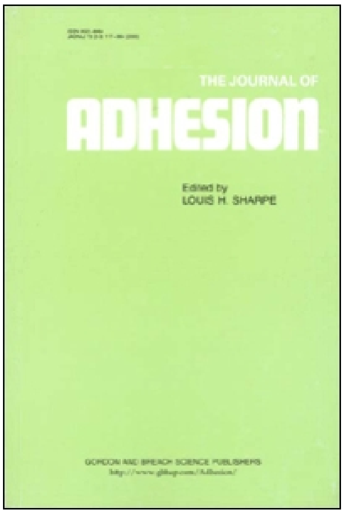

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Investigations of the Adhesion of Maleic Anhydride/Cyclic Olefin Alternating Copolymers to Silicon Substrates: Improved Materials for 193 nm Lithography

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To cite this Article Pasquale, Anthony J. , Long, Timothy E. , Truong, Hoa and Allen, Robert D.(2002) 'Investigations of the Adhesion of Maleic Anhydride/Cyclic Olefin Alternating Copolymers to Silicon Substrates: Improved Materials for 193 nm Lithography', The Journal of Adhesion, 78: 1, 1 — 13

To link to this Article: DOI: 10.1080/00218460210378

URL: http://dx.doi.org/10.1080/00218460210378

The Journal of Adhesion, 78: 1–13, 2002

0021-8464/02 $12.00 +.00

INVESTIGATIONS OF THE ADHESION OF MALEIC ANHYDRIDE/CYCLIC OLEFIN ALTERNATING COPOLYMERS TO SILICON SUBSTRATES: IMPROVED MATERIALS FOR 193 NM LITHOGRAPHY

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Various synthetic variations that affect the molecular weight, yield, and composition of maleic anhydride (MAH), norbornene (Nb), and tert-butyl 5-norbornene-2-carboxylate (Nb-TBE) terpolymers have been investigated. The adhesive properties of these polymers were evaluated from work of adhesion (W_{adh}) values to silicon substrates (treated with hexamethyldisilazane) using the method of fractional surface free energy from contact angle measurements of water and methylene iodide on the polymer films and substrate. These measurements showed that the W_{adh} increased with higher Nb-TBE content, and values were close to those of conventional 248 nm photoresist polymers. Furthermore, 193 nm resist formulations incorporating polymers with high Nb-TBE content showed increased imaging performance and successfully produced sharp and defined features as small as 110 nm, which were seen via scanning electron microscopy (SEM).

Keywords: 193 nm-lithography; Adhesion; Alternating copolymerization; Surface energy

Received 25 June 2001; in final form 12 October 2001.

Presented at the 24th Annual Meeting of The Adhesion Society, Inc., held at Williamsburg, Virginia, USA, 25–28 February 2001.

Financial support provided by the Jeffress Memorial Trust, Virginia Tech Department of Chemistry, National Science Foundation (CRIF CHE-9974632), and IBM is gratefully acknowledged. The authors would also like to thank the Center for Adhesive and Sealant Science (CASS) at Virginia Tech and the Adhesive and Sealant Council (ASC) for financial support through an ASC Education Foundation Research Fellowship.

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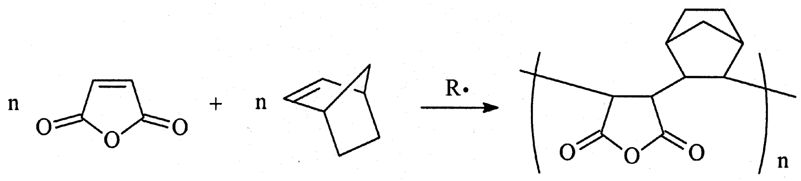
INTRODUCTION

Photolithography using 193 nm (Ar-F laser) light is the basis for the production of the next generation of microelectronic devices [1–6]. Current technology (Kr-F laser), including ultraviolet (UV) and deep-UV (DUV) photolithography, employs aromatic materials based upon phenolic polymers [7–8]. However, the photon energy of 193 nm light is high enough for aromatic polymers to absorb strongly at this wavelength, resulting in opaque materials that are not practical for 193 nm lithography [9]. Therefore, recent years have seen a large effort devoted to the design of materials that are optically transparent at 193 nm and also have the desirable etch-resistant and image-forming properties of phenolic-based materials [10].

