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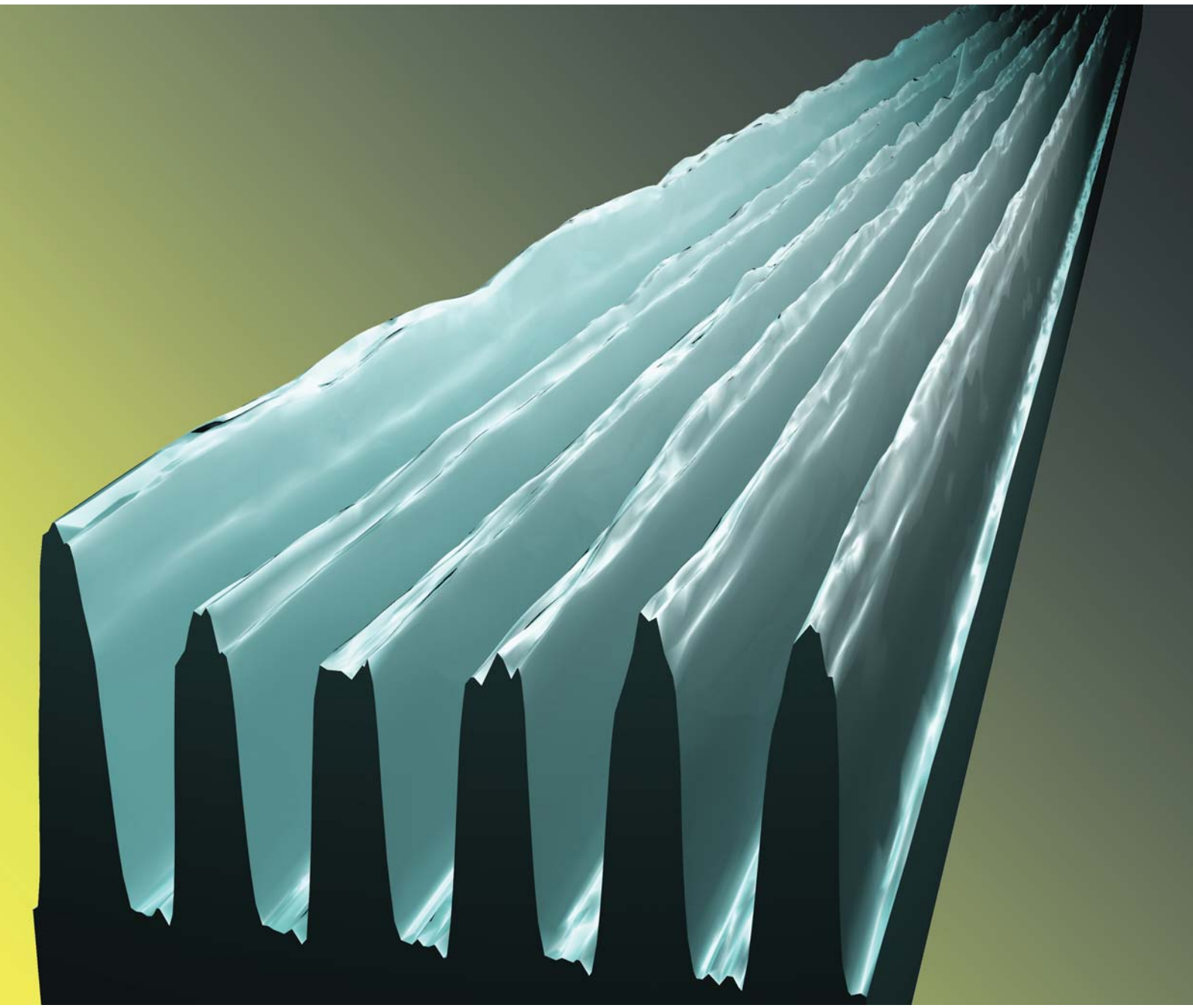

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COMMUNICATION

Enhanced polymeric lithography resists *via* sequential infiltration synthesis†

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Etch resistance of two commonly used lithography resists is increased significantly by sequential infiltration synthesis (SIS). Exposing films to trimethyl-aluminum and water with long dosage times infiltrates the bulk of the film with alumina, which renders them dramatically more resistant to plasma etching with no degradation to the patterns. Enhanced etch resistance eliminates the need for an intermediate hard mask and the concomitant costs and pattern fidelity losses. Moreover, by allowing for thinner resist films, this approach can improve the final pattern resolution.

