Microelectronic Engineering 191 (2018) 25–31

Contents lists available at ScienceDirect

Microelectronic Engineering

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

Research paper

Beyond 100 nm resolution in 3D laser lithography — Post processing solutions

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ARTICLE INFO

Article history:
Received 12 October 2017
Received in revised form 4 January 2018
Accepted 23 January 2018
Available online xxxx

Keywords:
3D laser lithography
Laser polymerization
Pyrolysis
Plasma etching

ABSTRACT

Laser polymerization has emerged as a direct writing technique allowing the fabrication of complex 3D structures with microscale resolution. The technique provides rapid prototyping capabilities for a broad range of applications, but to meet the growing interest in 3D nanoscale structures the resolution limits need to be pushed beyond the 100 nm benchmark, which is challenging in practical implementations. As a possible path towards this goal, a post processing of laser polymerized structures is presented. Precise control of the cross-sectional dimensions of structural elements as well as tuning of an overall size of the entire 3D structure was achieved by combining isotropic plasma etching and pyrolysis. The smallest obtainable feature sizes are mostly limited by the mechanical properties of the polymerized resist and the geometry of the 3D structure. Thus, the demonstrated post processing steps open new avenues to explore free form 3D structures at the nanoscale.

1. Introduction

Three-dimensional (3D) laser lithography has become an established technique that allows direct writing of arbitrary 3D structures at the microscale. The achievable resolution and versatility make this fabrication approach highly suitable for numerous applications ranging from micro-optical elements [1–4] and 3D templates [5] to micro-scaffolds for cell studies [6–9]. However, the growing interest in nanoscale 3D objects requires sub-100 nm resolution, which still remains demanding in practical applications.

Structuring by 3D laser lithography is based on local curing of a resist with a tightly focused laser beam. The obtainable resolution mainly depends on light-matter interaction and localization of photons. Both have been tackled to push the resolution limits. Solutions from the optical microscopy were successfully applied to deliver photons of a wavelength λ into a diffraction-limited spot size of ~λ/2, reaching fundamental limitations of light confinement in the far field. Hence, focal spot sizes of a few hundreds of nanometers can be achieved for lasers operating at visible to near infrared wavelengths. Interestingly, the smallest feature size of the exposed structure may still be smaller than the diffraction limited spot size due to nonlinear light-matter interaction effects and by taking advantage of selected cross-linking thresholds. To tailor the light-matter interaction and efficiently exploit nonlinear effects novel resist materials were developed [10–12]. Their application in multiphoton polymerization [13–15] as well as stimulated emission depletion techniques [16,17] resulted in achievable resolutions well below 100 nm. However, complicated writing setups and stability issues currently hinder practical applications of free form 3D structuring beyond 100 nm feature sizes and commercially available systems mostly offer writing resolution only down to 200 nm range.

An alternative approach to produce well defined nanoscale features is the pyrolysis of laser polymerized structures. A few studies reported that the size of 3D objects can be efficiently reduced by thermal decomposition of a resist in vacuum or inert gas atmosphere [18,19]. The decomposition results in mass loss of up to 80% while turning the resin into a glassy carbon [19–21]. This change is accompanied by shrinkage of the structure and reduction of its dimensions. Pyrolysis allows scaling of the entire structure; however, it does not leave much freedom to tune width/thickness of its building blocks.

To add nanoscale precision and flexibility to post processing approaches, we studied the combination of isotropic plasma etching and pyrolysis for the fabrication of 3D structures with sub-100 nm feature sizes. Plasma etching provides accurate control of cross-sectional dimensions of structural elements while an overall size of the entire 3D structure is down-scaled via pyrolysis.

2. Materials and fabrication

Two types of resists were used to polymerize test structures. The first one was an organic negative tone photopolymer known under the brand name IP-Dip and containing 60–80% of 2-(hydroxymethyl)-

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https://doi.org/10.1016/j.mee.2018.01.018
0167-9317/

2-[[(1-oxoallyl)oxy]methyl]-1,3-propanediyl diacrylate (also known as pentaerythritol triacrylate). The resist was developed by Nanoscribe GmbH and serves as an immersion and photosensitive material at the same time. The material (25 g bottle, batch: 1–600-0055) was obtained from Nanoscribe GmbH and used according to the provided standard operation procedures for 3D structuring using a commercially available laser lithography system Photonics Professional GT (Nanoscribe GmbH) with 63×, N.A. 1.4 objective lens.

The second type of resist was an organic–inorganic zirconium–silicon hybrid composite (SZ2080 [10]) doped with a quencher 2-(dimethylamino) ethyl methacrylate (DMAEMA) [22,23]. The resist is composed of an inorganic and an organic network. The inorganic network is built through Si-O-Si, Si-O-Zr and Zr-O-Zr bonds and is formed during the synthesis of the material prior to photo-polymerization. The organic network is the one formed during photo-polymerization by polymerizing the pendant methacrylate moieties.

