properties of the polymer structures. First, 4-vinylbenzene sulfuric acid sodium salt ($CH_2CHC_6H_4SO_2Na$) was dissolved into a N,N-dimethyl acetic amide ($CH_3CON(CH_3)_2$) saturated solution. Then, we mixed 20 vol.% of this solution with 80 vol.% of the Z7012C resin to form the new photopolymerizable material. This volume ratio was determined in order to maintain the robustness of the solidified resin for 3D fabrication.

Figure 5(a) shows a SEM image of a large $78\times58\ \mu m^2$ fabricated area of 3D silver coated polymer structures, made from the modified resin on a hydrophobic coated glass substrate. Figure 5(b) shows a 45° tilted view of an individual structure before coating by electroless plating, composed of a cube (2μm in size), holding a self-standing spring (height 2.2 μm, inner diameter 700 nm). The sample was written with about 700 exposure pulses (200 ms, laser power ∼270 mW) for a total fabrication time of 40 minutes. Despite the modification of the resin to improve silver deposition, the side view of the spring proves that the solidified resin is still rigid enough to allow 3D fabrication.

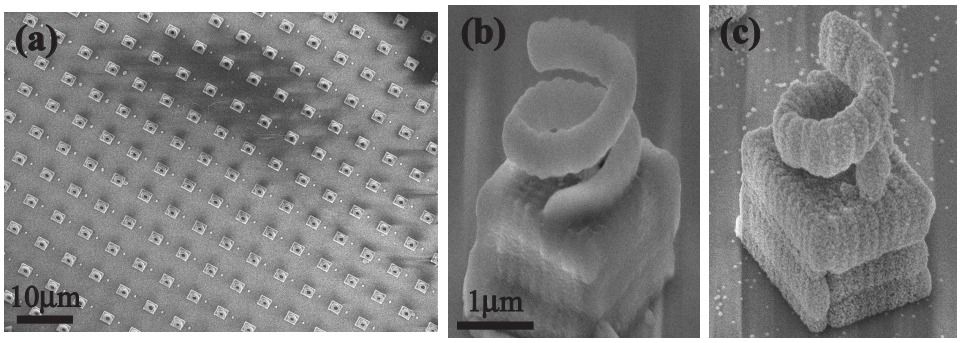

Fig. 5. (a) $78\times58\ \mu m^2$ SEM image of a 3D periodic silver coated structure fabricated on a hydrophobic coated glass surface. (b) Tilted magnified view of an individual uncoated polymer structure composed of a cube (2μm in size) holding up a spring (height 2.2 μm, inner diameter 1 μm). (c) SEM image of an individual silver coated structure after electroless plating.

To overcoat fine structures, the plating had to be optimized to reduce as much as possible the thickness of the metal film. To do so, we focused on the formation of very small silver particles, with diameters of 20 nm or less, by using a different reductant, changing the concentrations of

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the reagents and realizing two consecutive steps. The new plating solution was composed of a 0.3 mol/l $AgNO_3$ solution, mixed with a saturated solution of 2,5-dihydroxybenzoic acid ($C_7H_6O_4$) 300× diluted in water as reductant agent, in a 1:1 volume ratio. The reaction was performed at 37°C and stopped after 2 minutes. A second short plating (∼10 s) was realized with the same $AgNO_3$ solution, mixed with ammonia (0.2 mol/l) and benzoic acid (10× diluted). Figure 5(c) shows an individual structure after metallization of the sample. Only a few silver particles adhered on the substrate and the polymer structure was uniformly overcoated by a thin film, which we estimate to be about 50 nm thick by comparing on the SEM images the inner diameter of an individual spring before and after EP.

