Nanopatterning with 248 nm photolithography by photostabilizing bilayer photoresists

F.-Y. Tsai[a] and S.-J. Jhuo
Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

J.-T. Lee
Headway Technologies, 678 South Hillview Drive, Milpitas, California 95035

(Received 13 November 2006; accepted 8 February 2007; published 14 March 2007)

The authors demonstrated patterning of 35 nm isolated lines with 248 nm photolithography by photostabilizing a bilayer photoresist structure with a postdevelopment UV exposure. Overcoming the limitations of the conventional single-layer resist structure, the bilayer structure allowed the resist lines to drastically shrink in dimensions by ~70% upon photostabilization, while maintaining their critical attributes including sidewall profile, dry etch resistance, and ability to be stripped, and eliminating the need for high-temperature baking during the process. Comparing two types of photoresists, environmentally stable chemically amplified positive (ESCAP) and acetal, as the top layer in the bilayer structure, the ESCAP-type resist's shrinkage was ~67% that of the acetal-type resist, as a result of its lower free-volume reduction and extent of cross-linking. ^{13}C solid-state nuclear magnetic resonance spectra indicated that the photostabilized resists were cross-linked through bonding between the polymer backbones and between the backbones and the phenol side groups. The applicability of this photostabilization technique to device processing was confirmed with the fabrication of a ~35 nm insulator-metal-insulator junction, a structure similar to that of a typical giant magnetoresistive reader. Their technique may be readily extendable to other applications requiring nanopatterning. © *2007 American Vacuum Society.*
[DOI: 10.1116/1.2713404]

I. INTRODUCTION

With the advent of nanotechnologies, techniques capable of patterning nanometer-sized features in a commercially viable scale have become a subject of intensive research and development. Specifically, much effort has been devoted to extending the capability of photolithography, the predominant industrial patterning technique, to meet the needs for nanopatterning. Photolithography using short exposure wavelengths, e.g., 193 and 157 nm, has been demonstrated to allow patterning of sub-50-nm feature sizes, but its implementation is still limited, as it requires expensive equipments and uses resist chemistry that is not fully mature. A more practical solution has been to improve upon older-generation (i.e., longer wavelength) photolithography, e.g., 248 nm, by incorporating auxiliary techniques such as mask resolution enhancement and immersion lithography. These auxiliary resolution-enhancing techniques, although effective, add significant cost and complexity to the patterning process. Techniques that enhance resolution at minimum cost and process complexity are therefore highly desirable.

Previous studies have established that chemically amplified (CA) photoresists shrink when exposed to ultraviolet (UV) light at elevated temperatures in a process commonly referred to as photostabilization or UV hardening.[1–3] The shrinkage is known to occur mainly via the following mechanism: (1) UV activates the photoactive compound (PAC), which causes the protection groups to cleave from the polymer backbone of the resist; (2) at elevated temperatures, the detached protection groups escape the resist through permeation, reducing the volume; and (3) UV cross-links the resist to further densify it.[1–5] Eisele and Mohondro demonstrated the potential of this process as a resolution-enhancing technique by showing that when isolated lines of CA photoresists were simultaneously exposed to UV and heated at 230 °C, the width of the lines decreased by ~25%.[6] Employing this technique, Pollentier *et al.* reduced the width, from 100 to 75–80 nm, of isolated CA resist lines prepared with 248 nm photolithography, and then used the shrunk resist lines to successfully fabricate 50 nm gates.[7] This technique presents great promise as a low-cost, easy-to-implement method of nanopatterning, as it requires equipments and procedure that are already in common use.

Despite the promise of the photostabilization technique for nanopatterning, there are a few issues that may limit its implementation, including the following: (1) resist features shrink against their adhesion to the substrate, which causes severely slanted sidewall profile (or footing) and limits the extent of shrinkage; this problem may be partially alleviated by heating the resist at >200 °C, which, however, increases process complexity and decreases process flexibility; (2) the UV-exposed resist, being cross-linked, is insoluble in stripping solutions and therefore is incompatible with additive processes such as lift-off; (3) the resist's shrinkage is accompanied by thickness reduction, which lessens the resist's effectiveness as an etch mask.[6–8]

