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SPIE.

Event: 26th Annual International Symposium on Microlithography, 2001, Santa Clara, CA, United States

Resist Materials for 157 nm Microlithography: An Update

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ABSTRACT

Fluorocarbon polymers and siloxane-based polymers have been identified as promising resist candidates for 157 nm material design because of their relatively high transparency at this wavelength.¹ This paper reports our recent progress toward developing 157 nm resist materials based on the first of these two polymer systems. In addition to the 2-hydroxyhexafluoropropyl group, α -trifluoromethyl carboxylic acids have been identified as surprisingly transparent acidic functional groups. Polymers based on these groups have been prepared and preliminary imaging studies at 157 nm are described. 2-(Trifluoromethyl)bicyclo[2,2,1]heptane-2-carboxylic acid methyl ester derived from methyl 2-(trifluoromethyl)acrylate was also prepared and gas-phase VUV measurements showed substantially improved transparency over norbornane. This appears to be a general characteristic of norbornane-bearing geminal electron-withdrawing substituents on the 2 carbon bridge. Unfortunately, neither the Ni^{II} nor Pd^{II} catalysts polymerize these transparent norbornene monomers by vinyl addition. However, several new approaches to incorporating these transparent monomers into functional polymers have been investigated. The first involved the synthesis of tricyclononene (TCN) monomers that move the bulky electron-withdrawing groups further away from the site of addition. The hydrogenated geminally substituted TCN monomer still has far better transparency at 157 nm than norbornane. The second approach involved copolymerizing the norbornene monomers with carbon monoxide. The third approach involved free-radical polymerization of norbornene monomers with tetrafluoroethylene and/or other electron-deficient comonomers. All these approaches provided new materials with encouraging absorbance at 157 nm. The lithographic performance of some of these polymers is discussed.

Keywords: 157 nm lithography, 157 nm resist, 2-(trifluoromethyl)acrylates, fluoronorbornanes, metal-catalyzed addition polymerization, carbon monoxide copolymerization, dissolution inhibitor

1. INTRODUCTION

The design of 157 nm photoresists is a daunting task since air, water, and most organic compounds are opaque at this wavelength. Spectroscopic studies¹ led to the observation that fluorinated hydrocarbons and siloxanes offer the best hope for the transparency that is necessary for the design of an effective 157 nm photoresist, and these classes of materials have quickly become the prominent platforms for a variety of research activities in this field. Our approach to the design of the resist polymer requires identification of four "modules": a backbone that tethers the functional substituents and provides basic mechanical properties, an etch barrier that provides RIE resistance, an acidic group that generates tetramethylammonium hydroxide (TMAH) developer solubility, and an acid-labile protecting group that enables a chemical amplification type solubility switch. Here, the difficulty lies in identifying moieties that will not only perform these specific functions, but also provide transparency at the 157 nm wavelength. Our group identified the bistrifluoromethylcarbinol (1,1,1,3,3,3-hexafluoro-2-hydroxypropyl) (HFP) group as a transparent acidic module, and acetal protecting groups were shown to function effectively in conjunction with this structure in an acid-catalyzed, chemically-amplified system (**Figure 1**).²

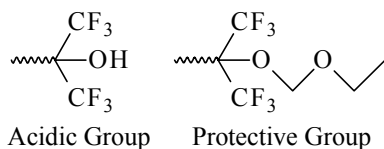


Figure 1. Transparent acidic module

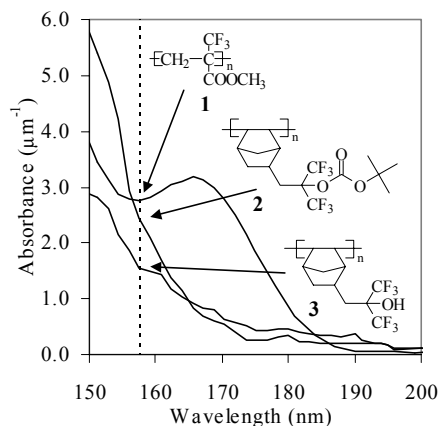


Figure 2. Absorbance of fluorinated polymers

Continuing with this "modular" approach, we reported the relatively low absorbance of poly(methyl 2-(trifluoromethyl)acrylate), which inspired the synthesis of a variety of fluorine-substituted poly(norbornane)s^{3a} (**Figure 2**). Our group has thereby identified polymers that are relatively transparent and fulfill the requirements of the backbone and etch barrier module functions of a 157 nm resist.

In this paper, we present our continuing synthetic efforts in the area of fluorocarbon-based 157 nm resist development. We have synthesized a number of fluorinated monomers and have incorporated these into polymer systems by a variety of methods including metal-catalyzed addition polymerizations, carbon monoxide copolymerizations, and anionic and free radical-initiated polymerizations. Investigation of these materials by VUV spectrometry and variable angle spectroscopic ellipsometry (VASE), along with actual imaging experiments of certain polymers, has shown encouraging results and provided a clear direction for the development of 157 nm lithographic resist materials.

2. EXPERIMENTAL

Section 2.1 Materials

All starting materials were purchased from Aldrich and these were used as received unless noted otherwise. 1,1,1-Trifluoro-2-(trifluoromethyl)pent-4-en-2-ol was received as a gift from AZ Clariant and 2-(trifluoromethyl)acrylic acid was received as a gift from Central Glass Co. All solvents were dried by fractional distillation either over Na/K metal or CaH₂. All liquid reagents used for VUV measurements were distilled from appropriate drying agents, thoroughly degassed by freeze-pump-thaw cycles, and sealed in glass ampoules under vacuum.

