A Bergman Cyclization Approach to Polymers for Thin-Film Lithography

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ABSTRACT: A new polymer, poly(3,4-bis(phenylethynyl)styrene), has been synthesized that undergoes a Bergman reaction upon heating to yield a highly aromatic material. The occurrence of the cycloaromatization reaction is characterized through thermal analysis and absorption spectroscopy. The plasma etch resistance of the polymer has been measured by reactive ion etching (RIE) in sulfur hexafluoride and oxygen plasmas and is shown to be superior to other conventional organic plasma etch barriers.

Introduction

In the past two decades, reductions in the size of semiconductor device features such as the transistor gate width have driven the dramatic progress in the microelectronics industry.[1,2] This reduction has been made possible through advancements in the lithographic tools and materials used to produce such patterns. As new lithographic exposure technologies are introduced to enable patterning of yet smaller device features, advances in photoresist technologies are also required.[3,4]

In conventional lithographic processing, the patterned photoresist generally serves as a mask for pattern transfer into other layers by means such as etching in a reactive plasma, wet chemical etching, ion implantation, or deposition of thin-film layers.[5,6] When the minimum feature size required in semiconductor devices dropped below 1 μm, plasma etching became the method of choice for pattern transfer due to its anisotropic nature. However, since plasma etching is, in general, less chemically selective than wet etching, plasma-based processes require thicker, less reactive, resist materials. The ideal resist is one that provides a high plasma etch resistance for pattern transfer but a low oxygen plasma resistance for stripping. The final selection of the polymer resin for application as a photoresist (lithography) involves obtaining the best compromise between (1) etch resistance, (2) oxygen plasma sensitivity, (3) and acceptable chemical and physical imaging properties.

As shorter exposure wavelengths (193 and 157 nm, EUV) are used for submicron and even nanometer scale patterning, new resist materials that function at shorter wavelengths are required. Organic materials typically have high absorbances at wavelengths below 200 nm, thus making them opaque at future exposure wavelengths. This opacity is a serious problem since both conventional nonchemically amplified (DNQ-Novolac) and chemically amplified (CA) resists require that a photoreaction occur throughout the entire thickness of the resist film in order to successfully image a pattern. Therefore, use of conventional resists and methods requires that current resist materials be implemented at reduced thicknesses or entirely new, more transparent materials must be developed. Reduction of the resist thickness leads to a number of problems and is fundamentally limited by the etch resistance of a specific material, while the development of transparent materials for imaging at UV wavelengths below 200 nm is difficult and may not be feasible.

One solution to this problem involves the use of so-called "top surface imaging" (TSI) techniques. In these methods, an exposure-induced reaction in a thin surface layer of a material is sufficient to allow subsequent pattern formation. The most widely investigated of these TSI methods have been silylation approaches that use the selective incorporation of silicon into the surface of an organic resist film to permit pattern formation.[7−9] However, a number of problems have been identified with silylation techniques, including pattern distortion resulting from lateral swelling during silylation and line edge roughness. It is a challenge to control selective silicon incorporation and to minimize silicon dioxide sputtering, and thus micromasking, during subsequent plasma-based etching. Such practical problems have effectively prevented the use of silylation in high-volume semiconductor manufacturing.

Our approach to the elimination of silicon-containing species as local etch masks involves the use of carbon-based or graphitic materials. This approach is based on previous investigations, as well as our studies of current polymer resist materials, that demonstrate that polymers with aromatic groups attached to the main chain and/or side chain are more resistant to plasma etch atmospheres.[10−12]

To better define the relationship between aromatic structure and etch resistance, we have prepared several carbon-rich, highly aromatic polymer materials that could be used in surface imaging techniques in place of silicon-based materials to function as etch masks. Recently, Smith and co-workers have described an approach to form highly aromatic polymers based upon bis(orthodiynylarene) (BODA) chemistry.[13] These precursors are designed to undergo cycloaromatization and cross-linking in a thermal, photochemical, or chemical consolidation step.

