Spinodal Dewetting–A Simple Method to Prepare Conjugated Polymer Array

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ABSTRACT: A novel, simple method was developed to prepare conjugated polymer array in a large scale by using a spinodal dewetting technique. Mica, silicon, and glass were selected as substrates. The results show that with a suitable concentration of poly(9,9-dihexylfluorene) (PF) in volatile organic solvent the polymer forms different sizes of array on the substrates. Atomic force microscopy measured the three-dimensional structure of the arrays, and the relative FFT and PSD analyses reveal the detail information of the dewetting process and the array formation mechanism. The size of spots in the arrays is controlled by the evaporation speed of solvent and concentration of the PF solutions. The photoluminescence of PF arrays were also measured. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1412–1417, 2005

Key words: conjugated polymer; array; spinodal dewetting; atomic force microscopy (AFM); photoluminescence (PL)

INTRODUCTION

Conjugated polymer is a kind of polymer with conjugated π–π bonds through its main chain. For their conductive and photoluminescence properties they are attracting much more attention for potential application in light-emitting diodes, organic flat panel displays, etc.[1,2] However, in multicolored displays, integrated electronics, and smart photonic structures, nanopatterned polymer films are usually required.[3–5] The nanopattern structure may also increase the photoluminescence efficiency of conjugated polymer film.[6,7] Recently, it was also reported that conjugated polymer arrays have potential application in the principle of distributed feedback lasers.[8]

Several patterning techniques have been proposed for conjugated polymers recently, such as holographic lithography,[9] laser photoablation,[7] nanoimprint,[10] cold molding,[3] site-selective chemical vapor deposition on pattern precursors,[11] and near-field optical lithography.[12] However, it is still necessary to develop new methods to prepare large-scale conjugated polymer patterns at low cost.

Dewetting is a novel, simple method to prepare a polymer pattern, which has been widely studied.[13,14]

For an unstable film, it dewets if an initial film thickness is smaller than a critical thickness.[13] Generally, in the dewetting process holes initially form, followed by their growth and coalescence, and finally droplets are formed on the substrate. Two possible rupture mechanisms for the hole formation are nucleation, initiated by defects, and the spontaneous amplification of capillary waves; the latter is the called spinodal dewetting.[13,15] Karthaus et al. reported the formation of a patterned polymer array by simple spinodal dewetting,[16] and time-resolved optical microscopy reveals that the pattern can be caused by fluctuations in polymer concentration near the three-phase line (the contact line among the solid, liquid, and gas phases) of a polymer solution and produce "order through fluctuation."[17] At the second stage of deweeting the holes grow to a size and touch the neighboring holes, resulting in a network of polymer strings. Then the strings break up into an array of polymer droplets. The driving forces for this kind of self-assembly are dissipative structures that occur in the solution and especially at the three-phase line. During solvent evaporation temperature and concentration fluctuations occur, and the concentration of the polymer increases mostly in the vicinity of the three-phase line. Finally, an ordered array is formed by the fluctuation. By this method, many different polymers, such as polyion complexes, saccharide-containing vinyl polymers, DNA complexes, photoactive dendrimers, and polystyrene, formed regular patterns.[18]

Additionally, in the linearized capillary wave instability model,[19,20] when a dried polymer film was heated upon its glass temperature, the film can be
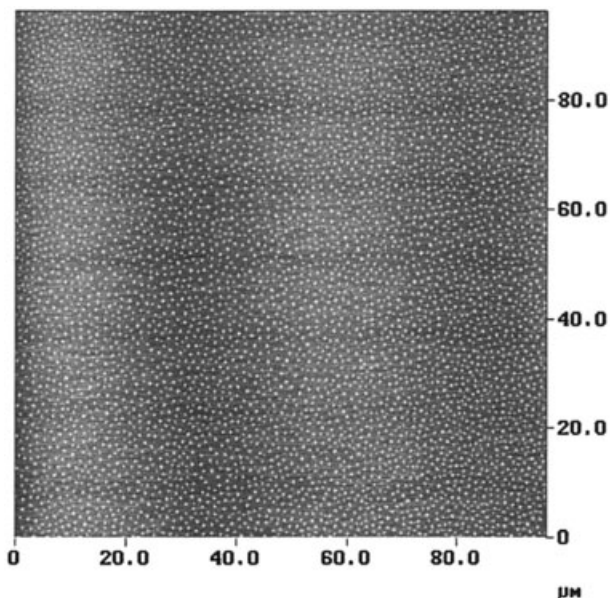
Figure 1 Typical AFM image of the PF array formed by nitrogen blew of 20 μL of PF solution (0.1 mg/mL) at sonic speed on the freshly cleaved mica at room temperature.

regarded as a liquid film and the thermally induced thickness fluctuations are exponentially amplified if the wave vector is less than the critical wave vector, which also called spinodal dewetting and can result in polymer pattern formation on the surface of the substrate.

