Integration of block copolymer directed assembly with 193 immersion lithography

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An integration scheme of block copolymer directed assembly with 193 nm immersion lithography is presented. It is experimentally shown that a thin silicon nitride film can be used as an antireflective coating (ARC). With such an ARC, directed assembly of a block copolymer (BCP) to triple the feature density of a chemical pattern was demonstrated. A high quality of assembly was obtained over a large area, and pattern transfer feasibility was illustrated. The integration of feature density multiplication via directed assembly of a BCP with 193 nm immersion lithography provided a pattern quality that was comparable with existing double patterning techniques, suggesting that the process could be a promising candidate for extending the use of current 193 immersion lithography tools to higher pattern densities. © *2010 American Vacuum Society.* [DOI: 10.1116/1.3501348]

I. INTRODUCTION

As the critical dimension of integrated circuits and memory devices approaches the resolution limit of 193 nm immersion (193i) lithography and while next generation lithography technologies may not be ready for another two or three years, double patterning (DP) techniques[1,2] could be the most viable candidate for bridging the resolution gap in the interim.[3] However, DP techniques, when compared to conventional single exposure patterning, require additional processing steps that increase the overall production cost dramatically. Directed assembly (DA) of block copolymer (BCP) films is an alternative patterning technique that has the ability to increase the density of features compared to those defined in a single exposure while at the same time offering decreased process complexity and therefore lower cost than DP.[4] Recently, feature density multiplication schemes incorporating BCP DA have been successfully demonstrated using e-beam, extreme ultraviolet (EUV), or 193i lithography.[4–7]

Compared with e-beam or EUV lithography, one of the key concerns regarding the integration of BCP DA with 193i lithography is that an antireflective coating (ARC) is required to resolve subwavelength patterns.[8] A consequence is that film stack design, pattern transfer feasibility, and chemical pattern formation for DA must be carefully engineered to include the ARC. Previous research has demonstrated the integration of an ARC by using a thick organic ARC. However, because the ARC was two to ten times thicker than the BCP template before selective removal of one of the do-mains, one may expect that the use of an additional hard mask layer for pattern transfer will be needed. In this work, we propose that an 8-nm-thick silicon nitride film can serve as an effective ARC, thereby alleviating the difficulty of pattern transfer. With the use of a silicon nitride ARC, we can readily adopt a previously reported process[7] that uses EUV lithography and provides exquisite control in chemical pattern formation. Large areas of perfect assembly and successful, precise pattern transfer are demonstrated, all in a process that is compatible with 193 nm immersion lithography.

II. EXPERIMENT

A. Materials

Cross-linkable polystyrene (X-PS) containing 4 mol % of glycidyl methacrylate (GMA) was synthesized as described previously.[9] The X-PS used in this study, before cross-linking, had a number average molecular weight (M_n, determined by gel permeation chromatography) of $\sim$60 000 g/mol and a polydispersity index (PDI) of 1.4. Poly(styrene-*block*-methyl methacrylate) (PS-*b*-PMMA) BCP was purchased from Polymer Source, Inc. and was used as received. The PS-*b*-PMMA used in this study had a M_n, PDI, and bulk lamellar spacing, L_o, of 18k-*b*-18k, 1.07, and $\sim$30 nm, respectively. A hydroxyl-terminated random copolymer of styrene and methyl methacrylate [P(S-*r*-MMA)], containing 43% styrene, was synthesized as before.[10] The photoresist (JSR ArF ARx2928JN-8) and developer (Futurex RD6) used in the patterning process were used as received. The surfactant used for rinsing was 0.01% DuPont Zonyl FSO-100 in de-ionized water (DIW). Toluene, *N*-methylpyrrolidone (NMP), and GMA were purchased

