Integration of Directed Self-Assembly with 193 nm Lithography

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Directed self-assembly (DSA), which combines self-assembled polymers with lithographically defined substrates, has been considered as a potential candidate to extend optical lithography. In order to assess the capabilities and limitations of DSA as a viable patterning technology for the fabrication of semiconductor devices, we seek to integrate DSA with state-of-the-art optical lithography in a straightforward and process-friendly manner. In this paper, we discuss several integration strategies which allow 193 nm immersion lithography to produce suitable topographical and chemical guiding patterns for DSA. The ability to use optical lithography and commercially available patterning materials to fabricate effective guiding patterns will enable DSA to be applied to 300 mm wafers with state-of-the-art fab tooling and will open the door to meaningful wafer-scale characterization of DSA performance.

Keyword: directed self-assembly, DSA, block copolymers, graphoepitaxy, chemical epitaxy, 193 nm lithography, immersion lithography

1. Introduction

Improvements in optical lithography have been the driving force behind scaling for over four decades; however, 193 nm water immersion lithography has already reached its physical resolution limit [1]. Several double patterning schemes [2] have been developed to further extend the patterning capabilities of 193 nm immersion lithography to the 22 nm node (and possibly beyond) while extreme ultraviolet (EUV) lithography is being readied for high volume manufacturing. Of the various double patterning techniques, self-aligned double patterning (SADP), a spacer based sidewall image transfer process, has gained traction in memory fabrication [3]. In SADP, a conformal coating of an inorganic material is deposited on top of a photoresist pattern and transformed into a series of spacers (one corresponding to each sidewall of the original photoresist line) thereby effectively doubling the pattern. Advantageously, SADP requires only one critical lithography step (although subsequent trim steps are necessary) and the critical dimension of the resulting features is determined by the deposition step rather than the lithographic resolution of the exposure tool. Smith et al. have presented an overview of various triple or quadruple patterning options for the extension of optical lithography beyond double patterning [4]; however, these higher order pitch division schemes would be extremely process intensive and demand even more stringent process control.

Compared to other higher order pitch division schemes, directed self-assembly (DSA), which combines self-assembling (SA) materials such as block copolymers with lithographically-defined directing prepatterns on a substrate, is a potentially attractive alternative since it retains a level of process complexity similar to or less than that of SADP but enables much higher levels of pitch division [5]. The lithographically-defined directing prepatterns may consist of topographical features...
Fig. 1. DSA via graphoepitaxy using a topographical hardmask prepattern.

(referred to as graphoepitaxy, see Figure 1) or chemical patterns (referred to as chemical epitaxy, see Figure 2).

Demonstrations of the DSA of block copolymers on directing patterns formed with electron-beam direct-write, EUV, and optical lithography have been reported [6-9]. In particular, DSA on chemical patterns fabricated using e-beam lithography is being explored for the creation of nanoimprint templates for the fabrication of bit-patterned magnetic storage media [6].

In order for DSA to emerge as a viable lithographic technology for the high volume manufacturing of semiconductor devices, integration of DSA with state-of-the-art 193 nm immersion lithography in a straightforward and process-friendly manner is required. Unfortunately, the organic casting solvents used to apply block copolymers and the high temperature annealing processes (required for rapid cycle times) destroy the fidelity of directing structures comprised of 193 nm positive tone photoresists. As a result, photoresist structures are typically only employed as sacrificial intermediates which are converted into more robust topographical or chemical prepatterns by pattern transfer into an underlying material such as a hardmask layer. These additional steps significantly increase the overall process complexity, cost of ownership, and difficulties in wafer rework.

Although cross-linked negative tone photoresists have been directly used as chemical [7] and topographical [8] guiding patterns for the DSA of block copolymers, few high resolution negative tone 193 nm immersion-compatible photoresists have been reported [10]. In order to facilitate the implementation of DSA in commercial lithography, we have developed a number of practical schemes to fabricate topographical and chemical patterns for DSA directly from commercially available positive tone 193 nm photoresist materials and imaging stacks. These schemes can be performed entirely on the wafer track with short cycle times and no intermediate dry etch processes.

2. Experimental

2.1. Materials

Poly(styrene-b-methyl methacrylate) (PS-b-PMMA) diblock copolymers were purchased from Polymer Source, Inc.

2.2. Poly(styrene-co-epoxydicyclopentadiene methacrylate)

Poly(styrene-co-epoxydicyclopentadiene methacrylate) (70:30) random copolymer was prepared by free-radical polymerization and formulated as described elsewhere [11]. M_n = 7400 g/mol. PDI: 1.40.