To address these issues of practicality, we propose a bilayer resist structure, where the top layer is a UV-shrinkable

[a]Electronic mail: ftsai@ntu.edu.tw

CA resist, and the bottom layer a nonshrinkable, non-cross-linkable resist. The bottom layer is to form an undercut to free a large portion of the top layer from adhesion, so that the top layer can freely contract without changing its sidewall profile. The need for heating the resist during shrinking is therefore eliminated. The non-cross-linkable bottom layer is also to allow the bilayer resist to remain strippable and to reinforce the etch resistance of the shrunk top layer. We studied the behaviors of UV-induced shrinkage of two types of 248 nm CA resists in both the bilayer and single-layer configurations. We examined the mechanism of the UV-induced cross-linking using solid-state nuclear magnetic resonance (NMR) spectrometry. The applicability of our bilayer method to device processing was verified with the fabrication of a ~35 nm insulator-metal-insulator junction (similar to the structure of a typical giant magnetoresistive reader) using a lift-off process.

II. EXPERIMENTAL SECTION

The isolated bilayer resist lines were prepared as follows: (1) 70 nm of polymethylglutarimide (PMGI) (Shipley) was spin coated onto an AlTiC substrate coated with a sputtered NiFe film; (2) 0.35 μm of a positive-tone environmentally stable chemically positive (ESCAP)-type resist (Shipley UV210) or a positive-tone acetal-type resist (Shinetsu I801) was spin coated onto the PMGI film; (3) the bilayer resist was exposed in an ASML PAS5500 KrF (248 nm) step-and-scan system (with dipole illumination, numerical aperture NA=0.74, and k_1=0.36) through binary reticles with optical proximity corrections; (4) the resist was developed in a developer (Shipley LDD26W), where the PMGI dissolved in the unexposed area to create an undercut of 0.3–0.5 μm into the edge of the top layer. The single-layer resist lines were prepared identically, but with the omission of the PMGI layer. A detailed description of the resist-processing procedure can be found elsewhere.[9] The resist pattern used in this study consisted of two large pads connected with a narrow line (<0.3 μm), as depicted in Fig. 1; the line in the bilayer structure became freestanding after the development removed the PMGI bottom layer. The developing time may also be shortened to retain a desired amount of PMGI under the line as an additional structural support and etch protection. For the photostabilization/shrinking process, the developed resists were flood exposed in a Fusion F300S UV system with wavelengths spanning 200–400 nm and intensity of 158.5 mJ/cm^2 min. The resists were not deliberately heated, but were circumstantially heated by the UV exposure to ~80 °C (for ~3–5 min). The atmosphere of the photostabilization process was not controlled.

The resist lines were observed and measured with an Applied Materials critical dimension scanning electron microscopy (SEM); their cross sections were observed with a Micrion focused ion beam system. Solid-state ^{13}C NMR spectra were collected using a Varian Infinity$^+$ 400 MHz spectrometer with the following conditions: rotor diameter =4 mm, rotor speed=12 kHz, proton $\pi/2$ pulse=3.3 μs, contact time=1.5 ms, spin rate=12 kHz, and recycle delay=4 s. The NMR samples were prepared as follows: (1) for the "before photostabilization" spectra, the acetal resist was flood exposed with 30 mJ/cm^2 of 248 nm light and then baked at 120 °C for 30 min to remove the PAC and protection groups; the resulted resist showed identical spectrum to pure poly(hydroxystyrene); (2) for the "after photostabilization" spectra, the resist from (1) was exposed to 3125 mJ/cm^2 of the broadband UV and then washed in acetone to collect its insoluble cross-linked product. The assignment of the spectral peaks was done by comparing the solid-state spectra to solution spectra collected from poly(hydroxystyrene) dissolved in acetone.