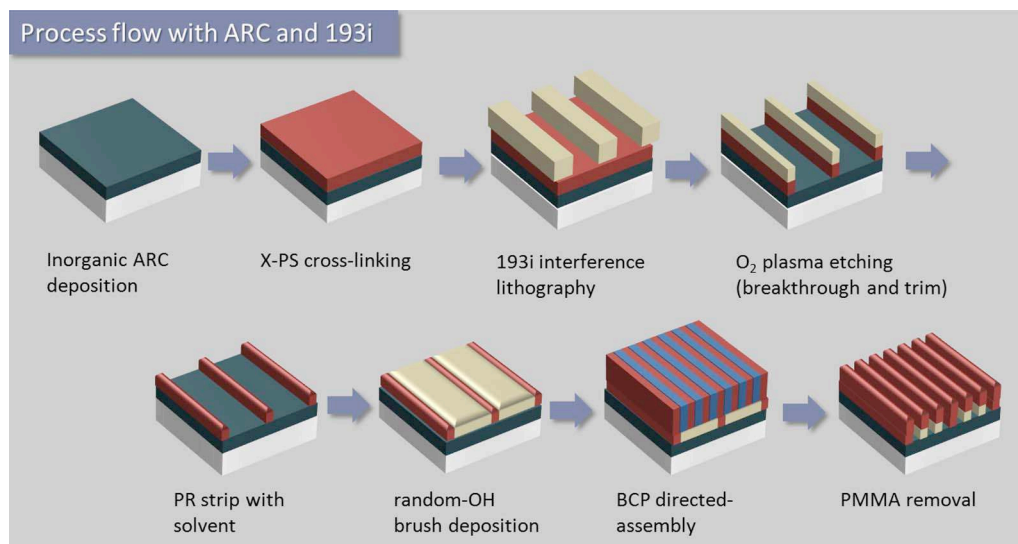[a)]Author to whom correspondence should be addressed; electronic mail: nealey@engr.wisc.edu

FIG. 1. (Color online) Schematic illustration of the proposed method.

from Aldrich and Fisher and were used without further purification.

B. Sample preparation and analysis

The process of sample preparation is illustrated in Fig. 1. A thin silicon nitride layer was deposited onto a freshly cleaned silicon wafer by plasma enhanced chemical vapor deposition, performed in a PlasmaTherm PT70 tool. The process temperature, pressure, plasma power, and gas flow rate were 250 °C, 900 mT, 45 W, and N_2 =900 SCCM/2% SiH_4=375 SCCM/5% NH_3=50 SCCM (SCCM denotes cubic centimeter per minute at STP), respectively. The thickness of the nitride was determined by ellipsometry. A dilute solution of X-PS (0.25 wt % in toluene) was spin-coated at 4000 rpm onto the nitride film, yielding a film that was 6–8 nm thick. The sample was heated to 190° C for 2 days under vacuum to drive the cross-linking reaction. The sample was then washed by repeated sonication in toluene to remove any unreacted X-PS. An 80-nm-thick layer of photoresist was spin-coated at 2500 rpm onto the X-PS on the substrate. The post-applied-bake condition was 120 °C for 90 s. The photoresist was subsequently patterned with 193i interference lithography using the parameters reported in an earlier work.[11] After the post-exposure-bake at 115 °C for 90 s, the sample was developed for 60 s followed by a 15 s DIW rinse and a 3 s surfactant rinse. The final structure in the photoresist was a grating pattern consisting of parallel lines with a period, L_s=90 nm ($3L_o$). The width of the lines, W, ranged from 20 to 50 nm depending on the exposure dose. Some of the samples were etched with an oxygen plasma (75 mT, 8 SCCM O_2, and 100 W in a PlasmaEtch PE-200 tool) to remove the X-PS in the non-photoresist-covered region and to decrease W. The photoresist was then removed with a warm solvent (NMP) and with repeated sonication. Hydroxyl-terminated P(S-*r*-MMA) was spin-coated from a 0.5 wt % toluene solution at 3000 rpm onto the samples. The substrate was then baked at 190° C for 4 h to graft the P(S-*r*-MMA)-OH onto the native oxide of the sample through a condensation reaction, resulting in a 5-nm-thick layer of P(S-*r*-MMA). Excess P(S-*r*-MMA) was washed away with toluene and sonication after the reaction. The PS-*b*-PMMA was spin-coated from a 1.0 wt % solution in toluene at 4000 rpm, resulting in a ~25-nm-thick film, which was then annealed for 1 h at 250 °C in a nitrogen environment. When desired, the PMMA domains were removed with an O_2 plasma (10 mT, 10 SCCM O_2, and 50 W in a Unaxis 790 tool)[12] to create an etch template. SF_6/C_4F_8 inductively coupled plasma etching (in a Trion Phantom tool) was used to demonstrate the pattern transfer of the PS template to the silicon substrate. A LEO 1550VP field-emission scanning electron microscope (SEM) was used to image the chemical patterns, assembled block copolymer films, and etched silicon.