Polyfluorene (PF) is a kind of potential polymer for high photoluminescence efficiency in the blue spectral region.[21] Recently, an ordered array in small scale of PF on mica was prepared[22]. In this paper, the large-scale arrays of poly(9,9-dihexylfluorene) (PF) were prepared by a simple spinodal dewetting method on mica, silicon, and glass, respectively. The topography of the samples was measured by AFM and their photoluminescence behavior was also reported.

EXPERIMENTAL

PF, M_n = 12,150 g/mol, M_w/M_n = 1.7, was synthesized according to the reported method.[23]

The solutions of PF were prepared by dissolving some PF in dichloromethane (CH_2Cl_2). The concentrations are 1.0, 0.1, and 0.05 mg/mL, respectively. Silicon and glass were cleaned before used. Three simple liquid film dewettiing methods, dried in air spontaneously, spun coated at high speed, and blew by high-purity nitrogen at sonic speed were employed. The first method is a slow process with a slower evaporation rate of the solvent, and the last one is very fast with a quick evaporatation rate of the solvent. Dewetting by spin-coating is also a quick process that depends on the spin speed. In addition, thermal in-

duced film spinodal dewetting by an annealing process was also applied to prepare the array of polymer. In the process, the PF film was initially heated at 140 °C for a period of time and then cooled down at room temperature under the protection of nitrogen. For all sample preparation, 20 μL of PF solution was initially transferred by a micropipette onto the surface of the substrates.

A NanoScope IIIa AFM (DI, CA) was used to image the topography of the samples. A silicon cantilever
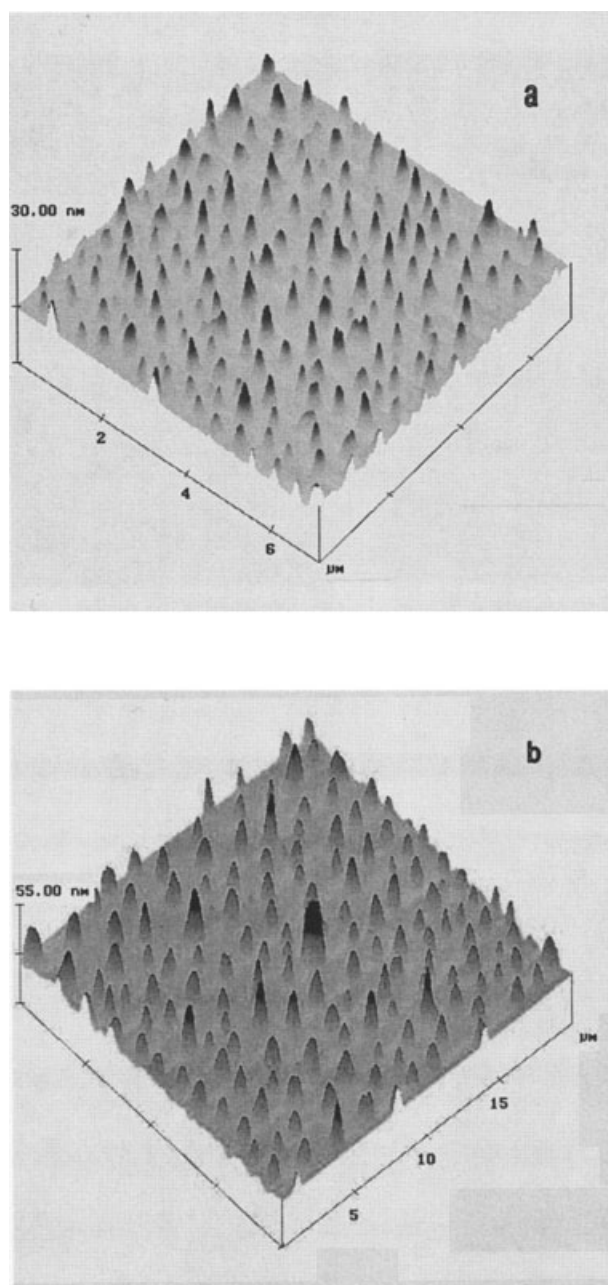

