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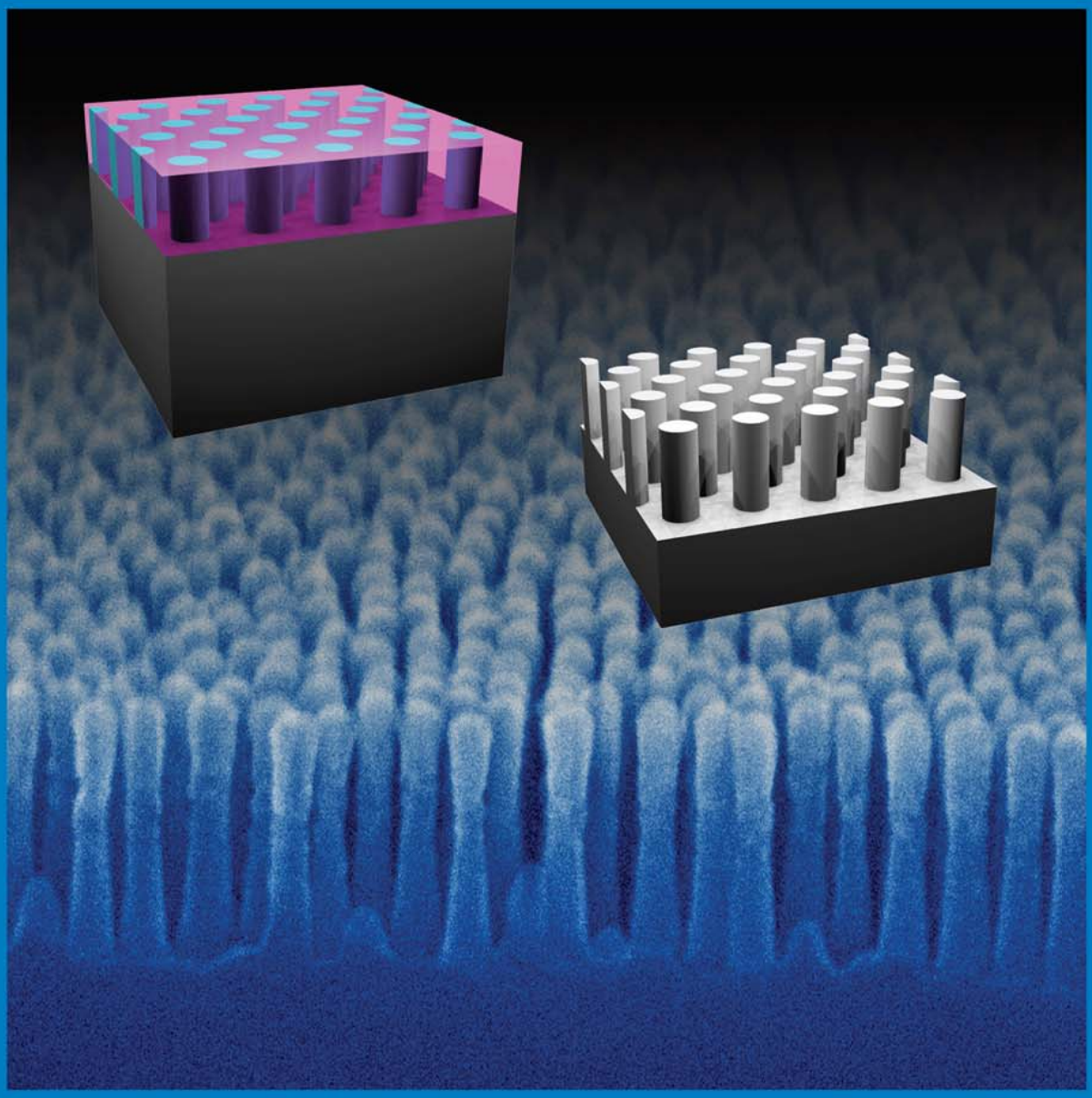

Nanopillar Array in Silicon Fabricated Using Sequential Infiltration Synthesis-Enhanced Block Copolymer Lithography (see page 5A)

