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Large-area microfabrication of three-dimensional, helical polymer structures

A L Elias¹, K D Harris², C W M Bastiaansen², D J Broer^{2,3}
and M J Brett¹

¹ Department of Electrical and Computer Engineering, University of Alberta, Edmonton, AB T6G 2V4, Canada

² Department of Chemical Engineering, Laboratory of Polymer Technology, Eindhoven University of Technology, PO Box 513, 5600MB Eindhoven, The Netherlands

³ Philips Research Laboratories, Prof. Holstlaan 4, 5656AA Eindhoven, The Netherlands

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Abstract

A technique has been developed to fabricate polymeric helices with sub-micron dimensions. These helices are made using a double-templating process, in which an inorganic thin film deposited using glancing angle deposition acts as the master. The shape, pitch, handedness and number of turns of the polymer helices can be tuned by altering the deposition parameters of the master film. The structure of this positive master is copied into a negative intermediate template of photoresist, which itself acts as a master for the templating of polymer helices. This process is demonstrated with four multifunctional acrylates. The master, intermediate template and polymer helices are characterized using scanning electron microscopy, and the polymer helices are characterized using energy dispersive x-ray spectroscopy. It is shown that a large number of polymer helical microstructures, which are anchored to both a thick substrate and a thin capping layer, can be made in parallel over areas of mm² to cm².

1. Introduction

The chemical, mechanical and electronic properties of polymers make these materials attractive for use in a variety of microsystems. Current fields of investigation include optical devices [1], microelectromechanical systems (MEMS) [2], thin-film transistors [3] and microfluidics [4]. Before the material properties of polymers can be exploited in microdevices and systems, repeatable means of structuring polymers with the desired dimensions must be developed.

There are a number of microfabrication techniques that are used to shape polymers on the micron and sub-micron scales [1–12]. An obvious example is the conventional lithography and etching processes developed by the semiconductor industry. While these techniques may be used to pattern polymers directly [2], they clearly fail to take advantage of the ease with which polymers can be processed. A more common approach in polymer microfabrication involves using

conventional lithographic processing to produce a master that is then used to cast or mold polymer replicas in subsequent processing steps. The master is coated or brought into contact with a liquid polymer precursor or softened solid polymer, the polymer is set or cured, and then the final product is physically separated from the master. Variations of this process are found in hot embossing [5], the production of compact disks [6], replica molding [7], nanoimprint lithography [8] and LIGA [9]. The resolution of each of these processes is dictated by the resolution of the master as well as by the ability of the polymer to coat the master effectively and to be removed once it is set. Features with dimensions of less than 100 nm and high aspect ratios can be achieved using many of these techniques [10]. However, complex three-dimensional structures such as helices and zig-zags are difficult to manufacture with the conventional replication techniques described above due to the fact that structures with undercutting cannot be released from the master.

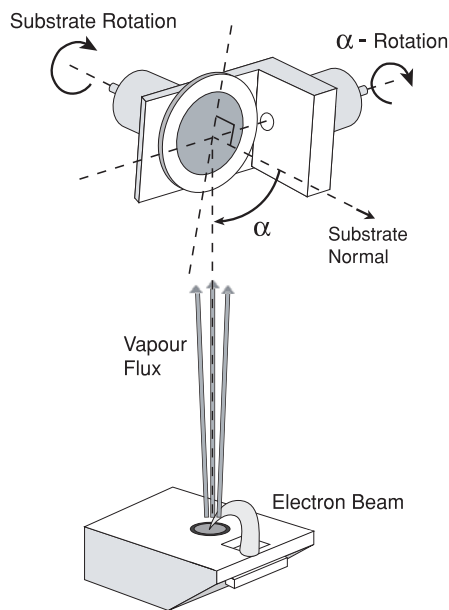


Figure 1. GLAD apparatus. Source material is evaporated using electron-beam excitation. The vapour flux is deposited on an obliquely oriented substrate, where the angle between the substrate normal and the flux (α) is controlled by a stepper motor. A second stepper motor is used to rotate the substrate.

One elegant technique to sculpt detailed three-dimensional structures with excellent resolution (~ 120 nm) is 2-photon lithography [11]. This process has been used to make a micro-oscillator system consisting of a spring and anchor [12]. However, the high cost and low throughput of this direct write process makes it rather impractical. It may be beneficial to a variety of fields to develop new techniques to manufacture three-dimensional polymer structures with undercutting.