Figure 2 The 3-D AFM images of the PF arrays on the surface of silicon prepared by (a) spin coating 20 μL of PF solution (0.1 mg/mL) at 4200 rpm and (b) drying in air spontaneously.
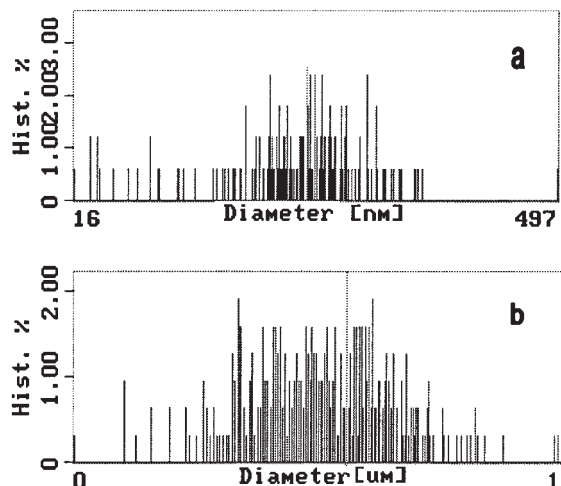
Figure 3 Histograms of the aggregate's diameter of the PF arrays in Figure 2. The mean diameter of the aggregates is 235.42 nm for (a) and 635.31 nm for (b), respectively.

Figure 4 The normalized PLs of the PF array on silicon, the unpatterned PF film, and the PF solution.

(FESP, DI) was used in tapping mode. The spring constant is 1–5N/m, the resonant frequency is 200–400 kHz, and the radium of the curvature is 5–10 nm. The scanning rate is 1.0 Hz, the operate setpoint is 0.95 V, and the drive amplitude is 300 mV. After measurement all images were analysed using AFM software and Photoshop 5.0.

The photoluminescence of the PF solution, unpatterned film, and PF arrays was measured by a spectrofluorophotometer (RF-5301 PC, Shimadzu, Japan).

RESULTS AND DISCUSSION

Freshly cleaved mica was selected as the substrate for its atomic level plane. Under blew of high pure nitrogen at sonic speed, the PF liquid thin film quickly dried in seconds. Figure 1 shows a typical AFM image of the formed structure of the film. There appears a homogenous PF array in an area as large as 100 μm^2, and the array is constituted of many conical or cylindrical aggregates with size in the nanometer scale.

Both the above image and early studies[22] show that a simple dewetting process forms PF arrays with spots in scale from nanometer to micrometer. However, mica is a nonconductive and opacity substrate; its potential application is limited. To prove that liquid thin film dewetting can be widely applied on different substrates for conjugated polymer arrays preparation, silicon and glass were selected as the other two substrates in this study.