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Enhanced Block Copolymer Lithography Using Sequential Infiltration Synthesis

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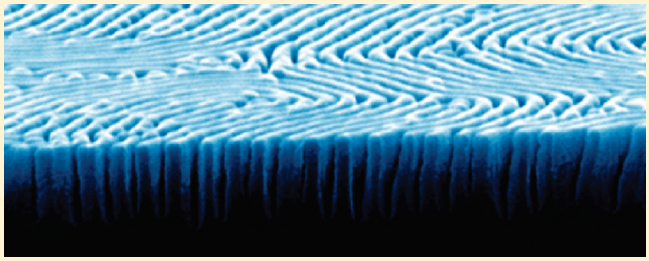
ABSTRACT: Block copolymer lithography is a promising approach to massively parallel, high-resolution, and low-cost patterning, but the inherently low etch resistance of polymers has limited its applicability to date. In this work, this challenge is overcome by dramatically increasing the plasma etch contrast of polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) using spatially localized sequential infiltration synthesis (SIS) of alumina. The PMMA phase of self-assembled PS-*b*-PMMA block copolymer thin films was selectively infiltrated with alumina yielding an inorganic nanostructure mimicking the original block copolymer template that serves directly as a robust etch mask. SIS-modified films are resistant to a variety of plasma etching chemistries enabling the direct patterning of a range of substrates, including silicon, indium tin oxide, and permalloy, without the need for intermediate hard mask layers. This method considerably simplifies the fabrication of nanostructures in technologically relevant materials over large areas with improved transfer fidelity and pushes block copolymer lithography closer to practical use.



INTRODUCTION

Self-assembly of block copolymer (BCP) thin films has been explored extensively as a strategy to make periodic nanostructures.[1−4] Because these nanoscale features can be formed reproducibly and at low-cost, there is tremendous interest in transferring such patterns to functional materials. In particular, BCP films are promising for microelectronics and data storage applications where highly dense and periodic nanoscale patterns are needed over a large area.[5−8] BCP films can self-organize to form nanostructures of various morphologies with tunable length scales. Furthermore, by guiding BCP self-assembly using surface topography, highly regular patterns can be generated over macroscopic area with low defect density.[9,10]

Since BCP films with a single layer of laterally ordered domains have a thickness on the order of the domain size, they are generally too thin for transferring patterns into the underlying substrate using plasma etching. Because carbon-based polymer blocks erode quickly in a plasma, the masking BCP film is completely removed before features with significant depth can be transferred. For example, polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA), one of the most widely studied BCPs (including in lithography experiments), has an overall poor etch resistance, and the etch contrast between the blocks is only about two.[11] As a result, the depth that can be etched is only on the order of the thickness of the film at best, which is tens of nanometers in most cases. Significant effort has been invested in developing BCPs containing etch-resistant blocks such as polystyrene-*block*-polydimethylsiloxane (PS-*b*-PDMS)[12,13] or polystyrene-*block*-poly(ferrocenylsilane) (PS-*b*-PFS),[14−17] but many of these BCPs have poor wetting properties or are difficult to remove after the etching process. The synthesis of these polymers can also be challenging. Furthermore, organometallic blocks (such as PFS) are undesirable for microelectronics manufacturing, a major potential application of BCPs, because the uncontrolled diffusion of metals in a semiconductor can degrade the performance of microelectronic devices.

For the reasons stated above, a BCP that is easy to synthesize, applicable over large areas, and resistant to plasma etching remains elusive. To etch high aspect-ratio structures, a common scheme is to first transfer the BCP pattern to an intermediate hard mask layer that provides greater etch resistance. The insertion of a hard mask layer adds complexity and cost to the fabrication process due to complications from stress and adhesion as well as the risk of damaging the underlying substrate during deposition. The interfacial interaction between the hard mask and the BCP may also change dramatically how the BCP self-assembles. Furthermore, transferring the pattern with high fidelity into the hard mask layer still requires etch contrast between the polymer blocks. Consequently, strong etch contrast between the BCP blocks is highly desired, regardless of the overall pattern transfer scheme.

