Etch properties of resists modified by sequential infiltration synthesis

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The etch resistance of electron-beam lithography resists, poly(methyl methacrylate) (PMMA) and ZEP520A, is increased significantly by sequential infiltration synthesis (SIS). This process infiltrates the bulk of the resist film with alumina, rendering it resistant to plasma etching. The enhanced etch resistance eliminates the need for an intermediate hard mask and the associated process costs and pattern fidelity losses. Furthermore, the improvement is realized with no degradation to the line-edge roughness of lithographically defined patterns. The enhancement in etch resistance is especially strong at the edges of the printed lines, owing to diffusion of the SIS precursors from the resist sidewalls. These improvements enable the anisotropic transfer of sub-100 nm patterns deeply into silicon without the need for an intermediate hard mask. © *2011 American Vacuum Society*. [DOI: 10.1116/1.3640758]

I. INTRODUCTION

Common methods for fabricating nanostructures generally employ a very thin polymer resist film as a medium to define a pattern that is subsequently transferred into an underlying substrate. For example, a resist film thin enough to circumvent forward scattering of electrons is needed for electron-beam (e-beam) lithography. In photolithography, the thickness of the photoresist is limited by the depth-of-focus of the lithography tool. In the promising area of block copolymer lithography, regularly ordered nanoscale patterns can be generated over large areas, but the film thickness is limited to about one layer of the polymer domains (10–50 nm), since a film with multiple layers of the polymer domains is not suitable for generating ordered patterns over large areas.

Thin carbon-based polymer films are however, poor etch masks, since they erode quickly during plasma etching. A thick polymer film can withstand plasma etching longer, but it is difficult to print or self-assemble high-resolution patterns in such thick films. A typical work-around involves etching the pattern first into an intermediate hard mask layer with greater etch resistance. The pattern in the hard mask is then transferred into the substrate. Inserting this layer can add significant complexity to the fabrication process because it needs to satisfy requirements on etch selectivity and adhesion to the underlying substrate. The deposition process also needs to be thermally compatible, and the hard mask needs to be removable after the etching process. A material that satisfies all these conditions can be difficult to find. The features transferred into the hard mask can have very different dimensions from the printed image, and additional line-edge roughness can result. Furthermore, an imaging layer with poor etch resistance may not allow pattern transfer into a hard mask thick enough for subsequent pattern transfers.

Many schemes to enhance etch resistance have been reported previously. Several of these etch-enhancement processes are based on resist silylation.[1–4] These processes only modify the surface of the resist film, and there is no modification to the resist sidewalls to protect them from plasma etching. There is also a previous report where atomic layer deposition (ALD) is performed on photoresists to increase their etch resistance.[5] It also only modifies the surface of the resist film. Another scheme uses patterned ALD films as etch mask, via lift-off from a patterned resist layer which serves as a diffusion mask for the precursors.[6,7] The lift-off of the ALD film is not straight-forward since the ALD process covers the resist sidewalls, leading to a rough pattern edge after lift-off. Also, many ALD cycles, at high process temperatures, are needed to deposit a film sufficiently thick for a hard mask. Such post-processing of resists at high temperature is generally incompatible with high-resolution patterning due to reflow of the resist polymer.

In contrast to these methods, which modify only the surface of the resist film, we present a procedure to harden the resist film by infiltrating its bulk with inorganic materials. We show that sequential infiltration synthesis (SIS) addresses the shortcomings of previous etch resistance enhancement methods by modifying the bulk of the resist layer and improving the etch resistance of the sidewalls via deep precursor diffusion. We show that the etch resistance of two e-beam resists, poly(methyl methacrylate) (PMMA) and ZEP520A (a copolymer of chloromethacrylate and methyl styrene from Nippon Zeon Corporation), can be improved by SIS.[8,9] The SIS-modified resist films can be used directly as an etch mask for generating high aspect-ratio nanostructures via plasma etching, without the need for an intermediate hard mask. In this approach, the resist film is infiltrated with Al_2O_3 by alternating exposures to trimethyl-aluminum (TMA) and water in an atomic layer deposition (ALD) chamber. Whereas short precursor exposure times of 10–1000 ms are typically used for Al_2O_3 ALD, much longer exposure times are used for Al_2O_3 SIS to allow the precursors to diffuse into the bulk of the resist layer and to ensure complete chemical reaction with the resist polymer. It is well known that TMA can diffuse deeply into polymer films,[10] with subsequent reaction of

