Dial-a-Size: Precision Quantum Dot Nanopatterning Using Cheap, Off-the-Shelf Copolymers

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ABSTRACT: In the use of block copolymers as templates for nanolithography, deposition, or etching, substantial time and cost savings can be achieved through the use of algebraic models for block copolymer feature size as a function of both the polymer's molecular weight and the relative concentration of a homopolymer additive. Desired average pore diameters and spacing can be achieved on the first try, using off-the-shelf polymers in a wide range of molecular weights. This allows precise nanoscopic components such as quantum dots to be patterned over large areas rapidly, repeatably, and at very low cost. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 3785–3794, 2008

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INTRODUCTION

The use of block copolymers as self-assembled nanoscale templates is well established.[1] Copolymers of polystyrene (PS) and polymethyl methacrylate (PMMA) have proven particularly useful, because both polymers are familiar resists in the semiconductor industry, and because the different photodegradation properties of the two materials make it relatively easy to remove one component of the self-organized film, with little damage to the other component.[2] The polymer self-organizes within a limited range of molecular weights, and the feature sizes of the resulting template are molecular-weight dependent, while the orientation is dependent on the relative weight fractions of the two components. For an array of vertically oriented cylindrical pores—useful in particle filtration, photonic materials, nanowire deposition, and etch masks for nanostructured capacitors and other electronic components—a PMMA fraction of $\sim 30\%$ is used.

However, certain applications such as quantum dots require nanometer precision in both the diameter and spacing of periodic features.[3] A usual solution is to design custom copolymers by slowly increasing the molecular weight until one is found that produces the desired features. This strategy presents little problem for a fully equipped chemistry department, but for small businesses and laboratories who must outsource the polymer synthesis, the costs and time involved (typically 10–14 days and several thousand dollars per sample) can be prohibitive. It is therefore desirable to use a predictive model that expresses the two critical dimensions—pore diameter and center-to-center spacing or period—as an algebraic function of the polymer's molecular weight. This way, a single custom copolymer can be designed and synthesized, with high confidence that it will function as intended.

Additionally, in the recent years, the addition of a homopolymer matched to one component of the block copolymer has been found to affect the pore diameter and spacing in predictable ways.[4] In the case of a PS-PMMA copolymer, which forms vertical PMMA cylinders in a PS matrix, a PMMA homopolymer additive migrates to the center of the cylinders, widening them. Because the volume of PS is not affected, the spacing between the cylinders must also increase.

This creates an even cheaper alternative for small laboratories to order an off-the-shelf block copolymer and homopolymer and to adjust feature size in the self-organized polymer film by adjusting the relative concentrations of these two components. Because off-the-shelf polymers can be ordered at much lower cost than custom polymers (typically around $200 a gram), and with shorter lead-times, the amount of research and development required can be dramatically reduced. This strategy also allows a small laboratory to tweak feature sizes on a regular basis without ordering new polymers, simply by adjusting the amount of homopolymer in the solution.

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METHODOLOGY

Ting et al.[6] demonstrates a relationship between the molecular weight of a 70% PS/30% PMMA block copolymer, and the pore size and period that results from spinning it onto a surface and dissolving away the PMMA with acetic acid. The first step in our process was to fit these data to an algebraic relationship and then confirm the model with additional experiments.

A styrene/BCB/MMA (proportions 56/2/42) random copolymer was dissolved to a 0.3% wt solution in toluene, spin coated onto a silicon surface at 3000 rpm, baked at 250°C on a hotplate for 30 min to crosslink it, and finally rinsed for 5 min in toluene to remove any residual polymer. This process creates molecular "brushes" ∼ 10-nm high, which serve as anchor points for the self-organized polymer film.[5] Next, a block copolymer containing ∼ 70% PS and 30% PMMA was dissolved to a 1% solution in toluene, spin coated onto a surface at 3000 rpm, and baked at 160–190°C in a vacuum oven for 12 h. The resulting self-organized copolymer film was ∼ 30-nm thick. According to the experiments of Ryu,[5]

Mansky, Black,[1] Hawker, Harrison,[3] Jeong,[4] and others, and from our own experience, the film will reliably self-organize within this temperature range, which is above the glass transition temperature and below the order–disorder temperature of the polymers.[3] The period of the self-organized structure is then a function of composition rather than thermal history. To cross-link the PS component of the film and render the PMMA component soluble, the sample was then cured in a vacuum under a mercury UV lamp for a total dose of >25 J/cm². Using an Edmund Scientific BondWand source, 25 mW/cm² at standard height, this means an exposure time of >1000 s or ∼ 17 min under a gasketed quartz window resting on a vacuum plate. For safety margin, exposure times of 35–45 min were used. The sample was then immersed in glacial acetic acid for 15 min to dissolve the PMMA, leaving empty cylindrical pores in the regions the PMMA had occupied. Finally, each sample was examined with a Veeco Dimension 3100 atomic force microscope.