Figure 2 shows the typical 3-D AFM images of the PF arrays formed on the surface of silicon by spin coated 20-μL PF solution (0.1 mg/mL) at 4200 rpm [Fig. 2(a)] or dried in air spontaneously [Fig. 2(b)]. Both images show an array structure similar to that in Figure 1. Figure 3 shows the histograms of particle
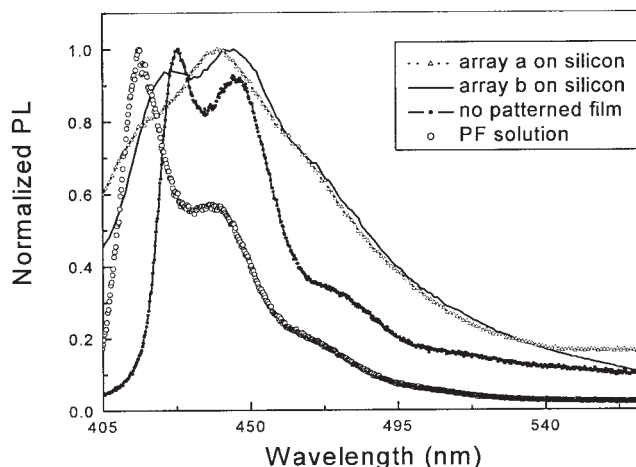
distribution, and the mean diameters of the aggregates in Figure 2(a,b) are 235.42 and 636.31 nm, respectively. The quick evaporation of the solvent results in a small array structure, which is consistent with the result of the arrays formed on the surface of mica.[22] Furthermore, the photoluminescence behaviors of the arrays on silicon were also measured (Fig. 4). Both the PL
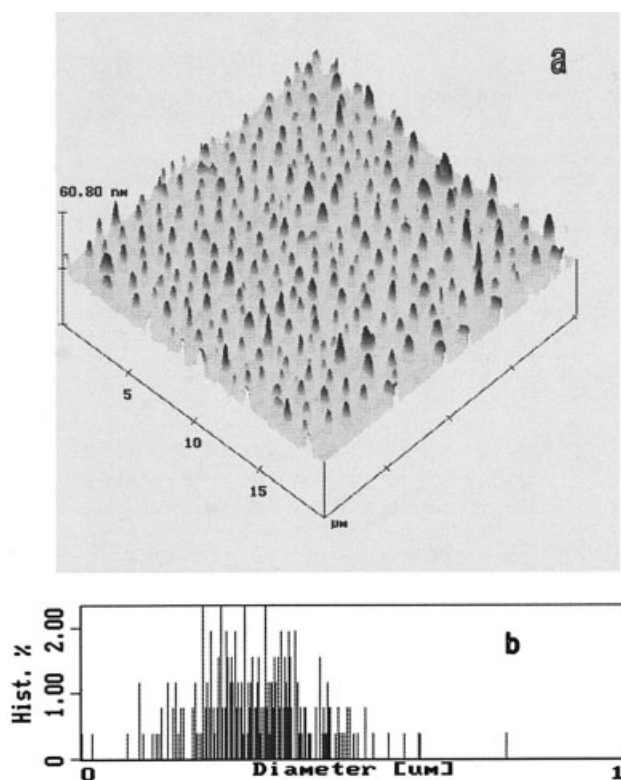

