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Simple and Versatile Methods To Integrate Directed Self-Assembly with Optical Lithography Using a Polarity-Switched Photoresist

Joy Y. Cheng,[†,*] Daniel P. Sanders,[†,*] Hoa D. Truong,[†] Stefan Harrer,[‡,§] Alexander Friz,[†] Steven Holmes,[‡] Matthew Colburn,[‡] and William D. Hinsberg[†]

[†]IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120, [‡]IBM Albany Nanotech, 257 Fuller Road, Albany, New York 12203. [§]Present address: IBM T.J. Watson Research Center, 1101 Kitchawan Road, Yorktown Heights, New York 10598

ABSTRACT **We report novel strategies to integrate block copolymer self-assembly with 193 nm water immersion lithography. These strategies employ commercially available positive tone chemically amplified photoresists to spatially encode directing information into precise topographical or chemical prepatterns for the directed self-assembly of block copolymers. Each of these methods exploits the advantageous solubility and thermal properties of polarity-switched positive tone photoresist materials. Precisely registered, sublithographic self-assembled structures are fabricated using these versatile integration schemes which are fully compatible with current optical lithography patterning materials, processes, and tooling.**

KEYWORDS: directed self-assembly · graphoepitaxy · chemical epitaxy · block copolymer · photoresist

Directed self-assembly (DSA), which combines self-assembling materials with lithographically defined directing prepatterns on a substrate, has been widely explored to produce nanoscale devices[1−3] and nanoscale patterns.[4−10] Early work on self-assembly demonstrated its utility in the creation of etch masks with sublithographic resolution.[11] More recently, concept demonstrations of frequency multiplication and/or pattern rectification using directing patterns formed using electron-beam direct-write, extreme ultraviolet (EUV) interference, and optical lithography have been reported.[12−21] In particular, much effort has focused on using DSA to create nanoimprint master templates for the fabrication of bit-patterned magnetic storage media.[12−15] Nanoimprint master template fabrication is a logical progression for the field as it requires that the DSA process performs only once, which relaxes the time and process constraints. In stark contrast, the application of DSA as an on-wafer lithographic technique for the direct fabrication of semiconductor devices is a much more challenging application due to the more stringent defectivity requirements as well as the more restricted wafer processing techniques, shorter cycle times, cost constraints, and other limitations inherent to the semiconductor industry.

Despite these challenges, there is a pressing need to integrate DSA with commercial optical lithography so an assessment of the resolution, line-edge roughness, overlay, and defectivity capabilities of DSA can be evaluated in a timely manner, since the practical resolution limit of 193 nm water immersion lithography has already been reached at 40 nm half-pitch.[22,23] Double patterning is being used to further extend the patterning capabilities of optical lithography until a next generation lithographic technique such as extreme ultraviolet (EUV), nanoimprint, and massively parallel electron-beam lithography is ready for high-volume manufacturing.[24,25] In particular, a self-aligned double patterning (SADP) technique, which doubles the spatial frequency of a photoresist prepattern by generating spacers next to the side walls, has gained the most acceptance[26] because it requires only one critical lithography step which eliminates the overlay issues associated with interlacing features created in separate exposures. However, the extremely strict process control requirements and exploding development and manufacturing costs of SADP become significant roadblocks for using sequential SADP to achieve higher order pitch splitting (*i.e.*, frequency multiplication).

Compared to alternative higher order pitch division schemes,[27] directed

*Address correspondence to chengjo@us.ibm.com, dsand@us.ibm.com.

Received for review April 5, 2010 and accepted June 28, 2010.

Published online July 15, 2010.
10.1021/nn100686v

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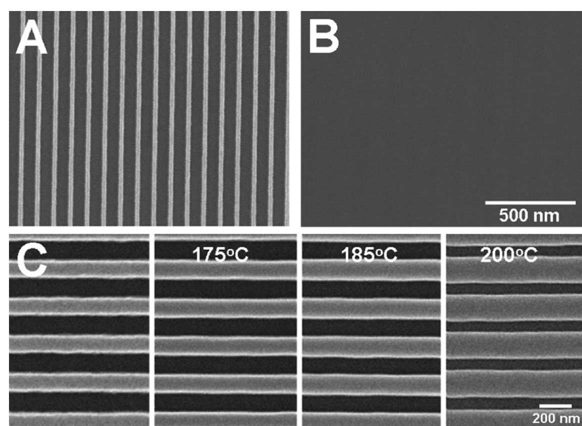