A 70% PS/30% PMMA polymer with a molecular weight of 77,000 was found to produce a pore diameter of 20–25 nm, which fits the model reasonably
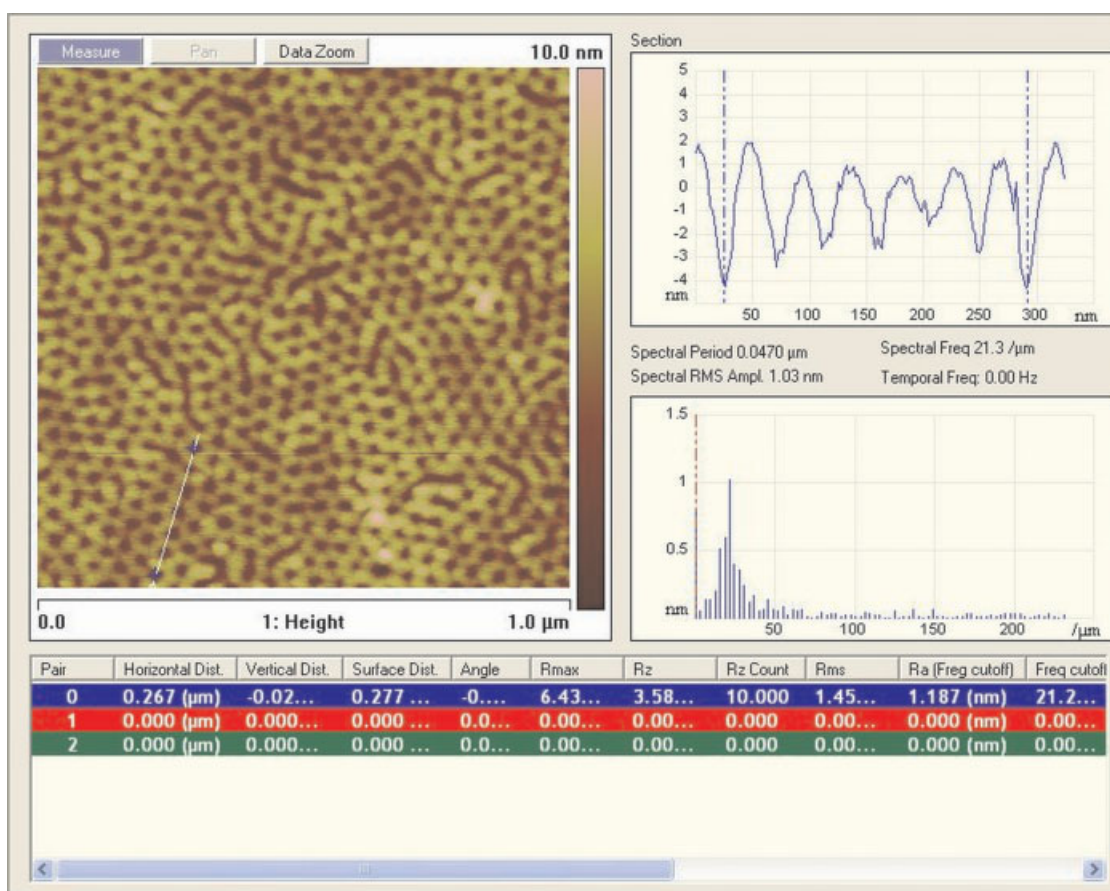

Figure 1 A 1-μm atomic force microscope scan of a film of 97,500 MW diblock copolymer on Si. The section line in the lower left quadrant of the image passes through seven regularly spaced pores, and makes an angle of +73.5° with the X-axis. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
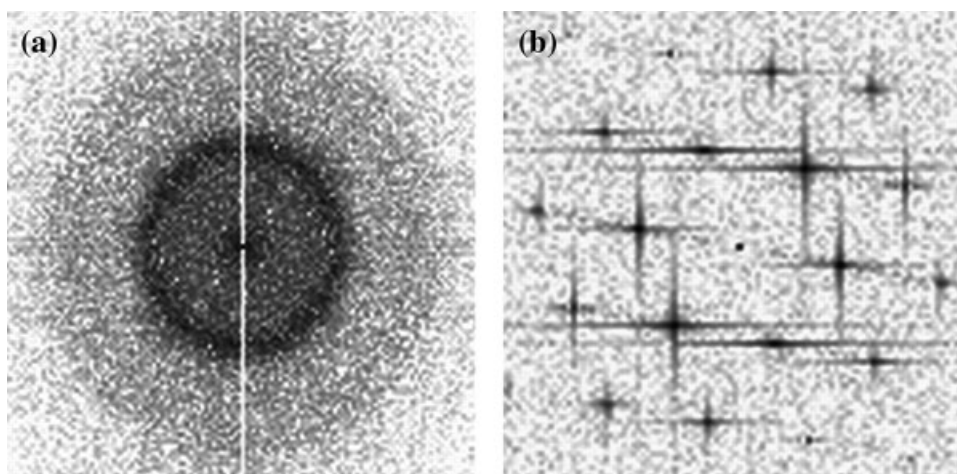
Figure 2 (a) A 2-D Fourier transform of the AFM scan shown in Figure 1. (b) A 2-D Fourier transform of a computer-generated ideal honeycomb pattern.

well, and period of 47 nm, which was ∼ 20% larger than the model predicted. Consistent with the previous results,[6] a polymer of molecular weight 132,000 was found to produce a poorly organized film with much less regularity in pore size and spacing. Nevertheless, measurements showed pore diameters falling into a range between 35 and 60 nm (11–58% larger than expected) and period of 55–70 nm (0–27% larger than predicted). The model was revised to account for these results, and when a polymer with molecular weight 97,500 was measured, the pore diameter of 25.5 nm and period of 45 nm matched the new model's predictions to within 1 nm. Based on this, and on the original curve-fit data, the model is believed to be useful over the entire range of self-organizing molecular weights for the 70% PS/30% PMMA copolymer, and thus to be a general solution for feature size estimation.

Because pore diameter was measured with an AFM using a TESP-SS "supersharp" probe (nominal ROC = 2 nm), the results may be affected somewhat by the exact size and geometry of the probe tip. Also, pore sizes are generally less uniform than pore spacing, the pores are not perfectly circular, and the

pore openings are curved downward rather than presenting a perfectly cylindrical edge. Finally, the AFM is unable to see the bottom or to render the sidewalls accurately when the pore is both narrow and deep. Instead, the scanning probe perceives the pore as a cone-shaped hollow rather than a cylinder. Thus, while the pore period is an easily and reliably measured property, pore diameter is somewhat subjective, and care must be taken to ensure the same measurement rules are applied in each case.

