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Embossed Polymeric Relief Structures as a Template for the Growth of Periodic Inorganic Microstructures

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ABSTRACT

A new method is presented for the glancing angle deposition (GLAD) of inorganic micro- and nanostructures using polymeric relief structures as seeding sites. Conventional embossing processes in thermoset resins are used to produce the relief structures, which potentially facilitates large scale production array production. By utilizing GLAD to control the film deposition conditions over these arrays, we have fabricated periodic lattices (2 μm periodicity) of both silicon dioxide pillars with a thickness of 1.58 μm and oblique nickel columns of thickness 0.60 μm.

The fabrication of periodic inorganic nanostructures by glancing angle deposition (GLAD)[1,2] is inherently dependent on shadowing of adatoms incident on the film surface. Utilizing a prefabricated seed layer of known density, geometry, and area can enforce this shadowing effect. We have previously demonstrated and described the growth of both helical and post nanostructures using the GLAD technique on a small seed array fabricated by an electron beam lithography process.[3,4] Unfortunately, this method of seed production has a low throughput that makes it undesirable for use in large area applications.

The reproduction of nano- and microrelief structures in polymers with embossing is extensively used in the large scale production of, for example, compact disks and holograms. Moreover, it was shown by Chou et al. that it is possible to reproduce nanostructures with typical dimensions as small as 20 nanometers in polymers over areas as large as 16 cm^2 [5,6] with a high throughput.

In this letter, the use of embossed, polymeric relief structures as a template for the growth of inorganic nano- and microstructures using GLAD is investigated. Special emphasis is devoted to the selection of suitable polymers and to the proper conditions for the reproduction of relief structures. We propose that the number of processing steps for growing periodic arrays of nanostructures can be reduced by using these polymer seeds and GLAD, a one step deposition technique (shown in Figure 1).

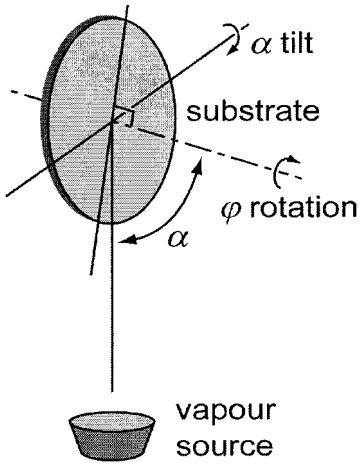

Figure 1. The GLAD apparatus. During a deposition, the flux incidence angle (α) may be varied between 0° and 90°, while simultaneously rotating the substrate about the axis perpendicular to its surface (ϕ).

Films of poly(tetrafluoroethylene-*co*-hexafluoropropylene), or Teflon FEP 100 (mp 260 °C) were produced by compression moulding (2.5 kgs, 1 min) at 330 °C between two cover slips. The resulting thickness of these films was estimated to be of the order of 200 μm. Silicon calibration gratings for a scanning probe microscope (SPM) patterned with