A number of approaches to materials with high transparency at 193 nm have been reported [11]. Initially, acrylic-based polymers seemed promising as new materials for 193 nm lithography. Acrylates were desirable materials due to only a weak carbonyl absorption at 193 nm, which resulted in good transparency when exposed to this wavelength of light [12]. Allen and coworkers described successful 193 nm patterning using an all-acrylic terpolymer made up of methyl methacrylate, *tert*-butyl methacrylate, and methacrylic acid [13]. However, the poor reactive-ion etch resistance of acrylics under the etching conditions used widely in the semiconductor industry has limited their application in 193 nm resist materials [14]. The primary design challenge that has emerged in the development of new materials for 193 nm photolithography is the trade off between imaging performance (broadly defined as resolution, adhesion, sensitivity, and compatibility with industry standard aqueous-base developers) and reactive-ion etch resistance [10]. The chemical modifications that were used to tailor the imaging performance of acrylic polymers also deleteriously influenced reactive-ion etch resistance [14]. Previously, it has been determined that there is a correlation between increased reactive-ion etch resistance and a high carbon-to-hydrogen (C/H) ratio [2, 15], helping to explain why phenolic materials that are currently used as resist materials, which have a high C/H ratio, exhibit good plasma etch resistance. Therefore, to improve the reactive-ion etching properties of acrylic-based materials by increasing the C/H ratio, a number of acrylic-based materials containing pendant alicyclic adamantane or norbornane functionality have been investigated [16–22]. Incorporation of the pendant alicyclic functionalities greatly improved the etch resistance of acrylic-based materials. The increase in etch resistance was also accompanied by decreased image performance, which has hindered the development of a 193 nm photolithography acrylic resist material with both etch resistant and image performing properties required for industrial application.

An alternative approach to increase the C/H ratio has been to incorporate alicyclic structures directly into the polymer backbone [12]. A variety of synthesis routes for producing resist materials with alicyclic backbones have been investigated. They include cyclic olefin alternating free radical copolymerization [23–30], metal catalyzed vinyl addition polymerization [23, 24, 31–33], and ring opening metathesis polymerization (ROMP) followed by hydrogenation [23–24]. In recent years, the most promising of these methods to emerge for synthesizing alicyclic materials for 193 nm lithography is the alternating free radical copolymerization of maleic anhydride with cyclic olefin monomers such as norbornene (Scheme 1). Cyclic olefins will homopolymerize poorly *via* free radical methods. However, when cyclic olefins are reacted with maleic anhydride, which is a strong electron acceptor, in the presence of a free radical initiator, they copolymerize in an alternating manner [3]. In addition, maleic anhydride also serves to incorporate oxygen into the material, providing necessary adhesion and solubility properties that are required for imaging performance while still retaining sufficient etch resistance to be successfully demonstrated as 193 nm resist materials [28]. The cyclic olefin character of these materials provides for excellent etch resistance, surpassing even currently utilized phenol-based resists. Furthermore, the increased etch resistance is of great importance because of the decreasing film thickness necessary for the achievement of increasingly smaller feature sizes [3]. In addition, the ability to modify the polymer properties *via* incorporation of cyclic olefin monomer derivatives to improve lithographic performance has further made this a very attractive route to new materials for 193 nm lithography.



SCHEME 1 Maleic anhydride and norbornene alternating copolymerization scheme.