Next, we added various concentrations of a homopolymer (PolymerSource P2716-MMA with a molecular weight of 31,800, PDI = 1.08) to solutions of block copolymer and observed the effects on pore size and period.

The homopolymer was added to the copolymer of molecular weight 97,500, such that the ratio of the total dissolved mass of the homopolymer to the total dissolved mass of the PMMA block, referred to as β, ranged from 0 to 34%. For each of several values of β, a film was prepared as described earlier. An atomic force microscope was then used to scan a 1-μm^2 area of each film. This topographic data was used to measure the pore period by taking cross-sections

TABLE I
Measurements of the Periodicity and Pore Diameter of Self-Organized Films of Diblock Copolymer with MW = 97,500 Containing Varying Amounts of Homopolymer

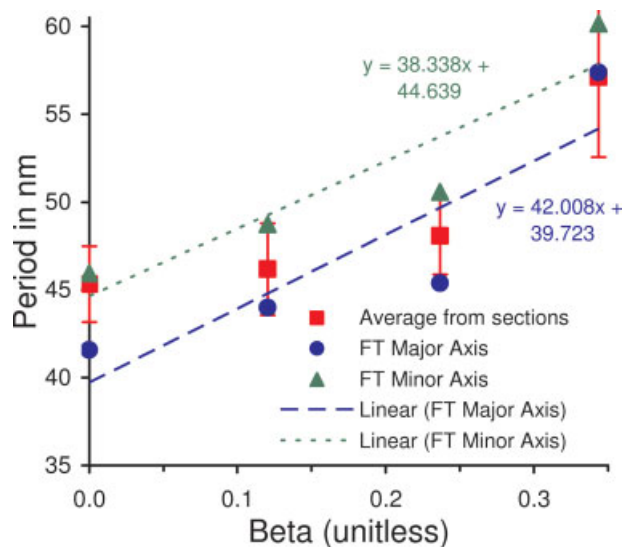|	Period in nanometers			Pore diameter in nanometer
	Via sections	Via fourier transform		
β (unitless)	Mean ± SD	Major axis	Minor axis	Mean ± SD
0.00	45.3 ± 2.2	41.6	46.0	25.5 ± 2.3
0.120	46.2 ± 2.6	44.0	48.7	27.3 ± 3.1
0.237	48.1 ± 2.2	45.4	50.6	28.2 ± 2.6
0.344	57.1 ± 4.6	57.4	60.2	32.0 ± 3.6

y = 38.338x + 44.639

y = 42.008x + 39.723

Figure 3 Period as measured directly via sections compared to the upper and lower bounds of the period as determined using Fourier transform data for a diblock copolymer of molecular weight 97,500 with added PMMA (α = 1). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

through straight rows of pores as shown in Figure 1. Eighteen sections were taken from each image, except for the last sample (β = 34%), which was less organized than the others. The sections passed through four to seven pores each. The orientation of the row of pores (i.e., the angle it made with the X-axis) was recorded for each section.

A second method was employed to extract periodicity information from the AFM data in a different way. Figure 2 shows a two-dimensional Fourier transform of the same data featured in Figure 1; next to it is a similar Fourier transform of a computer-generated "ideal" honeycomb surface for comparison. The surface of the copolymer film tends to self-organize locally, but several different orientations of the same basic pattern can be found on within a single 1-μm scan. Therefore, the transform of the real AFM data contains a central ring instead of the six equally spaced peaks shown in the transform of the ideal honeycomb. The ring is a composite of many sets of six peaks; this image is analogous to an X-ray diffraction pattern created by a polycrystalline sample. Note that the ring is slightly elliptical; this eccentricity corresponds to an anisotropy in the self-organized film. The measurements made by the cross-section method confirm that the period of the pattern appears to depend on direction.

The diameter of the pores produced by self-organization also increases as homopolymer is added.[3] Smaller sections were taken of nine pores from each film; each pore was sectioned along its major and

minor axis, and all 18 measurements were averaged together.

Table I shows the information obtained on all four films using both methods of measurement. Note that the "major axis" of ellipse in the Fourier transform yields a *lower* bound on the period of the pattern and vice versa.

One issue complicating the attempt to fit a model to the periodicity data is the large nonrandom spread in period values due to directional dependence. Because the Fourier transform method yields an upper and lower bound on the period for each sample, these bounds can be fitted separately to define a range of probable values for the period in a given region of the sample. Figure 3 compares the Fourier transform data with the directly measured data.

The average pore diameter is plotted against β in Figure 4. The ratio between average period and average pore diameter is 1.74 ± 0.05.

Figures 5–8 show the images from which these measurements were made, and the direction dependence of the period measurements. Each group of figures represents a film of 97,500 MW diblock copolymer on a Si substrate; the fraction of added homopolymer (given as β) increases from one sample to the next. The first image in each group is a 1-μm atomic force microscope scan (height mode), the next image is a two-dimensional Fourier transform of the height data, and the graph plots directly measured periods (see Fig. 1 for an example) against θ, the angle that a row of holes makes with the positive X-axis.
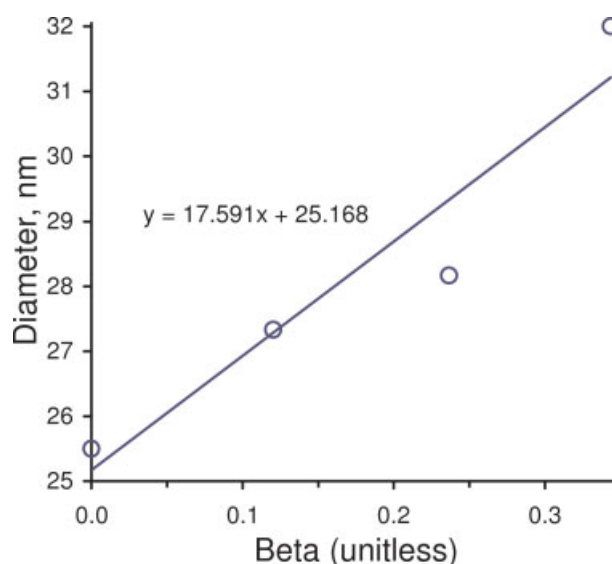

