Microelectronic Engineering 128 (2014) 7–11

Contents lists available at ScienceDirect

Microelectronic Engineering

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

Fabrication of high-aspect-ratio (up to 10) one-dimensional organic/inorganic hybrid nanogratings via holographic lithography

Jie Li, Shu Yang *

Department of Materials Science and Engineering, University of Pennsylvania, 3231 Walnut Street, Philadelphia, PA 19104, United States

ARTICLE INFO

Article history:
Received 19 April 2014
Accepted 3 June 2014
Available online 12 June 2014

Keywords:
High-aspect-ratio
Holographic lithography
Nanograting
Organic/inorganic hybrid
Organosilicate
Negative-tone photoresists

ABSTRACT

We fabricated high-aspect-ratio (up to 10) one-dimensional (1D) nanogratings with width ranging from 200 nm to 500 nm and pitch from 600 nm to 2 μm via holographic lithography. An organic/inorganic hybrid material, epoxy-functionalized polyhedral oligomeric silsesquoxane (epoxy-POSS), was used as negative-tone photoresist due to its enhanced thermal and mechanical stability. The periodicity of 1D structure was controlled by the incident beam angle, while the filling fraction could be altered by exposure dosage. The undesired surface roughness could be reduced by increasing POSS crosslinking density. Furthermore, we showed that the epoxy-POSS nanogratings could be directly converted to silica-like nanogratings upon calcination.

1. Introduction

One-dimensional (1D) periodic structures in micron- and nano-scale have been of interest for many applications, including diffraction gratings, linear polarizers [1–3], plasma etching masks [4,5] photonic [6] and phononic crystals [7]. There have been extensive studies to fabricate 1D structures using techniques, including photolithography [4,8], e-beam lithography [9,10], replica molding [11], holographic lithography (HL) [12,13] and nanoimprint lithography [14] in different materials [2,4–6,15]. 1D structures with high aspect ratio (AR = height/width) are desired for many applications. For example, as plasma etching masks, high AR structures that offer better etch resistance and structure fidelity are often desired [4,5]. As grating structures, high AR could lead to new properties, such as blazed transmission gratings via total external reflection on the grating sidewalls for X-rays incident at graze angles [2]. As 1D photonic crystals, high AR structures could offer higher intensity reflection peak at the photonic stop band [6].

However, direct fabrication of high AR structures has been challenging using conventional organic polymer resists, especially in the nanoscale. First, the major limitation is the depth-of-focus (DOF), which defines the maximum photoresist thickness. In photolithography, DOF and the critical dimension (CD, also the minimum feature size) are determined by [16]

$$\mathrm{CD} = k_1 \frac{\lambda}{NA} \tag{1}$$

$$\mathrm{DOF} = k_2 \frac{\lambda}{NA^2} \tag{2}$$

where λ is the wavelength of light, NA is the numerical aperture of the lens, and k_1 and k_2 are processing related constants. Decreasing λ and increasing NA could decrease CD. However, DOF is reduced more rapidly. For 193 nm lithography the AR is typically less than 3. Therefore, multi-step hard mask etching steps are necessary to create high AR structures for certain inorganic materials, which add complexity and cost to the fabrication. Secondly, high AR structures tend to pattern collapse due to the capillary force during solvent drying [17–20]. To address this problem, high AR structures are typically dried using supercritical CO_2 dryer to minimize surface tension.

Unlike photolithography, where DOF is closely related to lenses, depth-of-penetration in holographic lithography (HL) is solely dependent on λ of the incident light and the optical density (OD) of photoresist at the given λ. Thus, it is possible to create high AR structures with AR > 3 by carefully choosing photoresist with high transparency.

Here, we fabricated organic/inorganic hybrid high AR (up to 10) 1D nanogratings with variable feature size via HL. Epoxy-functionalized polyhedral oligomeric silsesquoxane (epoxy-POSS) was used as photoresist due to its high thermal and mechanical stability. The periodicity of the nanograting was controlled by the incident beam angle, while the filling fraction could be altered by exposure

* Corresponding author. Tel.: +1 215 898 9645.
E-mail address: shuyang@seas.upenn.edu (S. Yang).

http://dx.doi.org/10.1016/j.mee.2014.06.004
0167-9317/

dosage. We also discussed the surface roughness formation mechanism in the POSS nanogratings, and demonstrated roughness reduction by increasing exposure dosage. Furthermore, we showed that the epoxy-POSS nanogratings could be directly calcinated to silica-like nanogratings.

2. Experimental details

2.1. Fabrication

The 1D nanogratings were fabricated with controllable periodicity using the set-up and fabrication process shown in Fig. 1a. Epoxy polyhedral oligomeric silsesquoxane (epoxy-POSS, EP0408 from Hybrid Plastics) (Fig. 1b), an organosilicate, was used as photoresist, following the HL procedure reported earlier [21–25]. In brief, the photoresist film was prepared from 50 wt% to 70 wt% Epoxy-POSS and 0.9 wt% (relative to the mass of Epoxy-POSS) Irgacure 261 (visible photoacid generator (PAG), Ciba Specialty Chemicals) in γ-butyrolactone (GBL, Sigma–Aldrich), which was spun-coated on pre-cleaned cover glasses, followed by soft bake at 50 °C for 40 min and 95 °C for 2 min, respectively. The film was exposed to a diode-pumped Nd:YVO_4 laser (λ = 532 nm, Verdi-6, Coherent) with overall 1.0 W laser input (before beam splitting) for 2 s to 6 s. The angle between two laser beams could be varied to achieve different feature sizes. After exposure, the film was post-exposure baked (PEB) at 50 °C for 35 s to crosslink the exposed regions, followed by development in propylene glycol monomethyl ether acetate (PGMEA, Sigma–Aldrich) for 30 min. Before drying in CO_2 supercritical point dryer (SAMDRI®-PVT-3D, Tousimis), the wet samples were rinsed in isopropanol (IPA, Sigma–Aldrich) for another 30 min.