In this work, we demonstrate that the etch contrast between PS and PMMA blocks can be increased significantly using sequential infiltration synthesis (SIS).[18,19] In this method, Al_2O_3 is grown from gas-phase trimethyl-aluminum (TMA) and water within a thin film of PS-*b*-PMMA using an ALD reactor operating in semistatic mode as previously described.[18] Under these conditions, the precursors diffuse through the entire PS-*b*-PMMA film.

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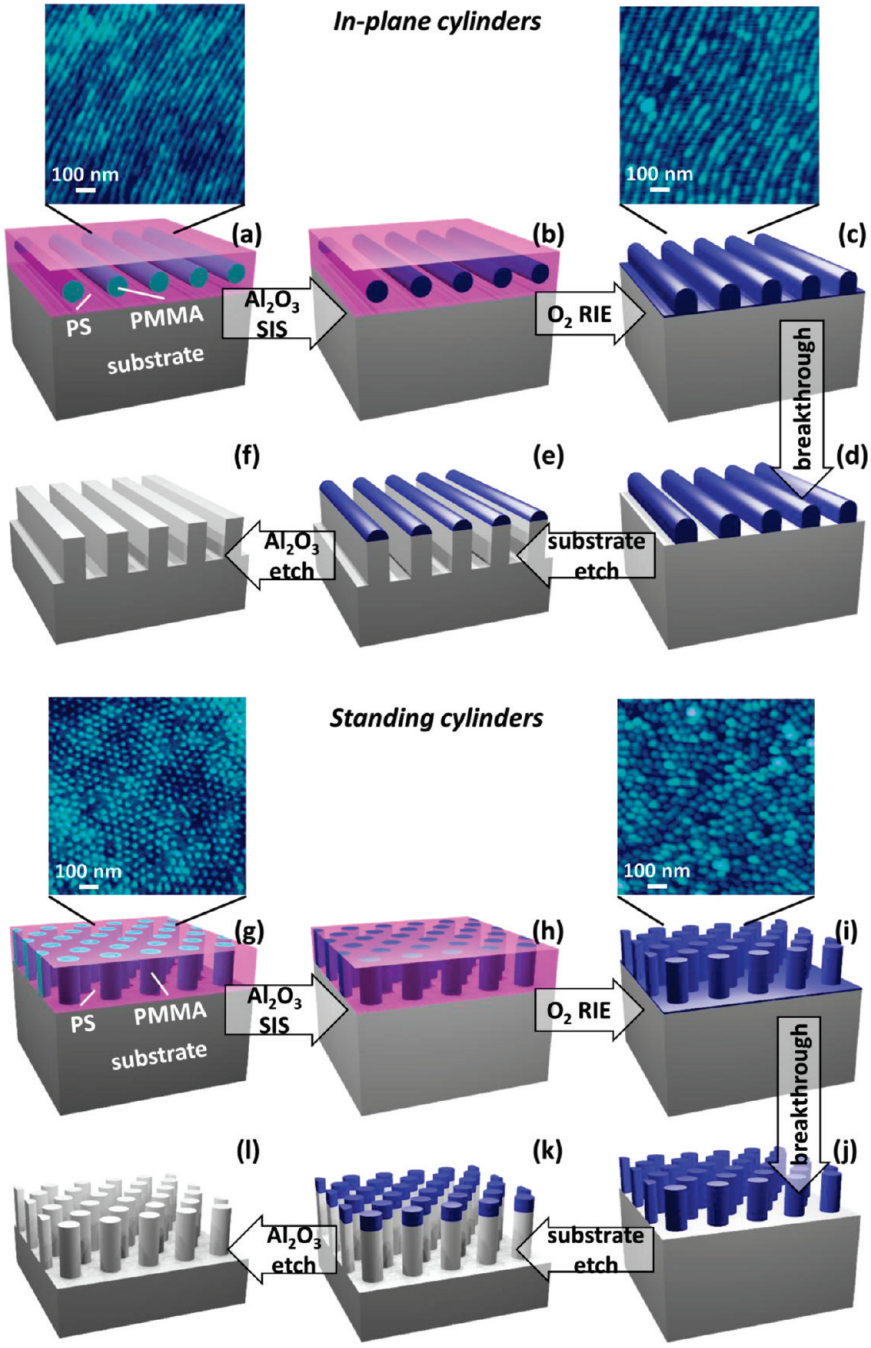

