Thin-Film Micropatterning Using Polymer Microspheres

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A new microlithographic strategy to create precise surface patterns in the submicron region was developed. Densely packed monolayers of monodisperse polymer microspheres (polystyrene) were deposited on a glass substrate using the Langmuir–Blodgett film technique. The spheres serve as a mask for the pattern to be created. Next, ZnS was deposited on the substrate as a thin film by thermal evaporation in vacuum. Finally, the mask (the spheres) was dissolved away to leave behind a surface with features (peaks) located where the interstitial spaces of the densely packed spheres had been. For 2-μm diameter shapes, the lattice spacing of the resulting pattern is ∼900 nm and the individual peaks approximate trigonal pyramids. Subsequent overgrowth of thin films on the micropyramids gradually changes their geometry to a hemispherical shape.

Introduction

Microlithography, used mainly for integrated circuit fabrication, is a technique with which precise high-resolution patterns can be created. However, for nanometer scale structures, electron beam or UV lithography is necessary.[1-3] This paper describes an alternative technique for forming a dense, regular array of features having nanometer or larger scale.

Experimental Section

Spherical polymer particles were synthesized by dispersion polymerization of styrene in ethanol solution. The starting reaction mixture is homogeneous, and the formed polystyrene precipitates out as spherical particles stabilized by a steric barrier of solvated stabilizer. The spherical shape of the particles is a result of the insolubility of the polymer in the solvent (minimization of contact surface). The procedure was essentially the same as that reported by Tseng et al.[4] and by Paine and McNulty.[5]

Unpurified styrene monomer (99%, Aldrich), poly(N-vinylpyrrolidone) (MW ∼40 000 g/mol, special grade, Aldrich) as the stabilizer and 2,2′-azobis(isobutyronitrile) (AIBN/Kodak) as the initiator were dissolved in ethanol, transferred to 30-mL polypropylene screw-cap bottles and placed on a rotor plate (see Table 1 for concentrations). The plate was submerged in a water bath (controlled at 70 °C) and rotated round its central axis at 30 rpm for 24 h. The reaction was stopped by cooling in an ice bath and the resulting particles were cleaned by centrifugation and redispersion in ethanol (three times). The results for the microsphere synthesis are summarized in Table 1. The table shows that—among other system parameters—the composition

Table 1[a]

sample	[styrene], vol %	[AIBN], wt %	[PVP], g/L	diameter, μm	CV, %	yield, %
1	5	1	16	1.78	8.71	56
2	20	1	16	2.78	12.06	94
3	10	0.25	16	1.38	9.26	38
4	10	2	16	2.25	13.55	89
5	10	1	25	1.78	7.44	91
6	10	1	10	2.31	13.48	89

[a] [styrene] is volume percent of styrene in ethanol solution. [AIBN] is weight percent of initiator to monomer. Yield is weight of isolated microspheres. The coefficient of variation (CV) given includes some background noise due to fines or dust. The actual CV's of sample 5 would be closer to 2–5%, in accordance with figure 2.

of the starting reaction mixture determines the final particle size and size distribution, expressed by the coefficient of variance CV (standard deviation of size measurement divided by average particle size). Particle sizes were measured with a 256-channel Coulter counter. In the subsequent procedures sample 5 was used.

The Langmuir–Blodgett film technique,[6] originally developed to deposit molecular monolayers, was successfully applied to prepare densely packed monolayers of monodisperse polystyrene microspheres (diameter = 1.78 μm) onto a glass substrate.

An ethanol dispersion of the spheres (concentration ∼0.1–0.2 g/mL) was slowly and steadily deposited on a clean water surface using a syringe until the whole water surface was covered. The syringe was held at an angle of ∼30° to the water surface (Figure 1) in order to reduce turbulence in the water. Under these conditions, two-dimensional regular microsphere arrays are formed, which show the typical imperfections (packing faults, fault lines between crystalites) expected in a two-dimensional lattice.

To transfer these regular microsphere arrays onto a substrate, a region of the water surface was cleared of microspheres, and a flat glass cover slide was submerged through this opening.