The photoresist was produced using the sol-gel method [24]. It consists of methacryloxy-propyl trimethoxysilane (MAPTMS), zirconium propoxide (ZPO, 70% in propanol), and DMAEMA. MAPTMS and DMAEMA were used as the organic photopolymerizable monomers, while ZPO and the alkoxysilane groups of MAPTMS were used to form the inorganic network. In our case, the organic–inorganic hybrid material was synthesized by mixing the above chemicals in the following molar ratios: MAPTMS:ZPO = 8:2, and (MAPTMS+ZPO):DMAEMA = 9:1. Michler's ketone (4,4-bis(diethylamino) benzophenone) used as a photoinitiator was added at 1% w/w concentration to the final solution of MAPTMS and DMAEMA composite. All chemicals were obtained from Sigma-Aldrich and used without further purification. The samples were prepared by drop casting onto 100 μm thick silanized glass substrates and the resulting films were dried in air for several days before photopolymerization.

A Ti:Sapphire femtosecond laser (Femtolasers Fusion, 800 nm, 75 MHz, <20 fs) was used as the light source for the fabrication of three-dimensional SZ2080 microstructures. The complete experimental setup and procedure has been described elsewhere [25]. The laser beam was focused using a high numerical aperture microscope objective lens 100×, N.A. 1.4, Zeiss, Plan Apochromat. The writing speed employed was 5 μm s^{-1} and the average light intensity in the focal spot was 0.11 MW/cm^2 (peak intensity ~0.35 TW/cm^2). After the completion of the component building process by Direct Laser Writing, the samples were developed for 20 min in a 50:50 solution of 1-propanol/2-propanol and were further rinsed with 2-propanol.

A buckyball structure shown in Fig. 1 was selected as a 3D model for our experiments. The geometry of the structure provides high mechanical stability that allows reaching sub-100 nm widths of the composing bars without a structural collapse. The focal spot of the laser is elongated along the optical axis and the voxel has an aspect ratio of around 1:3. To

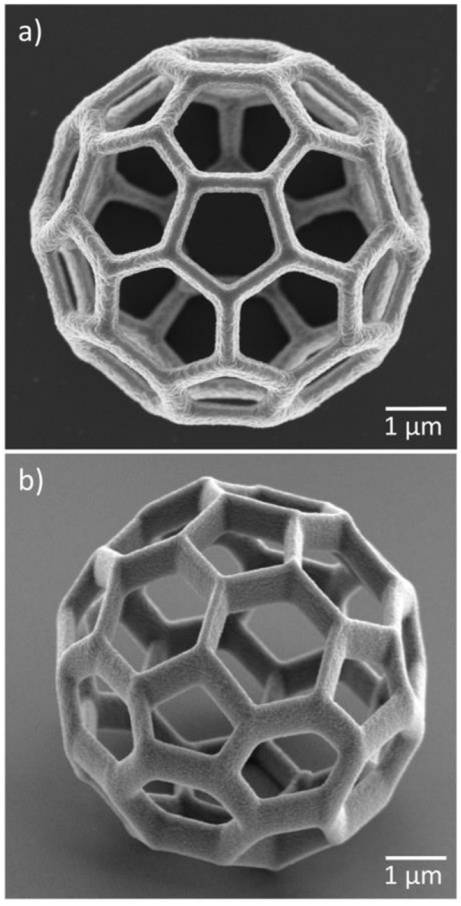

Fig. 1. 7 μm diameter laser polymerized buckyball used as a 3D model for experiments. The structure was produced using SZ2080 and imaged before the post processing steps. a) top view; b) 45° tilt view showing 1:3 aspect ratio of the composing bars.

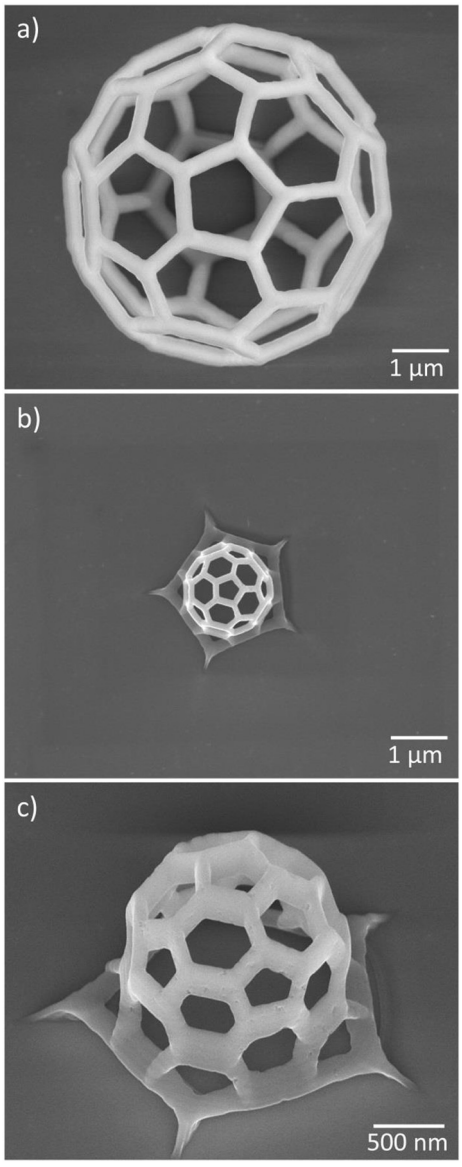

Fig. 2. Shrinkage of the polymerized structures due to pyrolysis: a) SEM images of the initial 7 μm diameter buckyball. IP-Dip resist and Nanoscribe system was used to produce the structures on a silicon substrate; b) corresponding structures after the pyrolysis; c) 45° tilt view of the pyrolyzed structure. Note: SEM magnification is the same in a) and b).