Figure 1. Solvent and thermal instability of 193 nm positive tone photoresist patterns. (A) Initial line-space photoresist pattern (100 nm pitch) formed using JSR AR2928JN. (B) Resulting pattern after 30 s anisole rinse. (C, left panel) Initial 220 nm pitch line-space pattern composed of JSR AR2928JN photoresist hardened with JSR NFC FZX 112 chemical freeze material. (C, three right panels): Resulting patterns after baking at 175, 185, and 200 °C for 1 min.

self-assembly of block copolymers may be a more efficient pitch division technique to extend optical lithography beyond double patterning. In order to be successful, directed self-assembly requires prepatterns consisting of complex combinations of topography and surface chemistry that are compatible with a variety of solvents and process conditions. Unfortunately, typical DSA processes use organic casting solvents and high-temperature annealing processes which destroy the fidelity of typical photoresist prepatterns. To circumvent these issues, most DSA demonstrations have used patterned photoresist only as a sacrificial intermediate that is converted into a more robust topographical or chemical prepattern by pattern transfer into an underlying material, such as a hardmask.[5−10,12−15] While insoluble prepatterns consisting of cross-linked negative tone photoresists patterned by electron-beam or i-line ultraviolet lithography have been used as chemical[16,17] and topographical[18−20] guiding patterns for DSA, few high-resolution cross-linking negative tone 193 nm immersion-compatible photoresists have been reported (with none being commercially available).[28]

In order to assess the viability of DSA as a lithographic technology for high-volume manufacturing of semiconductor devices, it is necessary to integrate DSA with state-of-the-art 193 nm immersion lithography in a straightforward and process-friendly manner. In this paper, we report simple and versatile integration schemes to fabricate topographical and chemical patterns for DSA using optical lithography and conventional 193 nm photoresists and imaging film stacks. In particular, we have found that polarity-switched chemically amplified photoresist materials can be utilized to fabricate topographical and chemical prepatterns for DSA as a result of their increased thermal stability and insolubility in casting solvents suitable for the application of self-assembling materials. These process schemes are advantageous for semiconductor manufacturing since they can be performed entirely on the wafer track of the lithography tool with short cycle times, thereby eliminating the additional dry etch processes and lengthy process steps found in previously reported efforts. While the work herein focuses on integrating DSA with 193 nm lithography, these general methods can also be applied to a wider range of chemically amplified photoresists to expand and accelerate the possible application of traditional lithography to the directed self-assembly of functional materials and the creation of novel assemblies, patterns, and devices.

RESULTS AND DISCUSSION

Issues in Integration of 193 nm Photoresist into DSA Process. When attempting to use photoresist patterns as directing structures in DSA, the solvent stability, thermal stability, and surface chemistry of the patterned photoresist layer and the uncovered underlayer are critical. As mentioned previously, patterned 193 nm positive tone photoresist materials are generally soluble in typical organic casting solvents used to apply block copolymers for DSA. For example, line-space patterns formed using a representative 193 nm positive tone photoresist (JSR AR2928JN) shown in Figure 1A are readily dissolved by common organic solvents such as anisole (as shown in Figure 1B) and propylene glycol methyl ether acetate (PGMEA). To combat this issue, photoresist "hardening" processes using chemical freeze materials or surface curing agents have been developed to render photoresist patterns stable to subsequent coating processes used in double patterning schemes.[29−34] Unfortunately, the effectiveness of such processes which rely primarily on surface modification depends strongly on the particular photoresist in question and may not provide sufficient thermal stability for use in DSA. For example, hardened 193 nm positive tone photoresist patterns (JSR AR2928JN treated with JSR NFC FZX 112 chemical freeze material) before and after a 60 s bake at various temperatures are shown in Figure 1C. The hardened photoresist lines reflow at temperatures greater than 175 °C, which is well below that experienced in the high-temperature (>200 °C) annealing processes required for rapid DSA pattern formation.[35] The pitch-dependent increase in line widths and the degradation of photoresist profiles at high temperatures prevent such photoresist structures from serving as precise and reliable guiding patterns for DSA.

In addition, the ability to selectively and independently control the surface chemistries of the various regions of the guiding prepattern in contact with the self-assembly materials is critical to the success of DSA processes, especially those which involve higher order pitch division. With respect to graphoepitaxy, successful pitch division by DSA generally requires the ability to specifically control the surface chemistry of the top sur-

faces, the side walls, and the bottom recessed surfaces of the guiding features. Vertically oriented lamellar or cylindrical domains (*i.e.*, oriented perpendicular to the substrate) which span the entire film thickness are preferred in order to facilitate subsequent pattern transfer of line-space and via patterns, respectively. Many materials, including self-assembled monolayers, polymer brushes, and cross-linked polymers, have been specifically designed to provide a substrate which is neutral (with respect to its affinities toward the various block copolymer domains) and thereby enable vertical orientation of the self-assembled domains.[36−42] In the pitch division of trenches using lamellae-forming block copolymers via graphoepitaxy, for example, it is desirable for the side walls of the guiding features to have a preferential affinity for one of the block copolymer domains to direct the lamellae to align parallel to the trench and for the bottom recessed surfaces to remain neutral to ensure vertical orientation of the self-assembled domains for straightforward etch transfer.