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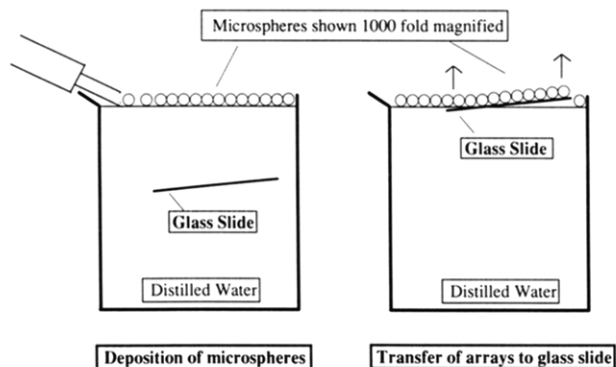
Figure 1. Particle injection and transfer onto glass slides.

The glass slide was recleaned under the water surface with a small brush which was passed through the same opening as well. Alternatively, a glass slide was submerged under water before the particles were deposited onto the surface of the water (Figure 1). The slide was then lifted nearly horizontally to pick up the dense microsphere packings on its upper side. The deposited monolayer was then dried in a clean atmosphere, or in vacuum. Thermal evaporation of ZnS from a tantalum boat containing ZnS chunks (99.99%, Johnson Matthey) was performed at 5 × 10⁻⁵ Torr chamber pressure. The substrate was not heated, and the growth rate was ~30 Å/s. Films of 0.75-μm thickness according to a quartz microbalance were grown. Finally, the microspheres were dissolved using hot, anhydrous HPLC-grade tetrahydrofuran (THF) in an ultrasonic bath. This process also removed the ZnS material that covered the spheres but did not damage the ZnS peaks that adhered to the glass substrate directly. The resulting micropatterns were analyzed by optical microscopy and scanning electron microscopy.

Results and Discussion

The different steps involved in the described technique are illustrated in the figures below. Parts a and b of Figure 2 show a scanning electron micrograph and an optical micrograph, respectively, of microsphere monolayers deposited on glass slides. All substrates characterized by SEM were sputter-coated with a 15-nm-thick layer of gold. Figure 3 shows an enlarged SEM image of the particle packing. Figure 4 shows, in gray scale, the wavelength-dependent diffraction of plane-polarized white light passing through a monolayer of 1.78-μm diameter microspheres deposited on glass. The monolayer after deposition of a 0.75-μm-thick layer of zinc sulfide is seen in the SEM in Figure 5. Near the edge of the support in the center foreground, two particles have broken off, revealing a set of six peaks located at the corners of a hexagon.

After ultrasonic treatment with tetrahydrofuran, only the zinc sulfide deposited in the interstitial spaces remains in the form of approximately trigonal pyramids in a hexagonal lattice (Figures 6 and 7). Subsequent deposition of two thin films transforms the trigonal pyramid peaks into near spherical sections (Figures 8: 0.5 μm ZnS; Figure 9: 0.3 μm Y_2O_3 on top of 0.5 μm ZnS).

Due to the fairly low melting point of polystyrene, substrate temperature was kept below 150 °C during processing. Care had to be taken to avoid excessive heating during thermal evaporation of ZnS.

