MICROFABRICATION OF 3D METALLIC INTERCONNECTS VIA DIRECT LASER WRITING AND CHEMICAL METALLIZATION

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We present a developed method based on direct laser writing (DLW) and chemical metallization (CM) for microfabrication of three-dimensional (3D) metallic structures. Such approach enables manufacturing of free-form electro-conductive interconnects which can be used in integrated electric circuits such as micro-opto-electro-mechanical systems (MOEMS). The proposed technique employing ultrafast high repetition rate lasers enables efficient fabrication of 3D microstructures on dielectric as well as conductive substrates. The produced polymer links out of organic-inorganic composite matrix after CM serve as interconnects of separate metallic contacts; their dimensions are: height 15 μm, width 5 μm, length 35–45 μm, and they could provide 300 nΩm resistivity measured in a macroscopic way. This proves the techniques potential for creating integrated 3D electric circuits at microscale.

Keywords: direct laser writing, laser nanolithography, 3D microstructures, electro-conductive polymers, 3D electric circuits, integrated electronics, SZ2080, MOEMS

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1. Introduction

Recently, there has been a lot of interest in the design and fabrication of 3D metallic micro-/nanostructures for applications in MOEMS, plasmonics, biosensors, and metamaterials. However, the fabrication of complex, high resolution, fully 3D metallic structures is still a challenging task, since traditional lithographic techniques involving the layer-by-layer structuring of metallic structures can only allow the deposition of a few layers or the creation of high-aspect ratio two-dimensional (2D) structures. Direct laser writing (DLW) can be used as an alternative technology for fabrication of 3D metallic micro-/nanostructures [1]. Much effort to develop highly efficient materials and attempts to enhance the resolution as well as improve the fabrication throughput of the technique have been performed during the last decade [2,3]. A special consideration was given regarding its potential application in tissue engineering and regenerative medicine [4,5]. In a most common case a negative photoresist is selectively exposed in a pin-point manner, later immersed in a developer bath resulting into revelation of a 3D polymer object materialized from a CAD model. By choosing specific material and subsequently applying chemical metallization (CM) it can be metallized by using electroless plating [6]. The method has attracted the most attention up to date and has been chosen for this work. DLW of photopolymers is based on two-photon polymerization which due to quadratic dependence of the two-photon absorption rate on light intensity is initiated only at a highly localized area at the focal point of the laser beam. It allows to create dielectric nanostructures with sub-100 nm resolution. Furthermore, electroless plating does not require external source of electric current. It is characterised by the selective reduction of metal ions only at the surface of a catalytic substrate immersed into an aqueous solution of metal ions.

During the last decade the direct laser polymerization technique [1] of cross-linkable materials has been successfully applied for the manufacturing of various functional microstructures applicable within diverse fields of photonics [7–9], miniaturized [10,11] and integrated [12,13] free-form optics as well as microfluidics [14,15]. As the majority of the materials are bio-compatible [16,17], this approach was employed for the manufacturing of artificial scaffolds for cell proliferation studies [18,19], medical implants for tissue engineering [20,21] as well as regenerative...
In all of the mentioned examples the materials were passive polymers sensitized only with a photoinitiator responsible for the efficient photostructuring [24]. In order to increase the functionality of the microstructures and metamorphose them into operating devices additional doping with optically active [25, 26], magnetic [27, 28], and biological [29, 30] ingredients has been applied. 3D micro-/nanostructures out of electro-conductive materials would enable realization of plasmonic metamaterials [31, 32] and creation of 3D complex microcircuits [33, 34]. Doping the material with carbon [35], mixing with ionogel [36], conductive polymer [37], subsequent metallization by electroless coating [8], direct fabrication of metals [38], infiltration [39] was employed. However, combining DLW with CM offers best structuring properties in the meaning of produced feature size and surface roughness [6]. Other ultrafast laser based techniques such as multiphoton reduction [40] or employment of positive tone resist [51] are limited to the produced structure uniformity, range of possible geometries and feature aspect ratio, respectively. Alternative approaches such as laser assisted direct metal deposition [41] provide only ~10 μm spatial resolution. On the contrary, atomic layer deposition ensures nanometre precision film deposition, yet still requires an initial template [42]. Thus, the DLW technique subsequently combined with the CM method offers a practical compromise of fabrication flexibility (structure geometry and resolution) and throughput for the creation of metallic interconnects for the design and investigation of 3D electro-conductive circuits [43].

Fig. 1. Chemical metallization: (1) silver ion binding to amine moieties on surface, (2) silver ion reduction to form silver nanoparticles and (3) silver bath/plating process to obtain the metal coated structures. Density and size of nanoparticles depend on seeding and reduction times [6].