In this paper, we described the synthesis and properties of poly(3,4-bis(phenylethynyl)styrene). Since polymers formed by radical chain processes such as polystyrenes are prone to chain scission during plasma etching, a consolidation step may be required to convert

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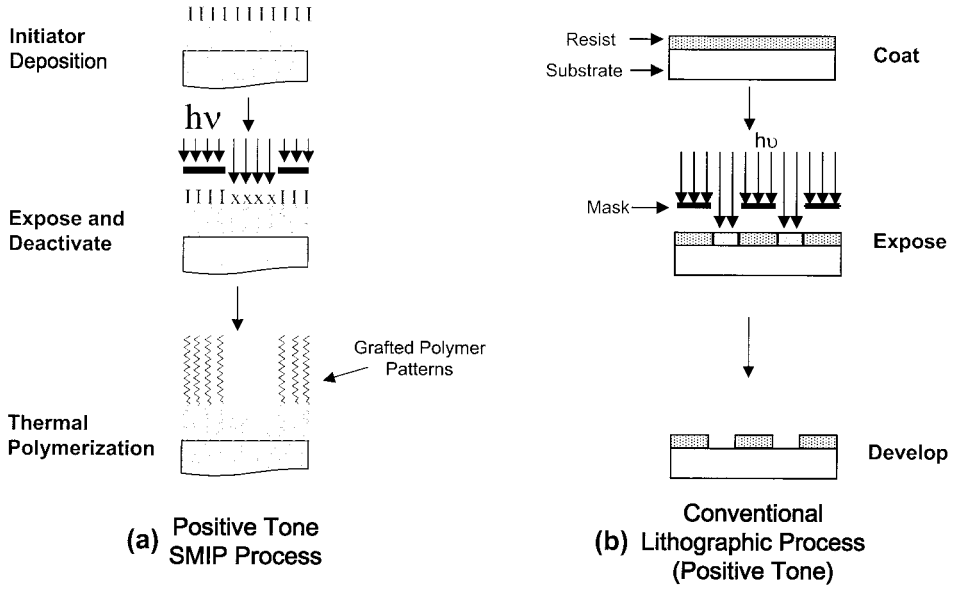

Figure 1. Schematic comparison of positive tone imaging using (a) a surface monolayer initiated polymerization (SMIP) process and (b) a conventional photoresist process.

the polymer into a more robust resist material. The polymer studied in this work, which is produced by AIBN-induced polymerization of the monomer, undergoes a thermal Bergman cycloaromatization that results in a highly aromatic material. The method of interest here is the production of patterned highly aromatic materials, and this paper demonstrates a candidate polymer that can be altered after patterning to produce such materials. One advantage of this material is that it is converted into an aromatic material after polymerization through a heat treatment, thus avoiding problems with solubility in solvents that may be encountered when attempting to directly coat a graphitic material. Furthermore, the monomer described in this work allows the patterned polymerization of the polymer precursor material directly onto a surface using a technique such as surface monolayer initiated polymerization (SMIP).[14] Surface initiated polymerization techniques utilize a photosensitive initiator that can be coated onto a surface, patterned, and subsequently used to selectively initiate polymerization and form the desired polymer patterns (Figure 1). The monomer and polymer described in this work were designed such that they could be used in conjunction with a SMIP process.[14] Both the precured and cured material have been characterized by thermal and spectroscopic means. Finally, the plasma etch resistance of the polymers has been measured by reactive ion etching (RIE) in both SF_6 and O_2 plasmas.

Experimental Section

A. Synthesis of the Monomers. 3,4-Dihydroxybenzaldehyde Bis(trifluoromethanesulfonate). To a solution of 3,4-dihydroxybenzaldehyde (0.340 g, 2.46 mmol) in 8 mL of triethylamine at −10 °C was slowly added trifluoromethanesulfonic anhydride (1.00 mL, 6.00 mmol). The reaction mixture was stirred at 0 °C for 5 min, then allowed to warm to room temperature, and stirred for 15 h. The reaction mixture was poured into water and extracted with ether. The organic extract was washed with water, 10% aqueous HCl, water, and saturated NaCl solution, dried with anhydrous $MgSO_4$, and concentrated in vacuo. Silica gel column chromatography (with hexane) yielded a pale yellow oil (710 mg, 70.6%). Spectral data: MS: M+: 402. ^{1}H NMR ($CDCl_3$): 10.0 (s, 1H), 8.05 (d, 2H), 7.65 (d, 1H). ^{13}C NMR ($CDCl_3$): 188.2, 144, 141.8, 136.6, 131.0, 124, 121.5, 116.4, 112.2. Anal. Calcd for $C_9H_4F_6O_7S_2$: C, 26.78; H, 1.00; S, 15.94. Found: C, 26.67; H, 1.25; S, 15.74.