2.2. Characterization

High resolution SEM images were taken from FEI 600 Quanta FEG Environmental Scanning Electron Microscrope (ESEM). The chemical compositions in the 1D structures were determined by energy-dispersive X-ray (EDX) analysis coupled on the same ESEM. The 1D nanogratings with thickness ~2 μm were supported on silicon wafers for EDX measurement.

3. Results and discussion

The 1D nanograting was fabricated by two-beam interference lithography (see Fig. 1) with an intensity profile shown in Fig. 1c. During exposure, photoacids were generated, which catalyzed the ring-opening reactions during the PEB process. In the regions where the exposure dosage is higher than the threshold value, epoxy-POSS becomes fully crosslinked. In the regions where the exposure dosage is below the threshold, the epoxy-POSS is not crosslinked or partially crosslinked, therefore, could be removed by an organic solvent during developing, leaving the high AR nanograting (AR = 10 in Fig. 1d).

Compared to conventional organic photoresist, e.g. SU-8, which is commonly used in ultrathick films to create high AR microstructures, epoxy-POSS offers three advantages: (1) as an organic–inorganic hybrid material, it has thermal and mechanical stability in-between silica and polymers [21,22]. (2) it can be directly converted to silica-like material by calcinations in O_2, and (3) it can serve as a template to backfill both inorganic and organic materials, where the template can be removed using hydrofluoric (HF) aqueous solution at room temperature [23,24]. Typically, the organic template has to be removed by calcination above 500 °C, making it impossible to template functional structures from another organic materials.

In HL, periodicity of the 1D structure is determined by

$$2d \cdot \sin\theta = \lambda \tag{3}$$

where d is the periodicity of the 1D structure. θ is the half angle between two incident laser beams, and λ is the wavelength of the light, which is 532 nm in our system. At this wavelength, epoxy-POSS was completely transparent. According to Eq. (3), the minimum periodicity in our case is 266 nm, half of λ. The calculated periodicity from different incident angles is summarized in Table 1.

From Table 1 we could see that periodicity as large as 15 μm is feasible with 532 nm HL with θ = 1°. However, when θ is very small, it becomes difficult to accurately control the incident angle. To demonstrate the flexibility of HL, we varied θ to create 1D gratings of different periodicities. As seen in Fig. 2, both samples had the same height, 2 μm. With θ = 7.5°, sample with pitch of 2 μm (in agreement with calculated value), line width of 500 nm, and

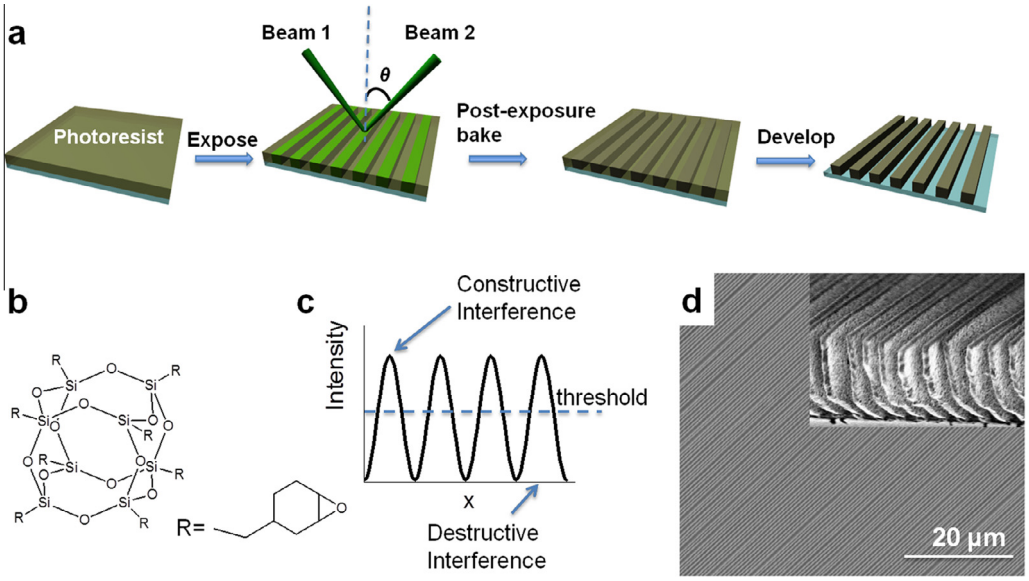

Fig. 1. Holographic lithography (HL) process to fabricate 1D high AR structures. (a) Schematics of HL fabrication process. (b) Chemical Structure of epoxy polyhedral oligomeric silsesquoxane (epoxy-POSS). (c) Two-beam interference intensity profile. 1D periodic structure is formed in the regions, where the light intensity is higher than the threshold. (d) Top-view and cross-sectional view (inset) SEM images of the 1D grating with 300 nm line width, 600 nm pitch and AR = 10.