y = 17.591x + 25.168

Figure 4 Pore diameter as measured from AFM data plotted against fraction of added PMMA for a diblock copolymer of molecular weight 97,500 (α = 1). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
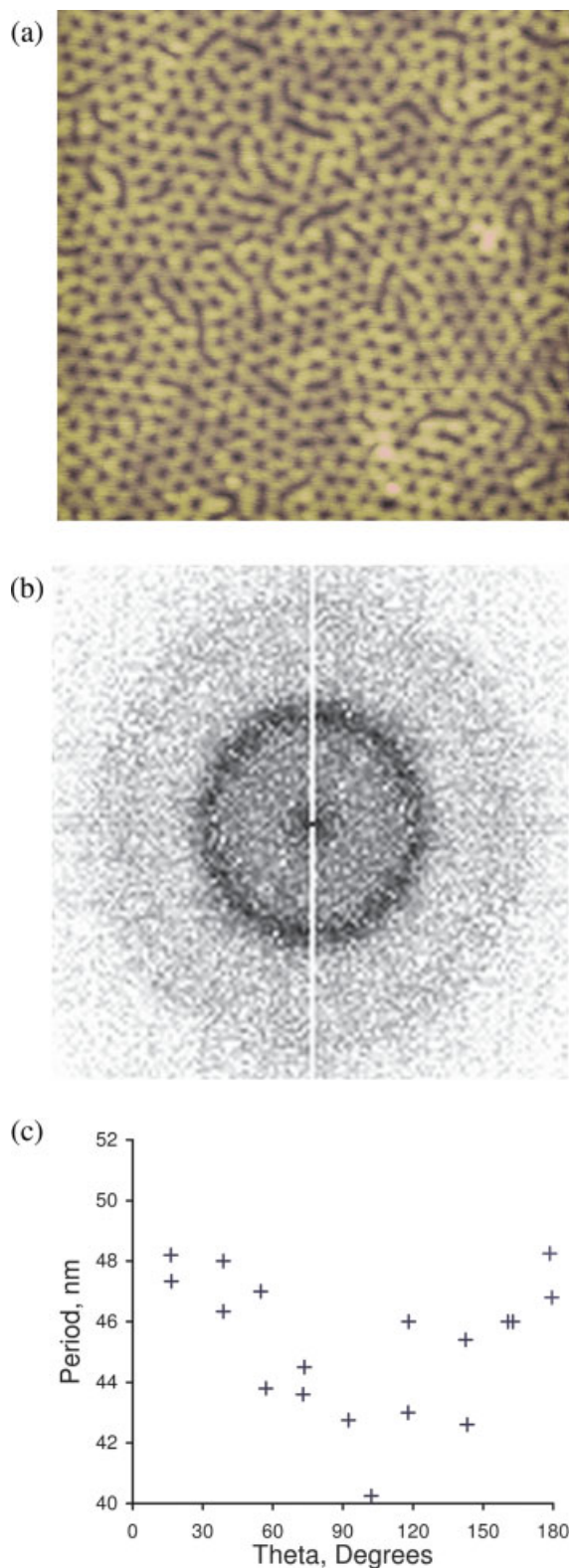
Figure 5 Diblock copolymer (97,500 MW) without homopolymer ($\beta = 0$); (a) AFM image, (b) 2D Fourier transform, and (c) period as measured from AFM data plotted versus direction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
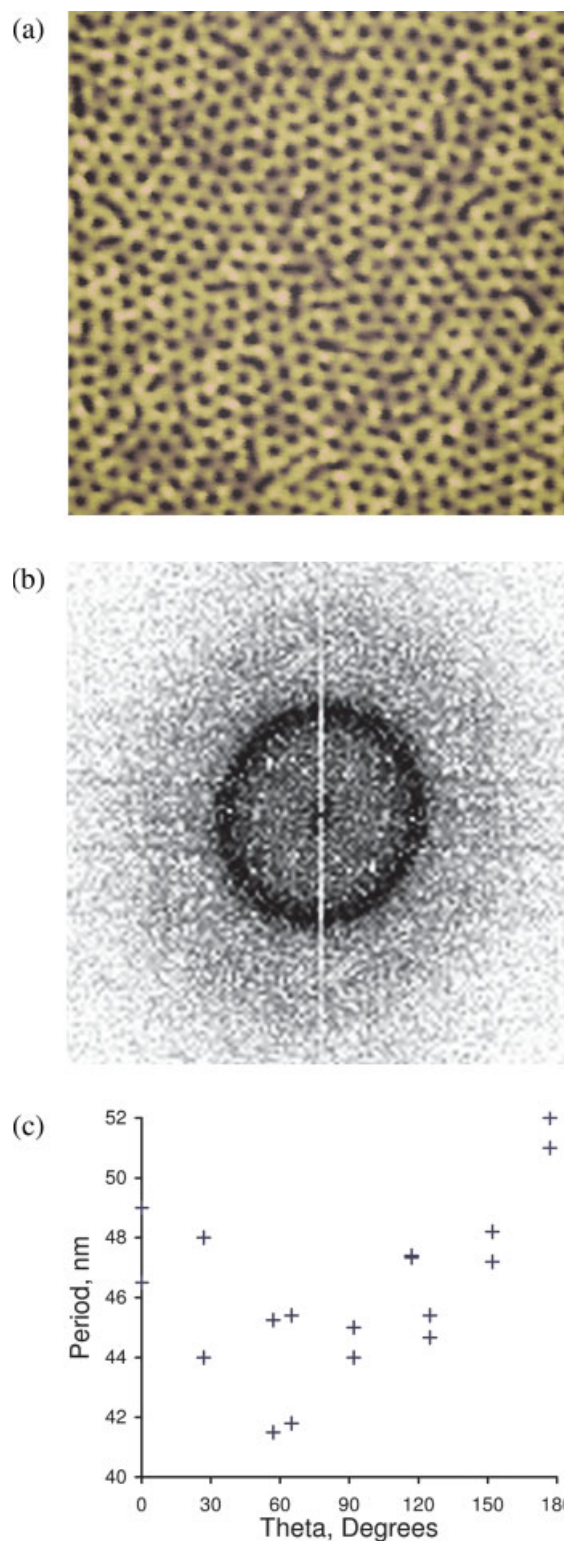
Figure 6 Diblock copolymer (97,500 MW) with homopolymer ($\beta = 0.120$): (a) AFM image; (b) 2D Fourier transform; and (c) period as measured from AFM data plotted versus direction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