3,4-Bis(phenylethynyl)benzaldehyde. To a deoxygenated solution of 3,4-dihydroxybenzaldehyde bis(trifluoromethanesulfonate (1.00 g, 2.48 mmol), triethylamine (10 mL), and DMF (10 mL) were added phenylacetylene (0.805 g, 7.84 mmol) and $Pd[P(Ph_3)]_2Cl_2$ (55.0 mg, 1 mol %). The mixture was heated at 60 °C for 5 h. Methylene chloride (100 mL) was added, and the organic fraction was separated and washed with 10% $NaHCO_3$, water, 10% HCl solution, water, and saturated NaCl solution and dried with anhydrous Na_2SO_4. The solvent was evaporated and the crude material isolated by silica gel column chromatography (hexane). After removal of hexane, a red oil (0.591 g, yield 78%) was obtained. Spectral data: MS: M+: 306. ^{1}H NMR ($CDCl_3$): 10.0 (s, 1H), 8.05 (s, 1H), 7.75 (d, 1H), 7.70 (d, 1H), 7.60 (m, 4H), 7.41 (m, 6H). ^{13}C NMR ($CDCl_3$): 88.0, 88.5, 95.5, 98.0, 122.5, 127.4, 128−129.5, 132.2, 132.4, 132.7, 133.2, 135.8, 191.5. Anal. Calcd for $C_{23}H_{14}O$: C, 90.17; H, 4.61. Found: C, 89.90; H, 4.65.

3,4-Bis(phenylethynyl)styrene. To a suspension of methyltriphenylphosphonium bromide (0.678 g, 1.9 mmol) in dry ether (50 mL) was slowly added phenyllithium (1.2 mL of 1.8 M hexane solution, 2.16 mmol) in 10 mL of ether. The solution was stirred in argon for 5 h. 3,4-Bis(phenylethynyl)benzaldehyde (0.522 g, 1.71 mmol) in dry tetrahydrofuran (20 mL) was added to the solution dropwise under argon. The solution was stirred for 2 h, heated to 60 °C, and heated at reflux for 10 h. The reaction mixture was concentrated to 20 mL. Toluene (50 mL) was added and the separated organic fraction washed with 10% $NaHCO_3$, water, 10% HCl solution, water, and saturated NaCl solution and dried with anhydrous $MgSO_4$. The solution was concentrated and subjected to silica gel column chromatography (hexane) to produce a red oil. Crystallization from methanol at 4 °C afforded a red solid (0.450 g, yield 87%); mp 28 °C. Spectra data: MS: M+: 304. ^{1}H NMR ($CDCl_3$): 7.31−7.60 (m, 13H), 6.60−6.75 (m, 1H), 5.82 (d, 1H), 5.35 (d, 1H). ^{13}C NMR ($CDCl_3$): 89.1, 93.2, 94.0, 100, 115, 124, 125.8, 126, 128, 129, 130, 132, 134, 136, and 138.

B. Polymerization. AIBN (azobis(isobutyronitrile)) was dissolved in dimethylformamide to produce a 5 mol % initiator solution. The monomer was added to the initiator solution to achieve a monomer concentration of 1 M. The mixture was degassed by three freeze−pump−thaw cycles. Subsequently, the degassed solution was polymerized thermally at 50 °C for 10 h. This solution was added to stirring methanol (300 mL) and filtered. The resulting solid was reprecipitated twice and then dried in a vacuum. The resulting polymer was characterized by ^{1}H NMR and ^{13}C NMR spectroscopy. ^{1}H NMR ($CDCl_3$,

ppm): 6.61−7.83 (m, 13H), 1.52 (m, 1H), 0.63−1.41 (m, 2H). ^{13}C NMR ($CDCl_3$, ppm): 130−132, 125−130, 122−124, 93.2−95.5, 86.3−89.0, 33.4, 26.1−28.2.

