



Alignment and reordering of a block copolymer by solvent-enhanced thermal laser direct write



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ARTICLE INFO

Article history:

Received 7 January 2014

Received in revised form

6 February 2014

Accepted 7 February 2014

Available online 15 February 2014

Keywords:

Block copolymer

Laser heating

Zone annealing

ABSTRACT

Block copolymer (BCP) thin films have shown high potential as a pattern transfer medium for ultra-fine (<20 nm) features. We introduce an effective approach for performing rapid local annealing of BCP films by focused laser spike (FLaSk) zone annealing, using a moving highly-focused circularly polarized visible wavelength laser spot. A poly(styrene-*b*-dimethylsiloxane) BCP was transformed from a metastable spherical micelle morphology to the bulk equilibrium cylindrical morphology aligned along the write direction within a region controlled by manipulation of the laser focal plane, even for curved paths. This simultaneous microdomain reordering and alignment was accomplished on the *tens of millisecond* time scale by creating a very large driving thermal gradient (estimated as 100–750 K/μm or, temporally, 3000–75,000 K/s), enhanced by incorporation of solvent vapor (here toluene) swelling of the BCP film. The extent of the thermal effects suggests that the role of solvent may extend beyond increasing the mobility of the BCP film to enhancing both the thermal gradient and also potentially the surface energy gradients, providing a thermocapillary shear mechanism. Further, enhanced domain alignment is greatest at higher scan speed, indicating as well the importance of the *temporal* thermal gradient.

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1. Introduction

Well-ordered thin films of microphase-separating block copolymer (BCP) domains are commonly assembled through the use of thermal annealing processes which allows the kinetically trapped, as-cast polymer microdomain structure to attain the equilibrium morphology *via* diffusion by increasing temperature to overcome the energetic barrier for chain reptation [1]. Several techniques for controlling the orientation, morphology, and long range order of the BCP microdomains have been developed, in particular, substrate patterning to direct the self-assembly by chemical epitaxy [2,3] and graphoepitaxy [4–9]. As an alternative or supplement to

thermal annealing, solvent vapor annealing involves placing the BCP in a vapor environment where solvent molecules can diffuse into the film and plasticize the polymer, decreasing the glass transition temperature and improving the mobility of the BCPs for self-assembly at ambient temperatures [10]. Solvent annealing can produce non-equilibrium morphologies if the solvent is selective to one of the blocks, changing the effective volume fraction, as has recently been studied in detail for poly(styrene-*b*-dimethylsiloxane) (PS-PDMS) cylindrical BCP [11–13]. Techniques for the generation of BCP films containing regions of different microdomain types (*e.g.* coexisting regions of spheres and cylinders) have also been investigated. These methods involve trapping the BCP in a first morphology determined by one annealing process, then immobilizing the chains in regions of the film by crosslinking to fix one of the two microphases. Both e-beam [4,14] or ultraviolet [14] exposure can be used to fix the initial microdomain structure. Then a further annealing step with a different (or no) solvent can produce a second morphology in the un-crosslinked regions. The second solvent annealing step has been accomplished locally with a direct write solvent vapor nozzle without the need for crosslinking [15].

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Most recently, spatially controlled positioning, thickness and tuning within the microphase diagram was demonstrated by electrohydrodynamic jet printing of multiple compositions of a BCP, including graphoepitaxy and chemical epitaxy for enhanced ordering and alignment [16].

While these techniques enable feature control down to the length scale of a single microdomain (using e-beam cross-linking), most require the inclusion of crosslinkable block chemistry and possibly an additional crosslinking initiator and in the absence of templating, do not provide control over the in-plane microdomain orientation or registration that may be desirable for subsequent pattern transfer applications. In order to develop a more general technique that enables both localized morphology and orientational control with short annealing times, we investigated focused laser spike (FLaSk) zone annealing as a route to BCP patterning and sub-second annealing.

Laser spike annealing (LSA) has been utilized as an alternative to a standard thermal treatment in semiconductor technology [17–19] and also for the annealing of soft materials, such as chemically amplified photoresists [20,21] and for BCP microphase separation [22]. In this technique, a high intensity continuous or pulsed laser is rapidly scanned across an absorbing surface, such as a silicon wafer substrate supporting the device or polymer film. The local temperature at the laser spot spikes to a high value and then, once the laser light is removed, very rapidly drops back to ambient temperature. Because of this, both the temperature and annealing time of the thin film can be controlled by selection of laser intensity and exposure time. Additionally, annealing can be performed while avoiding unwanted effects, such as material degradation or diffusion. For BCP systems, the first demonstration of LSA was performed in 2007 and utilized a high power (on the order of a Watt), ms pulsed CO₂ laser exposure, which could initiate microphase separation for ~1 min total exposures, but did not demonstrate good domain ordering and often resulted in considerable polymer damage including burning and void formation, ostensibly due to intrinsic optical absorption and degradation of the polymer [22].