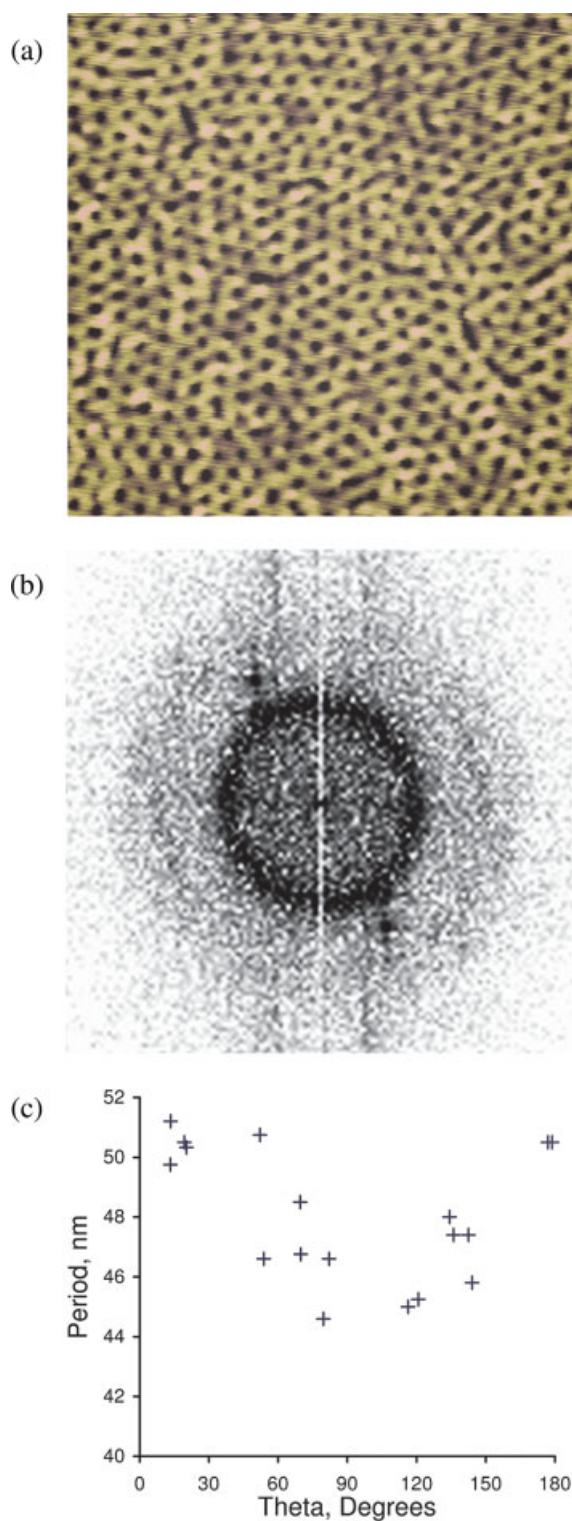
Figure 7 Diblock copolymer (97,500 MW) with homopolymer (β = 0.237): (a) AFM image; (b) 2D Fourier transform; and (c) period as measured from AFM data plotted versus direction. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
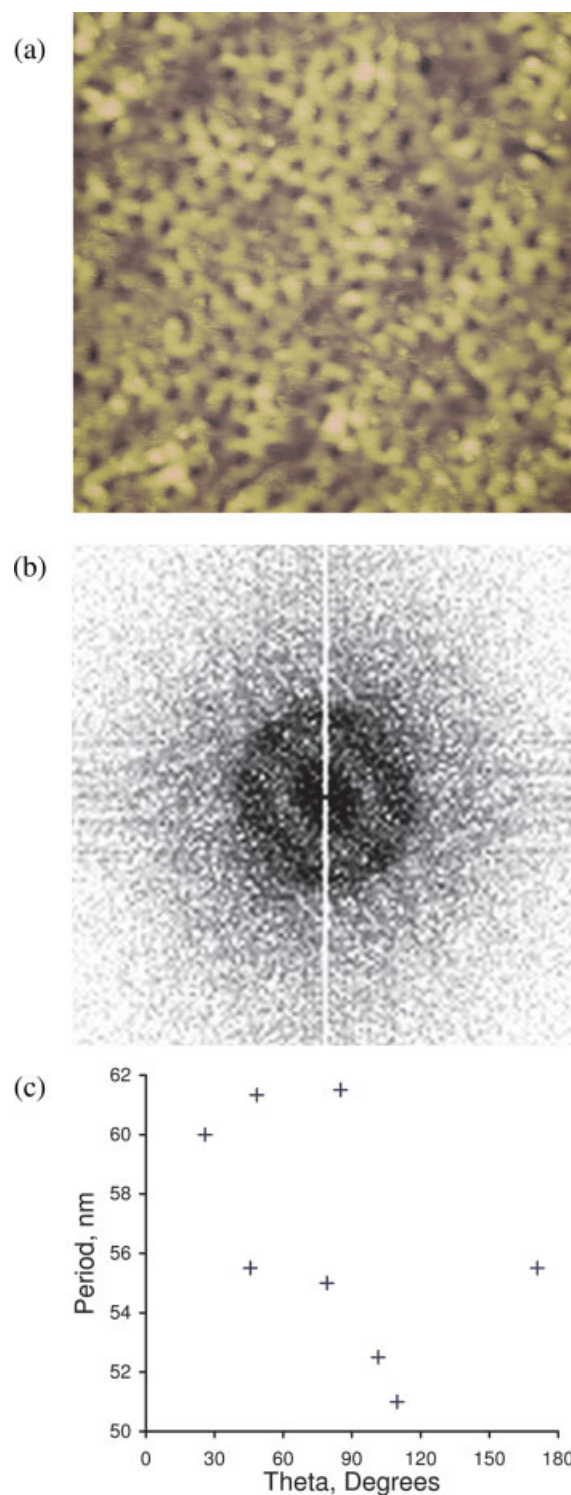
Figure 8 Diblock copolymer (97,500 MW) with homopolymer (β = 0.344): (a) AFM image; (b) 2D Fourier transform; and (c) period as measured from AFM data plotted versus direction. Note that the vertical scale of the graph is different from the previous three examples, due to the large variation in periodicity. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]
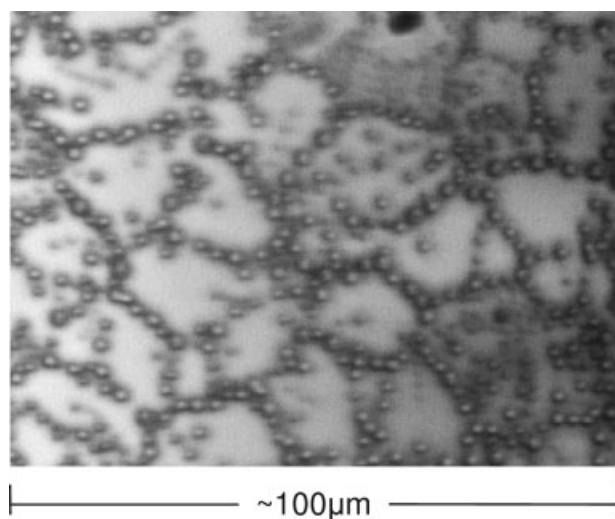
Figure 9 Photomicrograph of copolymer film with diblock MW = 77,000, α = 1.38, β = 0.034.