Owing to their spring-like shape helical structures are of interest for use in micromechanical systems [13]. While there are a number of techniques that can be used to fabricate inorganic helices described in the literature [14, 15], the same cannot be said for polymer helices, which can have favourable mechanical properties over inorganic materials. Therefore, a new technique is investigated here to batch fabricate three-dimensional polymer helices with diameters of around 100–200 nm using a double-templating process. In this process, the master template is a thin film fabricated by glancing angle deposition (GLAD), and is comprised of independent helical microstructures. The structure of this positive master is copied into a negative intermediate template, which is a layer of photoresist perforated with helical pores. The photoresist film then itself acts as a template for the final film of polymer helices.

2. Glancing angle deposition (GLAD)

Helical microstructures can be produced from a variety of metals, insulators and semiconductors using glancing angle deposition (GLAD) [16–18]. A diagram of the apparatus used in this process is shown in figure 1. GLAD is a physical vapour deposition process in which the substrate normal is oriented at an oblique angle of incidence ($>80^\circ$ as measured from the substrate normal) with respect to the vapour source.

The source material is then typically evaporated using e-beam excitation, although thermal evaporation or sputtering may also be used [19]. When the collimated flux reaches the substrate a shadowing effect results in the growth of isolated microstructures.

During the GLAD process, rotational substrate motion can be incorporated in order to make helical structures with engineered pitch and handedness. If the substrate is held stationary during deposition, the resulting microstructures resemble ‘slanted posts’ that tilt away from the substrate normal towards the vapour source. If the substrate is rotated continuously during the deposition the growth of the structures will track the direction of the source, resulting in the growth of helices, where the pitch and handedness are determined by the speed and direction of rotation. Thus, helices with a range of characteristics can be produced.

SiO_2 helices produced using GLAD have been found to behave similarly to macroscopic springs [13]. It is expected that polymer helices would have superior mechanical properties in terms of toughness and flexibility when compared with helices made from inorganic materials. However, it is unlikely that polymer helices could be deposited directly from the vapour phase using GLAD. While vacuum processes such as sputtering and evaporation (which are used in the GLAD process) can be used to deposit selected polymer thin films [20–22], the kinetics of these processes do not strictly mimic those of inorganic elements and compounds, because most polymers cannot exist in a vapour phase [20]. In PVD processes such as RF sputtering and evaporation, the polymer is fractured into volatile fragments that undergo repolymerization at the substrate [22]. Except in the case of a few extremely low molecular weight materials, the characteristics of the deposited film (i.e., chain length, molecular weight dispersion, crosslink density, elemental composition, etc) are therefore likely to be degraded, which could be detrimental to mechanical properties such as toughness, elasticity and flexibility.

3. Fabrication procedure

Polymer helices were fabricated in a double-templating process in which the structure of inorganic helices deposited vertically on a silicon substrate (the master template) were copied into a layer of photoresist (the intermediate template), which then acted as a template for the final helices (the replica). In this section, we will describe the fabrication of each of these three key parts of the process.

3.1. Master template fabrication

For this study, the SiO_2 master was deposited under high vacuum at an angle of 85° , and an average deposition rate of $0.3\text{--}0.6$ nm s^{-1} . The silicon substrate was rotated clockwise six complete times during the growth of the approximately 1950 nm thick film, resulting in the growth of a right-handed helical film with an average pitch of around 325 nm.

3.2. Intermediate template fabrication

For the intermediate template, the structure of the ‘positive’ GLAD master was replicated into a ‘negative’ layer of

photoresist, consisting of a thin film with helical pores. Photoresist was chosen as the intermediate template material because it fills GLAD films uniformly and reproducibly, and can be etched selectively using photoresist developer or organic solvents.

The negative replication was achieved using a process that has been employed previously to make optically active coatings [23]. The GLAD film was cleaned in a UV-ozone photoreactor, and spin-coated at 2300–2500 rpm with positive photoresist (Clariant, AZ1518). The photoresist was baked for 60 s at 110 °C in order to remove the residual solvent. To enable the removal of the SiO₂ GLAD film, it was first necessary to remove the top portion of the photoresist coating. This was accomplished by exposing the positive resist film to broadband UV radiation for 30 min, performing a post-exposure bake identical to the solvent removal bake, and briefly immersing the sample in photoresist developer (Clariant, AZ 300 MIF Developer). The GLAD film was then removed by immersing the sample for 5 min in buffered oxide etch (Sigma–Aldrich 40270, 12.5% HF, 87.5% NH₄F). SEM images illustrating each step of this process can be found elsewhere [24].