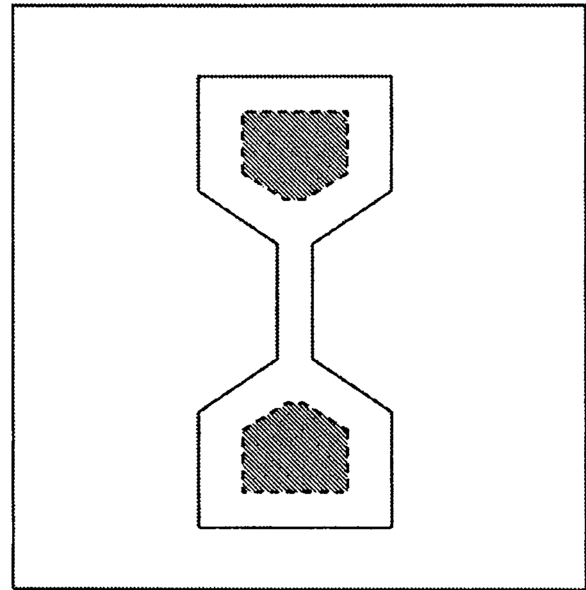

FIG. 1. Schematic illustration of the bilayer resist pattern used in this study. The dumbbell-shaped pattern is the outline of the top layer. The two shaded areas are the remaining bottom layer.

III. RESULTS AND DISCUSSIONS

The bilayer resist lines showed greater linewidth reduction upon photostabilization than the single-layer resist lines, as compared in Fig. 2. The width of the bilayer resist lines was reduced by ~60% upon ~3000 mJ/cm^2 of UV exposure, as opposed to ~25% for the single-layer lines, which agrees with previous results with single-layer resists.[6,7] The maximum achievable mass loss of the acetal and ESCAP resists was estimated to be ~25% and ~30%, respectively, assuming complete loss of the protection groups. This is consistent with the observed linewidth reduction of the single-layer resist but does not account for the ~60% reduction of the bilayer resists. The discrepancy between the estimated mass loss and observed linewidth loss of the bilayer resists may be explained in terms of the adhesion between the resist and the substrate. The bilayer resist lines were prepared with the top layer freestanding above the substrate (forming a bridgelike structure), as illustrated in Fig. 1, which eliminated the adhesion-imposed constraint to the linewidth-defining top layer. Therefore, the bridge section of the lines shrank due not only to mass loss but also to the tension

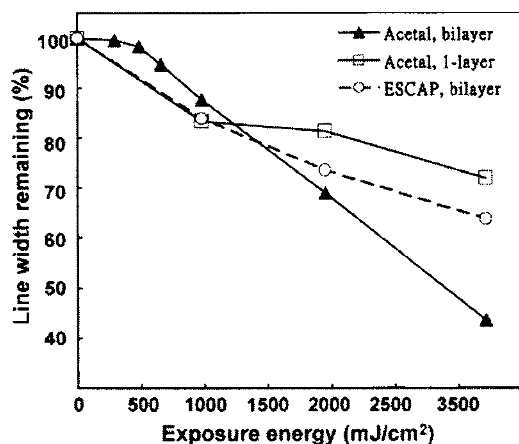

FIG. 2. Linewidth (in percentage of the initial value) as a function of UV exposure energy during the photostabilization process. The initial linewidth was 150 nm for the acetal bilayer lines and 180 nm for both the acetal single-layer lines and the ESCAP bilayer lines.

created by the retreating bridge ends, thereby showing greater linewidth reduction than was predicted based on mass loss.

The benefit of having the freestanding top layer in the bilayer resist lines was also manifested by the lines' straight sidewall profiles after the UV-induced shrinkage, as compared in Fig. 3 with the single-layer resist lines, whose sidewalls were significantly slanted with large foot formed (as indicated by the broadened bright bands at the line's two edges), as was observed in previous studies.[6,7] The cross-section micrographs [Figs. 3(e) and 3(f)] of the UV-exposed bilayer resist lines confirm their straight sidewalls and the absence of foot.