However, imaging a positive tone photoresist on top of the precisely tailored neutral materials discussed previously typically alters their surface properties and renders them unable to control the desired morphology and orientation of the block copolymer domains. In a positive tone imaging process, the underlying material in the exposed regions is subjected to deep UV radiation, superacids at elevated temperature, reactive chemical intermediates formed by photochemical reactions of the incident radiation with the PAG or photoresist components and/or resulting from photoresist deprotection fragments, strongly alkaline conditions during photoresist development, and any processes necessary to harden the photoresist structures. Any and all of these conditions may be sufficient to destroy the surface properties of the underlayer and ultimately produce DSA morphologies which are not useful for lithographic applications. For example, a hybrid morphology consisting of interconnected holes and lines was observed from a symmetric poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) diblock copolymer on a grafted hydroxyl-terminated poly(styrene-*r*-methyl methacrylate) neutral brush layer after TMAH treatment. For this reason, reported literature schemes typically use negative tone cross-linking photoresists to form directing structures on a neutral underlayer and rely on the photoresist material in the unexposed regions to protect the underlayer surface properties.[18,20]

Polarity Switched Photoresist. Given the aforementioned lack of commercial 193 nm immersion-compatible negative tone photoresists, we have explored alternative approaches to form negative tone photoresist patterns in order to overcome this neutral underlayer degradation issue. Negative tone development, which has been used to fabricate high-resolution negative tone patterns using 248 nm lithography by IBM[43] and, more recently, in 193 nm double patterning by Tarutani *et al.*,[44,45] has shown particular promise. Photoresists are typically classified by their solubility in the industry standard 0.26 N aqueous tetramethylammonium hydroxide (TMAH) developer. In positive tone chemically amplified 193 nm photoresists, a solubility switch is induced in the exposed region of the material which increases its dissolution rate in TMAH developer. This change in dissolution rate with respect to an alkaline developing solution is typically the result of the catalytic acidolysis of pendant tertiary ester groups in the photoresist resin by a photogenerated acid to produce carboxylic acid groups.[46] For example, Figure 2A shows the contrast curves of an exposed 193 nm positive tone photoresist (JSR AR2928JN) developed for 30 s using two different developing solvents. Above the dose to clear (E_0), a sufficient quantity of carboxylic acid groups has been generated to allow the photoresist materials to be completely removed by alkaline TMAH developer. Since the exposed material is dissolved in the developer, this process is referred to as positive tone development. However, if an organic solvent such as anisole is used to develop the same photoresist material instead, the non- and underexposed photoresist dissolves and the more polar deprotected photoresist material formed at exposure doses near and above E_0 remains insoluble. Since the non- and underexposed material is removed during development instead of the exposed material, such a process is referred to as negative tone development. In negative tone development, the same deprotection chemistry that is responsible for generating carboxylic acid groups (which increase the material's dissolution rate in alkaline developer via ionization at high pH) is used to decrease the material's dissolution rate in select organic solvents by changing its

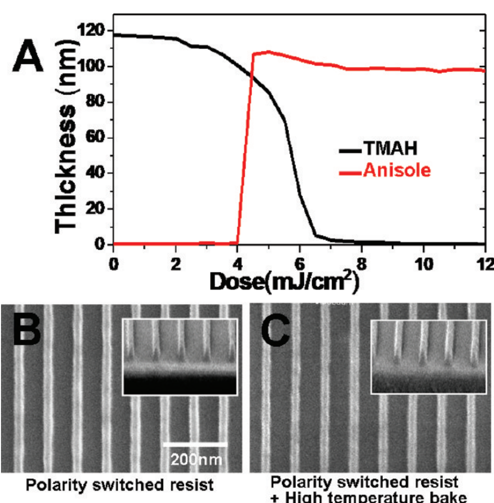

Figure 2. Solvent and thermal stability of polarity-switched 193 nm phororesist. (A) Contrast curves of a 193 nm photoresist (JSR AR2928JN) developed in the positive tone using standard developer (0.26 N TMAH) and in the negative tone using anisole. (B) Plane view and cross section of a 193 nm photoresist pattern (JSR AR2928JN) after deprotection. (C) Plane view and cross section after baking the pattern at 200 °C for 2 min.