Introduction

Electron-beam (e-beam) lithography is a successful and prolific method for defining patterns with spatial resolution below the diffraction limit of light. A beam of electrons having energy in the tens of thousands of electron volts traces a pattern on a substrate coated with a resist thin film sensitive to electron exposure. The choice and processing of the resist layer influence greatly the resulting image. In order to be used successfully, the resist material needs to satisfy requirements on resolution, exposure sensitivity, contrast, line-edge roughness, and etch resistance. A fundamental limitation to achieving high spatial resolution is the forward scattering of electrons in the resist. In this phenomenon, the electrons scatter from the resist molecules, resulting in a beam broader at the bottom of the resist layer than at the top. In practice, this effect is minimized by using a thin resist layer and increasing the electron energy.[1] A consequence of practical importance is that the thickness of the resist layer suitable for high-resolution patterning becomes limited.

This limit on the resist thickness is contrary to the requirements of pattern transfer by plasma etching, a process capable of transferring dense patterns with high fidelity. Whereas a thin resist film is desired for achieving high resolution, a thick film is better suited for an etch mask. Since most resist materials erode quickly during plasma etching, the resist pattern cannot be transferred deeply into the substrate using only a thin resist layer as the etch mask. To work around this problem, the resist pattern is usually first transferred to an intermediate hard mask layer that provides greater etch resistance. Inserting a hard mask layer can complicate the fabrication process significantly because this layer needs to have good etch resistance, good adhesion to the underlying substrate, be thermally compatible, and be easily removable after the etching process. It becomes difficult to find a material that satisfies all these criteria. This additional layer can increase image blur, and the transfer process into the hard mask can cause additional feature bias and line-edge roughness. Furthermore, a resist layer with poor etch resistance may not allow a complete pattern transfer into a sufficiently thick hard mask. This has motivated recent work to improve the etch resistance of a high resolution e-beam resist, by hardening the resist after its development through various techniques.[2,3] Silylation of resists has been employed in various schemes as a hardening process, but in each case only the surface is modified, leaving the bulk of the mask unhardened.[4–6] Several nanofabrication schemes have been devised to work around the low etch resistance of polymer films. In one such scheme, metal films are non-conformally deposited on top of the resist film after the resist development and used as an etch mask.[7,8] A previous report discussed selective-area atomic layer deposition (ALD) on photoresists to enhance etch resistance by modifying the surface of the resist layer.[9]

In contrast to previous etch-resistance enhancement schemes where only the surface of the resist film is modified, we present a method to harden the bulk of the resist film. In this work, we show that the etch resistance of two common resist materials, poly(methyl methacrylate) (PMMA) and ZEP520A (a copolymer of chloromethacrylate and methyl styrene from Nippon Zeon Corporation) can be improved by sequential infiltration synthesis (SIS).[10,11] The SIS-modified resists can be used directly as an etch mask for generating deep and high aspect-ratio nanostructures *via* plasma etching, without the need for an intermediate hard mask layer. In this approach, the patterned resist layer is reacted directly with trimethylaluminum (TMA) and water, the same precursors used for depositing Al_2O_3, in an ALD chamber operating in semi-static mode. In contrast to standard ALD processes for dielectric deposition, where the dosage times are on the order of 10–1000 ms, the dosage time for each precursor in SIS is several minutes to ensure diffusion into the bulk of the resist layer and to enable considerable reaction with (carbonyl moieties in) the resist layer. It is well known that TMA can

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† Electronic supplementary information (ESI) available: Step height *vs.* etch time; FTIR data showing changes to C=O vibration upon SIS reaction. See DOI: 10.1039/c1jm12461g

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diffuse deeply into polymer films, with large mass uptake in PMMA.[12] Subsequent reaction of the TMA with H_2O inside the film has also been reported.[10,11,13] Using this resist-hardening method, we endow these polymeric high-resolution positive resists with a large etch resistance typically encountered in inorganic dielectric materials.