III. RESULTS AND DISCUSSION

Previous reports have shown that without using an ARC in 193i lithography, the photoresist is generally not capable of resolving patterns with feature sizes smaller than the wavelength of irradiation.[13] The resulting resist patterns in such cases usually have numerous defects and large line-edge roughness (LER) values. The remaining resist will also be much thinner than the initial film thickness and thus cannot be used for efficient pattern transfer. A poor ARC, which could reduce but not minimize the reflection from the substrate, would result in standing waves in the resist and would cause a sinusoidal resist profile. Only an optimized ARC can generate an almost vertical sidewall in the resist profile. As shown in Fig. 2, the resist profiles on top of a layer of X-PS on various thicknesses of silicon nitride were nearly vertical. (One should note that the bright layer is the X-PS plus the silicon nitride.) Hence, we experimentally determined that the stack of X-PS (thickness of ~6 nm) on top of silicon
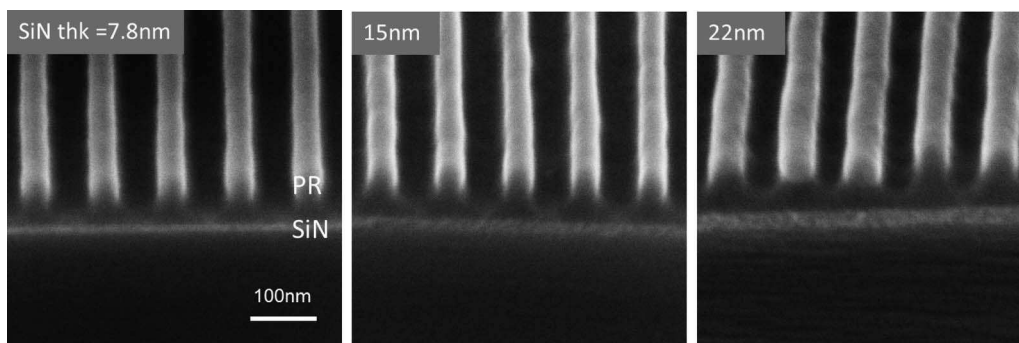
FIG. 2. Tilted SEM images of photoresist profile on different thicknesses of silicon nitride films. Note that the bright layer is a combination of X-PS and silicon nitride.

nitride (thickness of 7.8–22 nm) can serve well as an ARC. The nitride-to-PS etch selectivity in a conventional CHF_3/Ar plasma can be 5 or better. Thus, the etching of a ~20-nm-thick nitride layer using PS structures derived from assembled PS-*b*-PMMA as a template is relatively facile. The use of a thin layer of silicon nitride underneath the BCP and brush layer can simplify the process and can alleviate pattern transfer difficulties.

Along with developing a resist/ARC stack that is appropriate for etching and pattern transfer, it is also necessary to control the line width, i.e. critical dimension (or CD), of the chemical pattern as it is crucial to the quality of the assembled structures.[14] A trim etch of the resist, consisting of a controlled lateral etch of the exposed and developed pattern in the photoresist, was used to fine-tune the CD of the photoresist pattern and, therefore, of the chemical pattern as well. As shown in Figs. 3(a) and 3(b), the CD of the resist was trimmed from ~50 to ~15 nm, while the pitch was held constant at 90 nm. PS-*b*-PMMA was then directed to assemble on the chemical pattern, yielding a pattern consisting of parallel lines, effectively tripling the density of the lithographic pattern, as shown in Fig. 3(c). Our earlier work has shown that if the CD of the resist line does not equal ~$L_o/2$, the defect density of the directed assembly will increase.[14]

In addition to CD control, maintaining the minimum topography of the chemical pattern is also very important, which was achieved here by carefully choosing the initial X-PS thickness according to the thickness of the P(S-*r*-MMA) layer. A trim etch with a high ion energy etching condition, which may physically etch the nitride layer, may increase the topography of the chemical pattern and was hence avoided. The O_2 plasma employed in this work for trim etch was an unbiased plasma that had no additional ion energy applied. As a result, it had an excellent selectivity between the X-PS and the native oxide of the silicon nitride, and therefore minimum plasma damage of the nitride film could be expected. Additionally, one should note that the X-PS in the non-photoresist (PR)-covered regions needed to be completely removed during the trim etch so that P(S-*r*-MMA)-OH could be grafted onto these regions in the following process. Given that the etch rate of the X-PS was ~24 nm/min under the trim etch condition, a minimum etch

time of ~15 s was required to remove ~6 nm of X-PS. Compared to the typical trim etch time used in this work, ~60 s, the non-PR-covered region should be free of X-PS.