Figure 1. Scheme for pattern transfer using SIS-enhanced block copolymer with in plane (a−f) or out-of-plane (g−l) cylinder orientation. (a,g) Self-assembly of periodic structures on substrate using PS-*b*-PMMA thin film and corresponding AFM images (vertical scale: 4 nm). (b,h) SIS to selectively infiltrate alumina into PMMA domains. (c,i) Oxygen plasma treatment to remove the unreacted polystyrene phase and corresponding AFM images (vertical scale: 20 nm). (d,j) Break-through thin surface alumina layer using BCl_3-based plasma. (e,k) Etch into substrate using appropriate plasma chemistry. (f,l) Removal of mask to reveal nanopatterned substrate.

The Al_2O_3 grows selectively in the PMMA domains due to chemical interactions between the TMA molecules and the carbonyl moieties along the PMMA chains. These chemically bound TMA molecules seed the Al_2O_3 growth in subsequent SIS cycles, which renders the PMMA nanostructures significantly more resistant to plasma etching without affecting the PS domains. We further show that the SIS-modified PMMA domains are resistant to a variety of plasma chemistries. The SIS-modified BCP films enable pattern transfer via plasma etching directly into diverse substrate materials including silicon, indium tin oxide (ITO), and permalloy ($Ni_{0.8}Fe_{0.2}$), without the need for an intermediate hard mask layer. This nanofabrication scheme, which can be equally well applied to various BCP morphologies, is illustrated in Figure 1.

EXPERIMENTAL METHODS

SIS-modified PS-*b*-PMMA thin films were prepared as follows: A thin (∼50 nm) film of PS-*b*-PMMA was spun from

Table 1. Plasma Etch Conditions Used for Various Substrates

substrate	gas flow (sccm)	pressure (mTorr)	RF power (W)	ICP power (W)
silicon	HBr (20), O_2 (1)	14	100	250
ITO	CH_4 (25), H_2 (30), Ar (5)	40	200	0
permalloy	CO (20), Ar (10)	10	150	800
Al_2O_3 breakthrough	Cl_2 (20), BCl_3 (10)	7	100	800

toluene onto a substrate. The average molecular weight was 50 500 for the polystyrene block and 23 000 for the PMMA block. This composition led to self-assembly into cylindrical microdomains with a domain spacing of ∼42 nm, meaning the 50 nm-thick film accommodates a single layer of in-plane cylinders. Regions of the films having smaller film thickness display standing cylinders, as has been reported previously,[14] but a film with a vast majority of standing cylinders is achieved using a pretreatment with a random copolymer of PS-*r*-PMMA to obtain a neutral surface.[20] Ordering of the polymer domains was achieved by thermally annealing in a vacuum for 2 h at 250 °C. Five cycles of SIS reaction were then performed on the BCP film at 130 °C inside a commercial atomic layer deposition chamber (Sundew D200) as follows: The reaction chamber was first evacuated to a base pressure of less than 20 mTorr. Next, trimethyl-aluminum (TMA) was admitted into the reactor, at a pressure of 0.5 Torr, for a time of 80 s. The chamber was then evacuated to less than 20 mTorr to remove excess reactants and byproducts. The chamber was then purged with N_2 at 10 Torr for 30 s. The chamber was then evacuated again to below 20 mTorr. To complete the reaction, water was introduced to the chamber, and the sample was exposed to it for 80 s. Subsequently, the chamber was evacuated and purged by N_2 for 30 s at 10 Torr. The same evacuation−fill−purge−evacuation process was repeated for 5 cycles. Following a brief exposure to oxygen plasma (50 W, 1 min) to remove the unreacted polystyrene phase, the self-assembled BCP pattern was transferred directly into the substrate using an Oxford 100 inductively coupled plasma etcher. Table 1 shows the etch chemistries for each substrate used. The SIS process with other parameters has also been demonstrated to effectively infiltrate PS-*b*-PMMA films.[18]