2.3. Contrast curves using various developers.

A 150 nm thick layer of a commercial 193 nm positive-tone photoresist was formed on an anti-reflection layer (780 Å of ARC-29A, Brewer Science) on a silicon wafer. A 5 x 25 dose array of open field exposures was imaged on the material using 193 nm dry lithography (ISI ministepper, 0.6 numerical aperture (NA)). A post-exposure bake (PEB) was performed at 125° C for 60 sec and the thickness measured in each field using a Nanometrics Nanospec 6100. The photoresist pattern was developed for 30 seconds in anisole, 0.26N tetramethylammonium hydroxide (TMAH) (OPTIYIELD® CD, FujiFILM), or propylene glycol monomethyl ether acetate (PGMEA). After development, the wafer was spin dried and the remaining photoresist thickness was measured.

2.4. Graphoepitaxy using negative tone development of a 193 nm photoresist

A poly(styrene-r-epoxydicyclopentadiene methacrylate) neutral underlayer was spun cast on a substrate and cross-linked at 200 °C for 2 minutes. A 193 nm positive tone photoresist was applied, exposed, baked (30 sec), and developed in...
the negative tone using anisole for 60 sec to form a trench pattern. A PS-b-PMMA diblock copolymer was spun cast on the photosist pattern from anisole and baked at 200 °C for 5 minutes. The PMMA minority phase was selectively removed by an oxygen reactive ion etch (RIE).

2.5. Graphoepitaxy using a polarity switched positive tone 193 nm photosist pattern

Arrays of holes were made in a layer of 193 nm photosist on ARC29A with e-beam lithography (used for convenience). After positive tone development with TMAH, the remaining photosist pattern was flood exposed using a Hg/Xe deep ultraviolet arc lamp (Ushio America) and baked to form a DSA compatible photosist pattern. PS-b-PMMA was then spin coated onto the photosist pattern from anisole and baked at 200 °C for 2 minutes to form self-assembled domains within the guiding pattern. The PMMA domains were selectively removed by oxygen RIE.

2.6. Chemical epitaxy using sparse chemical patterns formed by 193 nm interferometric immersion lithography

A line-space pattern (30 nm line width, 90 nm pitch) was generated using 193 nm water immersion interference lithography by overexposing a positive tone 193 nm photosist on ARC29A. After positive tone development with TMAH, the photosist lines were flood exposed with a DUV lamp followed by a post exposure bake. A thin conformal layer of a proprietary neutralization material was applied and grafted onto the patterned wafer. The photosist was then removed by lift-off using an organic solvent to generate a sparse chemical pattern. A layer of PS-b-PMMA was applied onto the chemical pattern and thermally annealed. The PMMA domains were selectively removed by oxygen RIE.

2.7. Chemical epitaxy using sparse chemical patterns formed by 193 nm immersion lithography

Line-space patterns (30 nm line width, 100 nm pitch) were generated in a positive tone photosist on 300 mm wafers using 193 nm water immersion lithography (ASML 1700i, 1.35NA). The photosist lines were hardened by a DUV flood exposure and a post exposure bake. A thin conformal layer of a proprietary neutralization material was applied and grafted on to the patterned wafer. Lift-off of the photosist using standard 0.26N TMAH developer generated a sparse chemical pattern upon which PS-b-PMMA was applied and baked for 2 minutes. The PMMA domains were selectively removed by oxygen RIE.

3. Results and Discussion

3.1. Difficulties associated with using a positive tone imaging process in DSA

It is critical to precisely control the surface chemistries of all the materials in contact with the SA materials in DSA schemes which involve higher order pitch division. For example, vertically oriented lamellae which span the entire film thickness are preferred in order to facilitate subsequent pattern transfer. A number of underlayer materials including self-assembled monolayers, polymer brushes, and crosslinked polymers have been specifically designed to impart surface neutrality and thereby enable the perpendicular orientation of the SA domains [11-12]. Unfortunately, in a typical positive tone imaging process these carefully designed materials are subjected to deep UV radiation, superacids at elevated temperature, reactive chemical intermediates, and strongly alkaline conditions during photosist development. In addition, since 193 nm positive tone resists are generally soluble in typical organic casting solvents used to apply block copolymers for DSA, the patterned positive tone structures must be “hardened” in order to survive the DSA process. A number of photosist hardening processes based on 172 nm radiation, chemical freeze materials, or surface curing agents have been developed to render photosist patterns stable to subsequent coating processes used in double patterning schemes [13-16]. The conditions experienced by the underlayer during the patterning and/or the subsequent hardening process typically destroy the surface properties of the underlayer which leads to uncontrolled DSA morphologies that are not useful for lithographic applications. In addition, positive tone photosist patterns typically reflow at temperatures well below those used in the high-temperature annealing processes (> 200 °C) [17] required for rapid DSA pattern formation. To overcome such issues, many literature reports create directing structures comprised of crosslinked negative tone photosists and rely on the photosist material in the unexposed regions to protect the underlayer surface properties during patterning [7,8a,8c].
3.2. Advantages of negative tone development in the creation of DSA prepatterns