When the homopolymer was added, the pore period and diameter were observed to increase by roughly the same proportion, which is consistent with the homopolymer being confined to, and increasing the volume of, the cylindrical PMMA regions of the self-organized polymer film.[4] The algebraic model was expanded to encompass these observations. There is a geometric relationship between homopolymer mass and the increase in pore size,[4] which suggests that the effect of the homopolymer additive should be consistent across the useful range of molecular weights for the copolymer. Thus, an algebraic model can be found that applies to the entire range as well.

The data show a nonstochastic difference of up to 5 nm in the measured period as θ varies. Instrument calibration checks indicate that this is a real effect rather than a measurement or processing artifact. This directionality could be a result of spin-coating, that is, the preferred direction may extend radially from the center of the sample. For applications with stringent demands on pore spacing, further investigation is clearly warranted.

Readers should note that the molecular weight of the PMMA homopolymer does not need to be precisely matched to the weight of the PMMA block of the copolymer. If the ratio of the molecular weight of the PMMA homopolymer to the PMMA block is defined as α, acceptable results have been achieved by other groups using α values as low as 0.5 and as high as 3.[4] This greatly increases the probability that on-hand or off-the-shelf materials can be used to meet many different sets of design constraints without the need for a custom polymer each time. All of the above data is for α = 1.00. However, when using a block copolymer of W = 77,000 Da (22,000 PMMA

portion) and a homopolymer of W = 29,500 Da (α = 1.34), we were not able to obtain the same reliable relationship between β and pore period. Rather, the period increased as expected when a small amount of homopolymer was added (β = 0.0336), but then declined back toward the β = 0 value as the value of β grew larger, as shown in Figure 10. As shown in Figure 9, these films showed large-scale, pseudo-hexagonal patterning of large walls, >200 nm high and ~ 2 μm wide, with flat areas in between them that were >10 μm wide, in which the block copolymer had apparently organized normally, but with only small amounts of homopolymer incorporated. Ordinarily, the self-organization process drives the homopolymer into the center of the PMMA pores.[4] In these cases, we believe the homopolymer was instead driven out of the region to form the wall structures. It is not yet clear whether this malformation was due to operator error, the relative sizes of the PMMA blocks (i.e., α ≠ 1), or some other factor or combination of factors. Clearly, however, values of α close to 1.0 are likely to be the most reliable for industrial applications.