Section 2.2 Vacuum UV Spectroscopy

Gas-phase VUV measurements were made on an Acton CAMS-507 spectrophotometer fitted with a custom-made gas cell attachment. The details of the cell design and implementation are the subject of a separate paper.⁴ VUV spectra of polymer films were calculated from measurements made with a J.A. Woollam VU301 variable angle spectroscopic ellipsometer and/or measured with the Acton CAMS-507 spectrophotometer. The films were cast on calcium fluoride disks from solutions in propylene glycol monomethyl ether acetate (PGMEA) or cyclohexanone and baked at 110°C for at least 5 minutes prior to analysis. All absorbance data reported are in base 10.

Section 2.3 Synthesis

The polyfluorinated acrylate terpolymer (**4**) was prepared by anionic polymerization³ followed by hydrogenolysis of the benzyl ester to provide the free carboxylic acid. The 7,7-difluoronorbornane (**6**) was made by a 5-step synthesis that will be reported elsewhere. The synthesis of the other fluorinated norbornanes (**5**, **7**) was reported in a previous article.^{3a} Bicyclo[2.2.1]hept-5-ene-2-carboxylic acid *tert*-butyl ester (NBTBE, **8**) and bicyclo[2.2.1]hept-5-ene-2-(1,1,1-trifluoro-2-trifluoromethylpropan-2-ol) (NBHFA, **9**) were polymerized by a variety of methods to give poly(NBTBE-*co*-NBHFA) copolymers (**10**). 2-(Trifluoromethyl)bicyclo[2.2.1]hept-5-ene-2-carboxylic acid *tert*-butyl ester (NBCF₃TBE, **11**) was

prepared by the cycloaddition of the corresponding *t*-butyl ester and cyclopentadiene. These polymers were initiated with (a) (η^6 -toluene)bis(pentafluorophenyl) nickel(II) in toluene, (b) allyl palladium catalyst in dichloromethane without proton sponges, or (c) allyl palladium catalyst in dichloromethane with proton sponges.⁶ 4,4-Difluoro-3-(trifluoromethyl)tricyclo[4.2.1.0^{2,5}]non-7-ene-3-carboxylic acid methyl ester (TCNCF₃ME, **13a**) was synthesized from the cycloaddition of quadricyclane (**13**)⁵ with methyl perfluoromethacrylate¹³. Hydrogenation with Pd/C provided the reduced analogue **14** in high yield. Poly(TCNCF₃ME) (**15**) was initiated with an allyl palladium catalyst⁶ in dichloromethane at room temperature. The carbon monoxide copolymers (**16**, **17**, **19**, **20a**, **26**) were synthesized with Drent's catalyst⁷ in methanol in a sealed Parr reactor at 80°C overnight. Polymer **16** was reacted with di-*t*-butyldicarbonate and 4-dimethylaminopyridine to yield polymer **23**. The tetrafluoroethylene copolymers (**21**, **22**) were prepared at 90°C in Freon 113 (1,1,2-trichlorotrifluoroethane) with AIBN as the initiator. The reactions were run overnight.

Section 2.4 Imaging Conditions

The following were typical imaging conditions, unless noted otherwise. Wafers were coated with 150 nm of resist over 82 nm of bottom antireflective layer and softbaked at 140°C for 60 sec. Imaging was performed using an alternating phase shift mask on an EXITECH 157 nm Microstepper at SEMATECH using a numerical aperture of 0.6 and a partial coherence of 0.3. Wafers were then post-exposure baked at 130°C for 90 sec and puddle-developed for 20 sec in 2.38% TMAH. Top down scanning electron micrographs were collected with a JEOL 7550 and cross-sectional data were collected on a Hitachi 4500 scanning electron microscope.

3. RESULTS AND DISCUSSION

Section 3.1 Fluorinated Acrylate Platform

The relatively low absorbances of the alkyl 2-(trifluoromethyl)acrylates prompted the synthesis of a fluorinated acrylate polymer (**4**) similar to IBM's Version 1 193 nm resist.⁸ As shown in **Figure 3**, the absorbance of this polymer at 157 nm is approximately 3 μm^{-1} , which is several orders of magnitude lower than that of the commercially available 248 nm resist, UV-6. However, preliminary imaging experiments using 157 nm radiation (**Figure 4**), followed by SEM measurements, indicated that this fluorinated polymer backbone is not stable to e-beam radiation. Some of the polymer vaporized when exposed to high energy electrons from the scanning electron microscope (SEM). This result is not so surprising since this fluorinated acrylate platform was originally designed as an e-beam resist and is clearly very sensitive to main chain scission.⁹ This result led to the decision to explore incorporation of the fluorinated acrylates into polymer structures indirectly rather than directly. One method for doing this is to react the acrylates with cyclopentadiene to give norbornene analogues that can then be polymerized via vinyl addition using an appropriate metal catalyst.

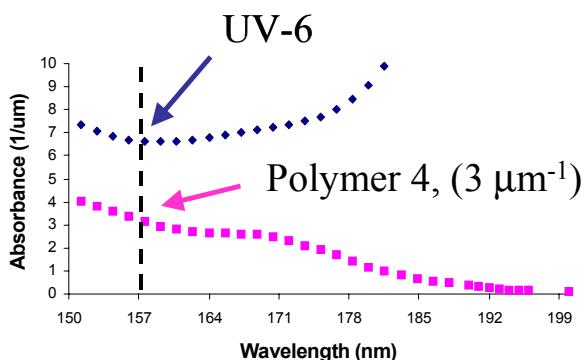
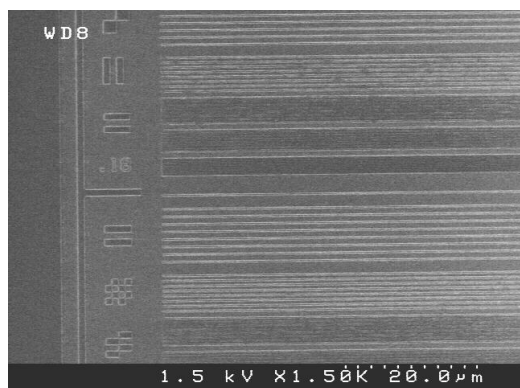
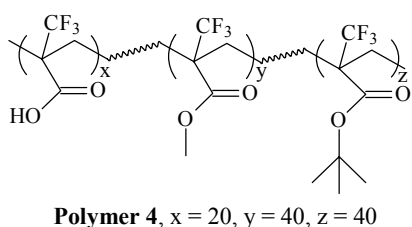