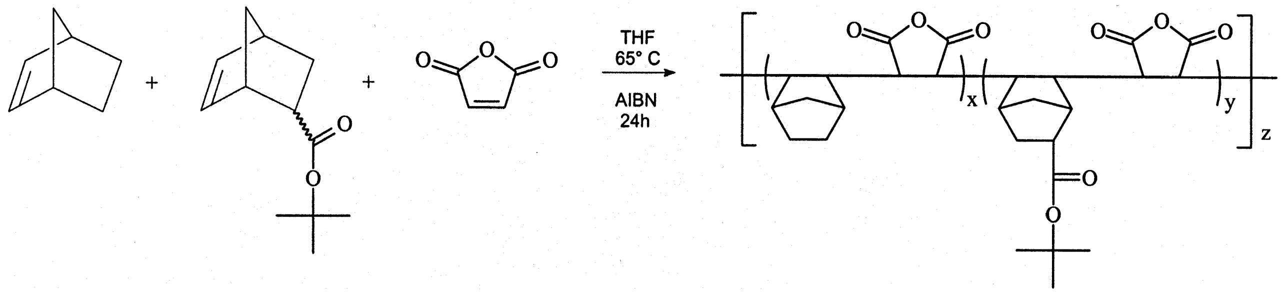
The adhesion performance of resist systems will be a critical performance criterion as microelectronic device features are pushed to smaller dimensions. The adhesion properties of chemically amplified resist polymers based on poly(hydroxystyrene) have been very successful in the production of patterned images using UV and DUV lithography. However, as device features are driven to below 100 nm, the properties of adhesion and resist rigidity become more important to prevent resist pattern collapse [34]. For example, Fréchet and coworkers have recently demonstrated the successful use of a hyperbranched polyester as a negative tone, chemically amplified resist that produced uniform 100 nm lines *via* electron-beam exposure [35]. However, the 100 nm features exhibited poor adhesion to the silicon substrate and resulted in random migration of the patterned lines. In an attempt to improve the adhesion of alicyclic resist polymers, Kim and coworkers have recently investigated the adhesive and lithographic properties of maleic anhydride/norbornene copolymers with the addition of an adhesion promoter [36]. They reported that the addition of hydrophilic 2-(2-methoxyethoxy) ethyl ester groups resulted in improved adhesion and 150 nm lines and spaces were successfully obtained using an ArF exposure system.

The focus of this research has been to investigate the adhesive and imaging properties of terpolymers composed of maleic anhydride (MAH), norbornene (Nb), and a norbornene derivative containing an acid labile *tert*-butyl ester functionality, *tert*-butyl 5-norbornene-2-carboxylate (Nb-TBE) (Scheme 2), which, when hydrolyzed to the corresponding carboxylic acid, lends aqueous base solubility. The *tert*-butyl functionality also serves to incorporate additional oxygen, which is anticipated to affect the adhesive properties of the resists. This study will describe the synthesis and characterization of these terpolymers based on MAH, Nb, and Nb-TBE. Thermodynamic work of adhesion values as a function of the Nb-TBE incorporation will also be discussed and successful patterning of these resist polymers using 193 nm ArF exposure technology will be demonstrated.

EXPERIMENTAL

Materials

All reagents were purchased from Aldrich and used as received unless otherwise noted. Nb-TBE was generously donated by BF Goodrich Company and the preparation has previously been reported by Willson *et al.* [24]. Tetrahydrofuran (THF) was distilled immediately before use using the classic sodium/benzophenone ketyl.



SCHEME 2 Alternating terpolymerization of Nb, Nb-TBE, and MAH.

In-situ FTIR

In-situ mid-FTIR spectra were collected with an ASI Applied Systems ReactIR 1000 reaction analysis system equipped with a light conduit and DiComp (diamond-composite) insertion probe. The details and capabilities of the ReactIR 1000 reaction analysis system based on attenuated total reflectance (ATR) have been described in detail previously [37].

Characterization

^{13}C NMR spectra were obtained from a Varian UNITY-400 spectrometer at 100 MHz in DMSO-d_6 solvent at ambient temperature. Apparent molecular weights and polydispersities were measured using a miniDAWN multiangle laser light scattering (MALLS) detector with a 690 nm laser (Wyatt Technology, Santa Barbara, CA) connected to a Waters SEC (515 pump, 717 autosampler, and 410 refractive index detector). The miniDAWN was connected in series after three 5 μm Plgel mixed-bed columns (Polymer Laboratories, Amherst, MA) and in front of the refractive index detector. Measurements were made at 40°C with THF as the solvent at a flow rate of 1.0 mL/min. Co- and terpolymer dn/dc values used for MALLS molecular weight calculations were estimated assuming 100% mass recovery.