To confirm the presence of silver and the quality of the coating, an energy dispersive X-ray spectroscopy (EDX) analysis was carried out on the sample composed of cubes and springs (Fig. 5). The EDX spectrum visible on Fig. 6(a) revealed different elements, mainly oxygen and silicon coming from the glass surface, carbon originating from remaining polymer traces, and silver ($L\alpha_1$ and $L\beta_1$ lines) resulting from the electroless plating. To observe the silver distribution over the sample, EDX images were taken at the energy of the main silver peak (∼3 keV). Figure 6(b) is a backscattered-electron image composed of several structures and Fig. 6(c) the EDX image simultaneously recorded at 3 keV. Figure 6(d) shows a magnified view of an individual structure. The clear contrast between the fabricated objects (bright regions) and the glass slide (dark regions) indicates that all the apparent polymer surfaces are well covered with silver. In the same time, almost no metal deposition occurred on the glass surface leading to the formation of individual conducting structures on a transparent substrate, which is important with regard to future experiments concerning the optical response of a sample, especially for its observation in transmission mode.

Electrical measurements were carried out on long polymer lines (length ∼600-900 μm, width ∼1 μm) connected to large silver electrodes formed by EP. These lines were fabricated on hydrophobic glass substrates and coated by EP with a ∼100 nm silver film (thickness measured by Atomic Force Microscopy) in order to form objects with dimensions comparable to the ones presented in this paper. The measurements revealed that the structures are very conductive with typical resistivities $\rho \sim 10^{-7}$ Ωm, only a few times larger that the value for bulk silver.

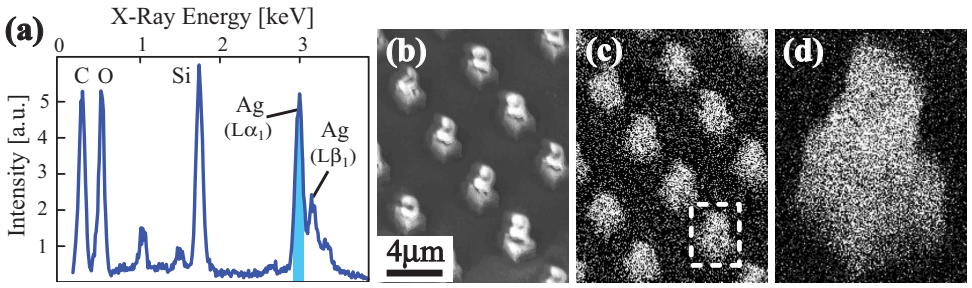

Fig. 6. (a) EDX spectrum of a silver coated polymer structure fabricated on a hydrophobic glass substrate. (b) Backscattered-electron image of several structures and (c) EDX image simultaneously recorded at the energy of the main silver peak (∼3 keV). (d) Magnified EDX image of an individual structure.

We have so far focused on coating polymer by silver because of its high conductivity. Yet, the possibility to fabricate structures with different metals is of great importance, notably since silver can be easily oxidized. We have previously reported on the deposition of gold on polystyrene and glass by using electroless plating and a pre-treatment with $SnCl_2$ [18]. Since gold as high positive standard electrode potentials, the reduction of gold ions in a plating bath

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is even more efficient then for silver and could be realized with alcohol instead of glucose. Thus, the realization of fine 3D polymer structures coated with gold is a straight forward step using our experimental protocol and is currently underway. Non-catalytic surfaces (such as polymers) can be coated with various metals after activation by a metal catalyst like tin [21-22]. For example copper plating is also conceivable but it would require a stronger reductant such as formaldehyde (HCHO).

4. Conclusion

In conclusion, we have developed a protocol to fabricate three-dimensional metallic structures over large areas on a glass substrate. Our TPP technique using a microlens array enables to simultaneously write more than 700 polymer structures uniform in size. The metallization of the structures was achieved through the deposition of thin films composed of small silver particles by means of electroless plating. A hydrophobic coating of the substrate prevents silver deposition and allows the formation of a large number of isolated and highly conducting objets. A chemical modification of the resin properties was performed to improve the formation and adhesion of metal onto the polymer surface. Using non-modified resin and regular glass slide can, in an opposite way, produce numerous isolated insulating polymer objects spread out over a metallic film. Our method opens the way to the fabrication of large 3D periodic metallic materials with features as small as 100 nm [8] by parallel processing. Since any shape can be designed for each individual structure, a straightforward application could be the realization of metamaterials [27] which require small and complex metallic objects.

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