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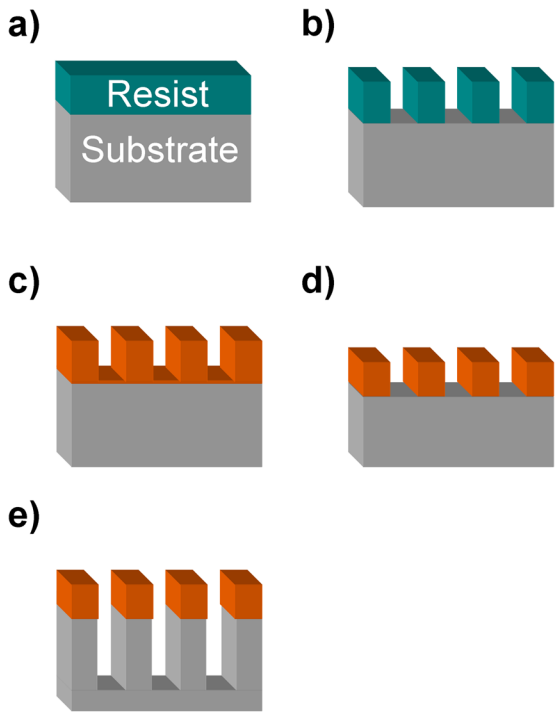

FIG. 1. (Color online) Process sequence for pattern transfer using SIS-modified resists as etch mask. (a) Spin coat substrate with resist. (b) E-beam exposure and development. (c) SIS reaction of resist with Al_2O_3. (d) Breakthrough etch to remove Al_2O_3 deposited on exposed substrate surface. (e) Pattern transfer into substrate.

TMA with H_2O inside the film. The resulting polymer film with deep infiltration of Al_2O_3 possesses a robust resistance characteristic of inorganic dielectric materials.

II. EXPERIMENT

The sequence for pattern transfer using SIS-modified resists is summarized in Fig. 1. Thin films of PMMA or ZEP520A were spun on silicon wafers previously cleaned using UV ozone. The e-beam resists were patterned using a JEOL JBX-9300FS e-beam lithography tool. After resist development, SIS was performed in a Sundew 200 atomic layer deposition chamber, at temperatures between 85 °C and 130 °C and a pressure of 0.6 Torr. Figure 2 summarizes the SIS timing sequence. Each precursor exposure consisted of a series of short pulses yielding total TMA and H_2O exposure times of 40 s. Nitrogen purge times of 60 s were used

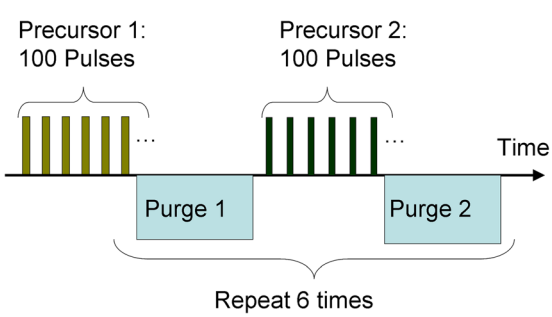

FIG. 2. (Color online) SIS reaction sequence. Pulse time for precursor 1 and 2: 400 ms. Delay between pulses: 400 ms. Purge 1: 60 s. Purge 2: 60 s.

TABLE I. Etch conditions for the Al_2O_3 breakthrough and Si etching steps. ICP: inductive-coupled plasma.

	Gas flow (sccm)	ICP power (W)	RF power (W)
Al_2O_3 Breakthrough	Cl_2 (20), BCl_3 (10)	800	100
Si main etching step	HBr (25), O_2 (1)	250	100

between precursor exposures to ensure out-diffusion and desorption of the unreacted precursors. Whereas the originally reported SIS reaction was performed in semistatic mode,[8,9] this continuous process also enabled deep precursor infiltration. The total exposure time to precursor 1 (TMA) and precursor 2 (H_2O) is 40 s each, while the purge time is 1 min long. Six cycles of the reaction were sufficient to significantly increase the etch resistance.

III. RESULTS AND DISCUSSION

The resists films modified via SIS were used directly as etch masks for plasma etching of silicon. An etch recipe based on HBr was used (Table I), in an inductively coupled plasma etcher (Oxford Plasmalab 100). In order to initiate etching into the silicon substrate, a brief Al_2O_3 breakthrough etching step was necessary to remove the thin layer of Al_2O_3 deposited on the exposed area. The etch parameters for the breakthrough step are listed in Table I.