Synthesis and *In-situ* FTIR of MAH/Nb/Nb-TBE Alternating Terpolymers

A typical synthesis of an Nb/Nb-TBE/MAH (25/25/50 mol ratio) alternating terpolymer with *in-situ* FTIR monitoring is described. In a 100 mL, round-bottomed, two-necked flask that was fitted with the ReactIR 1000 DiComp probe was added a magnetic stir bar, Nb (4.79 g, 51 mmol), Nb-TBE (9.89 g, 51 mmol), MAH (10.0 g, 102 mmol), 2,2-azobisisobutyronitrile (AIBN) (1.004 g, 6.12 mmol), and THF (16.5 mL). The flask was purged with nitrogen for approximately one minute and sealed tightly under positive nitrogen pressure (4–5 psi, ~0.03 mPa) with a rubber septum. An oil bath at 65°C was raised to the stirred (*via* magnetic stir bar) reaction flask and FTIR data collection was started. The ReactIR was programmed to collect a FTIR spectrum of the reaction mixture every 5 min. After 24 h, the reaction mixture had solidified at 65°C and was no longer stirring. The oil bath was removed and the reaction contents were allowed to cool to room temperature. The DiComp probe was removed from the reaction flask and THF (~50 mL) was added to dissolve the solid. The dissolved material was then precipitated into hexanes ($\sim$500 mL), filtered, washed with isopropyl alcohol ($\sim$200 mL) and dried overnight under vacuum (0.1 mm Hg) at approx. 75°C to give 19.6 g (80% yield) of white powder: $M_n = 6{,}700$ g/mol ($M_w/M_n = 1.60$).

Contact Angles

Nb/Nb-TBE/MAH terpolymers were spin coated (4000 rpm) on hexamethyldisilazane (HMDS) treated silicon wafers from 0.25 μm filtered 13% (w/w) cyclohexanone solutions. The films were baked at 120°C for approximately 2 min to remove residual solvent. Contact angles of water and methylene iodide on the terpolymer films and silicon substrate were measured using a contact angle goniometer.

RESULTS AND DISCUSSION

Synthesis and Characterization of Nb/Nb-TBE/MAH Alternating Copolymers

Free radical alternating terpolymerizations of Nb/Nb-TBE/MAH with various ratios of Nb to Nb-TBE (while maintaining a 50% molar feed of MAH) were performed using previously determined optimum conditions (3 mol% AIBN, THF (60% solids), 24 h). A more detailed discussion on the synthesis of these terpolymers will be published elsewhere [38]. Terpolymerizations were conducted using the following Nb/Nb-TBE/MAH monomer feed ratios: 50/0/50, 35/15/50, 25/25/50, 15/35/50, 0/50/50. The observed rate constants determined using *in-situ* FTIR (Figure 1), percent yields, molecular weights, and Nb/Nb-TBE composition in the resulting materials are summarized in Table 1. Several trends were apparent from the data analysis. First, the observed reaction rate is a strong function of the monomer feed ratio of Nb/Nb-TBE with a maximum of $6.68 \times 10^{-5}\ \text{s}^{-1}$ at a 50/0/50 Nb/Nb-TBE/MAH monomer feed ratio. The observed rate decreases with increasing Nb-TBE monomer feed to a minimum of $1.13 \times 10^{-5}\ \text{s}^{-1}$ at a 0/50/50 Nb/Nb-TBE/MAH monomer feed ratio. In addition, percent yield exhibited a similar trend with a maximum yield of 94% for a 50/0/50 Nb/Nb-TBE/MAH feed ratio and a minimum yield of 60% for a 0/50/50 Nb/Nb-TBE/MAH feed ratio. The observed decrease in rate with increasing Nb-TBE is proposed to be due to a combination of steric and polarity effects resulting from the *tert*-butyl ester functionality of Nb-TBE. Further experiments are planned to elucidate these effects more thoroughly. ^{13}C NMR analysis of terpolymers prepared from a 25/25/50 Nb/Nb-TBE/MAH monomer feed ratio further