Films of ZnS thicker than ~1 μm prevented removal of the polystyrene spheres, presumably because no free sphere
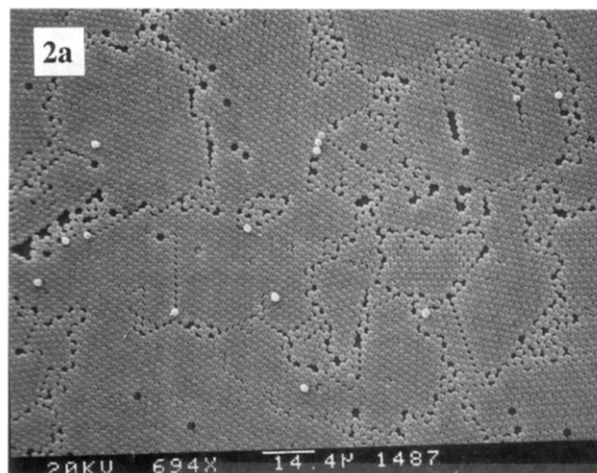
Figure 2. Crystalline arrays of monodisperse, polystyrene microspheres, diameter = 1.78 μm (view angle 90°). Areas of perfect dense packings are separated by crystal fault lines. (a) Scanning electron micrograph; (b) optical micrograph.
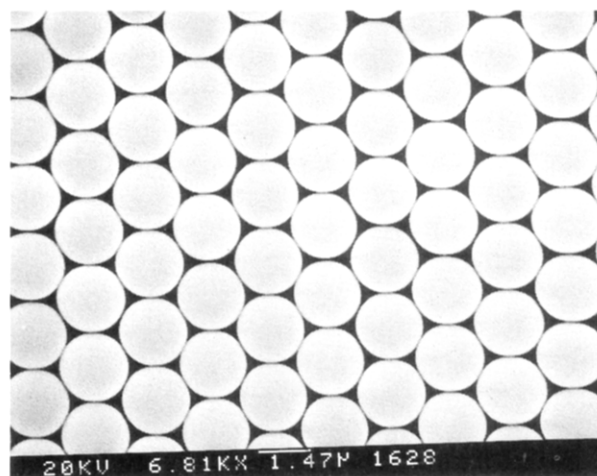
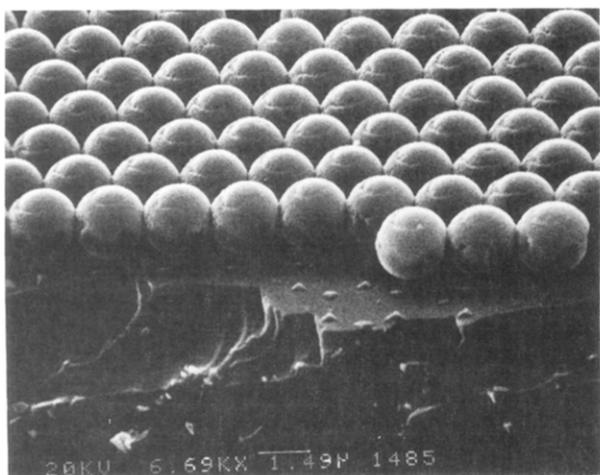
Figure 3. Scanning electron micrograph of one area of perfect dense packing (view angle 90°).

surface was available to the solvent. Thinner ZnS films leave the undersides of the spheres uncovered and accessible to the solvent.

The size of the crystalline arrays in the particle monolayer depends on the rate of particle injection onto the water surface. A high injection rate keeps up a constant "pressure" on the forming grains by the particle flow. Once this pressure is released, the dense-packed arrays break apart and rearrange themselves on the water surface in such a way that they cover it uniformly (density loss).
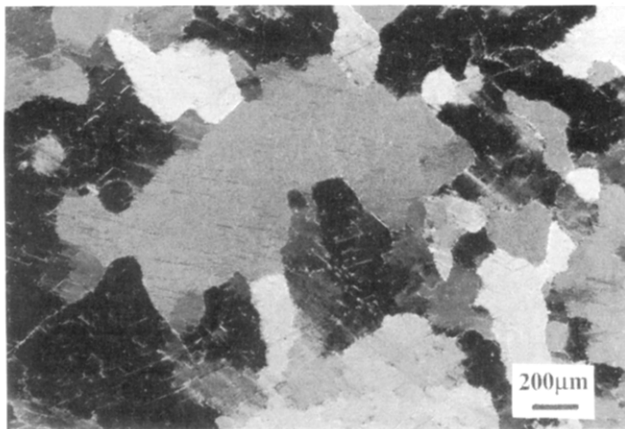
Figure 4. Optical diffraction effect observed when plane-polarized light passes through a monolayer of dense packed microspheres; areas of different crystal orientation appear in different colours (view angle 90°).
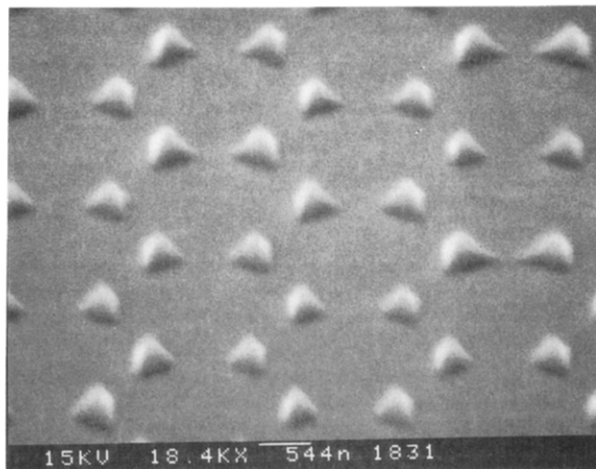