Experimental details

Al_2O_3 SIS was performed with alternating exposures to TMA/H_2O (at 85 °C). All precursors were introduced into the reaction chamber as room temperature vapors. After purging for 30 min with 300 sccm N_2 flow at 1 Torr, the chamber was evacuated to less than 20 mTorr before commencing the SIS process. The reaction was performed in a semi-static mode.[14] The first precursor (TMA) was admitted at 5 Torr into the reactor and held for 20 min. The chamber was then evacuated to less than 20 mTorr and purged with N_2 gas with a flow rate of 300 sccm at 1 Torr for a predetermined time. The above procedures were repeated for H_2O, which was also admitted at 5 Torr and held inside the chamber for 500 s to complete the reaction. The same evacuation-fill-purge-evacuation process was repeated 5 times. To verify the absence of gas phase homogeneous reaction, a bare Si substrate with native oxide was used as a control substrate for each run.

Results and discussion

The fabrication sequence is summarized in Fig. 1. Thin films of PMMA (33 nm) or ZEP520A (50 nm) were spun on silicon wafers cleaned in UV ozone. These films were patterned using a JEOL JBX-9300FS e-beam lithography tool. After a brief O_2 plasma removal of resist residues, SIS was performed on the patterned resist films using TMA and H_2O.

The resists modified *via* the SIS process were used directly as an etch mask for pattern transfer into silicon, using an HBr-based recipe (Table 1) in an inductively-coupled plasma etcher (Oxford Plasmalab 100). Both SIS-modified PMMA (SIS-PMMA) and ZEP520A (SIS-ZEP) showed substantially greater etch resistance than the untreated resist films. Based on the time needed to etch through the mask, SIS-PMMA and SIS-ZEP had respective etch rates of ~8 nm min^{-1} and ~20 nm min^{-1} during the silicon main etching step, substantially slower than the etch rate of silicon (~100 nm min^{-1}). Without the SIS treatment, PMMA and ZEP520A were etched at ~300 nm min^{-1} and ~100 nm min^{-1}, respectively. Fig. 2a shows that the improvement in

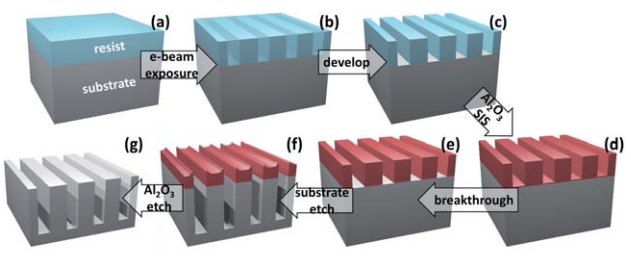

Fig. 1 Fabrication scheme for using SIS-modified resists directly as etch mask. (a) Spin-coat resist on Si substrate. (b,c) Exposure using electron-beam lithography and development. (d) SIS using reaction with tri-methyl-aluminum and water. (e) Al_2O_3 breakthrough plasma etching to reveal substrate. (f) Plasma etching of silicon to desired depth. (g) Etch mask removal using wet chemicals.