Figure 5 (a) The 3-D AFM image of the PF array formed on the surface of cleaned glass by dried spontaneously in air at room temperature. (b) The relative histogram of the particle's diameters.
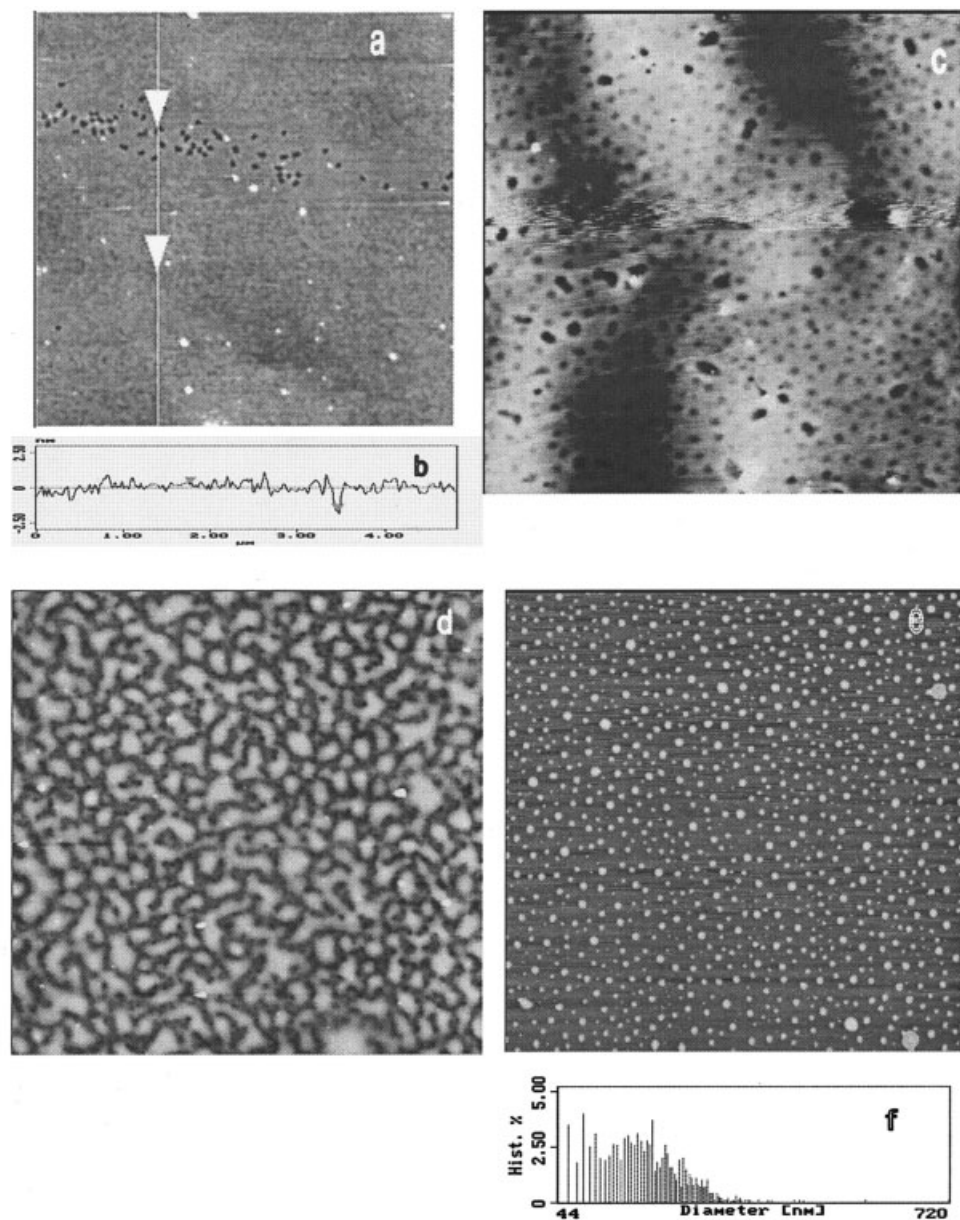
Figure 6 The AFM images of the topography structures of the PF films on silicon before and after annealing at 140 °C for different times. (a) Fresh film prepared by spin coated 20 μL of PF solution (1.0 mg/mL), 5.0 $\times$ 5.0 μm^2, (b) section line of (a), (c) annealing for 20 min, 20.0 $\times$ 20.0 μm^2, (d) annealing for 40 min, 20.0 $\times$ 20.0 μm^2, (e) annealing for 60 min, 20.0 $\times$ 20.0 μm^2, (f) the histogram of the particle's diameters of (e).

curves of the PF solution and the no-patterned film are plotted in Figure 4. The PL of the PF array prepared by spontaneous drying in air has a similar red-shift behavior to that of the arrays on mica,[22] indicating a decrease of the aggregative interaction among the PF molecules in the array compared to that of the no-patterned film. However, the PL of the array prepared by the spin coated method shows a smaller red-shift than that of array (b), indicating a much smaller β-phase aggregate formation than that in array (a).[24,25]

The array structure of PF can also be formed on the surface of glass by the spontaneously dried dewetting,

as shown in Figure 5. The spots have a narrow distribution with average diameter of 405.32 nm.

It can be said that with different substrates the spinodal dewetting of the liquid thin films is valid to prepare conjugated polymer arrays.

As mentioned above, when a dried polymer film was heated upon its glass temperature, the film can be regarded as a liquid film and may also result in array by a thermal spinodal dewetting. In this work, a homogeneous PF film was initially prepared by spin coated 20 μL 1.0 mg/mL PF solution onto the surface of glass, and then the film was annealed under nitro-

gen protection at 140 °C for 20, 40, and 60 min, respectively. The glass temperature of PF is 80 °C, so at 140 °C the film of PF can be regarded as a liquid thin film. The topographies of the films at different stages were measured by AFM. As shown in Figure 6, at the beginning there is a continuous film with only several little holes [Fig. 6(a)]. The thickness of the film is 29.6 nm, while the depth of the hole is 2.0 nm [Fig. 6(b)]. After 20 min annealing, more enlarged holes appear [Fig. 6(c)], and the depth of the hole is about 8 nm while the film is 30 nm in thickness. Forty minutes later, annealing develops the film into a bicontinuous structure and the holes enlarge further until neighboring holes coalesce [Fig. 6(d)]. At the end, subsequent annealing makes the bicontinuous structure break up into separated liquid droplets, which form spots in the form of an array after cooling down [Fig. 6(e)]. The distribution of the spots in the array is shown in Figure 6(f), and the average diameter of the spots is 186.95 nm.