ALGEBRAIC MODEL

Pore diameter was found to be a consistent fraction of pore period, regardless of molecular weight, whereas period was found to be an exponential function of molecular weight. Ting et al.[6] found that in the absence of a homopolymer additive, the relationship between lattice period and molecular
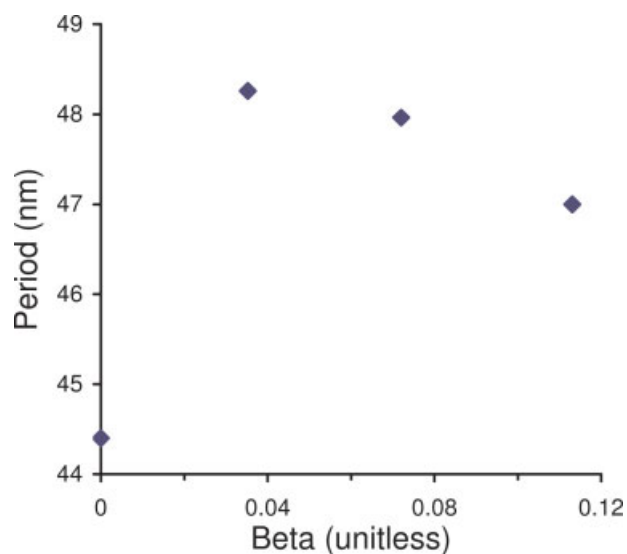

Figure 10 Period values plotted against β for samples prepared from a diblock copolymer with M_n = 77,000, (PMMA = 22,000), and a PMMA homopolymer with W = 29,500 Da (α = 1.34). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

weight follows a power law with an exponent of 0.64:

$$P = (0.5556) \times (W/100)^{0.64}$$

$$D = P/1.74$$

where P is the pore period or center-to-center spacing, W is the molecular weight in daltons, and D is the pore diameter as measured by atomic force microscopy. When a homopolymer is added to the solution prior to spin coating, the ratio of the molecular weights of the PMMA homopolymer and PMMA block is defined as α, the ratio of the total dissolved mass of PMMA homopolymer to the total dissolved mass of the PMMA block is defined as β, and the relationship requires additional terms. Assuming that the equation should reduce to the power law given above for $\beta = 0$, it can be expressed as the power law used above plus terms in β. An empirical power law equation in W and β yields:

$$P_{\text{section}} = (0.5556) \times (W/100)^{0.64} + 147.5 \cdot \beta^{2.574}$$

$$D = P/1.74 \quad \text{for } \alpha \sim 1.0$$

This equation is compared to the data in Figure 11.

Figure 11 Possible fit equation for the period of a film of a diblock copolymer with $W = 97,500$ Da and added homopolymer with $W = 29,500$ Da. The equation is of the form $(W/100)^{0.64}/1.8 + f(\beta)$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ETCHING OF QUANTUM NANOSTRUCTURES

Tunable quantum dots can be formed by dividing up a quantum well into microscopic allowed and forbidden regions using electric fields, produced for example by a pattern of holes in a charged thin-film electrode sitting on top of the well.[7,8] For room temperature operation, sub-50-nanometer features are required.[3] Electron beam lithography produces such features easily, but problems of scaling generally limit the patterned area to a few hundred microns on a side—too small for real-world applications such as tunable LEDs or optical filters. Block copolymers offer an attractive means of nanopatterning large areas, if the porous film is used as an etch mask.

To demonstrate, this possibility, a Si substrate was sputter coated with a 10-nm-thick film of 60% gold and 40% palladium alloy. Atomic force microscopy showed that except for occasional defects or inclusions in the surface, the metal film was of extremely high quality, being flat and dense rather than granular in nature. Next, a porous block copolymer film was added to the surface by the methods described earlier. To prepare it for chemical etching, the surface was exposed to oxygen plasma for 5 s to remove the random copolymer layer at the bottom of 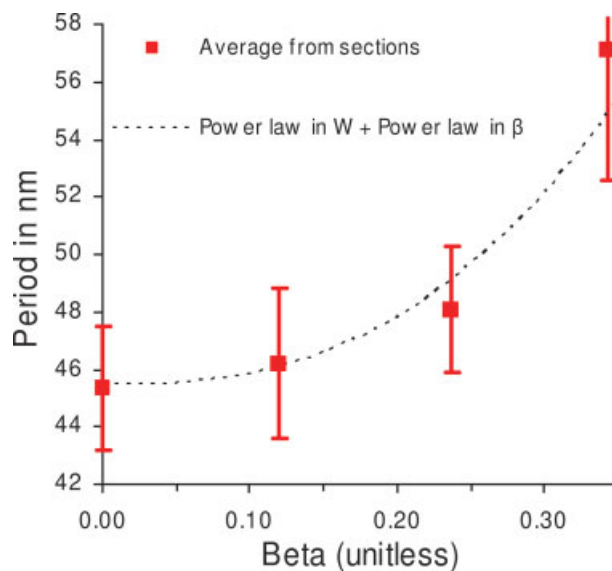the pores. Finally, the sample was immersed in commercial gold etchant (TFA type Gold Etch from Transene, etch rate 28 Å/s) for 5 s and then rinsed in deionized water. As a result of this process, the pore pattern in the polymer mask was transferred to the AuPd film in many areas, with feature sizes and spacing consistent with the formation of room temperature quantum dots (see Figure 12).

Unfortunately, this wet-etch process was difficult to control with precision, so that accidental underetching and overetching were common occurrences—usually both on the same sample. A dry etch process is therefore more desirable and is under the development at the time of this writing. A further complication arises because gold does not adhere well to many semiconductors, including GaAs, and can also act as a contaminant by slipping into the crystal lattice and "poisoning" it. For real-world applications, an adhesion layer and diffusion block, such as a thin film of titanium between the gold electrode and the semiconductor surface, is also required. Once the pores of sufficient depth are etched in the electrode material, a second etching step is therefore required to remove the adhesion layer from the bottoms of the pores, further complicating the etch process.