Another important consideration in the proposed integration scheme was the grafting of the P(S-*r*-MMA)-OH brush layer right before the copolymer assembly. This was done to avoid factors that may alter the apparent wetting behavior of the brush, such as photon damage, possible effects from ex-
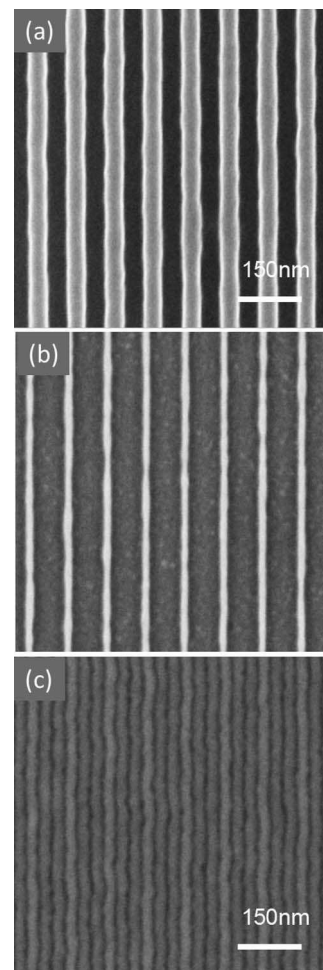

FIG. 3. Top-down SEM images of photoresist (a) before and (b) after trim etch and (c) block copolymer after directed assembly.
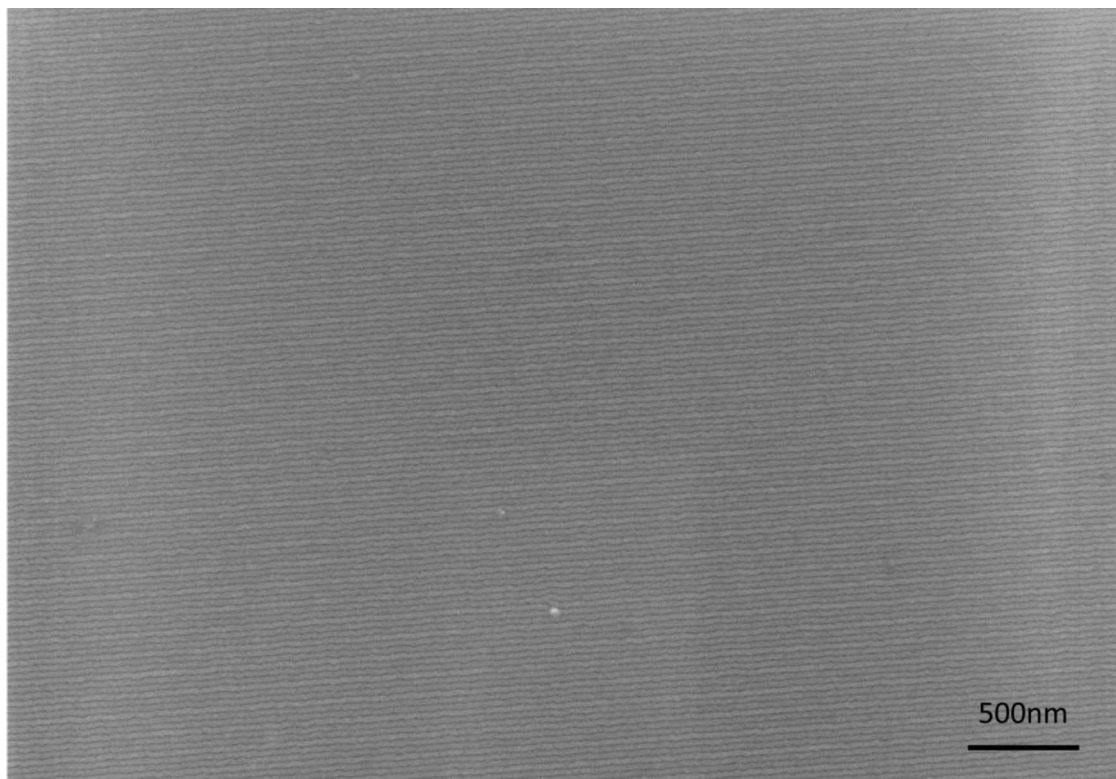
FIG. 4. Top-down SEM image of assembled structures of BCP with a large area of perfection. PMMA has not been removed; thus, the linewidth may be visually inaccurate.

posure to developer, and PR residue. Detcheverry *et al.*[15,16] demonstrated through molecular simulations that the interspatial region between X-PS stripes needs to be either weakly preferential or nonpreferential to both blocks so that a perpendicular morphology of a block copolymer could be obtained. Cheng *et al.*[5] experimentally achieved a perpendicular lamellae-like structure with a nonpreferential random copolymer. In the proposed approach, we intend to preserve the pristine chemistry of the P(S-*r*-MMA)-OH so that one could not only obtain the desired perpendicular morphology but also be able to further correlate the assembly results with the brush composition and acquire a greater understanding of the copolymer multiple patterning process.

