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Inorganic block copolymer lithography

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ABSTRACT

Block copolymer lithography, a process where block copolymer self-assembly is integrated with conventional lithographic patterning, is emerging as a promising technology for addressing the future needs of the semiconductor industry. The ability of block copolymers to self-assemble into ordered nanodomains allows for simple, low cost nanopatterning into underlying substrates. Since its initial conception, block copolymer lithography has been demonstrated using a variety of block copolymers, with research primarily focusing on all-organic diblock copolymers. The most notable example is polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) where long-range ordering of nanodomains has allowed applications on a commercial scale. However, scaling down of the feature sizes produced from the self-assembly of organic block copolymers is often limited due to the relatively low Flory-Huggins interaction parameter, χ. In addition, etch selectivity between the blocks, and their etch resistance for subsequent pattern transfers steps, is generally low. This review article provides an overview of how the introduction of segments containing inorganic elements into block copolymers can help to address these issues and can also allow the direct deposition of functional materials such as metal nanoparticles. This has led to potential interest for the next generation of block copolymer lithography applications.

1. Introduction

A constant commercial drive for smaller, faster and more energy efficient electronic devices has demanded increased component density in integrated circuits, and hence smaller component sizes. The use of lithography in the semiconductor industry has been paramount to the successful development of integrated circuit technology, and the continual realization of Moore's law [1]. State-of-the-art techniques, such as immersion lithography [2] and double patterning [3], when combined with a 193 nm UV light source, have been used by leading chip manufacturers for the latest 22 nm-node technology. It is expected that these techniques will be used for the fabrication of future 14 nm-node technology. However, due to the inherent limit of the wavelength of UV light sources, combined with prohibitively high costs of implementing new technologies, photolithography might be abandoned in the future, for a surrogate lithographic process capable of producing sub-10 nm features [4–7].

Alternative processes to photolithography include electron-beam lithography [8], ion-beam lithography [9], X-ray lithography [10] and nanoimprint lithography [11]; all are top-down processes that rely on pattern transfer through masks or via molded stamps. Bottom-up processes have also garnered the attention of the semiconductor industry, as viable alternatives for the fabrication of nanoscale features.

Block copolymers (BCPs) are macromolecular materials comprised of two or more chemically different polymeric segments. As a result of their segmented structures BCPs have a propensity to phase-separate and order themselves into a range of complex morphologies on the nanoscale. In the simplest case of an AB diblock copolymer, the driving force for phase-separation is due to the free energy cost of contact between blocks A and B, as described by the Flory-Huggins interaction parameter, χ_{AB}. Several experimental methods have been used to determine χ between distinct polymers, including small angle neutron scattering (SANS) [12–16], ellipsometry [17], light scattering [18–20], melting point depression and comparison of solubility parameters [21]. It has been shown both theoretically and experimentally that χ_{AB} has an inverse relationship with temperature, and thus lowering the temperature of a BCP melt favors the reduction of A–B contacts leading to phase-separation. The degree of polymerization, *N*, of each block, also plays a significant role in determining whether a block copolymer will phase-separate into an ordered system, or remain disordered. At large *N*, it is thermodynamically preferable to minimize A–B contacts and phase-separate the blocks into separate domains, even at the cost of the associated loss in translational and configurational entropy.

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Thus, it is the magnitude of χN that determines whether the block copolymer exists in an ordered (phase-separated) or disordered state. Above the order-disorder transition (ODT), where χN exceeds a critical value, denoted χN_{ODT}, the BCP phase-separates. The relative volume fractions (φ) of A and B determine the self-assembled morphology of the diblock copolymer, whereas the size of the domains is governed by the degree of polymerization of each block [22,23].

It is the ability of block copolymers to self-assemble into a range of morphologies that makes them suitable candidates for bottom-up lithographic processes. The infrastructure currently used in integrated circuit design is applicable for block copolymer lithography, with block copolymer films sharing many similarities with photoresist materials used in photolithography. The processability of BCPs in a variety of solvents allows polymer films to be spin-coated onto virtually any substrate, analogous to photoresist materials. The self-assembly of BCPs into ordered structures on the nanometer-scale allows for transferral of these features into an underlying substrate, via a plasma etch step. In this respect, they act as sacrificial templates, like conventional photoresist materials, but providing the template design in a bottom-up manner, saving the requirement of expensive optical set ups and complicated template designs.

Pattern transfer in block copolymer lithography relies on good etch selectivity between the coblocks. A reactive ion etch (RIE) step is commonly used to achieve pattern transfer into a substrate whereby the individual polymer segments degrade at different rates in the presence of different feed gas plasmas [24]. For example, when a thin film of polystyrene-*block*-polybutadiene (PS-*b*-PB) block copolymer is exposed to an ozone plasma, the unsaturated bonds along the PB backbone are cleaved, whilst the PS is cross-linked. Development of an ozone-exposed film leaves the cross-linked PS domains, which can be employed as a sacrificial mask for subsequent pattern transfer with a RIE step [25]. Similarly, exposure of a polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) film to UV light degrades PMMA whilst simultaneously cross-linking PS, allowing for the subsequent pattern transfer of the remaining cross-linked PS [26,27].