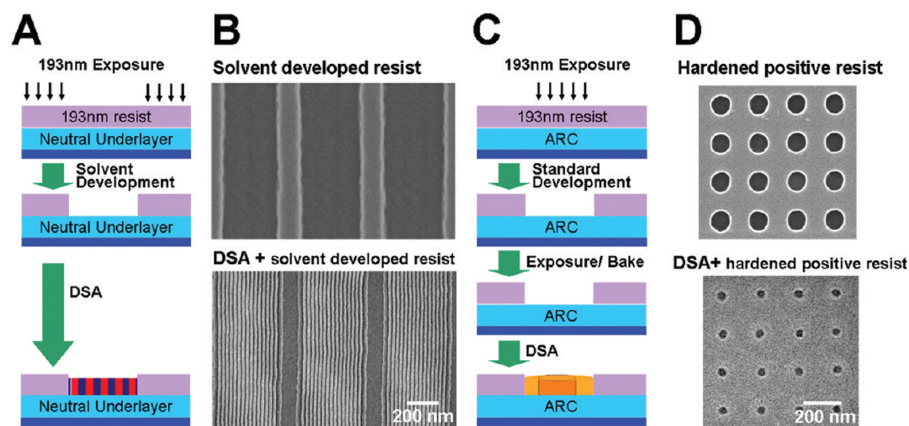

Figure 3. Graphoepitaxy using polarity-switched 193 nm photoresist as guiding features. (A) DSA prepatterns made from a negative tone, solvent-development scheme. (B, top) 370 nm wide photoresist trenches (JSR AM2073J) formed by negative tone development. (B, bottom) Resulting pattern formed by DSA of a lamellae-forming PS-*b*-PMMA block copolymer in the prepattern after removal of the PMMA domains and photoresist by oxygen RIE. (C) DSA prepatterns made from a positive tone development scheme featuring a subsequent flood exposure and bake step to switch the polarity of the photoresist. (D, top) 100 nm diameter via prepatterns in a photoresist (JSR AM2073J) after an ultraviolet flood exposure and bake. (D, bottom) Resulting 45 nm vias formed by DSA of cylinder-forming PS-*b*-PMMA block copolymer in the prepattern after selective removal of the PMMA domains by oxygen RIE.

solubility parameter. Herein, we will refer to such deprotected photoresist material as having been "polarity-switched". Unlike negative tone photoresists, which operate by a cross-linking mechanism, the polarity-switched photoresist material remaining after negative tone development can be easily removed for rework by stripping with either TMAH or highly polar organic solvents.

We have discovered that polarity-switched photoresists offer several advantages in the fabrication of directing structures for DSA. First, the polarity-switched photoresist is insoluble in select organic casting solvents suitable for applying common block copolymers for DSA. Second, the thermal stability of structures composed of a polarity-switched photoresist is much improved, allowing them to withstand the high-temperature annealing processes used to drive self-assembly in the short cycle times required for manufacturing. Although some photoresist profile change and film thickness loss is observed during the initial polarity-switching process due to the volatilization of deprotection products and densification of the photoresist film, no significant additional photoresist profile changes are observed as a result of subsequent high-temperature anneals, in striking contrast with the behavior of the "hardened" photoresist patterns shown previously in Figure 1C. For example, Figure 2B shows a line-space pattern composed of polarity-switched photoresist material in which the lines have an average CD of 31.1 nm and line-edge roughness (LER) of 3.2 nm. After an additional bake at 200 °C for 2 min, the CD is 30.8 nm and the LER is 3.0 nm (Figure 2C). Finally, the carboxylic acid rich polarity-switched photoresist material has a 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). Therefore, structures composed of a polarity-switched photoresist have surface properties which help orient the block copolymer domains parallel to the prepattern when used as topographic guiding features in graphoepitaxy and help to pin selective domains when used as chemical pinning features in chemical epitaxy.

DSA Topographical Prepattern Based on Polarity Switched Photoresist. In order to fabricate topographical guiding structures for DSA composed of polarity-switched photoresist material, two straightforward schemes are shown in Figure 3. In the first scheme illustrated in Figure 3A, a positive tone photoresist is developed in the negative tone using an organic solvent to produce topographical photoresist patterns suitable for grapheoepitaxy. The unexposed photoresist material is removed cleanly by the organic solvent developer to create a negative tone photoresist pattern with retention of the functional surface properties of the underlayer in the uncovered regions. As an example, a two-layer stack consisting of a positive tone 193 nm photoresist (JSR AM2073J) and a neutral underlayer is employed to create guiding structures with proper topographical confinement and surface chemistry for DSA in Figure 3B. The two-layer stack was exposed using 193 nm lithography and developed in the negative tone using anisole to form a 370 nm wide trench pattern shown in Figure 3B (top). A PS-*b*-PMMA (22k−22k) diblock copolymer was spun cast on the photoresist pattern from anisole and baked at 200 °C for 2 min. The affinity of the PMMA domains for the deprotected photoresist at the side walls and the neutrality of the underlayer at the bottom of the trenches induce the domains to align parallel to the trenches and orient perpendicular to the underlayer. The PMMA domains and the photoresist lines were subsequently removed by an oxygen RIE, which left the aligned PS line patterns (pitch = 24.8 nm) on the substrate, as shown in Figure 3B (bottom).