Figure 5. Scanning electron micrograph of packed spheres covered with ZnS. The picture is taken on the edge of the substrate; one sphere has broken off from the corner, giving here a view of the evaporated material in the interstitial spaces of the dense packings (view angle: 30°).
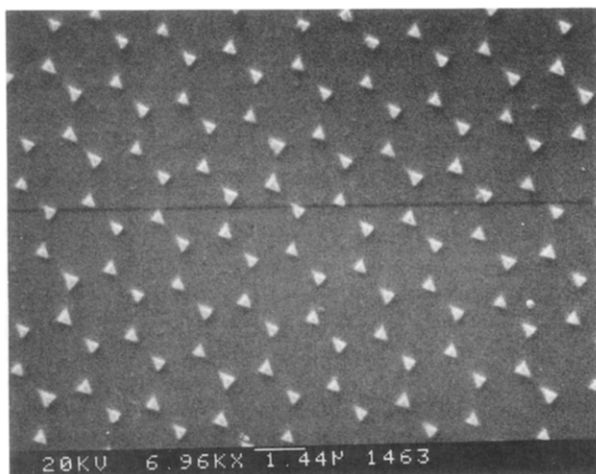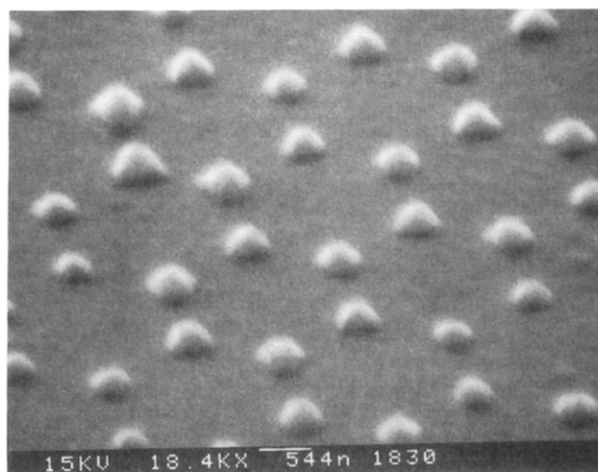

Figure 6. Scanning electron micrograph of the ZnS peaks – the residues of the evaporated ZnS after the dissolution of the spheres (view angle 90°).

Figure 7. Scanning electron micrograph of the peaks showing their geometry as trigonal pyramids with a height of approximately 0.2 μm (view angle 30°).

Figure 8. Electron micrograph of the peaks of Figure 6 after an overgrowth of a 0.5-μm-thick ZnS film (view angle 30°).

Figure 9. Peaks of Figure 7 after an additional overgrowth of a 0.2-μm-thick Y_2O_3 film.

dense packed arrays are stable after the whole surface is covered.

Conclusion

We have described a new technique for high-resolution microlithography.

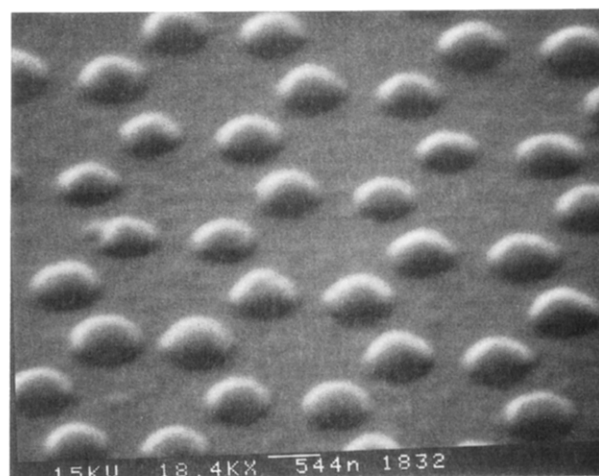This technique allows the production of regularly spaced micropeaks on smooth glass substrates. The micropeaks

Under the repeated application of pressure they move together again but form smaller grains. With a manual injection rate corresponding to $\sim$10 cm^2 surface coverage per second, array sizes up to 0.5 cm^2 can be obtained. The

consisted of zinc sulfide in this work; the choice of material, however, is only restricted by the requirement that thin films may be grown. The resolution of the obtained pattern is on the order of ~50 nm (for 1.78-μm spheres). Considering the fact that polymer microspheres in the range 0.1–100 μm are readily available[5,7,8] a wide range of lattice spacings may be prepaed with this technique. The optical properties of dense-packed polymer microsphere

monolayers and the resulting peak pattern may be useful as two-dimensional gratings. Experiments to investigate peak-patterned glass substrates in electroluminescent devices are currently being pursued.

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