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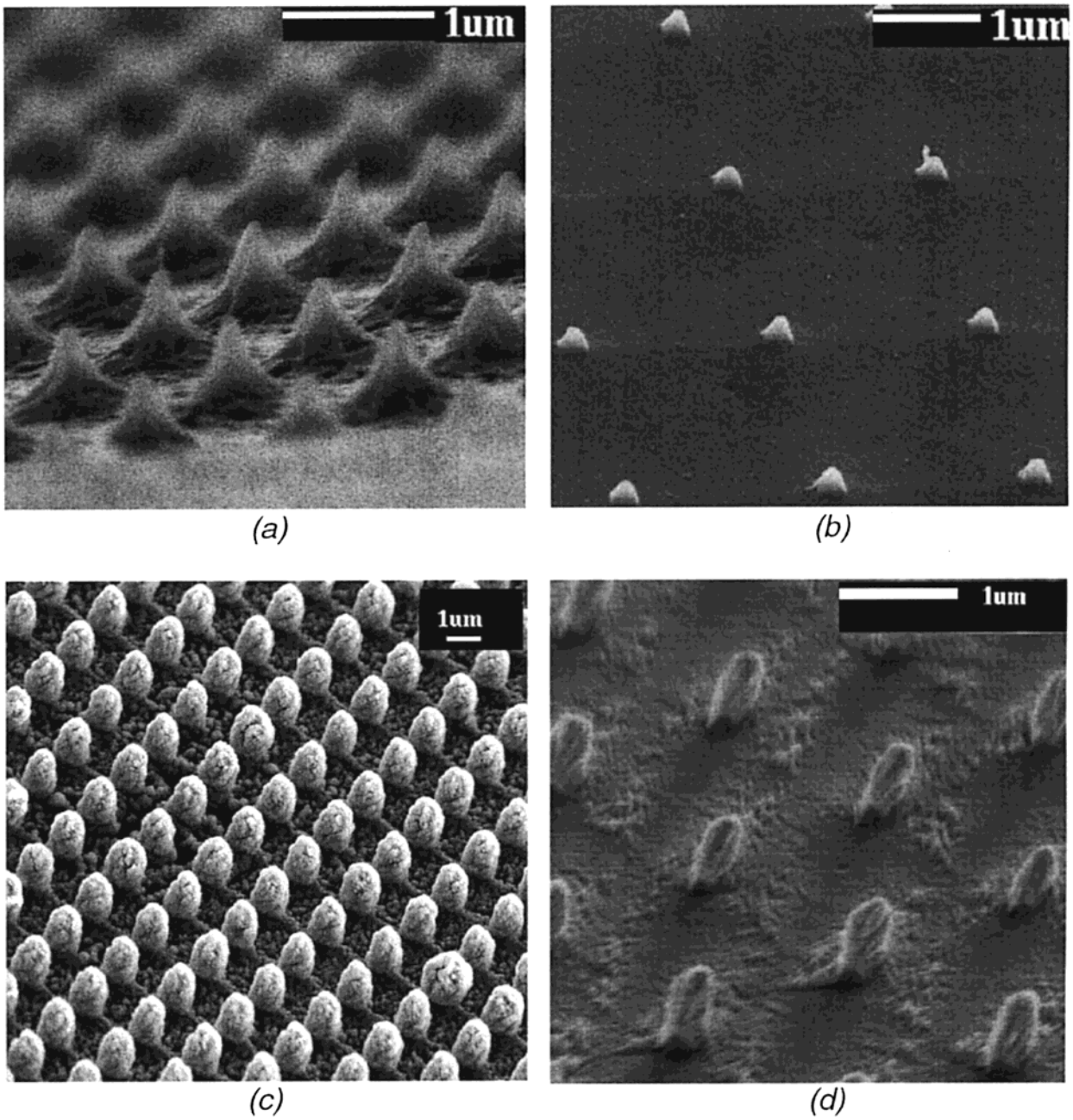

Figure 2. Two types of epoxy nanostructures prepared by embossing and shown before (a,b) and after film growth by GLAD (c,d). Both types have the same periodicity and pyramidal geometry though with different sizes: Approximate feature height of (a) $0.60 \pm 0.01\mu$ and (b) $0.15 \pm 0.3\mu$m. Part (c) is an oblique image of SiO_2 pillars grown on the patterned array shown in (a). The thickness of these pillars was determined by SEM to be $1.58 \pm 0.13\mu$m. Part (d) is an oblique image of oblique columns of nickel grown on the epoxy seed array shown in (b). Note the clear regions of flux shadowing on the surface caused by epoxy seeds. The thickness of this film was measured to be $0.60 \pm 0.03\mu$m

different grating sizes and shapes were used as masters. These masters were placed on the top of the FEP film, which was heated to 330 °C and subjected to a pressure of 100 g per 9 mm^2 for 1 min. Subsequently, the pressure was relieved, and the sample was quenched to room temperature. The master was then removed from the FEP film.

The embossed FEP films were then used as masters for the embossing of the resins. The epoxy resins were prepared from a mixture of diglycidyl ether of bisphenol A (DGEBA) with 4,4′-methylen-bis-(3-chloro-2,6-diethylaniline)(M-CDEA) in a stoichiometric concentration of 100 parts per weight of DGEBA for 51 parts per weight of MCDEA. The selection of the epoxy resin as the material for the microrelief structure was predominately motivated by the high temperatures used in the growth of inorganic nanostructures using GLAD. The mixture was degassed at 60 °C for 2 h under reduced pressure. A drop of resin was deposited on a glass slide and covered with a FEP mask with "spike" nanostructures. The samples were subsequently placed in an oven at 125 °C and subjected to the following curing cycle: 4 h at 125 °C, 4 h at 175 °C, and 4 h at 225 °C under reduced pressure to obtain a glass transition temperature in the order of 200 °C. After

the curing cycle, the samples were quenched to room temperature and the FEP master was removed from the embossed epoxy resins.