The SIS-modified e-beam resists showed substantially greater etch resistance than the untreated resists, with the SIS-modified films allowing pattern transfer into silicon. The feature depth was controllable by the etching time [Fig. 3(a) and 3(b)]. Based on the time needed to etch through the mask, SIS-modified PMMA and ZEP had, respectively, an etch rate of ~8 nm/min and ~20 nm/min during the silicon main etching step, substantially slower than the etch rate of silicon (~100 nm/min). This represents a 37-fold and five-fold improvement in the etch resistance over untreated PMMA and ZEP, respectively. The increase in etch resistance of the mask enabled high aspect-ratio trenches deeper than 300 nm, with a 50 nm width, to be easily etched in silicon without an intermediate hard mask (Fig. 4), using a

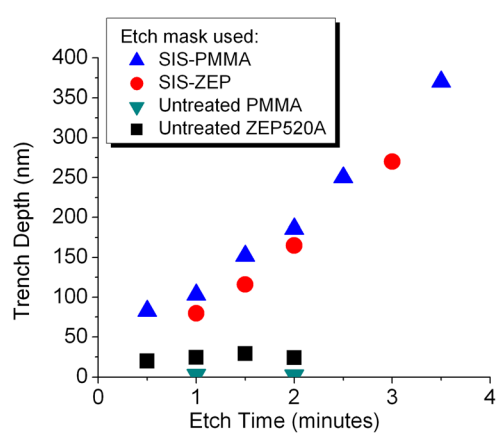

FIG. 3. (Color online) Trench depth in silicon as a function of etch time for resist masks with and without SIS treatment.

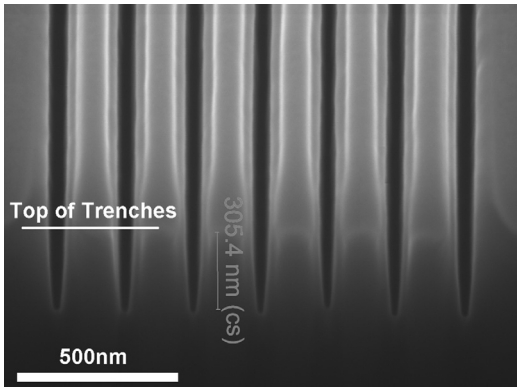

FIG. 4. 50 nm wide, high aspect-ratio trenches directly etched in Si using only SIS-PMMA as mask.

starting PMMA resist only 50 nm thick. Untreated PMMA film provided little etch resistance and no pattern transfer was possible. While the untreated ZEP resist had a higher intrinsic etch resistance than untreated PMMA, SIS-modification caused a greater improvement in PMMA, presumably due to deeper precursor diffusion, and a greater number of C=O nucleation sites. Figures 5(a) and 5(b) show spatially resolved energy dispersive X-ray images of PMMA and ZEP films after the SIS treatment. The larger aluminum signal in the PMMA film indicates that TMA and water diffuse through a much greater distance in PMMA, leading to greater enhancement in etch resistance.

In addition to etch-resistance enhancement, the SIS process preserves the quality of the printed pattern. The line-edge roughness (LER) does not change significantly, nor is there any significant swelling in the printed patterns. Table II lists the LER of PMMA and ZEP lines before and after the SIS treatment. Since the SIS process occurs equally well on surfaces of all orientation, roughness analysis of the AFM topography of the top surface of resist films also lead to the same conclusion (Table II). Previous methods of resist hardening using resist silylation increase the line-edge roughness of the printed pattern, due to low silylation contrast and the dependence of the polymer glass transition temperature on silylation.[1] 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.

TABLE II. Line-edge roughness (3σ) and surface roughness (1σ) of 70nm resist lines before and after SIS.

	LER (before SIS) (+/− 3 nm)	LER (after SIS) (+/− 3 nm)	Surface roughness before SIS (nm)	Surface roughness after SIS (nm)
PMMA	7	6.2	0.29	0.52
ZEP520A	4.4	5.4	0.75	1.2

Although the SIS reaction occurs deeply within the resist film, the etch resistance is particularly improved at the resist sidewalls, due to additional diffusion of the SIS precursors from there. This is particularly pronounced for PMMA treated by SIS at a lower temperature, where the enhancement occurs mostly at the edges of the pattern, leading to "spacers" after a relatively short etch time [Fig. 6(a)] of 2 min. The lowered temperature decreases precursor reactivity and diffusivity in the polymer films, leaving the bulk of the resist intact. However, the same SIS process performed at 95 °C enhances the etch resistance of the PMMA film more uniformly. The resulting mask, with a starting PMMA film 50 nm in thickness, is

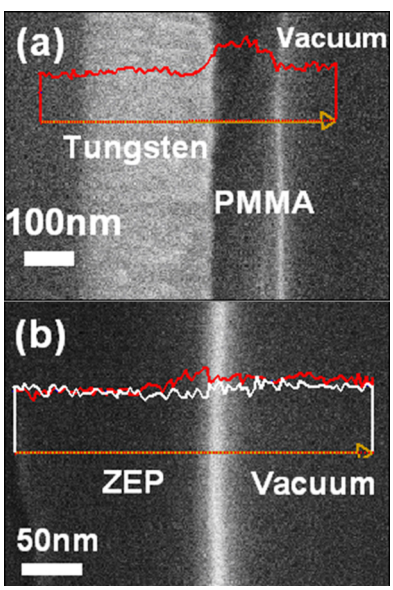

FIG. 5. (Color online) EDX linescan. The films are spun on tungsten-coated silicon. (a) cross-section of SIS-PMMA. Curve indicates aluminum signal along the arrow. (b) SIS-ZEP. Top curve (red): aluminum signal, Bottom curve (white): tungsten signal in the ZEP film. SIS process temperature: 130 °C.