C. Thermal Reaction. Poly[3,4-bis(phenylethynyl)styrene] was dissolved in dimethylformamide, spin-coated onto a quartz substrate, and heated in a vacuum at 250 °C/30 mmHg for 10 h. The UV spectra were subsequently recorded. Poly(3,4-bis-(phenylethynyl)styrene) was also directly heated in a vacuum under the same conditions. The resulting polymer was characterized by ^{1}H NMR and ^{13}C NMR spectroscopy and by GPC. ^{1}H NMR ($CDCl_3$, ppm): 6.73−7.85 (m, 13H), 1.64 (m, 1H), 0.70−1.64 (m, 2H). ^{13}C NMR ($CDCl_3$, ppm): 132−133, 127−130, 31.6, 28.3−29.2. From GPC, M_w = 2606 g/mol.

D. Polymer Film Etching. A Plasma-Therm RIE reactor was used to etch the polymer resist films spin-coated onto a silicon wafer. SF_6 and O_2 were used as the etchants. The flow rate of SF_6 was 30 sccm, the pressure was 100 mTorr, and the power was 50 W. O_2 RIE was performed at a pressure of 200 mTorr, a flow rate of 50 sccm, and a power of 100 W. The etch rates of the polymer films were determined by the changes in the thickness before and after the plasma etch using an Alpha-step 500 surface profilometer.

E. Characterization of Polymers and Films. Infrared spectra of the polymer films were measured with a Nicolet Fourier transform infrared spectrometer over the frequency range 4000−400 cm^{-1}. The spectra were obtained by averaging 1000 scans of films deposited on KBr crystals at a resolution of 4 cm^{-1}. The additional resonance at 3500 cm^{-1} is the result of residual water in the KBr pellet.

UV−vis spectra were recorded on a Perkin-Elmer Lambda 19 UV/vis/NIR spectrometer. Polymer samples were obtained by spin-coating onto quartz substrates. A Spex Fluorolog spectrofluorometer (components include 1680 0.22 m double spectrometer and 1681 0.22 m spectrometer) was used to record the fluorescence spectra.

All NMR spectra were measured in $CDCl_3$ solutions on a Varian Gemini 300 series spectrometer. The hydrogen and carbon contents were determined by elemental analysis (Atlantic Microlab, Inc.).

Differential scanning calorimetry (DSC) was performed with a DSC 2920 (TA Instruments). The heating rate was 5 °C/min from 25 to 250 °C (for the initiators) and to 350 °C for the polymers. Thermogravimetric analysis (TGA) was performed with a TGA 2050 (TA Instruments). The heating rate was 10 °C/min from 25 to 400 °C under a nitrogen atmosphere.

GPC measurements were performed using a Waters 2690 separations module and a Waters 2410 refractive index detector. The three columns used were Waters columns and had a MW range of 500−4 000 000 g/mol, with a solvent flow of 1 mL/min. Molecular weights were determined using a polystyrene standard calibration.

Results

Synthesis of Monomers and Polymers. 3,4-Bis-(phenylethynyl)styrene was synthesized by two different methods (Figure 2). In method A, 3,4-dibromobenzaldehyde was allowed to react with phenylacetylene using $PdCl_2(PPh_3)_2$ as the catalyst. Because of the differential reactivity of the two bromine atoms at the para and meta positions on 3,4-dibromobenzaldehyde, the coupling reaction required considerable time for completion; the reaction required 5 days for a 50% yield, with formation of a considerable quantity of the 3-bromo-4-phenylethynyl product. In method B, we used the reaction of 3,4-dihydroxybenzaldehyde bis(triflate) with phenylacetylene. Because the reactivity of the triflates in this coupling reaction was much higher than that of the dibromine-substituted derivatives, the reaction proceeded in several hours to form 3,4-bis(phenylethynyl)benzaldehyde in a relatively high yield (87%). The 3,4-bis(phenylethynyl)benzaldehyde products were

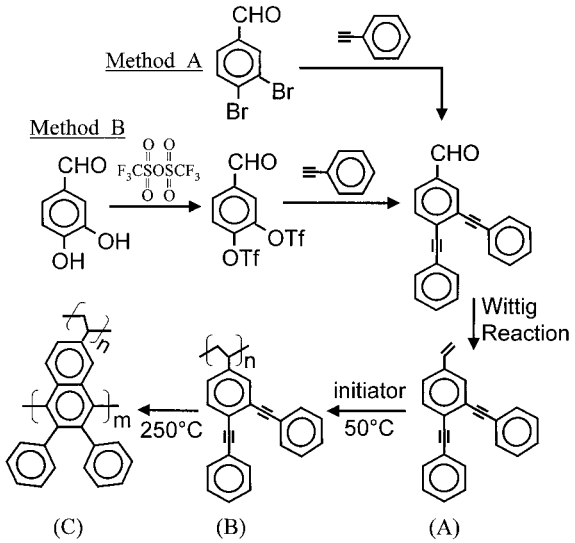

Figure 2. Synthetic route to formation of 3,4-bis(phenylethynyl)styrene followed by polymerization.