RESULTS AND DISCUSSION

SIS-modified PMMA domains in the BCP film are resistant to HBr-based plasma, enabling the etching of high aspect-ratio (∼10:1) trenches directly into silicon without the need of any intermediate hard mask. Essentially all previous reports on transferring PS-*b*-PMMA patterns required the utilization of a hard mask.[21−23] SIS modification can be applied to all commonly encountered morphologies in PS-*b*-PMMA thin films, enabling a variety of pattern geometries. Films with SIS-modified PMMA cylinders perpendicular to the substrate (Figure 1g) lead to densely packed, high aspect-ratio pillars (Figure 2a), whereas films with in-plane SIS-modified PMMA cylinders (Figure 1a) enable dense, regular-spaced trenches (Figure 2b). Many potential applications for BCP lithography require substantial lateral domain ordering. In combination with surface topography to guide the self-assembly of the PMMA cylinders,[24,25] periodic aligned structures with high aspect ratio can be easily achieved (Figure 2c). These prepatterned surface channels are ∼150 nm wide, which is approximately 3.5 times the natural domain spacing of the cylindrical domains, hence the observation of three parallel cylinders within each substrate channel. In this scenario, the lateral spacing of the cylindrical domains is similar to that observed on a flat substrate, but by manipulating the ratio of the channel width, it has been shown that the spacing of the cylinders can also be manipulated within a range of about ±10%.[24]

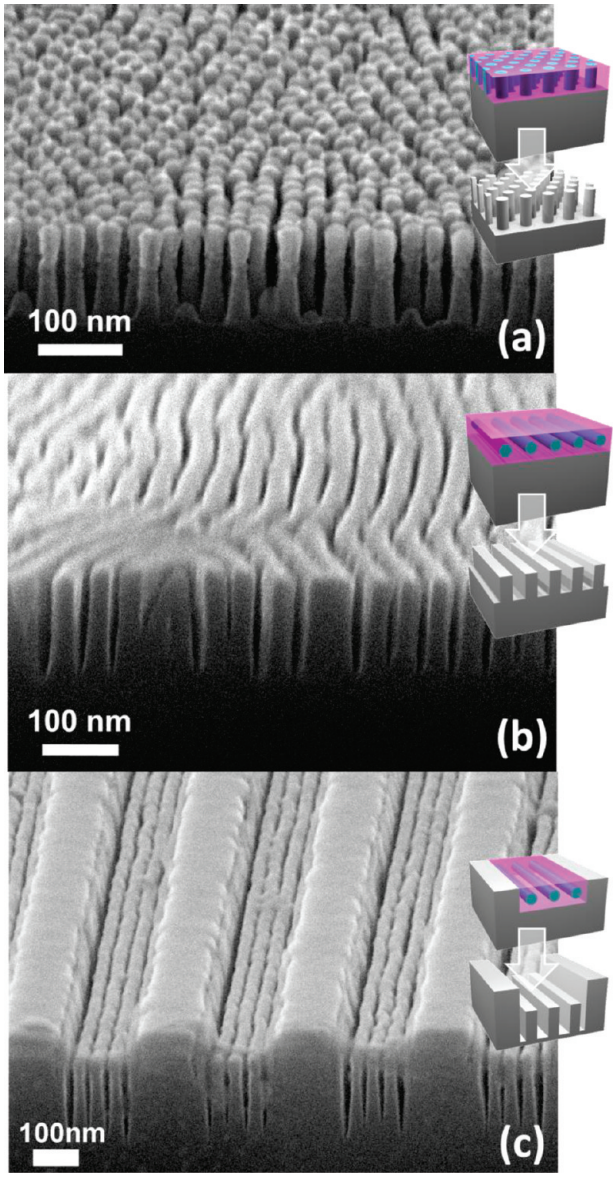

Figure 2. Pattern transfer directly and deeply into silicon using HBr-based plasma, with the SIS-enhanced PS-*b*-PMMA film as etch mask. (a) From standing PMMA cylinders. (b) From in-plane PMMA cylinders. (c) From in-plane PMMA cylinders aligned using graphoepitaxy.