Fig. 2. The main steps of formation of metallized polymeric link: glass substrate (1) is covered with conductive layer of metal (20 nm of Ag) (2). Dielectric scotch is formed using selective laser ablation (3) and then the polymeric link if fabricated over it via direct laser polymerization (4). The link is subsequently chemically metallized (5) and later measurements of resistance are performed (6).
In the paper, we present a way to create 3D conductive microstructures via laser nanolithography technique [1] on electro-conductive substrates separated by a dielectric scotch. The produced metallic interconnects are characterised by a scanning electron microscope (SEM) and their electrical conductivity is measured. Fabrication on electro-conductive surfaces has been shown before [44], yet not applied for the creation of electro-conductive structures.

2. Methods and materials

2.1. Chemical metallization

The polymer can be subsequently metallized by doping it with additive which has metal binding moieties and then using chemical plating [3]. The material used in this work was organic-inorganic hybrid composite SZ3070, produced by the addition of methacryloyloxypropyl trimethoxysilane (MAPTMS) to zirconium propoxide (ZPO). 30% of 2-(dimethylamino)ethylmethacrylate (DMAEMA) was added to provide the metal-binding moieties. Metallization process consists of three stages: seeding, reduction, and plating. First of all, the fabricated polymeric structure is immersed into 0.05 mol/l aqueous solution of silver nitrate (AgNO₃), where silver ions bind to amine moieties on surface and act like seeds for silver nanoparticles. In the second stage, silver ions are reduced in 4.4 mol/l aqueous solution of sodium borohydride (NaBH₄) and silver nanoparticles are formed. Finally, for plating the sample is immersed into aqueous solution mixed from 0.2 mol/l silver nitrate (AgNO₃), 0.9 mol/l ammonia (NH₃), and 1.9 mol/l glucose (C₆H₁₂O₆) as a reducing agent. Between each stage and after plating, the sample is rinsed in de-ionized water and dried in air at room temperature. The amount of silver plated onto the structures is proportional to seeding and reduction times.

2.2. Laser nanophotonic lithography

3D microstructures were fabricated by DLW. The SZ3070 + 30% DMAEMA composite was used for fabrication. 1% of 2-benzyl-2-dimethylamino-4-morpholynobutyrophenone (IRG) was used as a photoinitiator. A drop of photosensitive material was heated at 50 °C for 30 min in vacuum before photopolymerization. After fabrication, samples were developed for 30 min in 1-propanol.

The schematics and details of the nanophotonic system employed in this work are described elsewhere [21]. A high peak power femtosecond Yb:KGW laser amplifier (Pharos, Light Conversion Co. Ltd.) was used as an irradiation source. Its parameters are: 300 fs pulse duration, 200 kHz repetition rate, 1030 nm central wave-length (515 nm second harmonic was used in experiment). 350 μW of average laser power was used for link fabrication and 2 mW for arrays of 2D lines. It corresponds to 1.02 TW/cm² and 5.94 TW/cm², respectively (values are calculated for 100 × 1.4 NA (numerical aperture) and 20 × 0.8 NA objectives, which were the most practical for the fabrication of the microstructures). Sample translation velocities were 50 μm/s and 500 μm/s, respectively.

2.3. DLW of 3D metallic microstructures

Metallic 3D microstructures were obtained by combining DLW and chemical metallization. First of all, dielectric scotches were ablated in chromium (200 nm thickness) plated glasses using the same laser system. Then different numbers of polymeric links (height 15 μm, width 5 μm, and length 35–45 μm) were fabricated over separate scotches. Some areas were left unconnected for reference measurements. After that, microstructures were chemically metallized with Ag: seeding time 38 hrs and reduction time 40 min. Two final solutions for plating were prepared. Sample immersion time in each of them was up to 1 min. The microstructures were expected to be covered with 20 nm of silver using these times. Finally measurements of conductivity were performed. In order to measure resistance of structures more precisely, arrays of two dimensional lines (50 μm × 5 mm) on glass substrate were fabricated. Glass substrate before fabrication was immersed into 10% MAPTMS solution with ethanol for a few hours, then additionally rinsed in ethanol. It helps to increase adhesion of polymer to substrate and decrease amount of silver deposited on glass. After fabrication, samples were chemically metallized and measurements of conductivity were performed.