Given the benefits of a negative tone process with respect to maintaining the neutrality of the underlayer surface and the lack of a commercial 193 nm immersion-compatible negative tone photoresist, we instead explored the negative tone development of commercially available positive tone resists. Negative tone development has a long history in the semiconductor industry with the very first commercial application of chemically amplified photoresists being the manufacture of 1 Mb DRAM devices via the negative tone development of poly(4-t-butoxycarbonyloxystyrene) photoresist with anisole [18]. Tarutani et al. have more recently explored the negative tone development of 193 nm positive tone photoresists to create high resolution patterns for double patterning applications [19].

The basics of negative tone development are shown in Figure 3. A solubility switch is induced in the exposed regions of a positive tone chemically amplified 193 nm photoresist (typically the result of catalytic acidolysis of pendant tertiary ester groups in the photoresist resin by a photogenerated acid) which renders it soluble in alkaline developer [20]. Above the dose to clear ($E_0$), a sufficient quantity of carboxylic acid groups have been generated to render the photoresist material soluble in TMAH developer (Figure 3, squares); however, if an organic developing solvent such as anisole is used instead, the non- and underexposed photoresists dissolve and the more polar deprotected photoresist material formed at exposure doses near and above $E_0$ remains insoluble (Figure 3, circles). Since the non- and underexposed material is removed instead of the exposed material by the organic solvent, such a development process is referred to as negative tone development. Fortunately, the remaining photoresist material is not crosslinked after negative tone development and can be easily removed for rework by stripping with either TMAH or more polar organic solvents such as PGMEA (Figure 3, triangles).

With respect to DSA, directing structures comprised of deprotected photoresist have several advantages. First, the deprotected photoresist material is insoluble in select organic casting solvents suitable for applying common block copolymers for DSA. Additionally, the higher thermal stability of structures comprised of deprotected photoresist allows them to withstand the high temperatures of DSA annealing processes. Finally, the carboxylic acid rich photoresist material has strong preferential affinity for the more polar block(s) of a block copolymer (e.g., the poly(methyl methacrylate) block of a PS-b-PMMa diblock copolymer) and can help orient the block copolymer domains parallel to the photoresist structures.

In order to fabricate topographical guiding structures for DSA comprised of deprotected photoresist material, two straightforward schemes can be employed: (a) negative tone development or (b) positive tone development followed by subsequent polarity switching of the photoresist material.

3.3 Graphoepitaxy using photoresist features created via negative tone development

As shown in Figure 4, a negative tone development process can produce topographical photoresist patterns suitable for graphoepitaxy without damaging the surface properties of the underlayer. A 193 nm positive tone photoresist was applied on top of a neutral underlayer, exposed, and developed in the negative tone using anisole to form a trench prepattern (Figure 4, top right). A PS-b-PMMa diblock copolymer was spun cast onto the photoresist prepattern and baked to drive self assembly. After removal of the PMMA minority phase, a series of aligned holes or vias were formed within the original photoresist trench (Figure 4, bottom right).
3.4 Graphoepitaxy using photoresist features created via positive tone development and subsequent polarity switch

Since tooling for negative tone development processes are not widely available at present, an alternate approach to create suitable prepatterns for graphoepitaxy involves exposing a positive tone photoresist, developing in the positive tone with TMAH developer, and subsequently switching the polarity of the remaining photoresist material by various thermal, chemical, and/or photochemical processes. In order to obtain a similar result using commercially available positive tone photoresist materials, we switched the polarity of the positive tone photoresist patterns with a deep ultraviolet flood exposure using an arc lamp and a subsequent a post exposure bake. This simple photochemical treatment generates photoacid from the remaining photoacid generator within the photoresist lines in order to catalytically deprotect the remaining protecting groups during the post exposure bake.

An example of a via shrink process using this approach is shown in Figure 5. Arrays of holes were made in a layer of 193 nm positive tone photoresist. After development using TMAH developer, the positive tone photoresist pattern was flood exposed and baked to form a DSA compatible photoresist prepattern (Figure 5, top right). PS-b-PMMA was then spin coated onto the photoresist prepattern and baked to form self-assembled domains within the photoresist holes. The PMMA domains were selectively removed by oxygen plasma (Figure 5, bottom right) to afford holes with a reduced diameter.