3.3. Polymer helices replica fabrication

Densely crosslinked polyacrylate helices were made using the photoresist thin film with helical pores as a template. One per cent by mass photoinitiator (Irgacure 184) was added to a multifunctional acrylate monomer, and the mixture was stirred for 1 h at 50 °C in order to achieve homogeneity. Vacuum filling was used to apply this mixture to the intermediate template in order to ensure that the pores were completely filled. The samples were filled by placing the photoresist template and the acrylate/initiator mixture in a glass chamber, which was evacuated to ~1200 Pa. The template was then dipped in the mixture and allowed to sit until most of the trapped air was released. The chamber was slowly vented over 2–3 min, forcing the mixture into the pores. The fluid both filled the pores and formed a large cap of material on top of the template film (hundreds of microns thick). The acrylate was cured for 5 min under UV light (365 nm) in a light flow of nitrogen. The photoresist template was dissolved by soaking the sample in acetone for a few hours. In order to expedite this process, we found it useful to first cleanly remove the polyacrylate/photoresist composite film from the silicon substrate by immersing the sample into liquid nitrogen. The photoresist template could then be completely dissolved in acetone in less than 3 min. After dissolving the template the sample was rinsed in IPA to remove the residue from the acetone. The samples were then flipped upside-down so that the helices were on the top and mounted for SEM inspection.

This process was repeated a number of times using four different acrylates: (1) pentaerythritol triacrylate (Aldrich 24,679-4), (2) pentaerythritol tetraacrylate (Aldrich 40,826-3), (3) dipentaerythritol pentaacrylate (Polysciences Inc. 16311), (4) dipentaerythritol pentaacrylate/hexaacrylate mixture (Aldrich 40,728-3). Although the chosen materials all belong to the class of densely crosslinked glassy polymers, the varying functionalities and crosslink densities should result in somewhat different mechanical properties for this set of

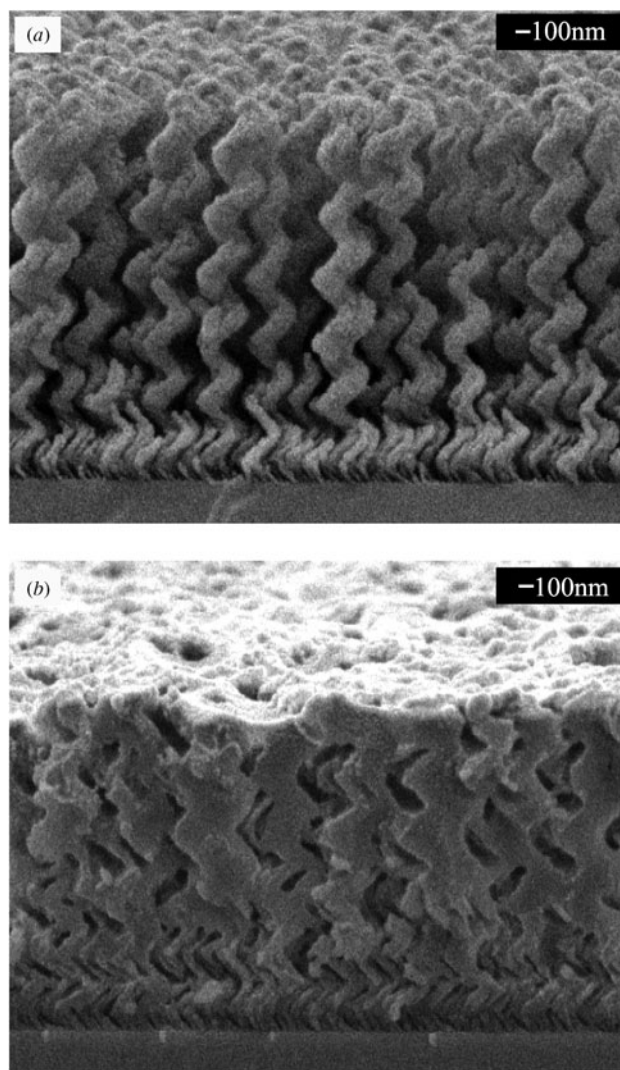


Figure 2. GLAD master template (a) and photoresist intermediate template (b).

helices. The monomers were chosen for this process based on two characteristics: (1) they are large molecules that do not dissolve the photoresist intermediate template and (2) the polymers themselves have high etch resistivity.