etch resistance enabled the fabrication of trenches deeper than 300 nm in silicon without any intermediate hard mask, with a starting PMMA film only 33 nm thick. In comparison, the untreated PMMA film provided little etch resistance and was completely eroded in less than 15 s of plasma etching. Fig. 2c–d show the resulting topography after 2 min of etching, with and without SIS modification to the PMMA resist. With SIS modification, the depth of the trenches can be easily controlled by the duration of the silicon etching step. On the other hand, without SIS modification, the trench depth was limited to only a few nanometres deep. Similarly, SIS-modified ZEP520A also shows greater etch resistance, as shown in Fig. 2b. The starting thickness of the ZEP520A film was 50 nm, larger than PMMA, but it was broken through in less time. This is possibly due to a smaller number of reactive C═O nucleation sites in ZEP520A, which leads to a lower density of etch-resistant Al_2O_3 in the SIS-ZEP film. Nevertheless, SIS treatment still significantly improved the etch resistance of ZEP520A. The untreated ZEP520A was completed removed in less than 30 s of plasma etching, allowing a trench depth of about 25 nm.

In order to initiate etching into the silicon substrate, a brief breakthrough etching step was needed to remove a thin layer of Al_2O_3 on the exposed area (Fig. 1d,e). This layer resulted from ALD on the exposed surface of the silicon substrate. The etch parameters for the breakthrough step are listed in Table 1. Details of the breakthrough step are important to initiate etching into the silicon substrate. Using a recipe designed to break through SiO_2 (Table 1), it was not possible to initiate substrate etching. In this scenario, the measured topographic height only decreased slowly from the initial mask thickness (Fig. S1, ESI†), indicating no etching into the silicon substrate.

It is important to note that the SIS process preserves the quality of the printed pattern—it does not change the line-edge roughness (LER) of the pattern, as shown in Fig. 3. LER is an important metric that describes quantitatively the quality of a lithographic pattern. For an advanced semiconductor device, for example, a large LER can have a negative impact on its manufacturability and reliability.[15,16] Improving the etch resistance of a resist layer has been attempted before by using silylated resists.[17,18] However, this method can increase the line-edge roughness of the printed pattern. Our results indicate that, using SIS, it is possible to combine the high-resolution capability of PMMA and ZEP520A with the etch resistance of Al_2O_3 without degrading the initial printed image.

Our previous work showed that Al_2O_3 does not simply deposit on the surface of a polymer film, but can infiltrate the bulk of a film.[11] Energy dispersive X-ray (EDX) imaging of the cross-section of a thick SIS-PMMA film shows a large, relatively uniform concentration of Al throughout the first 200–300 nm of the film (Fig. 4), under the reaction conditions described in the experimental section. Longer reaction time may allow deeper diffusion of the precursors into the film. Based on the etch selectivity described in previous paragraphs, the process parameters presented here should allow a surprisingly large etch depth of ~2 μm. In addition, we believe that the SIS process chemically changes the resist layer. On PMMA, Fourier transform infrared spectroscopy (FTIR) measurements (Fig. S2, ESI†) clearly indicate a reduction in the absorbance peak corresponding to the C═O bond (1720 cm^{-1}) with SIS treatment. This is consistent with our previous hypothesis that the carbonyl groups selectively react with the TMA molecules.[11,19] In ZEP520A, changes in the FTIR absorption are too small to be detected. The

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Table 1 Etch recipes for the Al_2O_3 breakthrough and Si etching steps. ICP: inductive-coupled plasma

	HBr (sccm)	Cl_2 (sccm)	O_2 (sccm)	ICP power (W)
Al_2O_3 breakthrough	5	20	0	600
SiO_2 breakthrough	0	20	0	600
Si etching	25	0	1	250