One limitation of this scheme is the inability to maintain the surface properties of the underlayer during the positive tone process.

3.5 Sparse chemical patterns for DSA created with 193 nm immersion lithography

The significant area taken up by the topographical directing features limits the potential utility of graphoepitaxial DSA processes in many semiconductor applications. Chemical epitaxy solves this problem by using patterns of differing chemical affinities on the underlying surface to direct the self-assembly process [6,7]. We have demonstrated chemical patterns may be formed in an additive fashion by patterning thin layers of a negative tone photoresist with e-beam lithography to form pinning regions on a neutral substrate [7]. Chemical patterns for chemical epitaxy may also be fabricated in a subtractive fashion by employing a sacrificial positive tone photoresist pattern to protect an underlying neutral surface while pinning regions are created by an intermediate etch process [6]. Kim and coworkers have used thermal reflow to shrink the size of the patterns prior to the etch step to overcome the resolution limitations of 193 nm dry lithography [9]. However, such subtractive methods require the use of an extra intermediate etch process as well as a non-traditional imaging stack having a neutral layer underneath the photoresist which may adversely impact reflectivity, photoresist adhesion, and photoresist profiles. Instead, we have developed a pattern first, neutralize last scheme which uses a positive tone 193 nm photoresist
patterned by 193 nm immersion lithography and a subsequent lift-off process to generate sparse chemical patterns for DSA as shown in Figure 6.

3.6 Lift-off process to create sparse chemical patterns for chemical epitaxy

A line-space pattern (30 nm line width, 90 nm pitch) was generated using 193 nm water immersion interference lithography by overexposing a positive tone 193 nm photoresist. After TMAH development, the photoresist lines were hardened by DUV flood exposure followed by a post exposure bake. A thin conformal layer of neutralization material was then applied and grafted to the surface. The photoresist was subsequently removed by lift-off using an organic solvent to generate a sparse chemical pattern consisting of alternating pinning and grafted neutral regions on the substrate (Figure 7, top). DSA was carried out by applying a layer of PS-b-PMMA on the sparse chemical pattern and thermally annealing. The strong affinity of the PMMA domains for the lift off regions pins some of the PMMA domains and directs the domains to align parallel to the pinning regions and orient perpendicularly to the grafted neutralization material. The resulting frequency tripled PS lines (16 nm line width, 30 nm pitch) are shown in Figure 7 (bottom) after selective removal of the PMMA domains.

In comparison to previously reported methods, this lift-off approach provides a fully 193 nm compatible process which can be performed with existing photoresists, anti-reflective coatings, and film stacks. Since the neutralization layer is applied last in the lift-off scheme, the photoresist pattern can be slimmed, trimmed, or otherwise manipulated in order to overcome the restrictions of the optical lithography tool without concern of damaging the surface properties of the underlayer.

In another demonstration, line-space patterns (30 nm line width, 100 nm pitch,) were generated from a trilayer photoresist stack on 300 mm wafers using 193 nm immersion lithography (ASML 1700i, 1.35NA). After switching the photoresist polarity with a DUV flood exposure and post exposure bake, a thin conformal layer of neutralization material was applied and grafted onto the surface. Lift-off using standard 0.26N TMAH developer generated a sparse chemical pattern (Figure 8, top). PS-b-PMMA was spun cast onto the sparse chemical pattern and baked for 2 minutes to produce a frequency quadruple DSA pattern. Atomic force microscopy (AFM) images of the resulting aligned block copolymer domains are shown in Figure 8 (bottom). After removal of the PMMA domains by oxygen RIE, polystyrene lines (13.1 nm wide, 25 nm pitch) with low roughness (LER 2.1 nm (3σ), LWR 2.3 nm (3σ)) can be obtained with champion results having sub-2 nm LER.
4. Conclusions

The fabrication of topographical and chemical directing structures for DSA using conventional 193 nm immersion lithography has been demonstrated by taking advantage of the thermal and solubility properties of unprotected 193 nm photoresists materials. These schemes are compatible with existing lithographic wafer tracks and 193 nm imaging materials. Compared to SADP which requires two sequential pitch splitting processes to achieve frequency quadrupling, a chemical epitaxy DSA process based on 193 nm immersion lithography can provide a similar result using a single DSA process. While further advancements in materials for DSA will result in additional improvements, process schemes such as those described here will allow DSA to be implemented in state-of-the-art facilities with the automated wafer track, immersion exposure, and metrology tools necessary to enable meaningful evaluations of the resolution, LER/LWR, overlay, and defectivity capabilities of DSA.

5. References