3.4. Characterization

The master, intermediate and replica films were examined by scanning electron microscopy (SEM, Philips XL 30 ESEM-FEG) in secondary emission and high vacuum modes. Samples were cleaved either in liquid nitrogen or at room temperature. All samples were coated with approximately 10 nm of gold for imaging. Additionally, uncoated tetraacrylate helices were examined using energy dispersive x-ray spectroscopy (EDX, Princeton Gamma Tech, IMIX).

4. Results and discussion

The master GLAD film and the intermediate template described in sections 3.1 and 3.2 are shown in figure 2.

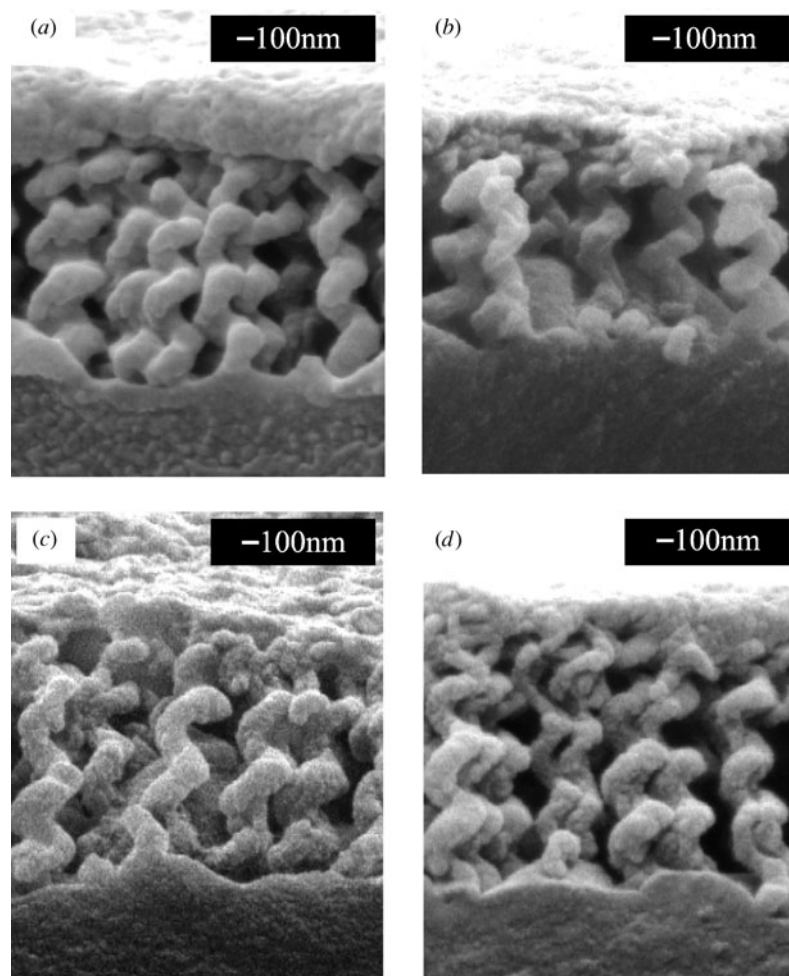


Figure 3. Pentaerythritol triacrylate helices (a), pentaerythritol tetraacrylate helices (b), dipentaerythritol pentaacrylate helices (c) and dipentaerythritol pentaacrylate/hexaacrylate helices (d). The helices shown in this image are upside-down with respect to those in figure 2, and the large capping layer that formed on top of the intermediate template during filling forms a bulk layer beneath the helices. These films are independent of the original silicon substrate.

The master film consists of 6-turn, right-handed helical microstructures, where the average pitch is approximately 325 nm. The pitch, spacing and structure of the pores in the intermediate template closely resemble the microstructures of the master film. The thickness of the intermediate template film is slightly less than that of the original GLAD film due to the etch-back of the photoresist. For this study, intermediate photoresist films were usually produced on a quarter of a 4 inch wafer at a time.

The helices made from the four types of acrylates described in section 3.3 are shown in figure 3. Typical sample sizes were on the order of a few mm² to cm², and when the edges of cleaved samples (5–10 mm in length) were examined, helices were uniformly present along most of each edge. The images in figure 3 are shown at the same magnification as figure 2. It can be noted that the overall pitch of each helix has decreased by as much as 30%, and examinations of the sample at various stages of the filling process have shown that this reduction occurs primarily once the template is dissolved, likely because the helices are not stiff enough to maintain the higher pitch in the presence of internal stresses. An important source for the internal stresses is polymerization shrinkage, which is considerable for these

polyfunctional acrylate monomers (>5 vol% depending on conversion and polymerization temperature). As is confirmed with energy dispersive x-ray spectroscopy, the replicated helices are composed purely of organic materials and the silicon dioxide of the master is absent. The spectrum for the sample that was examined had strong C and O peaks, but no identifiable Si peak. Furthermore, the helices shown are fully chemically resistant to buffered oxide etch, showing no observable changes after long-term exposure to concentrated glass etchants.