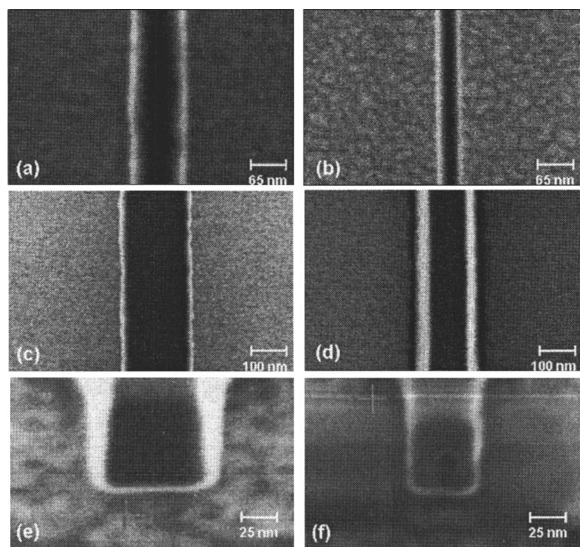

FIG. 3. Top-view SEM micrographs of (a) bilayer resist line, before photostabilization, (b) bilayer resist line, after photostabilization, (c) single-layer resist line, before photostabilization, and (d) single-layer resist line, after photostabilization. Cross-sectional micrographs of the resist lines in (a) and (b) are shown in (e) and (f), respectively.

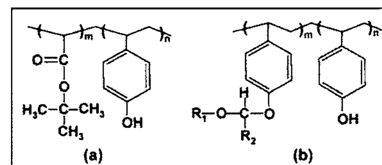

FIG. 4. General structures of (a) the ESCAP-type CA photoresist and (b) the acetal-type CA photoresist.

With the same bilayer structure (resist on top of PMGI, with the resist line freestanding), our acetal-type resist showed considerably more shrinkage upon UV exposure than our ESCAP-type resist, as shown in Fig. 2. The ESCAP-type resist lines had a maximum linewidth reduction at ~40%, compared with the acetal-type resist's ~60% under the same UV dose. This difference is consistent with previous results on the change in thickness of CA resists during photostabilization, which showed that acetal-type resists lost more thickness than ESCAP-type resists.[2] This may be explained in terms of the structural difference between these two types of resists (Fig. 4): the ESCAP-type resist is a copolymer of poly(*t*-butyl acrylate) (PBA) and poly(hydroxystyrene) (PHS), while the acetal-type resist is of PHS and alkylalkoxy PHS, which upon photostabilization is deprotected to become a homopolymer of PHS.[10] The PBA moieties do not cross-link upon photostabilization, while the PHS moieties cross-link readily.[11] Therefore, the acetal-type resist, being a PHS homopolymer upon photostabilization, underwent more cross-linking-induced densification than the PBA-containing ESCAP-type resist.

Solid-state ^{13}C NMR spectra of UV-exposed PHS in Fig. 5 indicate that cross-linking of the PHS moieties occurred through linkages between (1) the polymer backbone and the phenol side group and (2) two polymer backbones. Before the UV exposure, the PHS moieties contained six types of carbon atoms (designated as C_A, C_B, C_C, C_D, C_E, and C_F) and therefore produced six peaks in the spectrum. Four new peaks (designated as P_1, P_2, P_3, and P_4, from high δ to low δ) appeared after the UV exposure, all of which are in the range of alkyl carbons, indicating the formation of new intermolecular bonds at the backbone (C_E or C_F). The two high-δ

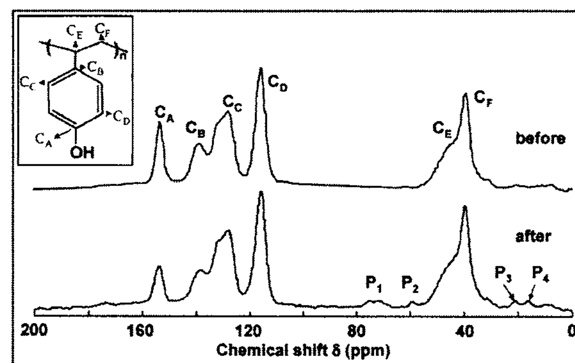

FIG. 5. ^{13}C solid-state NMR spectra of PHS before and after photostabilization. The inset shows the structure of PHS.