Figure 3. Absorbance of fluorinated acrylate (**Polymer 4**)

Figure 4. SEM of Pt coated sample of **Polymer 4**

94.9% Polymer, 5% TPS-Nf, 0.1% Bu₄NOH

157 nm exposure (0.6NA-0.7 σ), binary mask, 190 nm thick on 70 nm of DUV30, 130°C-60s PAB, 130°C-90s PEB, 60 sec development (0.05N TMAH)

Section 3.2 Absorbances of Fluorinated Norbornanes

The norbornene analogues derived from 2-(trifluoromethyl)acrylates will surely be more absorbing at 157 nm than the acrylates alone, but offer a trade-off between absorbance and stability. Our group has studied different fluorine substitution patterns on norbornane and how the absorbance of the ring system is influenced by substitution patterns.³ Absorbance at 157 nm is decreased dramatically by selectively fluorinating the norbornane skeleton at key positions (**Figure 5**). These studies showed that introduction of geminal fluorosubstituents at the two-carbon bridge (**5**), rather than the one-carbon bridge (**6**) is the most effective substitution pattern. We therefore reasoned that the introduction of geminal electron-withdrawing groups such as a trifluoromethyl or carboxylalkyl at the 2 position of norbornane should also improve absorbance relative to the parent hydrocarbon.

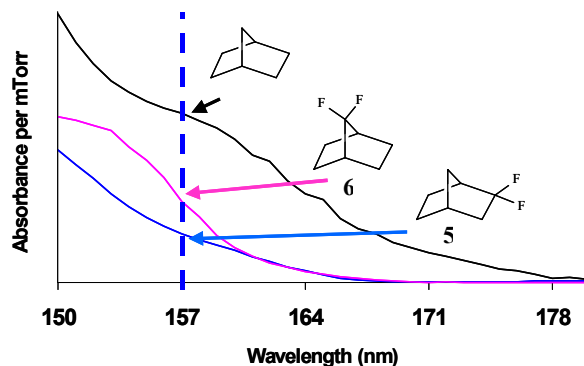


Figure 5. Absorbances of fluorinated norbornanes

Several 2,2-disubstituted norbornanes were therefore prepared by the Diels-Alder addition of cyclopentadiene to some 2-(trifluoromethyl)acrylates, and the products were reduced with hydrogen and Pd/C to give the corresponding substituted norbornanes (**Figure 6**). The absorbance of one of these norbornanes, the methyl ester (**7**), is compared to the absorbance of norbornane and 2,2-difluoronorbornane in **Figure 7**. This 2-trifluoromethyl-substituted compound is more absorbing at 157 nm than 2,2-difluoronorbornane, most likely due to carbonyl absorption, but it is far more transparent than norbornane.

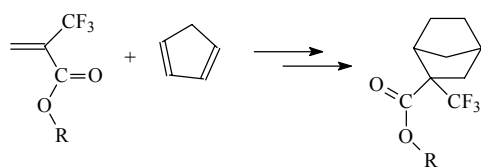


Figure 6. Synthesis of fluorinated 2,2-disubstituted norbornanes

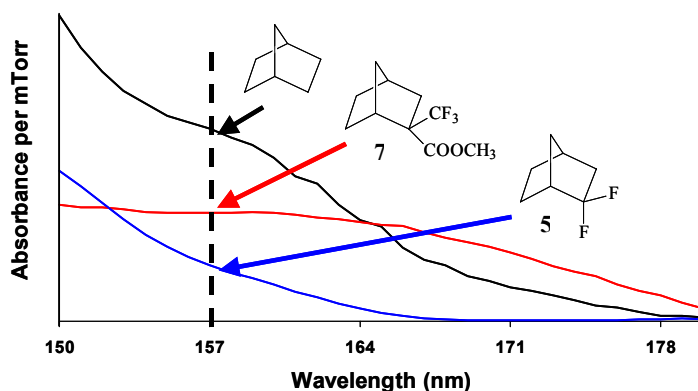


Figure 7. Absorbance of fluorinated norbornane methyl ester

Section 3.3 Metal-Catalyzed Addition Polymerization Studies

We have previously reported the syntheses and absorbances of a polynorbornene substituted with a HFP group and its *t*-BOC protected derivative (**Figure 2**).³ These polymers, to our surprise, are less absorbing than poly(methyl 2-(trifluoromethyl)acrylate). This discovery led us to design resist platforms based on vinyl addition copolymers that incorporate this monomer. The copolymers (**10**) of NBHFA (**9**) and NBTBE (**8**) were successfully made using (η^6 -toluene)bis(pentafluorophenyl) nickel (II) as the vinyl addition catalyst (**Figure 8**). The absorbance of one of the co-

polymers ($x = 80$, $y = 20$) is approximately $2.3 \mu\text{m}^{-1}$ at 157 nm. Preliminary imaging results using this co-polymer showed that although the material provides good film coatings, wets well during development and has a high contrast, it suffers from swelling during development. We believe that the high molecular weight of the polymers produced by the nickel catalyst is a major contributor to swelling, and efforts are underway to lower the molecular weight of polymers produced by this catalyst.