The flexibility of the SIS-enhanced BCP lithography approach can be demonstrated through its application to pattern a broad

variety of substrate materials. SIS-modified PS-*b*-PMMA is also effective, for example, as an etch mask for pattern transfer into indium tin oxide (ITO). Figure 3a and b shows an ITO surface directly patterned using SIS-modified PS-*b*-PMMA. Following pattern transfer, the SIS-modified mask can be selectively removed from ITO using a concentrated aqueous solution of tetramethylammoniumhydroxide (TMAH, 25%). In contrast, an untreated PS-*b*-PMMA film is essentially useless as a mask and does not allow the self-assembled pattern to be transferred. Rather, the polymer film is completely and rapidly removed during plasma etching, and the surface morphology of ITO is unchanged (Figure 3c) relative to the starting surface (Figure 3d).

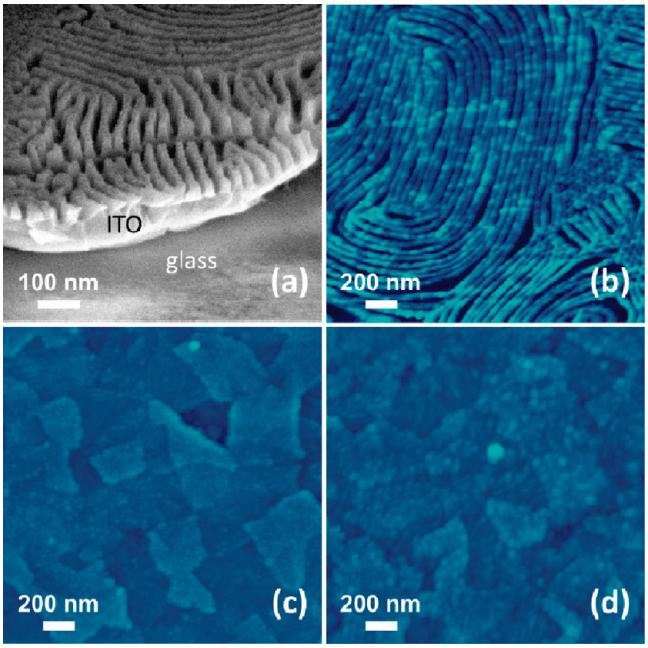

Figure 3. SIS-enhanced BCP pattern transfer into indium tin oxide using plasma etching. (a) Tilted SEM view image of 150 nm-thick ITO film on a glass substrate patterned using SIS-modified BCP film as mask. (b) AFM topography of patterned ITO showing etch depth of ~50 nm. (c) Topography of ITO surface after plasma etching with an untreated BCP film as mask, showing no sign of pattern transfer. (d) Starting ITO surface, prior to any etching. AFM vertical scale: 100 nm.

SIS-modified PS-*b*-PMMA also enables direct pattern transfer into permalloy ($Ni_{0.8}Fe_{0.2}$) using CO-based plasma etching (Figure 4a,b).[26] As in the previous cases, without SIS treatment, the PS-*b*-PMMA layer does not resist well to plasma etching, and no pattern is transferred (Figure 4c). Thickness segregation on this sample leads to regions with single and double layers of in-plane PMMA cylinders, facilitating visualization of the efficacy of the mask. The thicker regions prevent the permalloy from plasma etching, while the thinner, single-layer PMMA cylinders allow permalloy to be etched with nanoscale features. Deeper pattern transfer should be possible using optimized plasma chemistries and also through the use of alternate SIS chemistries such as TiO_2,[18] which has a large selectivity as compared to permalloy.[26]