Since negative tone development using organic solvents is not yet widespread, we have achieved a similar result using a scheme illustrated in Figure 3C that uses a positive tone photoresist and standard TMAH development. After producing a positive tone photoresist pattern in the typical manner, the polarity of the resulting photoresist lines can be subsequently switched by various thermal, chemical, and/or photochemical processes. Since our goal was to utilize existing photoresist materials, we used a simple flood exposure with a deep ultraviolet arc lamp and a post-exposure bake to induce this polarity switch. This simple photochemical treatment generates photoacid from the remaining photoacid generator (PAG) within the photoresist lines, which catalyzes the deprotection of the remaining protecting groups during the subsequent post-exposure bake.

An example of this process suitable for the shrinking of contact holes or vias using directed self-assembly involves forming arrays of 100 nm diameter holes in a layer of the 193 nm photoresist (JSR AM2073J) using standard TMAH development. After development, the remaining positive tone photoresist pattern was flood exposed and baked to form a DSA-compatible photoresist pattern (Figure 3D, top). An anisole solution of cylindrical PS-*b*-PMMA (96k−35k) was then spin coated onto the polarity-switched photoresist pattern and baked to form self-assembled cylindrical PMMA domains within the guiding pattern. The center PMMA domains were selectively removed by oxygen plasma (Figure 3D, bottom) to afford holes with a reduced diameter of 45 nm. This DSA process provides a simple and controllable route to substantially reduce the CD of vias patterned with a positive tone photoresist (currently the preferred photoresist for via patterning) using optical lithography. In this example, we used a standard bottom anti-reflection coating (which is not neutral to PS-*b*-PMMA) during photoresist patterning since the underlying surface would not remain neutral during the positive tone patterning process for reasons discussed previously. As a result of the non-neutral recessed surfaces of the prepattern, the central PMMA domains formed in this manner do not extend all the way to the substrate, presenting an additional challenge to the subsequent etch transfer of the DSA pattern.

DSA Chemical Prepattern Based on Polarity Switched Photoresist. The significant area taken up by topographical directing features limits the utility of graphoepitaxial DSA processes in many semiconductor applications. In addition, the imperfectness of the guiding topographical prepattern used in graphoepitaxy (*e.g.*, the line-edge roughness of the photoresist side walls) may propagate into the adjacent self-assembled domains and cause additional CD variation and placement error. Chemical epitaxy resolves these problems by using patterns of differing chemical affinities on an effectively planar surface located underneath the self-assembled material to direct the self-assembly process.[4−10] Unfortunately, it is quite challenging to fabricate sparse chemical patterns suitable for DSA by optical lithography. Although photopatternable neutralization materials have been reported,[40−42] developing a neutralization material that also acts as an immersion-compatible negative tone photoresist with state-of-the-art resolution capabilities is extremely difficult. While sparse chemical patterns composed of a cross-linked negative tone photoresist on a neutral substrate have been created using e-beam lithography,[16,17] optical lithography has insufficient resolution to print the desired line widths in an ultrathin layer of negative tone photoresist. Alternatively, a positive tone photoresist layer (patterned by e-beam lithography) may be used as a mask to protect the surface properties of an underlayer, while sparse chemical patterns (*i.e.*, pinning or preferentially wetting regions) are created by etching the unprotected areas of the underlayer.[12−15] Kim *et al.* have extended this work to optical lithography by using thermal reflow to shrink the openings in the photoresist prior to etching the underlayer.[21] However, this approach still requires the use of a nonconventional imaging stack for which the reflectivity, photoresist adhesion, and photoresist profiles are not optimized with respect to 193 nm lithography. In addition, the pitch dependence of thermal reflow (to narrow the photoresist openings) and the additional etch step increase process complexity and cost of ownership.