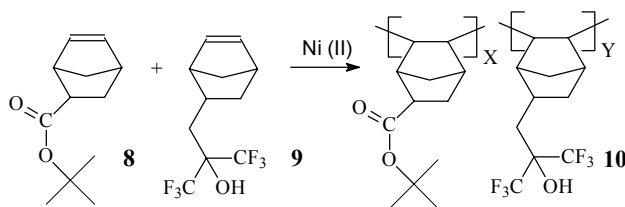


Figure 8. Synthesis of poly(NBHFA-co-NBTBE)

All efforts to incorporate the 2-trifluoromethyl-substituted norbornene esters into a polymer by vinyl addition using the nickel catalyst were unsuccessful. For example, NBCF₃TBE (**11**) was only incorporated by an amount less than half the feed ratio, when copolymerized with NBHFA (**9**) (**Figure 9**). Polymer yields from this reaction are also extremely low (< 10 %). NBCF₃TBE also did not copolymerize with NBHFA with an allyl palladium catalyst prepared using a literature procedure.⁶

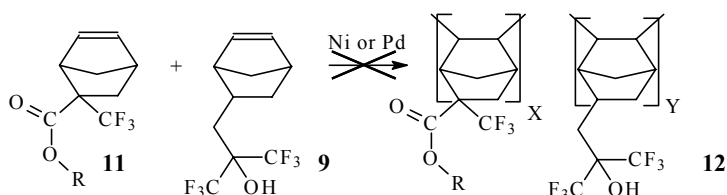


Figure 9. Attempted synthesis of poly(NBHFA-co-NBCF₃TBE, R = *t*-butyl, $x = 14$, $y = 86$)

The allyl palladium catalyst does copolymerize NBHFA and NBTBE to yield polymer **10**, but the acid-labile functional groups can be deprotected in reactions based on this allyl palladium catalyst. The formation of carboxylic acids is observed from attempts to polymerize NBTBE using this catalyst. The source of the strong acid that causes this deprotection may be reductive elimination of palladium hydride that forms during the polymerization. Whatever the source of this acid, the best solution is to quench it using sterically hindered, polymer-bound pyridines or “proton sponges”. These hindered amines can neutralize any residual acid without significantly affecting the active catalyst (by irreversible binding to the active catalyst). The other problem with this polymerization is that it generates product with very high molecular weight. The use of typical chain transfer agents on the polymerization of monomer **9** was unsuccessful (**Figure 10**). Addition of 1-hexene did not reduce the molecular weight of the polymer to an acceptable degree. Another, more expensive, solution is to simply use a higher catalyst loading. This method worked well with the palladium catalyst (**Figure 11**), but did not work with the nickel catalyst. In summary, we successfully solved both of the problems that plagued the allyl palladium catalyzed addition polymerization by using proton sponges and higher catalyst loadings. The use of large amounts of expensive catalyst is not a satisfying solution but it is a workable one, and provides resist material while we search for an effective chain transfer agent.

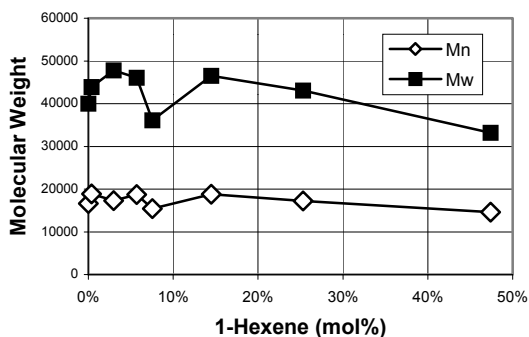


Figure 10. Effect of 1-hexene as a chain transfer agent on the molecular weight of polymer **3** (from monomer **9**)

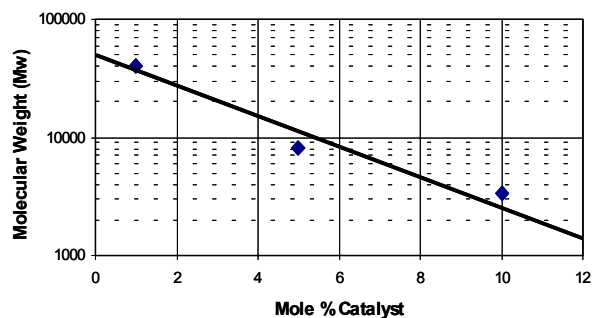


Figure 11. Effect of added Pd catalyst on molecular weight of polymer **3** (from monomer **9**)

Section 3.4 Incorporation of Geminal Substituted Monomers

Incorporation of geminal substituted monomers such as NBCF_3TBE into a polymer did not work well using either nickel (II) or palladium (II) catalysts. The reason for this may stem from the reduced electron density of the double bond resulting from the close proximity of the electron-withdrawing groups, from steric inhibition, or both. It should be noted that these vinyl addition catalysts typically polymerize electron-rich olefins much faster than electron-poor olefins.⁶ We have explored several approaches to incorporating these monomers into a polymer system. The first was to move the trifluoromethyl group further away from the double bond by synthesizing the corresponding tricyclononene (TCN) analogues. The second method involved copolymerization of carbon monoxide with the trifluoromethyl-substituted norbornene monomers using a different catalyst system. The third method was to use free-radical mediated polymerization with electron deficient monomers, for example, tetrafluoroethylene (TFE) to make alternating copolymers.

Section 3.4.1 Tricyclononene (TCN) Monomers

We have successfully synthesized the TCN model compound **14** (Figure 12) and compared its absorbance to that of norbornane and 2,2-difluoronorbornane (Figure 13). Compound **14** shows improved transparency over the norbornane hydrocarbon, so a variety of TCN derivatives are currently being prepared. The TCNCF_3ME monomer was successfully polymerized by the allyl palladium catalyst described earlier (Figure 14), and its absorbance at 157 nm was found to be $2.8 \mu\text{m}^{-1}$. Therefore, the TCN system has significantly improved reactivity towards vinyl addition polymerization while retaining a remarkable absorbance at 157 nm.