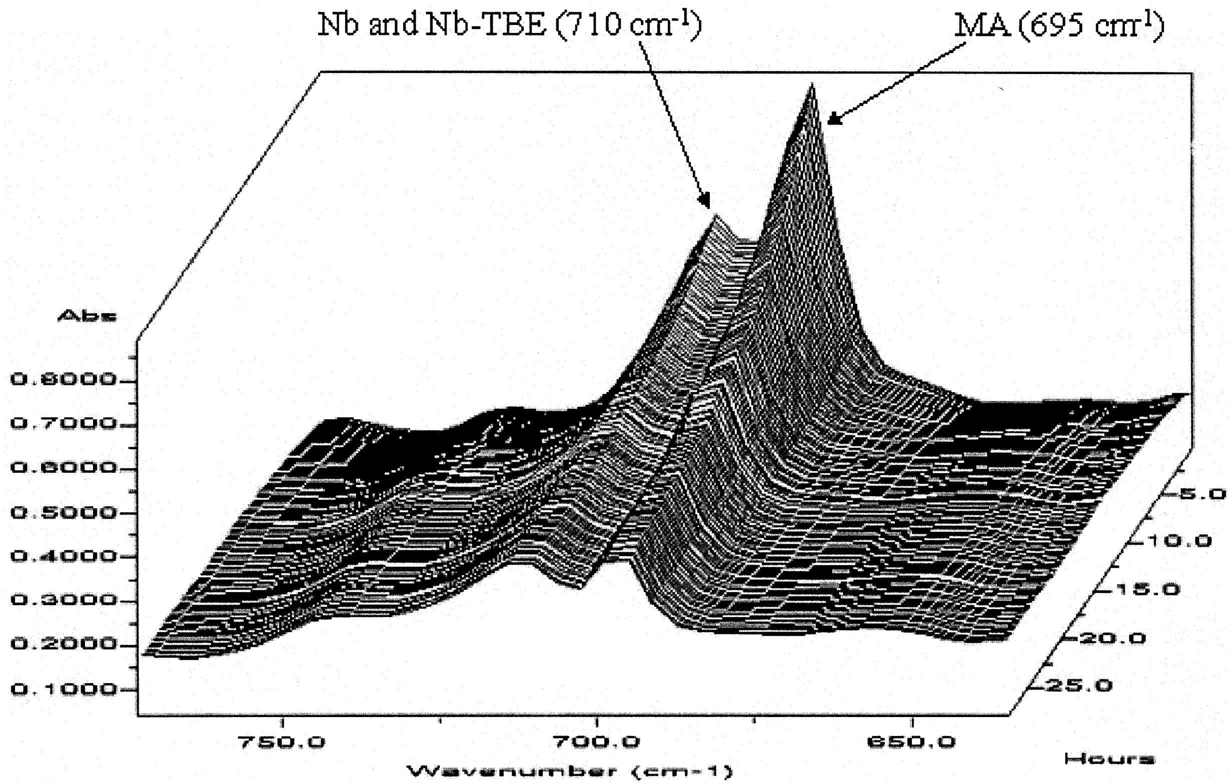


FIGURE 1 Vinylene region of "Waterfall Plot" for Nb/Nb-TBE/MAH (25/25/50 mol ratio) terpolymerization (in-situ FTIR, spectrum acquired every 5 minutes).

TABLE 1 Summary of Nb/Nb-TBE/MAH Terpolymerizations Varying the Monomer Feed Ratio of Nb to Nb-TBE

	Observed rate (FTIR)				
Nb/Nb-TBE/MAH	$\times 10^5\,s^{-1a}$	Yield (%)	$M_n{}^b$	M_w/M_n	Nb/Nb-TBE^c
50/0/50	6.68	94	7,300	1.63	
35/15/50	5.26	87	6,500	1.46	3.2
25/25/50	3.83	80	6,700	1.64	1.4
15/35/50	2.61	75	6,600	1.49	0.68
0/50/50	1.13	60	6,900	1.59	

[a] Determined from first-order kinetic plot using MAH/Nb peak area *via in-situ* FTIR for first 4 h of reaction.

[b] Wyatt miniDAWN MALLS detector coupled with Waters GPC with external 410 RI detector viscometer, THF solvent at 40°C and 1.0 mL/min flow rate.