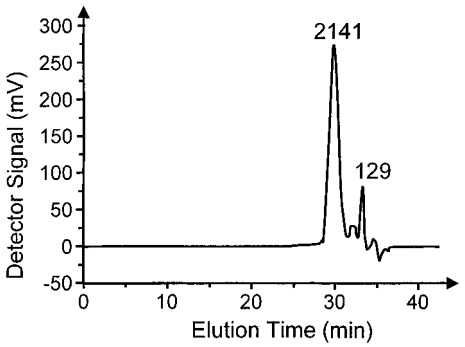

Figure 3. Molecular weight of poly(3,4-bis(phenylethynyl)-styrene) as measured by GPC.

subjected to a Wittig reaction to produce 3,4-bis(phenylethynyl)styrene.

The polymerization of 3,4-bis(phenylethynyl)styrene was performed with azobis(isobutyronitrile) (AIBN). A polymerization temperature of 50−55 °C provided the best conversion efficiency of the double bonds into poly-(3,4-bis(phenylethynyl)styrene) combined with minimal incorporation of the triple bonds, as indicated by the retention of sp-hybridized carbon residues in the infrared and ^{13}C NMR spectra (see below). The material was consolidated at 250 °C by analogy with previous preparations of similar compounds to yield a glassy material which retained the solubility characteristics of the untreated polymer.

The molecular weights of poly(3,4-bisphenylethynylstyrene) as measured by GPC using polystyrene standards were M_w = 2606 and MP = 2141 (Figure 3), corresponding to ∼7−8 repeat units in each polymer chain.

Thermal and Spectral Properties upon Heat Treatment. The ^{13}C NMR spectrum of poly(3,4-bisphenylethynylstyrene) displayed aromatic carbon peaks at 127−129 and 131−132 ppm, aliphatic backbone carbons at 26−28 and 33 ppm, and triple bond carbons at 86−89 and 93−95 ppm. After curing in a vacuum at 250 °C for 10 h, the peaks at 93−95 ppm disappeared, which indicated that the chemical structures of the polymer changed during the curing process due to cross-linking of the triple bonds. Similarly, the IR spectrum of the uncured polymer (Figure 4) showed triple bond

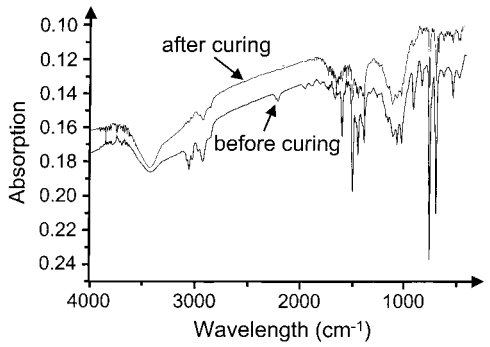

Figure 4. FTIR spectra of poly(3,4-bis(phenylethynyl)styrene) before and after the curing process.

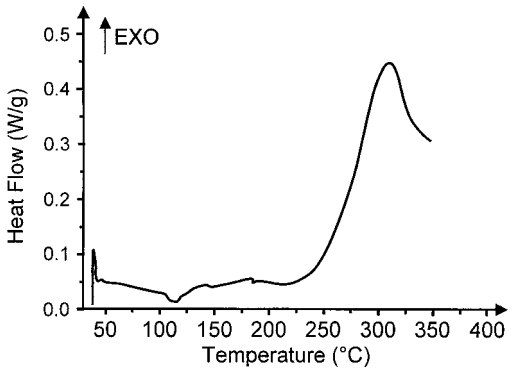

Figure 5. DSC of poly(3,4-bis(phenylethynyl)styrene). The heating rate was 5 °C/min from 25 to 350 °C.

