

Polymers for 157 nm Photoresist Applications: A Progress Report

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Abstract

Finding materials that offer the all of the characteristics required of photoresist matrix resin polymers while trying to maintain a high level of transparency at 157 nm is a daunting challenge. To simplify this task, we have broken the design of these polymers down into subunits, each of which is responsible for a required function in the final material. In addition, we have begun collecting gas-phase VUV spectra of these potential subunits to measure their individual absorbance contributions. Progress on developing materials for each of these subunits are presented along with plans for future studies.

Introduction

The extension of optical lithography to 157 nm has garnered widespread support within the past year as it offers the prospect of extrapolation from experience gathered during decades of optical lithography. Existing photoresist materials designed for use at DUV or 193 nm wavelengths are so strongly absorbing a 157 nm that they can only be used at film thicknesses so small that issues are raised about acceptable defect density. To avoid these potential problems, new photoresist materials must be designed that offer improved transparency at 157 nm. The SIA roadmap dictates that the 100 nm node, the current most probable insertion point for 157 nm photolithography, should enter pilot plant production in 2002. Considering that the development cycle for DUV photoresist materials spanned at least 10 years (1980-1990) and the 193 nm resist development program took approximately eight years (1991 to 1999), the 157 nm photoresist development program is faced with an extremely abbreviated schedule and significant technical challenges.

A single layer photoresist process for imaging at 157 nm is the favored approach among potential industry consumers. Fundamentally, the design of materials for single-layer 157 nm photoresists is identical to that used in the previous lithographic generations in as much as the materials developed for use in 157 nm photoresists must adhere to the set of requirements common to all chemically-amplified photoresist materials. Specifically, potential materials designed for use in a single layer photoresist must offer three fundamental properties: high transparency at the exposure wavelength, resistance to plasma etching processes, and the ability to undergo efficient photochemical transformations that change their solubility in developer solutions. There is another long list of secondary characteristics the new photoresist materials must have including accessibility through reasonably simple synthetic schemes,

glass transition temperatures above typical processing temperatures, adhesion to a wide range of substrates, acceptable shelf storage lifetime, and minimum toxicological risk. To accelerate the development of 157 nm photoresist materials, we have taken an approach that involves new materials development based on results of early studies on various polymer classes¹ in parallel with fundamental studies designed to refine current, and focus future development efforts.

Modular Approach to the Design of Photoresist Polymers

Our research group has adopted a modular approach to the design of new photoresist materials for 157 nm lithography. This technique allows a polymer design to be broken down into several functional subunits that may be addressed in a somewhat independent fashion. It is important to note that transparency requirements must be considered in the design of all subunits.

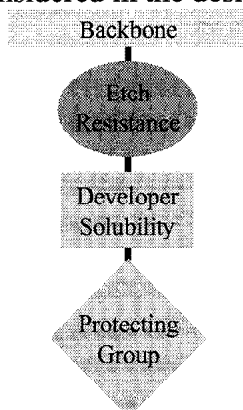


Figure 1: A design for a new photoresist matrix resin can be broken into individual subunits, each responsible for a fundamental property of the final material

Developer solubility unit

Solubility in tetramethylammonium hydroxide (TMAH) developer solutions is achieved by designing matrix resins that include acidic functional groups. DUV photoresists are primarily based on poly(*p*-hydroxystyrene) (PHOST). With a pK_a value of approximately 11, the hydroxyl groups in these resins are sufficiently acidic to render the polymer soluble in basic developer solutions. However, not all hydroxyl groups are so acidic. The acidity of phenolic hydroxyl groups such as those on PHOST is best explained by a concept known as resonance stabilization of an anion. This states that an anion can be made more stable by distributing the charge over several atoms in the molecule. In the case of PHOST, the negative charge can be distributed throughout the π -electron system of the adjacent aromatic ring. Stabilization of the conjugate base (anion) increases acid strength.