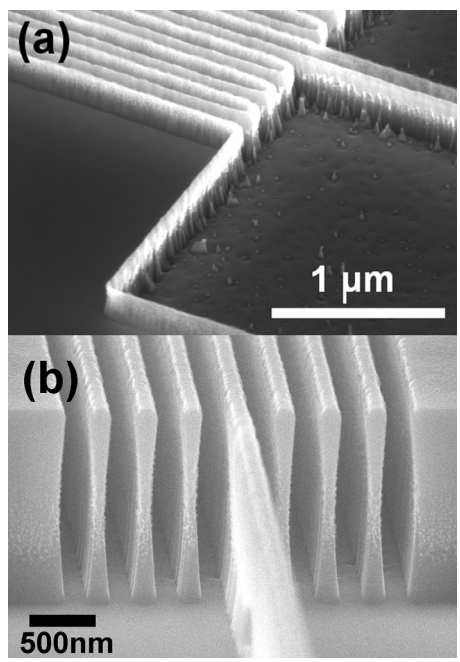

FIG. 6. (a) Result of HBr-plasma etching using SIS-PMMA processed at 85 °C, showing the formation of "spacers." (b) Etch result using PMMA modified in a 95 °C SIS process.

etch-resistant over a longer time (10 min), resulting in 1500 nm-deep trenches in silicon [Fig. 6(b)].

Following the etching process, the SIS-modified resists can be easily stripped in an aqueous solution of tetra-methyl-ammonium-hydroxide (TMAH) under ambient conditions. The SIS-modified resists are also removable 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 stripping are not effective in removing the SIS-modified resists. This is further evidence of substantial chemical modification of the resist film.

IV. SUMMARY AND 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. These improvements are realized with no degradation to the line-edge roughness of the printed features. A few cycles of SIS reaction with long precursor exposure times are sufficient to infiltrate the bulk of the resist films with Al_2O_3. This approach for improving etch resistance enables the transfer of sub-100 nm patterns deeply into silicon, without the need for an intermediate hard mask. The low thermal budget of SIS also makes it compatible with many materials and processes. The low temperature of the SIS (occurring below the glass transition temperature of PMMA), as well as its ability to enhance etch resistance of the resist sidewalls, enables this technique to be applicable to very small patterns where preventing resist reflow and reducing sidewall roughness present significant challenges. 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 polymer/SIS precursor/plasma combinations should make this process applicable to a broad range of mask and substrate materials.

ACKNOWLEDGMENTS

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[1]M. H. Somervell, D. S. Fryer, B. Osborn, K. Patterson, J. Byers, and C. G. Willson, J. Vac. Sci. Technol. B **18**, 2551 (2000).
[2]F. Coopmans and B. Roland, Solid State Technol. **30**, 93 (1987).
[3]E. K. Pavelchek, J. F. Bohland, J. W. Thackeray, G. W. Orsula, S. K. Jones, B. W. Dudley, S. M. Bobbio, and P. W. Freeman, J. Vac. Sci. Technol. B **8**, 1497 (1990).
[4]S. Tedesco, C. Pierrat, F. Vinet, B. Florin, M. Lerme, and J. C. Guibert, Proc. SPIE Int. Soc. Opt. Eng. **1263**, 282 (1990).
[5]A. Sinha, D. W. Hess, and C. L. Henderson, Electrochem. Solid State Lett. **9**, G330 (2006).
[6]E. Farm, M. Kemell, M. Ritala, and M. Leskela, J. Phys. Chem. C **112**, 15791 (2008).
[7]G. Gay, T. Baron, C. Agraffeil, B. Salhi, T. Chevolleau, G. Cunge, H. Grampeix, J. H. Tortai, F. Martin, E. Jalaguier, and B. De Salvo, Nanotechnology **21**, 7 (2010).
[8]Q. Peng, Y. C. Tseng, S. B. Darling, and J. W. Elam, Adv. Mater. **22**, 5129 (2010).
[9]Q. Peng, Y. C. Tseng, S. B. Darling, and J. W. Elam, ACS Nano **5**, 4600 (2011).
[10]C. A. Wilson, R. K. Grubbs, and S. M. George, Chem. Mater. **17**, 5625 (2005).