Rather than employing such subtractive methods, we have developed a pattern-first, neutralize-last process (shown in Figure 4A) to fabricate chemical prepatterns. This process uses a positive tone 193 nm photoresist prepattern formed on a conventional film stack using 193 nm immersion lithography to mask areas of the substrate during the grafting of a neutralization layer. Subsequent lift-off of the photoresist generates sparse chemical patterns suitable for DSA. In an analogous fashion to the photopatternable neutralization materials,[40−42] this lift-off procedure is an additive process in which areas of the substrate are selectively neutralized. However, rather than requiring a single material to serve as both an ultrahigh resolution photopatternable material and a neutral material, this scheme separates the roles and delegates the photopatterning role to a conventional photoresist which already has been rigorously optimized for imaging performance. As a result of the aforementioned insolubility of the polarity-switched photoresist material in selected organic solvents, it is possible to overcoat a polarity-switched photoresist pattern with a neutralization material from an organic casting solvent, graft it to the unprotected surface areas of the substrate to provide neutral regions, and then selectively remove the photoresist using an appropriate developer (such as TMAH) to form pinning regions.

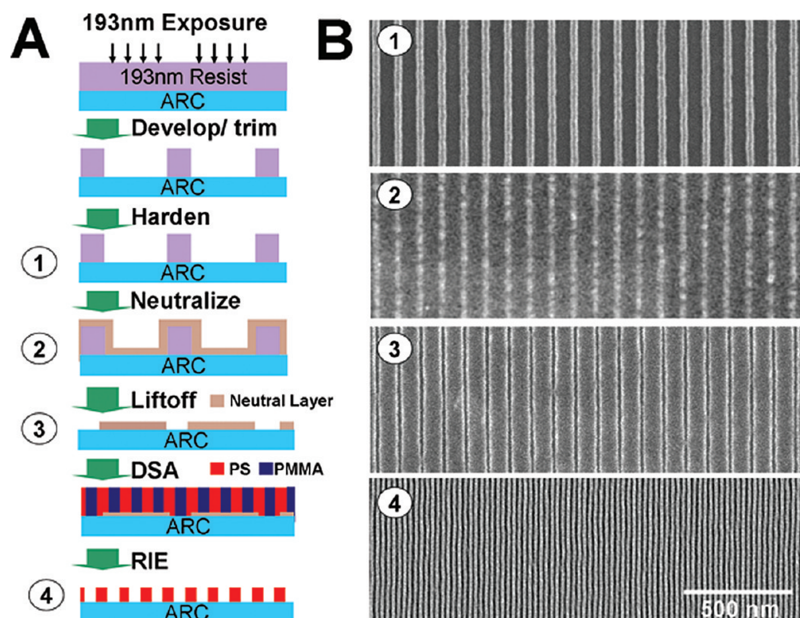

Figure 4. (A) Chemical epitaxy DSA process flow using sparse chemical prepatterns made by a pattern-first, neutralize-last approach featuring a lift-off step. (B) Scanning electron micrographs at various stages of the process illustrated in (A). (1) Polarity-switched photoresist prepattern consisting of ~30 nm lines (100 nm pitch) formed using 193 nm water immersion lithography (1.35 NA, ASML 1700i). (2) Topography after a thin layer of neutralization material is coated on top of the photoresist prepattern. (3) Sparse chemical patterns after lift-off of the photoresist lines using standard TMAH developer. (4) PS lines of 25 nm pitch formed by DSA using a lamellae-forming PS-*b*-PMMA block copolymer after removal of the PMMA domains with an oxygen RIE.

A line-space pattern (100 nm pitch, 30 nm line width) was generated from a trilayer stack consisting of a layer of positive tone photoresist (JSR AR2928JN), a silicon-containing bottom anti-reflective coating (Si-ARC), and a spin on carbon layer using 193 nm water immersion lithography (ASML 1700i, 1.35 NA) on 300 mm wafers. A flood exposure and post-exposure bake process was used to harden the photoresist lines to the casting solvent from which a neutralization material will subsequently be applied (typically PGMEA). The resulting patterned substrate is shown in Figure 4B-1. A thin conformal coating of neutralization material was applied over the photoresist pattern and grafted to the surfaces of the photoresist pattern and the uncovered substrate (as shown in Figure 4B-2) by heating. The photoresist (and any neutralization material grafted to it) was removed by lift-off using standard 0.26 N TMAH developer to generate a sparse chemical pattern consisting of alternating pinning and grafted neutral regions on the substrate (Figure 4B-3). A number of neutralization materials were screened for this process including hydroxyl-terminated poly(styrene-*r*-methyl methacrylate)[36] and various epoxy-functionalized poly(styrene-*r*-methyl methacrylate) terpolymers.[40,42] Although the particular choice of the neutralization material impacted the optimal grafting and lift-off conditions, successful demonstration using each were achieved. The higher content of reactive sites in the epoxy-functionalized neutralization materials advantageously reduced the length of the grafting step to 2 min or less.