2.4. Electric conductivity measurement

Prior to the macroscopic electric conductivity measurement the inspection of the produced microstructures was performed by a SEM (TM-1000, Hitachi). No additional sample preparation was performed prior to observation. Later, the electric conductivity measurements were performed using Mastech MS8222H multimeter. For chromium plated glasses, no additional electrodes were necessary. For resistance measurement of arrays of two dimensional lines, 20 nm thick Ag electrodes were made at the ends of lines using a sputter coater Quorum Q150R S. Resistance of electrodes was many times smaller than of the laser written lines, so one can assume that it had not significantly inuenced the conductivity measurement of a single line.
3. Results

The results showed that during metallization process some silver was deposited on dielectric scotches between two chromium surfaces, and conductivity appeared even between unlinked areas. However, resistance between surfaces connected with polymeric links (varies from 200 Ω to 340 Ω where 3 links are, and from 600 Ω to 1 kΩ where 1 link is) is much less compared to resistance between unconnected (varies from 150 kΩ to over 20 MΩ, this wide range could be an artifact of the before-mentioned silver deposition on dielectric scotches). The measured values are exactly the same despite the measurement, though vary from sample to sample. Additionally, some aging effect (increase of resistivity 3–10 times) was noticed as the same samples where measured after months of keeping them in ambient conditions.

So metallized polymeric links significantly reduce resistance and work as interconnection, but deposition of silver on glass should be decreased.

Inspection of samples with arrays of two dimensional lines showed that selective metallization can be achieved by using MAPTMS as an solating agent. Only metallized polymeric lines were conductive. Their resistivity varied from 296 nΩm. It is from 17 to 439 times more than the bulk silver (15.9 nΩm) [45].

4. Discussion

Using DLW of polymers approach and subsequent CM the fabrication of 3D electro-conductive microstructures was successfully realized. This method has been successfully implemented in 2006 using acrylate [46] and in 2007 using epoxy-based materials [47]. Up to now much effort has been made in hybrid (organic-inorganic) material synthesis specially designed for DLW 3D micro-/nanostructuring [18]. ORMOCER (ORganically MOdified CE-ramics) and ORMOSIL (ORganically MOdiefied SIlica) class materials offer optimal laser structuring, mechanical, chemical, and biological properties [48]. Sequentially, composite sol-gel synthesized hybrids with metal binding affinities were introduced [8]. In our case, the micrometre sized links were directly laser manufactured in between the insulating ridge of contacts. The achieved minimal resistivity (296 nΩm) can be compared to the values achieved using alternative protocols employing a combination of DLW an CM. For example, Maruo et al. reported fabricating continuous silver microstructures by the photoreduction of polymer film containing silver ions and attained 348 nΩm resistivity [38]. Terzaki et al. studied how seeding and reduction times affect resistance of polymeric films created using the same approach as ours [8]. Using seeding and reduction durations similar to ours, 729 Ω resistance was achieved. Also, it was shown that resistance can be reduced more than 10 times using extended reduction time.

Direct writing processes of electrically conductive metallic 3D microstructures have potential for application to integrated electrical wiring of microelectronic devices and production of 3D MEMS and MOEMS devices. Also, it should allow to create complex structures.
metallic microstructures for applications in plasmonics [50], metamaterials [51], and photonics [52], to mention a few.

5. Conclusions

We have demonstrated a successful fabrication of metallic polymeric microlinks (height 15 μm, width 5 μm, and length 35–45 μm) connecting two conductive surfaces. The DLW and CM method produced metal interconnects serving as 3D wires in between chromium contacts. In order to measure resistance more precisely, arrays of two dimensional lines (50 μm × 5 mm) were fabricated. The measured resistivity varied from 296 nΩm to 7.07 μΩm and it is from 17 to 439 times more then the value of a bulk silver (15.9 nΩm) [45]. Though it was not covered within the scope of the described study, the conductivity might be increased by extending the duration of seeding and reduction processes, as it has been reported elsewhere [6]. Using MAPTMS as an isolating agent helped to decrease deposition of silver on glass and selective metallization was achieved. The proposed combination of DLW and CM approaches opens new pathways for exibly creating custom 3D free-form metallic structures which can be applied in integrated microelectronics and / or nanophotonics.

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References


Santrauka

Darbe tiriama galimybė formuoti trimates metalines mikrojungtis tarp elektrai laidžių paviršių panaudojant tiesioginį lazerinį rašymą fotopolimeruose ir cheminį metalizavimą. Ši technologija leidžia laisvai parinkti darinio geometriją, o cheminis metalizavimas pasižymi selektyvumu ir jam nėra reikalingas išorinis elektrinis laukas.

Naudojant šį metodą eksperimentiškai suformuotos metalinės jungtys, kurios veikia kaip mikrolaidai tarp dviejų elektrai laidžių chromo paviršių. Nustatytos jų pagrindinės fizikinės savybės, palyginamos su kitais metodais pasiekiamais rezultatais (pasiektas atsikartojumas gana mažas). Be to, reikia imtis papildomų priemonių siekiant visiškai selektyvaus padengimo siadbru.

Vis dėlto naudojant šį metodą galima formuoti trimąčius metalinius mikrodarinius, kurie gali būti panaudoti taikant įvairias mikroelektromechanines sistemas, plazmoniką, metamedžiagas bei nanofotoniką.