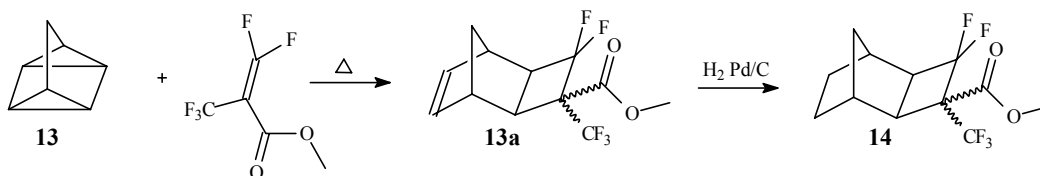


Figure 12. Synthesis of a fluorinated TCN compound

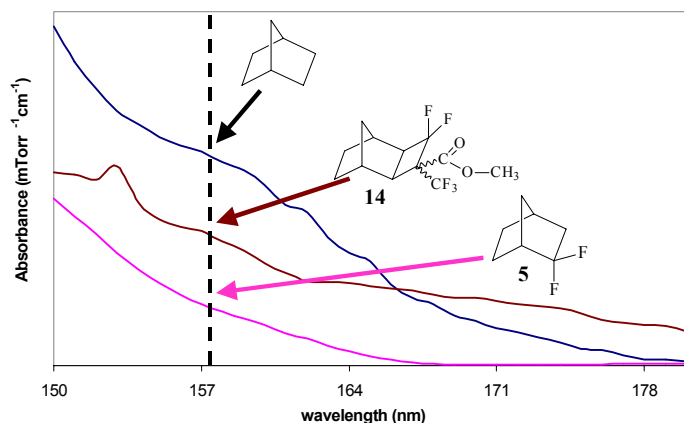


Figure 13. Absorbance of fluorinated TCN compound

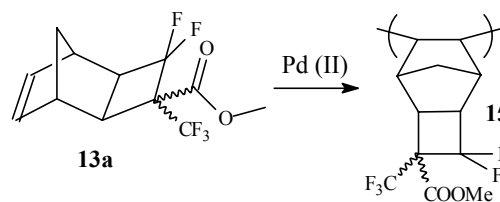


Figure 14. Synthesis of fluorinated TCN polymer

Section 3.4.2 Carbon Monoxide Copolymerization

The use of carbon monoxide as a comonomer enabled the production of polymers from geminal CF_3 -substituted monomers that could otherwise not be polymerized by vinyl addition. Carbon monoxide polymerization yields two types of polymer backbones, a ketal form and a ketone form, depending on the type of catalyst, solvent and reaction temperature (Figure 15).¹⁰ The ketone form can be reduced or fluorinated by the appropriate reagents.¹¹ These polymers will not be discussed in this paper. The current discussion will involve the spiral ketal form of the polymer.

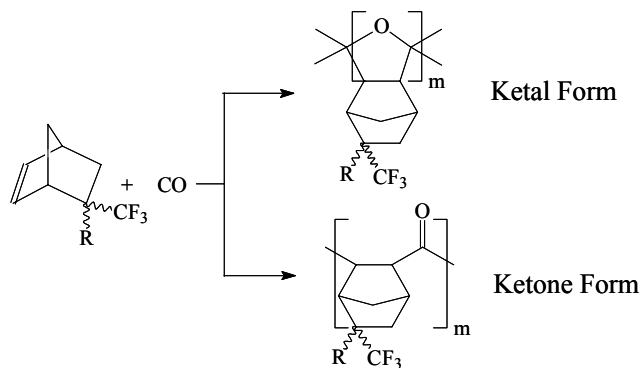


Figure 15. Products of carbon monoxide polymerization

We prepared two model ketal polymers (**16**, **17**) for absorbance measurements. **Figure 16** shows the absorbance spectra of the models. Polymer **16**, has an absorbance of $2.5 \mu\text{m}^{-1}$ while the acetate-substituted polymer **17** has an absorbance of $3.1 \mu\text{m}^{-1}$. These materials are approximately one thousand times less absorbing at 157 nm than commercially available 248 nm resists. The main reason for studying these ketal polymers was to find a way to incorporate our geminal substituted norbornene monomers into a resist material. Therefore, monomer **18** was copolymerized with carbon monoxide using Drent's catalyst (**Figure 17**). The absorbance of the resulting polymer (**19**) is $4.0 \mu\text{m}^{-1}$. Hydrolysis of the acetate provided polymer **20** with an absorbance of $2.7 \mu\text{m}^{-1}$. Polymer **20a** was also made successfully from the corresponding monomer (**11**). Clearly, it is possible to incorporate the geminal substituted norbornene monomers into a polymeric structure by an alternating copolymerization with carbon monoxide. All the carbon monoxide copolymers have low molecular weights ($M_w = 1000\text{-}2500$). The imaging characteristics of one of these copolymers will be discussed in a later section.