Achieving large areas of pattern perfection is necessary for a copolymer multiple patterning process to be considered as a viable enhancement to existing lithographic techniques. An idea of the extent of pattern perfection that could be achieved with copolymer multiple patterning in this work could be observed in Fig. 4, which shows an area of ~3.5 $\times$5 μm^2. (To permit feature recognition, Fig. 4 is only about half the size of the 7×5 μm^2 original image.) Although there were a few defects in the middle, most of the lines cross the entire field without defect. Further studies would be needed to clarify which types of defects were caused by particles or pattern defects and which defects originated from the directed assembly process. In Fig. 4, one of every three PS stripes was brighter than the others because it had an underlying X-PS guiding line. Despite the contrast difference observed in the assembled PS-*b*-PMMA, once the
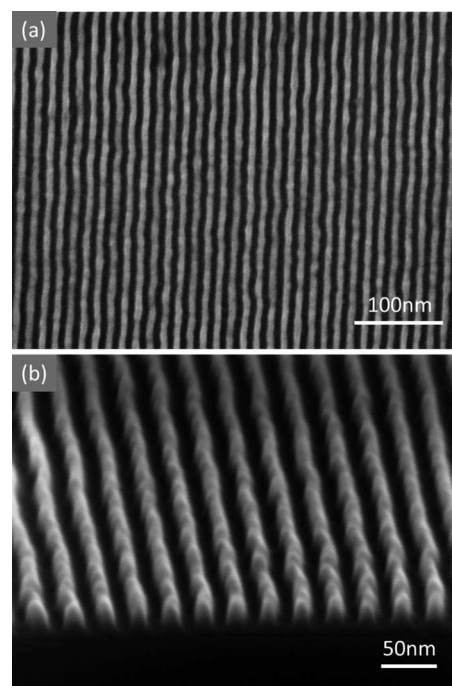

FIG. 5. (a) Top-down SEM image after PMMA removal. (b) Tilted cross-sectional image after pattern transfer.

PMMA domains were removed, the patterns exhibited uniform lines and spacing, as shown in Fig. 5(a).

The assembled BCP film could be used as a Si etch template by selective removal of the PMMA domains, as shown previously.[12,17] The quality of the PS template in this work, after the removal of the PMMA, is shown in Fig. 5(a). We used a plasma etch to transfer the PS pattern into the Si substrate, as shown in Fig. 5(b). Because we only wished to demonstrate the pattern transfer feasibility, the same etching recipe was used for silicon nitride and silicon etching, in which the etching selectivity of nitride-to-PS was not optimized. A better etching profile, LER, and higher aspect ratio could be obtained by using a better etching chemistry and processing condition.[18]

The resolution limit of a single exposure by 193i lithography is ~80 nm pitch.[19] Without using a higher density multiplication factor or multiple cycles of DP techniques, 40 nm pitch features would be the smallest that could be obtained by combining 193i lithography and one DP process. Although we only demonstrated a 30 nm pitch structure, which is already beyond the limit of one cycle of DP, by applying a copolymer with a smaller natural period combined with a properly designed chemical pattern, it may be possible to allow a finer feature size using the exact same process proposed in this work.[4] If a different copolymer system, e.g., PS-*b*-PVP, is required in order to generate features smaller than what PS-*b*-PMMA is capable of, our approach for chemical pattern fabrication will still be feasible using the corresponding random brushes.[20] However, other assembly related issues may arise for different block copolymer systems and have to be further studied. Also, before the proposed method can be implemented, further design for manufacturability studies, e.g., application of the gridded-design rule,[21] may be required.

IV. CONCLUSION

In this article, an integration scheme of block copolymer directed assembly with 193i lithography is presented. We experimentally show that a thin silicon nitride film can be used as the ARC. With such an ARC, it is possible to use directed assembly of a BCP to triple the feature density of a chemical pattern. A high quality of assembly was obtained over a large area, and pattern transfer feasibility was demonstrated. The integration of feature density multiplication via directed assembly of a BCP with 193i lithography provides pattern quality that is comparable with existing DP techniques. Thus, if carefully combined with design for manufacturing, directed assembly could be a promising candidate for extending the use of current 193i lithography tools to higher pattern densities and for lowering the overall patterning cost.

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