In the theory of spinodal dewetting, the droplets come from a "fingering instability" at the rim of three-phase line during dewetting, and the fingering wavelength (λ_s) equals the maximum probability of the distance among the aggregates, which provides a characteristic parameter to describe the fluctuatives array. It is reported that the fingering wavelengths of the samples are also decided by the evaporation rate of the solvent[26]. The slower the solvent evaporates, the bigger the fingering wavelength is. The preferred wavelength λ_s can be obtained from $\lambda_s = 2\pi/q^*$, where q^* is the characteristic wave vector corresponding to the size of the most unstable surface undulations, which can be determined from the power spectral density (PSD) curve.[22] Figure 7 shows the PDS curves of AFM images in Figure 6. The freshly prepared film has a smooth curve, indicating the continuity of the film. After annealing, there appear peaks in the PDS
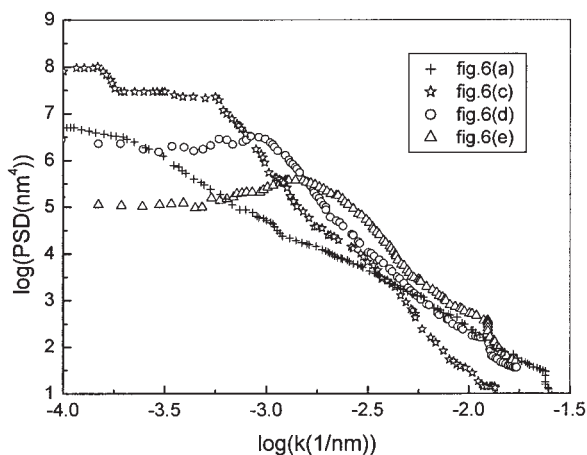

Figure 7   The power spectral density (PSD) curves of the AFM images in Figure 6 obtained from 2D FFT.
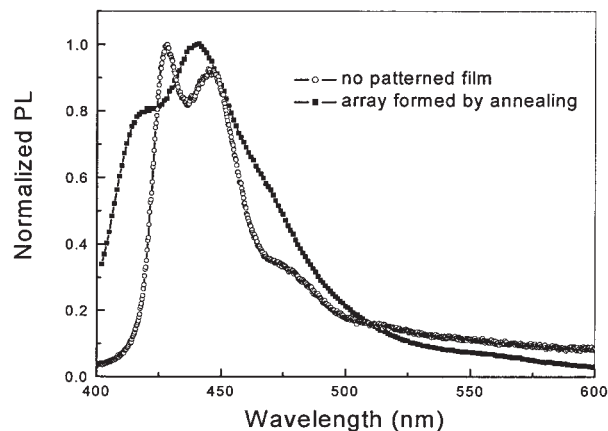

Figure 8   The normalized PLs of the PF arrays on glass prepared by the annealing method and the unpatterned PF film.

curves, revealing the beginning formation of a regular structure on the surface. The PDS curve of the formed array is similar to the arrays formed by a liquid thin film dewetting process.[22] For the bicontinuous structure [Fig. 6(d)] the $\lambda_s = 1.08$ μm and for the array structure [Fig. 6(e)] the $\lambda_s = 745.45$ nm.

Figure 8 shows the PLs of both the PF array formed by the thermal induced spinodal dewetting and the no-patterned film. The PL of the PF array also shows a similar red-shift behavior to that of the PF array prepared by liquid film dewetting at room temperature.

CONCLUSIONS

In conclusion, a very simple method was applied to prepare the conjugated polymer arrays by spinodal dewetting of a polymer liquid thin film or thermal-induced spinodal dewetting of a homogeneous PF film. By controlling the solvent evaporation speed, different array sizes were prepared. The PL of the PF arrays shows a smaller red-shift behavior than that of the no-patterned film, indicating less β-phase formation in the PF arrays. The size of the aggregates in the array is decided by the evaporation rate of the solvent. The PF arrays can also be formed on different substrates such as silicon and glass.

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