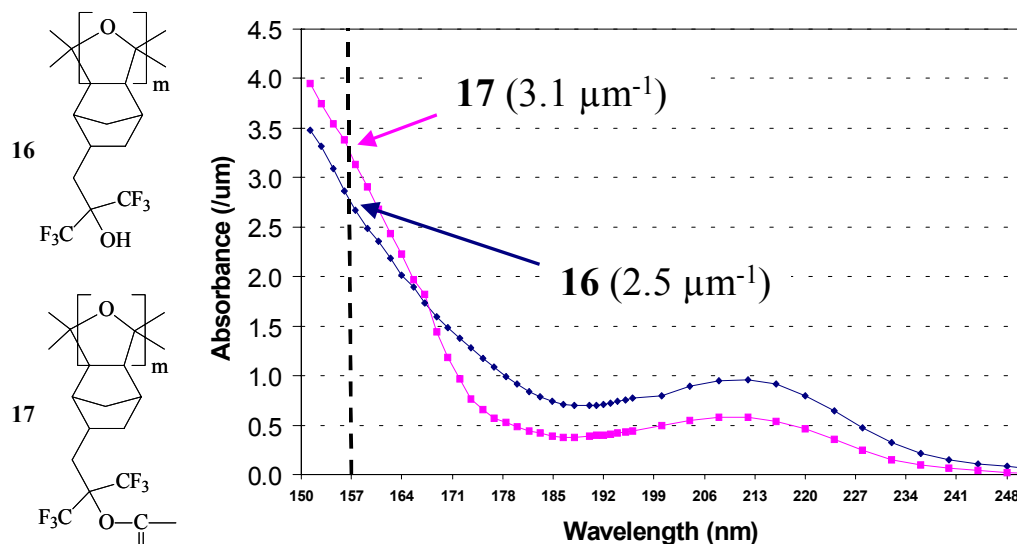


Figure 16. Absorbances of carbon monoxide polymers

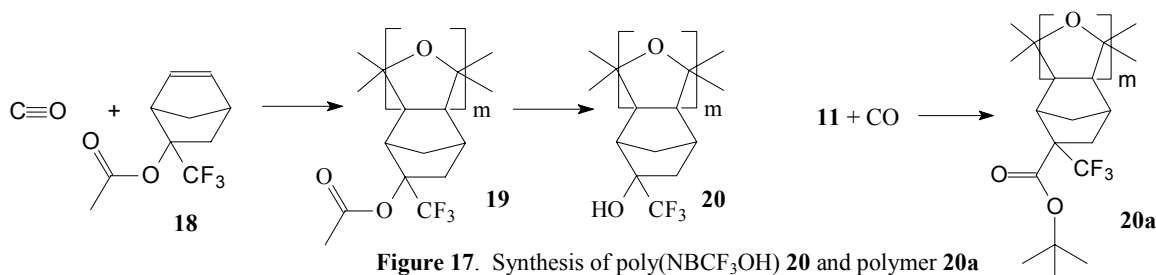


Figure 17. Synthesis of poly(NBCF₃OH) **20** and polymer **20a**

Section 3.4.3 Radically-Initiated Copolymerization

Preliminary work in the area of free-radical initiated polymerization has focused on the use of tetrafluoroethylene (TFE) as a comonomer. We are continuing the search for a transparent monomer that will undergo free-radical copolymerization with our norbornene monomers, analogous to the way maleic anhydride or sulfur dioxide undergoes radical polymerization with norbornene. A variety of comonomers are being auditioned in this study. A model polymer, poly(NB-co-TFE) (**21**), was made and its absorbance was found to be $1.1 \mu\text{m}^{-1}$ (**Figure 18**). A functional derivative, poly(NBTBE-co-TFE) (**22**), has also been made, and its characterization is now in progress.

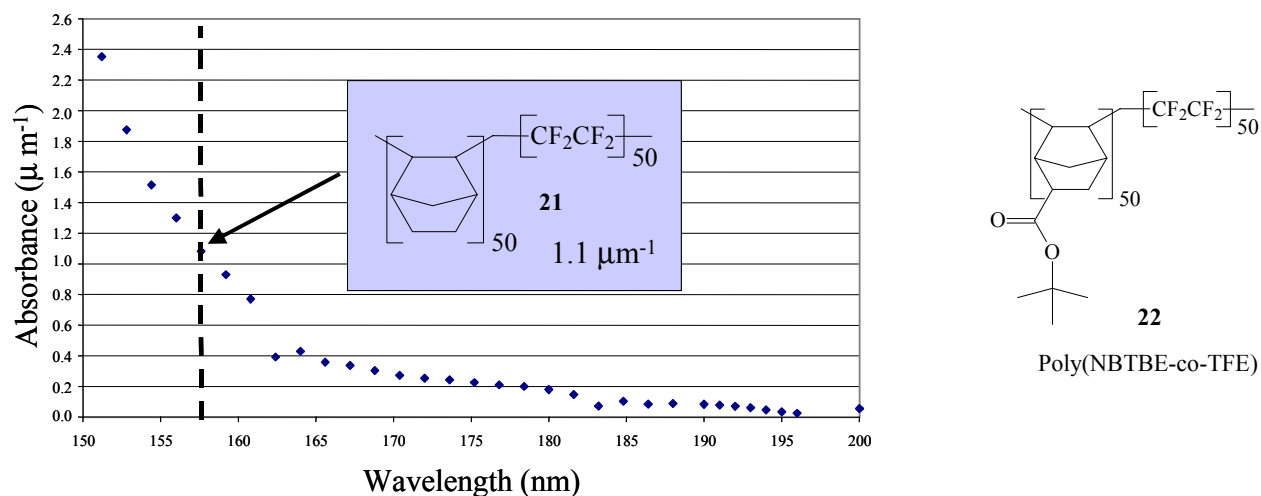


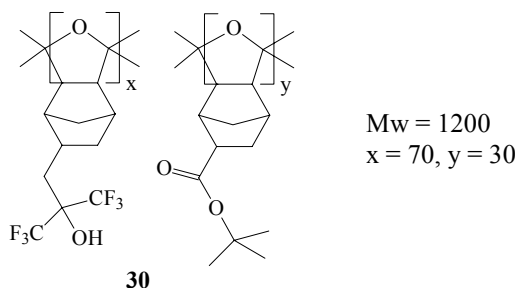
Figure 18. Absorbance of poly(NB-co-TFE) **21**

Section 3.5 Lithographic Evaluation

The functional characteristics of some of the polymers described in the paper have been assessed in preliminary imaging experiments.

Section 3.5.1 Imaging of Carbon Monoxide Copolymers

Preliminary 157 nm imaging studies were done on the carbon monoxide norbornene terpolymer **30**. The resist formulation and imaging conditions are shown in **Figure 20**. This polymer showed good lithographic processing properties; the polymer coated well, wetted well during development, did not leave residues or swell after development, showed promising resolutions, and has high contrast. However, the surface of the developed resist was very rough. The roughness is presumed to be due to the polymer's poor mechanical properties, which in turn may be due to the low molecular weight and rod-like character of the polymer.