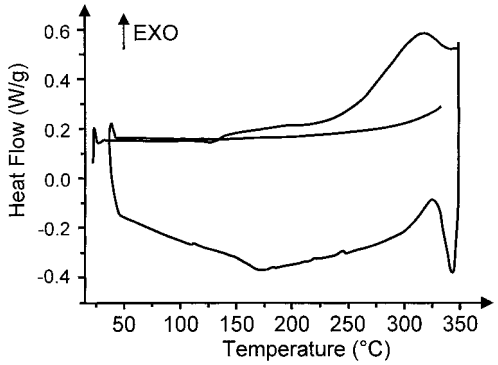

Figure 6. DSC of poly(3,4-bis(phenylethynyl)styrene) in heating−cooling−second heating cycle. The heating rate was 5 °C/min from 25 to 350 °C.

stretching peaks at 2230 cm^{-1}. After curing, no absorptions were present in this region.

DSC measurements showed a polymer glass transition temperature at 110 °C and melting point at 140 °C (Figure 5). At 250 °C, the heat flow increased, reaching a maximum at 310 °C. This dramatic change in heat flow is assigned to the exothermic Bergman reaction. After cooling to room temperature, a second heating cycle was performed, and no glass or melting transitions were observed (Figure 6). Apparently, this is due to polymer cross-linking and formation of the aromatic structure. During the curing process, the Bergman reaction resulted in the aromatization of the triple bonds in poly(3,4-bis(phenylethynyl)styrene). The polymer structure became more rigid, eliminating the phase transition at higher temperature. Until the temperature reached 270 °C, the heat flow increased. This may be due to the fact that the Bergman reaction was not complete when cooling began, so that when the polymer was reheated, cross-linking was still proceeding. TGA

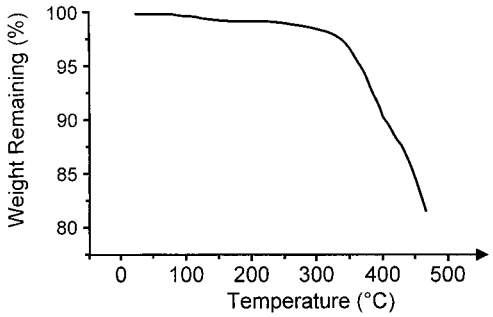

Figure 7. TGA of poly(3,4-bis(phenylethynyl)styrene). The heating rate was 3 °C/min from 20 to 430 °C under a nitrogen atmosphere.

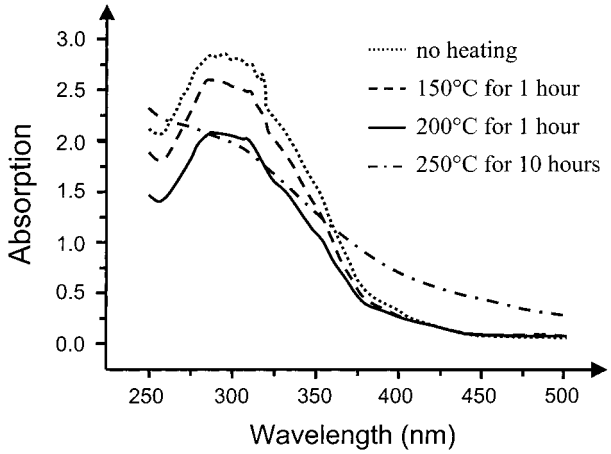

Figure 8. UV spectra of poly(3,4-bis(phenylethynyl)styrene) as a function of curing conditions.

Table 1. Plasma Etch Resistance of Poly(3,4-bis(phenylethynyl)styrene) before and after Curing Compared to that of Other Materials in SF_6 (100 mTorr, 30 sccm, 50 W) and O_2 (200 mTorr, 50 sccm, 100 W) Plasmas

	etch rate (nm/min)	
material	SF_6 RIE	O_2 RIE
poly(3,4-bis(phenylethynyl)styrene)	18.3	80
cured poly(3,4-bis(phenylethynyl)styrene)	11.6	52.5
poly(1-vinylpyrene-*co*-styrene)	18	75
Novolac	32.3	153.5
polystyrene	20	90
silicon	680	

analysis (Figure 7) indicated that polymer degradation started at 320 °C; at 390 °C, ~10% weight loss occurred.