Note that the helices shown in figure 3 are upside-down with respect to the original GLAD film, since the large cap that formed on top of the photoresist template now acts as a mechanical support layer beneath the helices, and the polymer has been removed altogether from the silicon substrate. The thickness of this cap depended primarily on the way that the samples were handled, and, to a lesser extent, on the viscosity of the monomers used. Polymers with high viscosities at room temperature were selected for this process, since the large size of the constituent molecules impedes interdiffusion with the photoresist template.

It is possible to foresee applications in which the cap could interfere with the function of the polymer helices, for example,

in the field of optics where a beam passes through the sample. In this case, it may be desirable to produce polymer helices anchored to a transparent substrate with a minimal capping layer. Therefore, we employed a number of different methods to reduce the thickness of the cap. If the monomer is applied to the photoresist template and cured without any additional attempts to remove excess material, the thickness of this layer ranged from 400 to 700 μm , depending on the viscosity of the monomer. However, a thinner cap could be achieved either by spin coating the sample or simply by holding the substrate vertically to allow excess monomer to drain off the surface of the intermediate template before crosslinking. Using these two methods the overall thickness of the cap at the thickest point could be reduced to 4 μm (pentaerythritol tetraacrylate spun at 5000 rpm) or less than 200 μm (pentaerythritol tetraacrylate held sideways). However, overall we found that samples with thicker caps were easier to handle with tweezers as they were less brittle. For applications in which a cap is completely undesirable it may be necessary to use an altogether different monomer with lower viscosity.

In the images shown in figure 3, a thin continuous layer of polymer can be seen on top of the helical structures. Since the samples in these images are upside-down with respect to their original configuration, this layer was actually formed underneath the photoresist template. It is suspected that the thin layer of polymer results from poor adhesion between the intermediate photoresist template and the silicon substrate. During the filling a small amount of acrylate was able to seep under the photoresist and form a continuous layer, as shown. The resulting structure thus consists of parallel layers of polymer films connected by polymer springs. Different surface treatments could potentially be used in the future to achieve different composite structures, including single-sided polymer helices or free-standing polymer springs.

In order to assist comparisons between the films, a single 325 nm pitch 6-turn GLAD film was used as the master for the work presented in this paper. However, it should be possible to use this technique to replicate any of the microstructures that can be achieved using GLAD, including helices with larger or smaller pitches, different heights and number of turns, opposite handedness, etc. Additionally, the GLAD technique can be used to make structures other than helices including slanted posts, square spirals and chevron or zig-zag shapes. It should be possible to copy all of these structures into polymers using our technique. Furthermore, structures can be deposited in periodic arrays by depositing onto lithographically produced seeds [25], thus it should also be possible to make periodically arranged polymer helices.

Inorganic thin films deposited by GLAD have been demonstrated for application in a number of fields, including sensors [26], carbon thin-film electrodes [27], supercapacitors [28] and photonic crystals [29]. The advantages of the GLAD process include the simultaneous fabrication of a large number of structures at a time, highly tunable structure geometry and the large surface area of the film itself. The process that we have described in this paper allows us to combine the control over microstructure achievable using GLAD with the control over mechanical and chemical characteristics that can be achieved by varying the polymer used in the final

step of our templating process. We have shown that we can make polymer helices from an assortment of acrylates; however, there is no reason that they cannot be made from other types of polymers as well, provided that the polymer will not dissolve the intermediate template, will coat the pores of the intermediate template completely, and will survive the solvent used to remove the intermediate template at the end of the process. This technique should be a viable means of structuring many different types of polymers with varying elastic moduli, for use in resonant devices, sensors and other microsystems.

5. Conclusions

A technique was presented for the production of polymer helices based on double templating of an inorganic GLAD film. It was shown that a negative copy of the GLAD film could be produced using photoresist in which the pores of the photoresist film very closely resemble the structures in the master GLAD film. It was also shown that this negative copy could itself be used as a template to impart chiral structure to achiral polymers. Polymeric helices are produced in densely crosslinked acrylates with typical helical pitches in the sub-micron range. It is suggested that the presented technique can be used for a large variety of other sub-micron structures such as zig-zags and slanted posts, and can also be extended to a variety of other polymers with elastic moduli varying from a few MPas to GPas.

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