In considering LSA of a thin BCP film, there are obvious similarities to zone annealing, a technique previously utilized for both thin and thick films of BCP for achieving simultaneous annealing and alignment. In zone annealing, a BCP film is moved over an induced thermal gradient resulting in alignment along the direction of the motion over the heat source. One important distinction among various zone annealing techniques is whether they are ‘hot’ (above the order-disorder transition (ODT)) [23,24] or ‘cold’ (below ODT) [25–27] at their maximum temperature. In both cases, microdomain ordering and alignment happens primarily in the regions of the thermal gradient: for hot zone annealing, ordering occurs as the BCP passes back through its ODT, while in cold zone annealing it was shown that a majority of ordering occurs in the cold-to-hot portion of the gradient and was relatively independent of subsequent baking, indicating the importance of a gradient for driving the reordering and alignment of the domains [25]. A combined approach of cold zone annealing with thermal expansion-induced surface shear by a top PDMS film resulted in exceptionally high order and alignment for annealing rates of up to 200 $\mu\text{m/s}$ (traveling through a 0.045 K/ μm , 9 K/s gradient) and film thicknesses from a single layer of microdomains up to 1 μm [28]. Additionally, it was shown that without the presence of the top PDMS layer, thermal gradients of a similar magnitude could lead to vertical alignment with respect to the substrate [29], which was most recently used to accomplish roll-to-roll perpendicular alignment of BCP domains [30].

We introduced FLaSk annealing which utilizes continuous wave visible or near-IR light and a high numerical aperture objective (in this study, NA = 0.4) to accomplish LSA on a micron or sub-micron

scale, for the post-exposure bake of absorbing-dye-doped chemically amplified resists [31] and, more recently, for thermocapillary dewetting of polymer thin films [32]. Here, as in the latter study, we utilize a FLaSk technique similar to conventional LSA in that it takes advantage of the quasi-2D absorption of the substrate to generate heat (Fig. 1), but still allows for LSA on a region of polymer of limited size, creating an effective instantaneous confinement by the surrounding unheated immobile polymer. As with conventional LSA, the duration, effective size, and temperature of this confined annealing are controllable by the laser power, writing speed, and tightness of focus. Circularly polarized light is employed to avoid directionally-dependent polarization effects in the absorption.

In this study, we employed a 42 kg/mol PS-PDMS (31 kg/mol-11 kg/mol) BCP trapped in a metastable state consisting of spherical micelles after spin-coating and utilize the FLaSk anneal to transform to the equilibrium phase (*i.e.* cylindrical PDMS domains). From a zone anneal standpoint, PS-PDMS is strongly segregating (room temperature $\chi N \approx 95$, where χ is the interaction parameter and N is the degree of polymerization) and the ODT (~3000 °C) is not reached before significant polymer degradation. The ODT of PS-

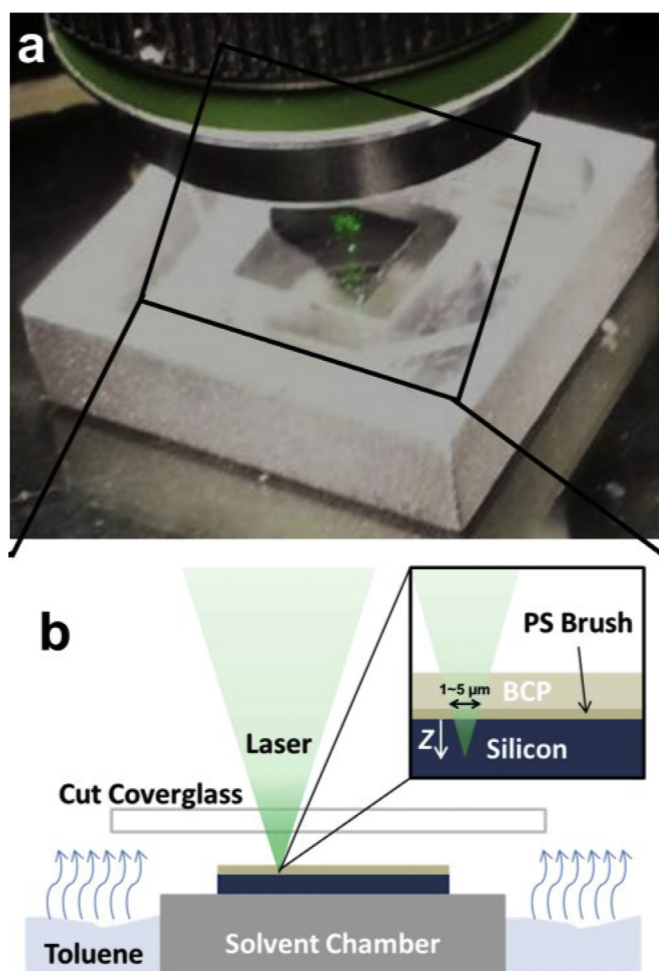


Fig. 1. Photograph (a) and schematic (b) of FLaSk zone annealing solvent setup. The solvent chamber (grey aluminum box in (a)) includes a platform surrounded by a solvent reservoir. The sample is placed on the platform underneath a cut cover glass. The surrounding solvent reservoir is filled with solvent (here, toluene) which slowly evaporates to generate a steady-state partial pressure of solvent under the cover glass. For the patterning, the BCP is spun on top of a PS brush on a silicon wafer, and the circularly polarized laser is focused through the glass with spot size controlled by axial translation away from surface “in-focus” position (Z).

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