CONCLUSIONS

Our analysis shows clear anisotropy in the values of pore diameter and period, that is, these values vary deterministically based on the orientation of the
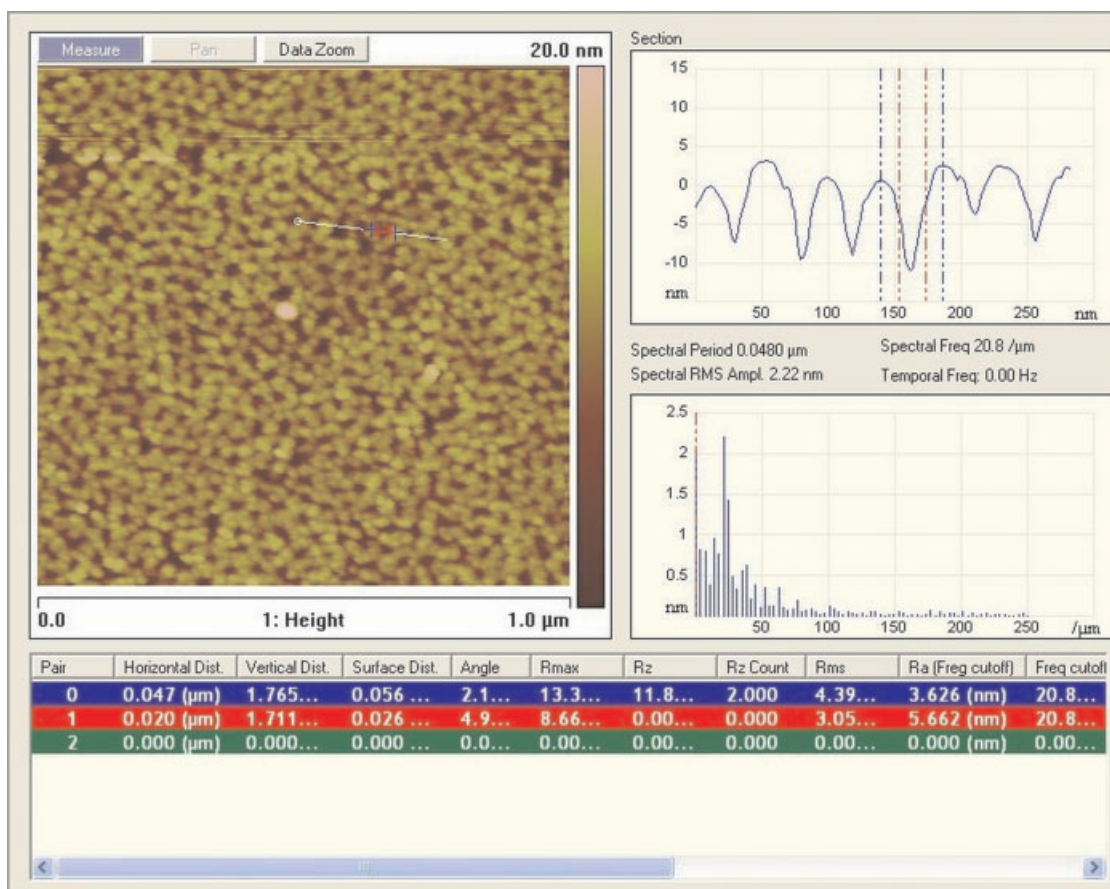
Figure 12 Using a block copolymer with vertical pores as an etch mask, an AuPd surface was treated with an oxygen plasma, immersed in a commercial gold etchant, and rinsed in deionized water. The feature sizes and spacing are suitable for the creation of electrostatically confined quantum dots that operate at room temperature. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

measurement line. When the anisotropy was first observed, the AFM was checked against a calibration standard to verify that the scale is the same in the X and Y directions. The major axes of the ellipses in the Fourier transform images point in different directions from one sample to the next; this would argue against the anisotropy being an artifact of the scanning hardware. The cause of the anisotropy is currently unknown. The spin coater is one obvious candidate for a strong directional influence on the film as it is deposited and suggests an interesting direction for future research.

The Fourier transform method of measuring the period has the virtue of using the entire image rather than just selected rows of pores and thus reducing measurement bias. The major axis/minor axis measurement offers a convenient way to express the anisotropy of the self-organized film, that is, the fact that the period is not just one number, but a function of direction.

However, the Fourier method is only suitable for well-organized surfaces. In the case of the $\beta = 0.344$ sample, the Fourier ellipse ceases to be a well-defined ridge.

We believe that this algebraic model is useful across a broad range of molecular weights[6] ($42,000 \leq W \leq 132,000$), homopolymer weights[4] ($0.5 < \alpha < 3$), and homopolymer concentrations ($0.0 \leq \beta \leq 0.344$). Although the model was developed specifically for PS-*b*-PMMA copolymers, we believe that the same relationships—quantitatively but not qualitatively different—should apply to other copolymer chemistries as well. This work is obviously preliminary, covering a single molecular weight combination, but we believe it suggests a promising approach whereby a more general empirical formula can be developed for producing a desired pore spacing using a combination of available diblock copolymer and homopolymer components.

With these issues well understood, the fabrication of nanostructures such as electrically tunable quantum dot arrays is facilitated by polymer masks, formed from solutions of block copolymer and homopolymer. For off-the-shelf polymers of known, fixed molecular weight, an algebraic model allows the user to predict or adjust the size and spacing of vertical pores in the mask by adjusting the relative concentrations of copolymer and homopolymer, without the need to fabricate a custom polymer for each

application. This allows significant savings of both time and money in a research and development effort.

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