DSA was carried out by applying a 40 nm thick film of PS-*b*-PMMA (22k−22k) diblock copolymer on the sparse chemical pattern and baking at 240 °C for 2 min. The Si-ARC and any residual polarity-switched photoresist in the lift-off regions have a preferential affinity for PMMA and pin some of the PMMA domains. As a result, the domains align parallel to the pinning regions and orient perpendicular to the grafted neutralization material. Figure 4B-4 shows the frequency quadrupled PS lines with a pitch of 25 nm and a CD of 13.1 nm after the PMMA domains were selectively removed by oxygen RIE. The average line-edge roughness (LER) and line-width roughness (LWR) of the polystyrene lines formed by this DSA process are 2.1 and 2.3 nm, respectively. Further optimization of the etch transfer process is in progress to improve pattern profiles and LER/LWR values.

In comparison to previously reported DSA methods, this lift-off approach provides a fully 193 nm compatible process which can be performed with existing 193 nm positive tone photoresists, anti-reflective coatings, and film stacks. Since the neutralization layer is applied last in the lift-off scheme, the photoresist pattern can be trimmed, cut, or otherwise manipulated to overcome the restrictions of the optical lithography tool without concern of damaging the surface properties of any underlayer. Finally, since no intermediate etch or deposition steps (which would require the wafer to be transferred from the litho track to another tool) are required, this combination of DSA and 193 nm lithography is potentially simpler and more efficient than com-

peting alternatives. In particular, if defect levels can be reduced to an equivalent level, the DSA process shown here could have significant cost advantages compared to sequential SADP-based pitch-splitting processes.

CONCLUSIONS

In conclusion, we have demonstrated a versatile platform based on using polarity-switched photoresists for the fabrication of topographical and chemical directing structures via conventional optical lithography. Since polarity-switched photoresist materials are compatible with casting solvents and high-temperature annealing bakes used in typical DSA processes, they provide a simple means by which to spatially encode topographical and/or chemical information on a substrate for use as guiding structures in DSA. Since these schemes are fully compatible with conventional lithographic processes and cycle times and can be performed entirely in the wafer track of an immersion lithography tool, they will allow DSA to be implemented on 300 mm wafers using fully automated processes in state-of-the art development lines. Such progress is necessary to enable a true assessment of the resolution, line-edge roughness, line-width roughness overlay, and defectivity capabilities of DSA.

While the work herein has focused on integrating DSA with 193 nm lithography for obvious reasons, these same general principles can be applied to a wider range of chemically amplified photoresists suitable for use with other lithographies. Moreover, since only commercially available lithographic materials are required to implement them, these processes will expand and accelerate the possible application of traditional lithography to the directed self-assembly of functional materials such as nanoparticles and nanowires to create novel assemblies, patterns, and devices.

EXPERIMENTAL SECTION

Materials: ARC 29A anti-reflective coating was obtained from Brewer Science. A940 anti-reflective coating was obtained from Shin-etsu Chemical. TCX-041 topcoat, NFC FZX 112 chemical freeze agent, HM8006, AR2928JN photoresist, and AM2073J photoresist were obtained from JSR Micro, Inc. The 0.26 N aqueous tetramethylammonium hydroxide (TMAH) developers OPTIYIELD CD and OPD 7262 were obtained from Air Products and FujiFILM, respectively. Propylene glycol monomethyl ether acetate (electronic grade) was obtained from Ultra Pure Solutions, Inc. All other chemicals were obtained from Aldrich Chemical and were used without further purification unless otherwise noted.

DSA Polymers: PS-*b*-PMMA diblock copolymers were purchased from Polymer Source, Inc. in various molecular weights. Lamellar PS-b-PMMA: M_n = 22k−22k, PDI = 1.09. Cylindrical PS-b-PMMA: M_n = 96.5k−35.5k, PDI = 1.11. Homopolymers: Poly(styrene), PS: M_n = 21k, PDI = 1.04.

Neutralization Materials: Neutralization materials were prepared by traditional free-radical polymerization in methyl ethyl ketone using 2,2′-azobis(2-methylpropionitrile) (AIBN) initiator. Solutions of the neutralization materials were made in PGMEA with *N*-phthalimide triflate, a thermal acid generator (TAG), (10 wt % relative to polymer) as described elsewhere.[42]

Poly(styrene-*ran*-epoxydicyclopentadiene methacrylate), P(S-*r*-EDCPMA). Styrene/epoxydicyclopentadiene methacrylate feed ratio = 70:30. M_n = 7400 g/mol, PDI = 1.40.