Formulation: 93.95% Polymer **30**, 6% TPS-Nf, 0.05% TBAH in PGMEA
 Conditions: 157 nm exposure (0.6NA-0.7 σ , 2 mJ/cm²), binary mask, 180 nm thick resist on 70 nm anti-reflective layer (DUV30), 130°C-60s PAB, 130°C-90s PEB, 20 sec 0.26N TMAH development

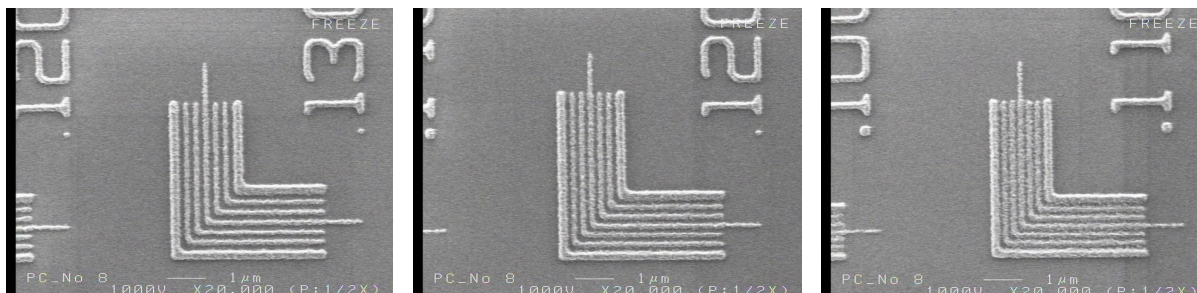
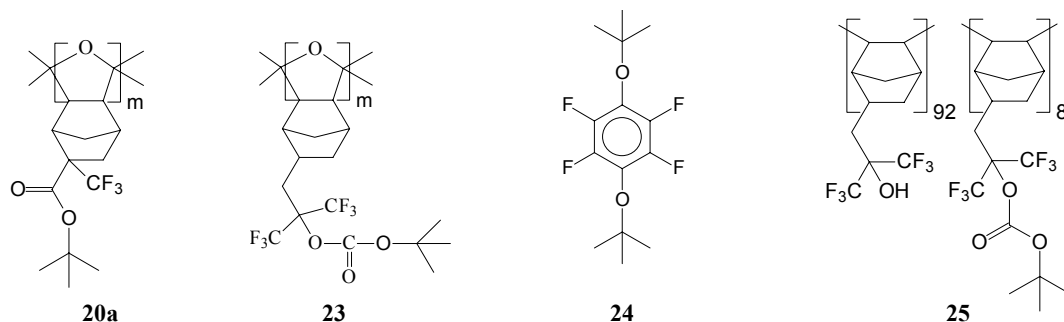


Figure 20. SEMs of carbon monoxide norbornene terpolymer **30**

Section 3.5.2 Dissolution Inhibitor (DI) Studies

Efficient imaging of addition polymers is reported to require dissolution inhibitors.¹² We have therefore surveyed a variety of compounds that may be used as dissolution inhibitors for 157 nm lithography. Since the carbon monoxide copolymers (**20a**, **23**) typically have very low molecular weights, they were tested as dissolution inhibitors. Other compounds tested include 1,4-di(*t*-butoxy)tetrafluorobenzene (**24**), because it is sufficiently transparent at 157 nm, and related monomeric species. The compounds were tested in polymer **25** (Mw = 40,000), which was prepared by palladium(II) catalyzed vinyl addition polymerization.



Solutions of **25** and each of the dissolution inhibitors were made in the appropriate solvent (20 wt%). The films were baked at 110°C for 90 sec and thickness measurements were made before and after 120 sec development time. The carbon monoxide copolymer blends gave clear, glassy films appear to be phase compatible with **25** over the entire concentration range studies. The dissolution rate was plotted against dissolution inhibitor loading, as shown in Figure 19.

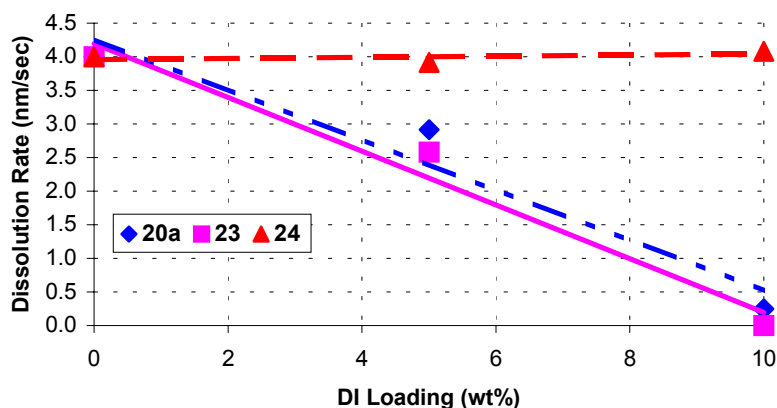
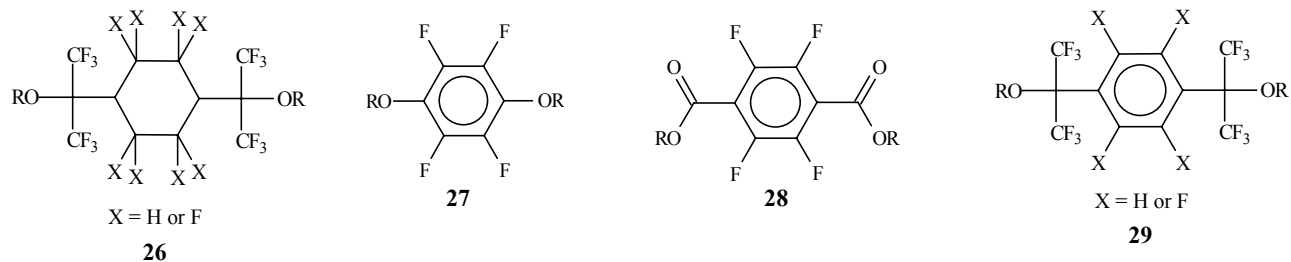