[c] Determined using ^{13}C NMR (Varian Unity-400) at 100 MHz, DMSO-d_6, ambient temperature. Ratio calculated from integration of the quaternary carbon of *tert*-butyl ester group (δ 80 ppm) of Nb-TBE to the total carbonyl region (δ 170–176 ppm). For calculation, a 1:1 ratio of MAH to total cyclic olefin (Nb and Nb-TBE) is assumed.

indicated that the terpolymers were enriched in Nb and depleted in Nb-TBE. The ratio of Nb to Nb-TBE in the terpolymer was subsequently determined *via* integration of the quaternary carbon of *tert*-butyl group (δ 80 ppm) to the carbonyl region (δ 170–176 ppm). Assuming a 1:1 ratio of MAH to the total cyclic olefin (Nb and Nb-TBE) incorporated into the terpolymer, the ratio of Nb to Nb-TBE incorporated was subsequently determined to be 1.4:1.0.

Adhesion and Lithographic Performance

Adhesive properties of the terpolymers were evaluated from calculating the work of adhesion (W_{adh}) between the polymer and an HMDS treated silicon substrate using the method of fractional surface free energy as demonstrated by Owens and Wendt (Eqn. 1) [39]:

$$W_A = 2(\gamma_1^d \gamma_2^d)^{1/2} + 2(\gamma_2^p \gamma_1^p)^{1/2} \qquad (1)$$

This equation developed by Owens and Wendt is based upon the Fowkes hypothesis of surface energy separation [40] and states that if the dispersion and polar force components of the surface energy are known, the work of adhesion is determined by the sum of the square roots of their products. Kim and coworkers have previously used this approach to study the adhesive properties of alicyclic 193 nm resist polymers [36]. Contact angles of water and methylene iodide and W_{adh} values are summarized in Table 2. W_{adh} increased with higher Nb-TBE composition in the terpolymer with a minimum of 58.6 dyne/cm for a 50/50 Nb/MAH copolymer and a maximum of 64.9 dyne/cm for a 50/50 Nb-TBE/MAH copolymer. In addition, lithographic evaluation of the terpolymers demonstrated that the 50/50 Nb-TBE/MAH showed excellent imaging capability at 193-nm. Scanning electron micrographs (SEM) of imaged films for a 50/50 Nb-TBE/MAH copolymer and a 25/25/50 Nb/Nb-TBE/MAH terpolymer are illustrated in Figure 2. Semi-dense 110 nm and 120 nm lines (1:1.5 line/space) were printed with sharp and defined features. The imaged 50/50 Nb-TBE/MAH copolymer resist formulation exhibited vertical and consistent sidewalls. In comparison, the patterned lines produced from the resist formulation using the 25/25/50 Nb/Nb-TBE/MAH terpolymer had significantly increased line thinning and sloping sidewalls. All of the resist polymer compositions exhibited good adhesion (qualitative observation based upon SEM of patterned images) to the silicon substrate after imaging and no movement of the patterned images was observed. The method discussed above for calculating the W_{adh} values of the resist polymers to the silicon substrates provides a useful technique for the estimation of the adhesive properties of resist polymers to the silicon substrates and it was demonstrated that the calculated W_{adh} increased with increasing Nb-TBE content. However, the essential performance criterion is whether the final patterned images adhere to the substrate and all of the patterned images produced from the MAH/Nb/Nb-TBE resist compositions investigated in this study did show good adhesion after exposure and development.

TABLE 2 Water and Methylene Iodide Contact Angles and W_{adh} Values for Nb/Nb-TBE/MAH Terpolymers

Polymer	Contact angle (H_2O)[b]	contact angle (CH_2I_2)[b]	W_{adh}[c]
50/0/50[a]	94 ± 0.82	68 ± 0.82	58.6
35/15/50[a]	91 ± 0.92	65 ± 1.2	60.6
25/25/50[a]	87 ± 1.1	62 ± 1.2	62.5
15/35/50[a]	85 ± 0.92	60 ± 1.1	63.8
0/50/50[a]	82 ± 1.0	58 ± 0.70	64.9
Si wafer	94 ± 1.0	47 ± 1.1	

[a] Nb/Nb-TBE/MAH monomer feed ratio.