The UV spectra of poly(3,4-bis(phenylethynyl)styrene) at room temperature, 100 °C, 150 °C, and 250 °C for 1, 1, and 10 h, respectively, are shown in Figure 8. After heating at 250 °C for 10 h, the intensity of the absorption at short wavelength decreased, while the absorption at longer wavelength increased, indicating an increase in conjugation, but without well-defined chromophores.

Plasma Etch Resistance. The plasma etch resistance of poly(3,4-bis(phenylethynyl)styrene) before and after the curing process was measured with both SF_6 and O_2 plasmas. The etch resistance of poly(3,4-bis(phenylethynyl)styrene) was higher than that of a conventional Novolac-based photoresist by a factor of nearly 2, which is comparable to the etch resistance displayed by polystyrene and poly(styrene-*co*-vinylpyrene) (Table 1). After curing, the etch resistance of the polymer increased to 3 times that of a Novolac resist. The selectivity of the cured poly(3,4-bis(phenylethynyl)-

styrene) to the silicon substrate was 1 to 58 in SF_6 RIE. This value is higher than that normally used in pattern transfer from the resist to the silicon substrate. As observed in the GPC results, there are only about 7−8 repeat units in each polymer chain. After the Bergman reaction, the cured material becomes more cross-linked and more aromatic, which accounts for the higher etch resistance in both the SF_6 plasma and the O_2 plasma.

Discussion

As measured by GPC, the initial polymer had a molecular weight corresponding to 7−8 repeat units. This low molecular weight can be attributed to two factors. First, the relatively high initiator concentration (5 mol %) necessarily produces low molecular weights, which was desired to maintain the resulting solubility. Second, stabilized monomers, e.g., *p*-vinylbiphenyl, are known to propagate inefficiently. As discussed below, molecular weight per se is not critical to efficient barrier properties.

The changes in the physical properties and chemical structure of poly(3,4-bis(phenylethynyl)styrene) upon curing are consistent with the Bergman cycloaromatization reaction. Indeed, thermal and photolytic cycloaromatization reactions of enediynes have been reported previously.[15,16] In the current study, the carbon−carbon triple bond absorption at 2230 cm^{-1} disappears from the infrared spectrum and the sp-hybridized ^{13}C resonances at 85−95 ppm vanish from the NMR spectrum. Moreover, the well-defined absorption at 300 nm shifts to a broad and featureless long-wavelength absorption. Such bathochromic shifts and broadening are consistent with the formation of a more delocalized polyaromatic structure, perhaps involving chain-transfer processes. Additionally, the glass transition in the polymer precursor disappears, and the high-temperature exotherm also disappears. Whether this occurs with simultaneous cross-linking to form a poly(1,4-naphthylene) structure is unclear. However, it is instructive to note that the parent 1,2-bis(phenylethynyl) benzene undergoes a consolidation reaction even in the presence of a good hydrogen donor, 1,4-cyclohexadiene.[14] Nevertheless, the molecular weight is high enough that simple thermal ablation is not significant. Higher molecular weights, as opposed to higher aromaticity, do not seem to play an important role.

The relative etch resistance of the cured polymer to silicon in a fluorine plasma is 58 to one, an increase of over 50% over the uncured polymer. Thus, the presence of aromaticity is a clear advantage to resist stability at the same C/H ratio. Since the minimum depth profile for active devices in silicon is 50 nm, this suggests that, in principle, a protective barrier can be achieved with a minimum thickness of 1 nm. This represents ca. 3 monolayers of an aromatic substrate and makes "nanolithography" within range for highly aromatic materials. The application of these materials to high-resolution pattern formation is the subject of ongoing investigations.

Conclusions

The highly aromatic prepolymer, poly(3,4-bis(phenylethynyl)styrene), has been synthesized and can undergo cycloaromatization during curing at 250 °C to form a cross-linked material. This aromatization or consolidation enhances the plasma etch resistance during subsequent plasma pattern transfer processes. The polymer was etched in both SF_6 and O_2 plasmas, and the plasma etch resistance was compared with a conventional Novolac resist (Shipley 1813). After curing, the etch rate of the cured polymer decreased to one-third that of a DNQ-Novolac resist. The selectivity of the cured poly(3,4-bis(phenylethynyl)styrene) to the silicon substrate was 1 to 58 in SF_6 RIE. Thus, cured poly(3,4-bis(phenylethynyl)styrene) and structurally analogous materials may meet the resist mask requirements for plasma etching under high-resolution conditions.

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