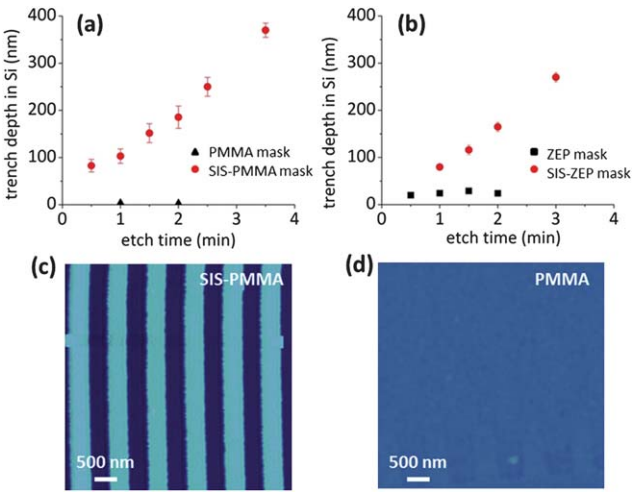

Fig. 2 Effect of SIS treatment on the etch resistance of PMMA and ZEP520A. (a) Depth of trenches etched into silicon with PMMA as the imaging resist and etch mask, with and without SIS. (b) Trench depth with ZEP520A as the resist and etch mask, with and without SIS. (c) AFM topography image of trenches etched into silicon with SIS-PMMA as the mask, after 2 min of silicon etching. (d) AFM topography image, using untreated PMMA as the mask, after 2 min of silicon etching. Vertical scale is 200 nm for both AFM images.

smaller number of C═O reaction sites in the backbone of the ZEP520A polymer relative to PMMA likely lead to fewer reactions with the precursors. This observation is also consistent with the faster etch rate of the SIS-ZEP film. The SIS treatment does not harden ZEP520A as effectively as PMMA, although there is still a dramatic improvement relative to the native resist.

Although the SIS reaction occurs deeply within the resist film, the etch resistance of the mask is particularly good at the resist sidewalls, likely due to the diffusion of the SIS reactants from the sidewall of the resists. As Fig. 1f shows schematically and Fig. 5a–c show experimentally, prolonged plasma etching breaks down the middle of the masked region first, while the edges hold up longer. The middle of the masked region is roughened more significantly as etch time is increased (Fig. 5b–c), whereas the edges remain smooth. The ruggedness of the modified resist line edges implies that under prolonged plasma etching, the SIS modified mask should retain the printed feature sizes, without degrading the line-edge roughness. This quality is desirable in essentially all etching processes.

In addition to having enhanced etch resistance, the SIS-modified resists can be readily removed in a bath of tetra-methyl-ammonium-hydroxide (TMAH) under ambient conditions. TMAH is a commonly used chemical in microelectronics fabrication known to attack aluminum. It is also possible to remove the SIS-modified

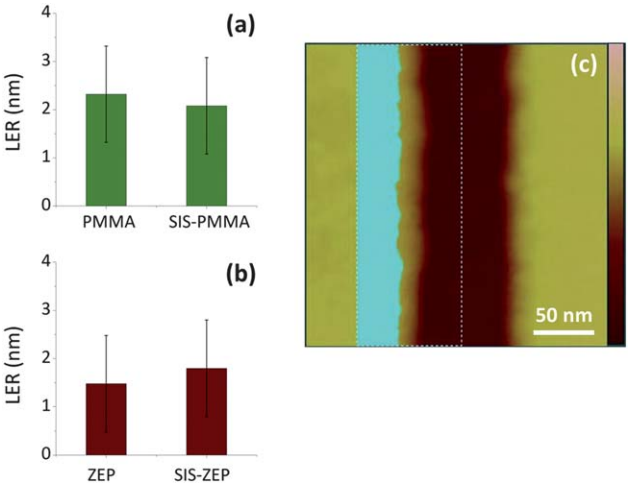

Fig. 3 (a,b) Line-edge roughness (1-sigma) of the resist patterns before and after the SIS treatment. The LER number is calculated from AFM images taken with super sharp tips (AppNano ACTA-SS, radius < 5 nm). (c) Methodology to calculate LER. The line edge is selected as in the figure, and the "Width" function of in the image analysis software (Veeco NanoScope version 7.3) is used. "Highest Peak" is used as reference, and the line edge is defined as the position where the topography height is 10% of the full resist thickness below the reference. This results in the blue region in the figure. A distribution of the x-coordinates of the blue region is calculated, and the standard distribution "X-Sigma" is taken as the LER.