In a block copolymer system where $\chi N >> 10$, known as the strong segregation limit, the width of the interfaces separating block A from B can be described by $\alpha\chi^{-1/2}$ where α is the characteristic segment length of a monomer unit. Thus, block copolymers with a higher χ will exhibit sharper interfaces between each block, allowing for the creation of features with a smaller edge roughness if used in a lithographic process. Additionally, the period of the phase-separated microdomains can be described as $D \sim \alpha N^{2/3}\chi^{1/6}$. This implies that reducing N, whilst maintaining an appropriate χN over the critical value for phase-separation, would lead to smaller features with a smaller period [23].

Since the early work by Register, Chaikin et al. [28] demonstrating the use of polystyrene-*block*-polyisoprene (PS-*b*-PI) films to create an array of 10^{11} holes/cm^2 in Si_3N_4 [29], substantial advances have been made in the field of block copolymer lithography. This has enabled the fabrication of air-gap interconnects [30], capacitors [31,32], field effect transistors [33], flash memory devices [34,35] and ultra-high density magnetic-dot arrays [36]. Improving the long-range ordering of the phase-separated block copolymer domains, as well as the manipulation of their morphology, has been an important development in the field [37]. Nealey et al. demonstrated the fabrication of highly-ordered, nanometer-scale jogs, junctions and isolated lines, all essential for integrated circuit technology, from ternary blends of PS, PMMA and PS-*b*-PMMA on chemically patterned substrates [38]. Highly-ordered, square-packed arrays of holes in a silicon oxide substrate have been prepared via block copolymer lithography using a blend of poly(ethylene oxide)-*block*-poly(styrene-*r*-4-hydroxystyrene) and poly(methyl methacrylate)-*block*-poly(styrene-*r*-4-vinyl pyridine) [39]. Russell and co-workers utilized a sawtooth patterned substrate to produce a single grain of hexagonally arranged cylinders from thin films of polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO), with exceptionally high orientational and translational order, over an area of ~4 cm^2 [40]. We direct the reader to a list of reviews describing many of the latest accomplishments in the field [34,41–45].

Whilst organic systems, such as PS-*b*-PMMA, PS-*b*-PI and PS-*b*-PB have been shown to be potential candidates for lithographic patterning, their relatively low χ-values limit both the scaling of domains to relatively large features, and also the definition of the domains created. Whilst organic block copolymer systems with high χ-values do exist, such as amphiphilic polystyrene-*block*-poly(4-vinylpyridine) [46,47] and PS-*b*-PEO [48], the low etch selectivity between the organic blocks hinders their potential. The incorporation of inorganic segments into block copolymers is an attractive prospect, as it addresses both of these issues. Inorganic–organic BCPs tend to have higher χ-values and greater etch selectivity between the blocks, due to the formation of robust oxide surface layers within the inorganic polymer domains when exposed to an oxygen plasma. The introduction of inorganic blocks also offers the potential for materials with useful physical or chemical properties to be directly fabricated from the BCP film, giving functional, as opposed to sacrificial, resist materials, thereby reducing the number of required steps for device fabrication. This review will focus on the introduction of inorganic segments into block copolymers for lithographic applications.

2. Silicon-containing block copolymers

2.1. Poly(dimethylsiloxane)-containing block copolymers

The introduction of silicon into a segment of a BCP has several advantages in the field of block copolymer lithography. Firstly, exposure of a silicon-containing polymer to an oxygen plasma leads to the formation of SiO_x species at the polymer/plasma interface, which gives far greater etch resistance than a solely organic polymer. Poly(dimethylsiloxane) (PDMS), a polymer comprised of a Si–O backbone, has been combined with various organic blocks as a means of patterning substrate layers. As noted previously, BCPs with a larger χ can phase-separate at lower N, giving smaller domains with a smaller period. Sharper interfaces between the phase-separated blocks are also obtained, resulting in a lower edge roughness of the patterned features. For PS-*b*-PMMA, $\chi = 0.04$–0.06 [49], whilst for PS-*b*-PDMS, $\chi = 0.26$ [50]. Thus, for a PS-*b*-PDMS diblock copolymer, phase-separation can be achieved with a lower degree of polymerization, allowing for the potential fabrication of smaller, more well-defined features with a smaller period. This behavior can also be described in terms of the difference in solubility parameters between each homopolymer, which is correlated to the value of χ [51].

Work by Chen, Fu et al has focused on self-assembled thin films of PS-*b*-PDMS for potential use as nanolithographic templates. Solutions of PS-*b*-PDMS were spin-coated onto silicon wafers, and solvent annealed in either THF or acetone to give a monolayer of spheres of PDMS in a matrix of PS, where a PS layer is formed at both the air/polymer and polymer/substrate interfaces. Subsequent exposure to UV irradiation combined with ozonation (UV/O_3) removed the PS matrix and gave a hexagonally-packed monolayer of PDMS spheres [52]. It was also demonstrated that addition of PS homopolymer to the sphere-forming PS-*b*-PDMS before solvent annealing allowed for greater long-range ordering to be achieved in a shorter annealing time [52,53].