Thus, the above method of increasing the etch resistance of PS-*b*-PMMA enables the direct transfer of nanoscale patterns into several types of technologically relevant substrates. BCPs are intensively studied as a potential method to enhance photolithography for semiconductor manufacturing. In this application, photoresist or BCP patterns almost always need to be transferred deeply into underlying substrates to enable the fabrication of densely packed electronic devices. However, the lack of etch resistance necessitates the deposition of a hard mask layer under the BCP film, complicating the fabrication process. The enhancement in etch resistance described here circumvents this need and could simplify considerably lithographic schemes employing BCPs. Nanostructured ITO is of technological interest because of its potential application in photovoltaics and optoelectronics. ITO is commonly used as an electrode material in photovoltaic devices based on organic semiconductors. The patterning scheme described here allows one to create ordered periodic structures on the order of exciton diffusion lengths, facilitating the extraction of photogenerated carriers. Thin permalloy films are widely used in magnetic devices and storage media. Because of the generally low etch rate of nickel, intermediate hard masks are almost always required, the use of which may degrade the final transferred pattern. Recently, BCP-based patterning has emerged as a promising route to easily pattern high-density storage media.[27−29] As demonstrated here with the permalloy layer, SIS modification could enhance this technique by transferring the self-assembled pattern directly into a magnetic medium with no intermediate hard mask and minimal loss in pattern quality.

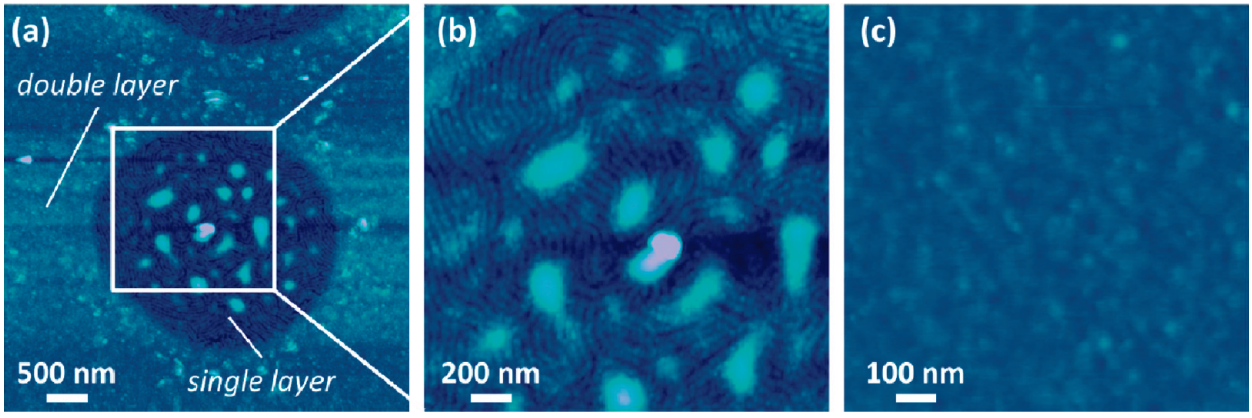

Figure 4. SIS-enhanced BCP pattern transfer into permalloy ($Ni_{0.8}Fe_{0.2}$) using CO-based plasma etching. Vertical scale: 20 nm. (a,b) Etching with SIS-modified block copolymer mask (unpatterned regions were covered by a thicker, double layer of the BCP mask). (c) Etching with an untreated BCP film showing no evidence of pattern transfer.

CONCLUSIONS

In summary, one of the foremost challenges in transitioning BCP lithography from science to technology, low inherent differential etch resistance of polymers, has been addressed. Self-assembled PS-*b*-PMMA thin films, selectively modified using SIS of Al_2O_3, exhibit significantly increased resistance to a variety of plasma etch chemistries. The self-assembled BCP patterns were transferred directly and deeply into silicon, with additional patterning demonstrated for indium tin oxide and permalloy, without the need for an intermediate hard mask. The remarkable increase in etch resistance will simplify nanofabrication schemes involving BCP lithography and ultimately enable the facile generation of high-aspect-ratio nanoscale structures over large area.

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