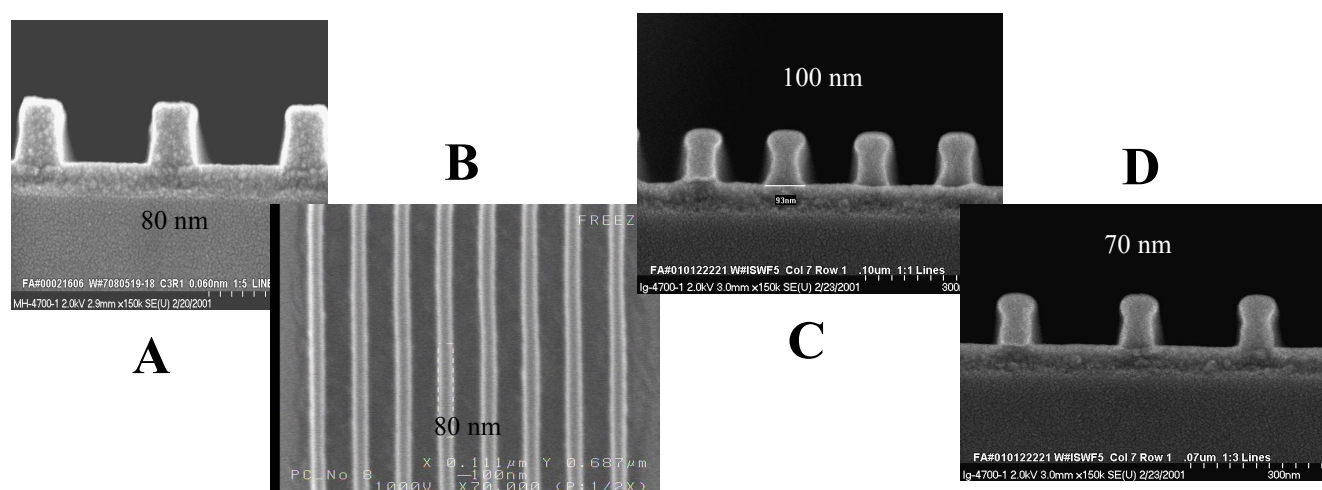
Figure 19. Dissolution rate of polymer **25** vs. DI Loading

Compound **24** did not inhibit the dissolution of the base polymer at all, even at a high loading. Both of the carbon monoxide copolymers completely inhibit the dissolution of the base polymer at only 10 wt% loading. These two polymers are therefore both promising candidates for use as dissolution inhibitors for 157 nm lithography. We have also explored the use of other dissolution inhibitors. The structures of some of these compounds are shown below. The protecting group, R, may be *t*-BOC or *t*-butyl. These compounds do not have to be *para*-substituted, but can also be *ortho*- or *meta*-substituted.



Section 3.5.3 Imaging of Vinyl Addition Copolymers

We are currently optimizing the formulations and imaging conditions required to print sub-100 nm features. This is a tremendous task since it is necessary to explore a variable space that includes photoacid generator, base, dissolution inhibitor, base polymer, exposure, bake, and development. **Figure 21** shows some of the images we are able to print at this point in the program.



A, B: 50/50 blend of 80/20 vinyl addition copolymer **10** with CO copolymers **20a (DI)**

C, D: 70/30 blend of 70/30 vinyl addition copolymer **10** with CO copolymers **20a (DI)**

Conditions: 157 nm exposure (0.6NA-0.3 σ , 50 mJ/cm²), phase shift mask, 148 nm thick resist on 70 nm anti-reflective layer (DUV30), 140°C-60s PAB, 130°C-90s PEB, 20 sec 0.26N TMAH development.

Figure 21. SEMs of vinyl addition copolymers exposed at 157 nm

9. CONCLUSION

We have shown that α -trifluoromethyl carboxylic acid groups can serve as an acidic module in our “modular” design of 157 nm resist materials. These groups, along with the hexafluoroisopropanol groups, are relatively transparent at the imaging wavelength. *t*-Butyl esters and *t*-BOC groups are acceptable protecting groups, even though the carbonyl contribution increases the absorbance. The carbonate group is surprisingly transparent. As our etch barrier, we have continued to use norbornene groups. The parent norbornane hydrocarbon is quite strongly absorbing at 157 nm, but judicious fluorination of norbornene can significantly decrease this absorbance. Norbornene bearing geminal electron-withdrawing groups on the two carbon bridge are precursors to transparent polymers but these monomers resist direct polymerization by vinyl addition. Fortunately, several synthetic approaches were found to circumvent this problem. These include Pd(II) catalyzed

polymerization of TCN monomers, copolymerization of norbornene analogues with carbon monoxide, and free-radical copolymerization of norbornene analogues with TFE. The carbon monoxide copolymers have been shown to function as effective dissolution inhibitors for 157 nm lithography, and resist formulations based on addition polymers and these dissolution inhibitors have provided 70 nm images.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge International SEMATECH for financial support of this work. Dr. Ralph Dammel from AZ Clariant and Central Glass Co. are also acknowledged for their generous donation of key monomers. We are indebted to JSR Corporation for support of Mr. Chiba, Shipley Co. for support of Dr. Yamada and ITRI for support of Dr. Vincent Jean. We are also indebted to Danny Miller and DC Owe-Yang from SEMATECH for their imaging work. Matthew Pinnow, Brian Osborn, and Colin Brodsky are gratefully acknowledged for their contributions to monomer synthesis and VUV measurements. Dr. Scott MacDonald is thanked for his helpful insights. Finally, we acknowledge the help of our undergraduates Anthony Vander Heyden and Jennifer Wunderlich.

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