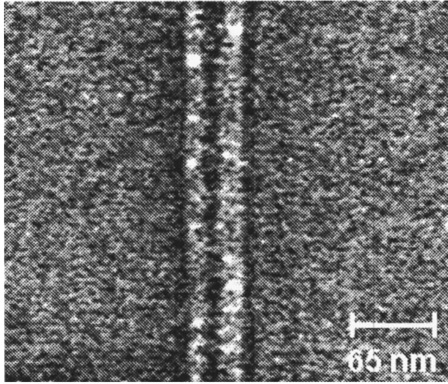

FIG. 6. Top-view SEM micrograph of the insulator-metal-insulator junction prepared with the UV-shrunk bilayer resist line.

peaks, P_1 and P_2, may be attributed to an intermolecular C_E-O-C_A bond and C_F-O-C_A bond, respectively, while the two low-δ peaks, P_3 and P_4, may be attributed to an intermolecular C_E-C_E and C_E-C_F bond, respectively.

Both the ESCAP and the acetal resists became insoluble in the stripping solution (80 °C N-methyl-2-pyrrolidone (NMP) upon UV exposure, as they were cross-linked, making their stripping difficult in the single-layer configuration. This difficulty was bypassed with the bilayer structure, where the PMGI bottom layer remained soluble throughout the UV exposure, thereby serving as a release agent in the stripping process.

The applicability of the UV-shrunk bilayer resist lines to device processing was confirmed by the fabrication of an insulator-metal-insulator junction, whose top-view SEM micrograph is shown in Fig. 6. Bilayer resist lines (with the acetal resist) were shrunk from 105 to 35 nm by the photostabilization process before undergoing the subsequent patterning process, which consisted of ion beam milling to remove ~800 Å of a metal film, ion beam deposition to deposit ~900 Å of Al_2O_3, and lift-off. The resist lines, despite their reduced thickness (Fig. 3, insets) after the UV process, were still adequate to withstand the milling and lift-off steps, producing a junction width (L) of ~35 nm, roughly equal to their linewidth. The lift-off was complete, as is evident from the smooth line edge in Fig. 6, confirming the effectiveness of the PMGI bottom layer as a release agent during stripping.

IV. CONCLUSIONS

We studied the photostabilization-induced linewidth reduction of two types of 248 nm photoresists, ESCAP and acetal, in a bilayer configuration, where one of the photoresists overhung above a PMGI bottom layer. Contrasted with a single-layer structure (i.e., a resist without the PMGI layer), the bilayer resist lines showed ~140% more width reduction, retained their sidewall profiles, were readily strippable and required no high-temperature baking during the process. With the same bilayer structure, the ESCAP resist shrunk less than the acetal resist, as its PBA moieties lowered the extent of cross-linking and the reduction in free volume. The cross-linking accompanying photostabilization was found to occur through bonding between the resist backbones and the phenol side groups and between two backbones. An insulator-metal-insulator junction ~35 nm in width was fabricated using the photostabilized bilayer resist lines, demonstrating the applicability of our technique to device processing.

ACKNOWLEDGMENT

This work was supported in part by the Taiwan National Science Council through Grant Nos. 94-2216-E-002-035 and 95-2623-7-002-010-ET.

[1]L. Pain, C. LeCornec, C. Rosilio, and P. Paniez, Microelectron. Eng. **30**, 271 (1996).
[2]R. A. Carpio, R. A. Martinez, and R. D. Mohondro, Proc. SPIE **3678**, 235 (1999).
[3]R. D. Mohondro, Solid State Technol. **46**, 69 (2003).
[4]C. Liu and M. Cheng, J. Microlithogr., Microfabr., Microsyst. **4**, 033001 (2005).
[5]G. Wallraff, J. Hutchinson, W. Hinsberg, F. Houle, P. Seidel, R. Johnson, and W. Oldham, J. Vac. Sci. Technol. B **12**, 3857 (1994).
[6]J. A. Eisele and R. D. Mohondro, U.S. Patent No. 6,117,622, 12 September 2000.
[7]I. Pollentier, P. Jaenen, C. Baerts, and K. Ronse, Future Fab Int. **12**, 161 (2002).
[8]E. F. Reznikova, J. Mohr, and H. Hein, Microsyst. Technol. **11**, 282 (2005).
[9]J. T. Lee, U.S. Patent Application No. 20040166419, 26 August 2004.
[10]H. Ito, Adv. Polym. Sci. **172**, 37 (2005).
[11]T. H. Fedynyshyn, R. R. Kunz, R. F. Sinta, R. B. Goodman, and S. P. Doran, J. Vac. Sci. Technol. B **18**, 3332 (2000).