[b] Measured using a contact angle goniometer. Reported value is the average of ten measurements.

[c] Work of adhesion to a HMDS treated silicon wafer (dyne/cm).

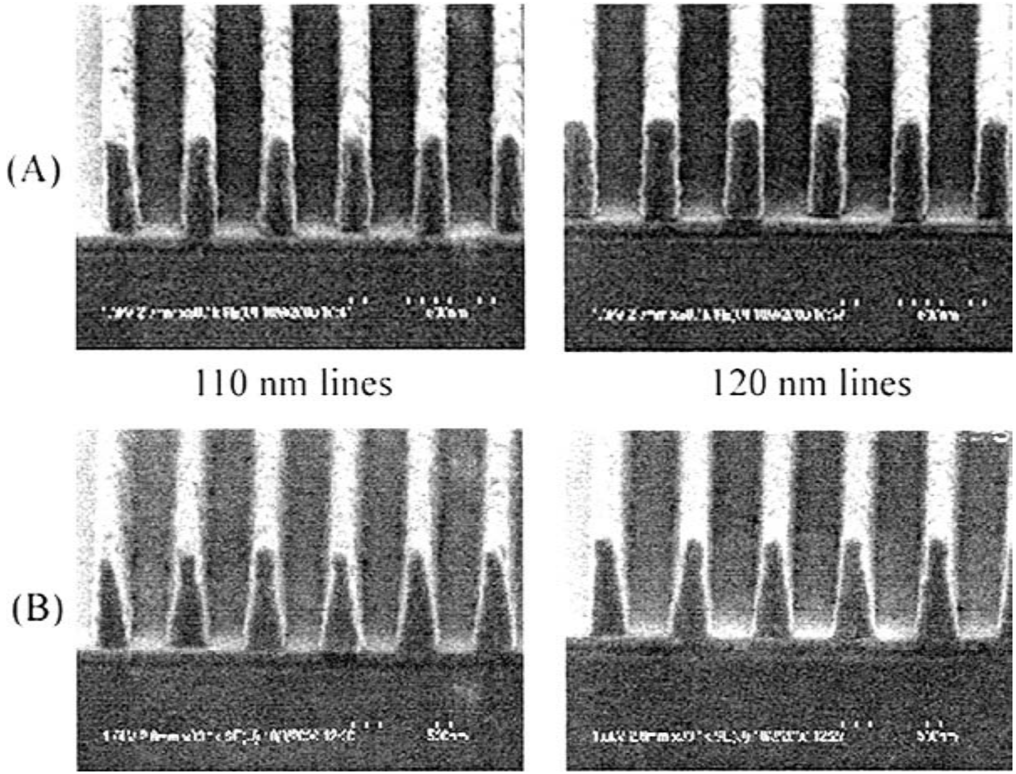


FIGURE 2 Scanning electron micrographs of 110 nm and 120 nm 1:1.5 line/space patterns (ISI Ar-F 193-nm Micostep, NA = 0.6). (A) 50/50 Nb-TBE/MAH copolymer (at a dose of 19 mJ/cm^2). (B) 25/25/50 Nb/Nb-TBE/MAH terpolymer (at a dose of 36 mJ/cm^2).

CONCLUSIONS

Real-time monitoring *via in-situ* FTIR spectroscopy of alternating terpolymerizations of MAH with Nb and Nb-TBE was utilized to evaluate the relative rates of varying Nb/Nb-TBE monomer feed ratios. Pseudo first-order kinetic plots constructed from the *in-situ* FTIR absorbance data indicated that the rate of reaction was a strong function of the Nb/Nb-TBE ratio and decreased with increasing Nb-TBE. In addition, percent yields were also observed to be a function of the Nb/Nb-TBE ratio and decreased with increasing Nb-TBE. Calculated work of adhesion (W_{adh}) values of Nb/Nb-TBE/MAH terpolymers demonstrated a linear increase in W_{adh} with increased Nb-TBE composition in the terpolymer. Furthermore, SEM of developed 193 nm resist formulations showed increased imaging performance in polymers with high Nb-TBE content.

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