The thermodynamic mismatch of different segments in a block copolymer drives microphase separation, while their covalent bonds limit the phase separated domains to the nanometer scale. As a result, densely arranged high resolution patterns, the goal of lithography, form a thermodynamically preferred equilibrium state for block copolymers. For production new annealing methods are being explored to speed up and improve structure formation. Solvent vapor annealing is a powerful technique to control the ordering process and the morphology of block copolymers by selectively or non-selectively swelling polymers. In recent years high $\chi$ block copolymers are attracting more and more attention due to their potential to form small patterns. However, the ordering process of high $\chi$ block copolymer is kinetically slow, thus using solvent vapor or increased temperature to enhance the polymer chain mobility is a key to increase ordering rate. In this paper, we review recent work on using solvent annealing to control the morphology and report high speed laser annealing of high $\chi$ for lithographic applications.

Keywords: DSA, high $\chi$, block copolymers, laser annealing

1. Introduction

Moore’s law has been the driving force for the semiconductor industry for 50 years. The requirement for lithography, shrinking the critical dimension of patterns, becomes more challenging than ever especially beyond the 22 nm node. The resolution, line edge roughness and sensitivity tradeoff for chemically amplified resist still awaits a major breakthrough. EUV lithography, although it has made great progress in delivering high power source, is still too costly for many non-logic applications. Instead densely arranged high resolution patterns are a thermodynamically preferred equilibrium state for block copolymers.

Directed self-assembly (DSA) is a relatively low cost method since the alignment and the ordering process of block copolymers does not require expensive optics or masks like photolithography. Although the defectivity of DSA is currently higher compared to conventional photolithography, the capabilities and the low cost of DSA make it a practical alternative method for some applications in lithography.

Block copolymers have been investigated for photolithographic materials since the late 1980s. Si containing block copolymer were utilized due to their higher etch resistance [1]. The bottom-up approach of utilizing the self-assembled microstructure of block copolymers directly as an etching mask for lithography purposes was introduced less than 20 years ago [2,3]. Many methods later invented to direct the self-assemble of block copolymers, such as chemically predefined patterns by Nealey et al. [4], greatly improve the alignment of the patterns. In recent years, the collaboration between the semiconductor industry and universities has transferred the DSA idea from lab to fab [5,6].

2. Solvent vapor annealing

Solvent vapor annealing is a powerful technique to accelerate the ordering process of block copolymers through increasing chain mobility. If a solvent only selectively swells one block, the solvent vapor annealing process will change the volume ratio between blocks thus altering the anticipated morphology. Different solvent interaction parameters with each polymer block could tunably generate different morphologies. Studies of PaMS-b-PHOST showed that the order-order transition occurs when solvent vapor annealing using THF and
acetone in sequence. When a non-selective solvent (THF) was used, a cylindrical morphology suggested by its dry-state volume fraction was achieved, while when a PHOST-selective solvent acetone was used, block polymers can be altered to a spherical morphology assumed in the highly swollen state [7]. Utilizing a closed chamber with constant N₂ flow and in situ thickness monitoring by filmmetrics can achieve precise control of the swelling ratio and the ordering process [8]. These two morphologies of PnMS-b-PHOST were found to be reversible during in situ GISAXS measurements and were maintained by fast quenching.

Later Chavis et al. further showed that careful control of solvent vapor annealing conditions could in a single block copolymer selectively form lamellar, spherical, cylindrical or gyroid morphologies using specific solvent mixtures. This work is meaningful since very often synthesis of a block copolymer with a precisely selected composition for a specific polymer is challenging especially for a bicontinuous gyroid phase, which only occurs within a narrow range of compositions. The order-order transition of poly(2-hydroxyethyl methacrylate)-block-poly(methyl methacrylate), (PHEMA-b-PMMA) during controlled-flow solvent vapor annealing was studied. Methanol which selectively swells the PHEMA block and THF which selectively swells the PMMA block were mixed in various ratios. Annealing in an 80/20 (v/v) mixture of THF/MeOH vapor leads to a lamellar morphology, while a 20/80 (v/v) mixture of THF/MeOH leads to a cylindrical morphology. In addition, short annealing times in 50/50 (v/v) mixture of THF/MeOH yields a gyroid morphology which forms a spherical morphology after prolonged annealing.

Poly(α-methylstyrene)-block-poly(4-hydroxystyrene) (PaMS-b-PHOST) has unique properties for lithographic purposes since it not only self-assembles but also can form DUV patterns in the presence of cross-linker and photoacid generator [10]. These crosslinkable properties of PHOST can be used to vary morphology during annealing. Conventional photolithography utilized crosslinking to prevent exposed film from dissolving in solvents. Similarly, the initial morphology of annealed PaMS-b-PHOST is locked after crosslinking upon DUV or e-beam exposure since solvent can no longer swell the PHOST block. Writing 75 nm wide lines with 1:4 spacing using e-beam lithography can partially lock the film resulting in the coexistence of two types of morphologies after a second solvent vapor annealing step.