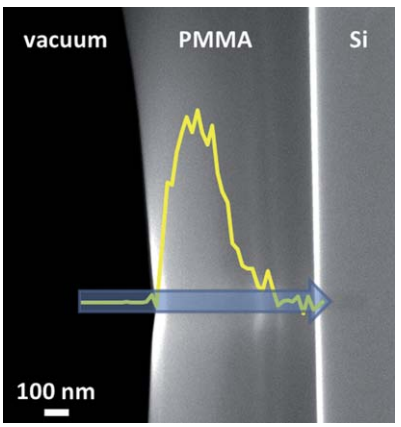

Fig. 4 Energy-dispersive X-ray imaging of the cross-section of a thick SIS-PMMA film. The yellow graph shows the Al K signal as a function of depth along the indicated path.

resists using commercially available wet aluminum etchant, consisting of an aqueous mixture of H_3PO_4, CH_3COOH, and HNO_3. In contrast, organic solvents typically used for resist removal (acetone, remover PG[18]), are not effective in removing the SIS-modified resists. This is further evidence of substantial chemical modification of the resist film.

In a previous report, ALD was performed on resists prior to development to increase their etch resistance.[9] As a result, there was no ALD reaction on the resist sidewall to protect it from lateral erosion during plasma etching. That process also only modified the surface of the resist layer. The present SIS process modifies the bulk

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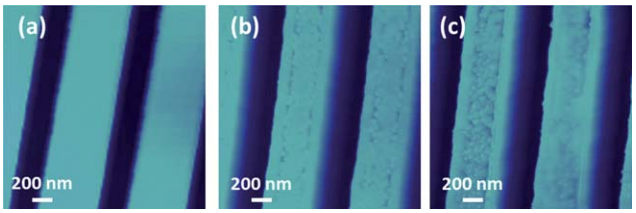

Fig. 5 Mask breakthrough. AFM topography images of silicon trenches fabricated with SIS-PMMA as the etch mask shows that the edges of the resist lines are significantly more rugged than the center of the lines. Vertical scale: 400, 800, 900 nm, respectively. (a) 2.5 min of etching. (b) 4.5 min of etching. (c) 5.5 min of etching.

of the resist layer, and enhances not only the etch resistance of the top side of the resist, but also the sidewalls, thus providing significant transfer fidelity even for very small features. There are several reports of using a patterned resist layer as a diffusion mask for area-selective ALD,[13,20] and using the patterned ALD film as a hard mask. In that approach, the ALD film needs to be lifted off from the polymer. Lift-off usually increases the line-edge roughness. Also, many ALD cycles would be needed to deposit a film sufficiently thick for a hard mask. The present work differs in several important ways: the positive image of the pattern is transferred (as opposed to transferring the negative image with a lifted-off mask), and many fewer cycles of the SIS process are sufficient to modify the bulk of a resist film with no concomitant degradation in the line-edge roughness.

Conclusions

Using sequential infiltration synthesis, the etch resistance of PMMA is improved by a factor of 37 and that of ZEP520A by a factor of 5 compared to the untreated resists. These improvements come at no expense to the line-edge roughness of the printed features. A few cycles of SIS reaction with long dosage time are sufficient to infiltrate the bulk of the resist films with Al_2O_3. This approach for improving the etch resistance of these common e-beam resists enables the transfer of printed patterns deeply into silicon, without the need for an intermediate hard mask. Since the SIS process can occur below the glass transition temperature of the resist polymer, resist reflow can be avoided and the pattern resolution retained. The low thermal budget of SIS also makes it compatible with most microelectronic fabrication processes. Potential problems encountered during hard mask deposition, such as the stress and adhesion of the film, can be circumvented as well. The wide variety of resist/SIS precursor combinations should make this process applicable to a broad range of resist and substrate materials.

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