To grow nanostructures films on top of the periodic seed layer, the GLAD technique was used. This technique, described in detail elsewhere,[1,2] is depicted in Figure 1 and is described only briefly here. Using external computer software sending signals to two vacuum compatible motors, both the substrate motion about the axis perpendicular to the plane of the substrate (φ) and the flux incidence angle (α) can be controlled during deposition. Two types of GLAD nanostructures are presented in this work: Posts are fabricated by rotating the substrate at greater than one revolution per minute about the φ axis at constant α, whereas oblique columns are fabricated by holding the substrate stationary with respect to φ and at constant α.

Because of the extreme angle of the incoming flux (typically, $\alpha > 75°$), deposition occurs only at, or near, the top of seeds, whereas other areas are shadowed. The substrate motion engineers the structure and geometry of the film growth above each seed (see Figure 2).

Two types of source material were used in our experiments: nickel and silicon dioxide. These two materials were chosen because they (including cobalt and titanium) have been used successfully in the formation of periodic and aperiodic microstructures on PMMA.[3,4] Before deposition, the system base pressure was typically 2.5×10^{-4} Pa, whereas the deposition pressure was 2.7×10^{-3} Pa for SiO_2 and 3.0×10^{-4} Pa for nickel. The deposition angle, α, was set to 85°, and the average growth rate (at normal incidence) was measured as 15 Å/sec for both SiO_2 and nickel. The growth rates were measured in situ using a Sycon STM-100 crystal thickness monitor. The substrate temperature during deposition was approximately 175 ± 25 °C, as monitored via a thermocouple fastened to the substrate during similar depositions, but without substrate motion. The source purities were 99.99% for silicon dioxide and 99.995% for nickel and were deposited using electron beam evaporation.

Figure 2, parts a and b, consist of an array of epoxy "bumps" that serve as seeding sites for the later growth of GLAD nanostructures. The seed periodicity in both images is 2 μm. These images were obtained using scanning electron microscopy (SEM).

Both posts and oblique columns were grown on these epoxy arrays, and the resulting nanostructures are shown in Figure 2, parts c and d. In these images, the film in Figure 2c has been grown using the seed images in Figure 2a, whereas the film in Figure 2d corresponds to the seed array in Figure 2b. Note that for both nanostructure types shown, the nanostructure periodicity matches that of the underlying seed, and only a small amount of film growth between individual nanostructure elements can be observed. This observation is expected due to the shadowing of the substrate surface by each seed element. Previous work on periodic helical structures has suggested that the growth of helices requires further optimization of the seed geometry, periodicity, and deposition angle to create ideal shadowing conditions.[3,4]

The area of the array is approximately 3.6 mm^2, containing over 10^6 individual elements. Although, in this demonstration, both the area and the number of elements is not very large with respect to both typical wafer sizes and other lithographic techniques,[9] a large number of arrays can be stamped quickly by the embosser and subsequent use depends only on the epoxy curing time. Previously, we mentioned that other authors[6] have demonstrated both larger area arrays (up to 16 cm^2) and smaller periodicities between seed elements, without noticeable degradation of the embossed pattern or increase in processing time. It is possible that larger area embossed patterns can be realized by step-and-repeat embossing.

The use of epoxy seeds coupled with the GLAD technique represents a simple and efficient way of manufacturing periodic arrays of unique nanostructures including posts, helices, and zigzags. The latter two examples are not known to be easily fabricated by other nanoimprinting techniques. As shown in Figure 2b, the size structure of individual seed elements can be made to less than 75 nm in diameter, and we foresee that this dimension can be reduced further. In addition, periodicities of less than 100 nm for embossed structures have previously been reported.[5] Once the FEP master is optimized and fabricated for a particular application, large area arrays of epoxy mounds can be easily embossed. Periodic nanostructures (e.g., pillars, oblique columns, or helices) of density greater than 10^{10} elements per square inch then require only one subsequent processing step using the GLAD technique.

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