3. High χ block copolymers

The Flory Huggins polymer-polymer interaction parameter χ is defined by the mixing enthalpy of two blocks, thus high χ block copolymers are thermodynamically preferred to phase separate. The product of χ and the degree of polymerization N has to be larger than 105 for a disorder-order transition to be observed. Therefore, a high χ block copolymer requires fewer repeating units for phase separation to take place, resulting in morphologies over a smaller length scale. Previously mentioned PHEMA-b-PMMA and PaMS-b-PHOST as well as Si containing block copolymers such as PS-b-PDMS are some examples of high χ block copolymer.

High χ block copolymer is a trend for DSA as the CD requirements within a few years will be sub-10 nm. Although solvent annealing is very versatile in terms of controlling morphology and accelerating the ordering process, it could be less desirable for a manufacturing process compared to thermal annealing since introducing solvent vapor might incur environmental concerns and process delay. However, thermal annealing temperatures should not normally exceed the ceiling temperature of a polymer, hence conventional thermal annealing time has an effective rate limit as well.

4. Laser Spike annealing

Many ultrafast annealing techniques such as rapid thermal annealing, microwave annealing or laser annealing have proven to reduce the processing time for high χ block copolymers. Laser spike annealing is an ultra-fast heating method in which a substrate is heated to high temperatures for time periods ranging from a sub-millisecond to several milliseconds. First used in shallow junction annealing [11], it has also recently been applied to organic systems [12-14]. Under laser induced heating, the degradation temperature of photopolymers may be extended.
by 200°C to 600°C, and the reaction time required for acid catalyzed deprotection of photopolymers decreases from minutes to milliseconds. These properties of ultrafast high temperature annealing are particularly useful for block copolymers with high glass transition temperatures and low ceiling temperatures.

In this study, we report using laser annealing for directed self-assembly of PS-b-PDMS. A continuous wave (CW) laser at 980 nm was used to heat the Si wafer via bandgap absorption. Laser temperature was calibrated using a thin film platinum thermistor with Si and gold melting temperature as references (Figure 1).

PS-b-PDMS (M_n,PS = 16 kg mol^{-1}, M_n,PDMS = 6 kg mol^{-1}; PDI = 1.1) with 23% of vinyl methyl siloxane was used in this study. PS-b-PDMS was dissolved in toluene and spin coated onto a hydroxyl-terminated polystyrene treated Si wafer. CF₄ plasma etching followed by O₂ plasma etching was used to reveal microstructure for SEM imaging. As shown in Figure 2a, non-equilibrium state was trapped in the as cast film. Toluene vapor annealing for 5 hours was able to achieve the finger prints structure of this cylindrical forming block copolymer at the swelling ration of 1.2 (Figure 2b). Laser exposure was used to anneal across large areas of block copolymer film by overlapping the scans. Microphase separation was achieved during 3 ms second laser annealing with 50W power (Figure 2c). This method greatly reduced the required annealing of hours using solvent vapor annealing to millisecond regime by laser annealing.

Figure 1. Laser temperature calibration

Figure 2. PS-b-PDMS thin film morphology a) as spun b) toluene vapor annealed for 5 hours c) laser annealed for 3ms

Figure 3. SEM images of PS-b-PDMS on PS brush modified substrate. The substrate is pre-patterned with periodic lines. The width of trenches and mesa are 275nm and 100nm respectively. The annealing conditions for a) hotplate 230 °C 5min, and b) laser 440 °C (45 W) 20 ms.
With proper guiding structures, annealing laser annealing can produce aligned microstructures that form in the millisecond timescale. In experiments with shallow trenches as guiding structures, standard hotplate annealing led to pinned microstructures that could be revealed in etched BCP films. In contrast, very fast laser spike annealed BCP films showed far fewer defects and had good long range order. With advances such as these, rapid processing of complex BCP morphologies are becoming possible.

5. Conclusions
In this paper we review the work of solvent annealing and report laser annealing of high $\chi$ block copolymers for lithographic applications. A single block copolymer can switch between different morphologies by carefully selecting the ratio and the types of solvents with a precise control of flow rate and swelling ratio. Two types of morphology can coexist in the same block copolymer film by crosslinking one block followed by another solvent annealing step. Laser annealing for a 3 millisecond dwell time achieved microphase separation of PS-b-PDMS which could requires hours of solvent or more conventional hot-plate annealing.

Reference