Poly(styrene-*ran*-methyl methacrylate-*ran*-epoxydicyclopentadiene methacrylate), P(S-*r*-MMA-*r*-EDCPMA).[42] Styrene/methyl methacrylate/epoxydicyclopentadiene methacrylate incorporation ratio = 57:39:4 by mole. M_n = 12.3 kg/mol, PDI = 1.55.

Poly(styrene-*ran*-methyl methacrylate-*ran*-glycidyl methacrylate), P(S-*r*-MMA-*r*-GMA).[40] Styrene/methyl methacrylate/glycidyl methacrylate incorporation ratio = 56:42:2 by mole. M_n = 12.1 kg/mol, PDI = 1.59.

Contrast Curves: A 150 nm thick layer of AR 2928JN photoresist was formed on an anti-reflection layer (78 nm of ARC 29A) on a silicon wafer. A 5 × 25 dose array of open field exposures was imaged on the material using a 193 nm mini-stepper (ISI, 0.6 numerical aperture (NA)). A 60 s post-exposure bake (PEB) was performed, and the film thickness was then measured using a Nanometrics Nanospec 6100. After development of the photoresist pattern for 30 s using anisole or 0.26 N TMAH developer, the wafer was spin dried and the residual thickness was again measured.

Graphoepitaxy Using Negative Tone Development of a 193 nm Photoresist: An 80 nm thick P(S-*r*-EDCPMA) neutral layer formulation was spun cast on a substrate and cross-linked at 200 °C for 2 min. A 80 nm thick layer of JSR AM2073J photoresist was spun cast on top of the neutral layer, baked at 110 °C for 60 s, exposed using 193 nm lithography (0.6 NA, COG mask), post-exposure baked at 110 °C for 60 s, and developed in the negative tone using anisole for 60 s to form a trench pattern (370 nm trenches). A PS-*b*-PMMA diblock copolymer (22k−22k) was spun cast on the resist pattern from anisole (2 wt % solution) and baked at 200 °C for 5 min (in air). The PMMA minority phase and the photoresist were removed by a short oxygen reactive ion etch.

Graphoepitaxy Using Polarity Switching of a 193 nm Photoresist: A layer of JSR AM2073J on an anti-reflection coating (78 nm of ARC 29A, Brewer Science) was exposed using e-beam lithography, baked at 120 °C for 90 s, and developed with 0.26 N TMAH developer for 60 s, rinsed with DI water, and spun dry. After development, the remaining positive tone resist pattern was flood exposed (40 mJ/cm^2) using a Hg/Xe deep ultraviolet arc lamp (UXM-501MA from Ushio America) and baked at 115 °C for 60 s to form the DSA-compatible resist pattern composed of 100 nm diameter holes. A 1 wt % solution of a 8:2 blend (by weight) of PS-*b*-PMMA (96k−35k) and PS (21k) was then spin coated onto the resist pattern from anisole and baked at 200 °C for 5 min in air to form self-assembled domains within the guiding pattern. The central PMMA domains were selectively removed by oxygen plasma to afford holes with a reduced diameter.

Chemical Epitaxy Using Sparse Chemical Patterns Formed by 193 nm Immersion Lithography: Line-space patterns (100 nm pitch, 30 nm line width) were generated from a trilayer stack consisting of 80 nm of JSR AR2928JN, a 35 nm thick layer of Shin-etsu A940 bottom anti-reflective coating (Si-ARC), and a 100 nm thick layer of JSR HM8006 spin on carbon layer on 300 mm silicon wafers using 193 nm water immersion lithography (ASML 1700i, 1.35 NA) at Albany Nanotech. A layer of JSR TCX-041 topcoat was applied onto the photoresist prior to patterning using an immersion lithography step and was removed during the photoresist development process using TMAH developer. The wafers were then shipped to IBM Almaden Research Center, where the photoresist lines were hardened by a DUV flood exposure process described above (20 mJ/cm^2) and a post-exposure bake (115 °C for 1 min and 185 °C for 2 min). A 1 wt % formulation of P(S-*r*-MMA-*r*-GMA) in PGMEA was spun cast over the pattern and grafted to the resist pattern and the uncovered substrate by baking at 200 °C for 2 min. The photoresist lines were removed using standard 0.26 N TMAH developer to generate a sparse chemical pattern consisting of regions of remaining surface-grafted neutralization material (approximately 7 nm thick). A 2 wt % solution of

PS-*b*-PMMA (22k−22k) in PGMEA was spun cast on the sparse chemical pattern and the resulting film baked at 240 °C for 2 min in air. The PMMA domains were selectively removed by oxygen RIE.

Acknowledgment. The authors thank Charles Rettner, Greg Wallraff, Ho-Cheol Kim, and Hikaru Sugita for helpful experiments and discussions, and JSR Micro and Shin Etsu for providing 193 nm lithographic materials.

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