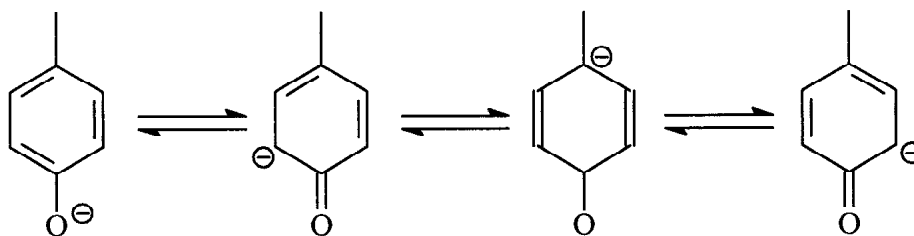


Figure 2: In phenolic systems, the delocalization through resonance of the negative charge throughout the adjacent aromatic system is responsible for the acidity.

In 193 nm photoresist materials, the aromatic groups were replaced with alicyclics bearing carboxylic acids functional groups to provide sufficient developer solubility. The anion of a carboxylic acid is also stabilized through resonance. In this case, the negative charge is distributed between the two equivalent electronegative oxygen atoms of the carboxylate anion. As a result, carboxylic acids have pK_a values between 4 and 5. This means that carboxylic acids are nearly 10^6 times more acidic than phenols but much more transparent at 193 nm.

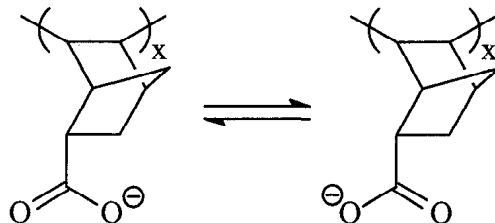


Figure 3: Resonance is also responsible for the acidity of the carboxylic acid groups found in 193 nm photoresist polymers.

Unfortunately, both carboxylic acids and phenols are strongly absorbing at 157nm. Therefore new acidic functional groups must be found for use in 157 nm photoresist materials. Earlier work¹ has shown that materials containing π -systems are, in general, strongly absorbing at 157 nm. This makes resonance stabilization unavailable for use in the design of 157 nm photoresist materials, so a different method of creating acidic functional groups must be utilized.

Negatively charged species can also be stabilized by adjacent electron-withdrawing functional groups that “pull” charge away through an effect known as inductive stabilization. Since inductive effects do not require π -electron systems, they hold promise for creating base-soluble groups that can be utilized in 157 nm designs. The hexafluoroisopropanol group is an example of a hydroxyl group that is fairly acidic as a result of inductive stabilization of the conjugate base. The two trifluoromethyl groups adjacent to the alcohol moiety result in acid strengths near that of phenol ($pK_a \sim 11$)².

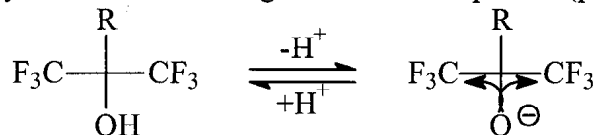


Figure 4: In a hexafluoroisopropanol derivative, the anion is stabilized through inductive effects

Based upon the high fluorine content of this acidic functionality, its absorbance at 157 nm is expected to be minimized. However, this assertion must be confirmed by some sort of spectroscopic method. While facilities have been created to measure the absorbance of solid films at 157 nm, this does not lend itself well to our modular approach where the individual absorbance contribution of small molecules is important. These results are important, not only because they will facilitate our “ground-up” design of new polymers, but they also generate critical data for developing useful simulation tools.

Gas-phase measurements

Vapor phase vacuum UV (VUV) spectra were measured at the National Institute of Standards and Technology (NIST, Gaithersburg, MD) using a custom built gas cell system illustrated in Figure 5. All seals between the gas chambers and the surrounding atmosphere were made with metal gaskets to

ensure that sample purity was maintained during the measurements. Samples were purified by appropriate techniques, vacuum distilled twice, and sealed in glass ampoules under an inert atmosphere.

The procedure for data collection began with loading an ampoule containing a sample of interest into the flexible bellows attached to the gas manifold. The entire system was then heated to approximately 50 °C and evacuated thoroughly. Upon reaching a satisfactory base pressure, the measurement cell was isolated from the gas manifold and a background spectrum was recorded. After collection of the background spectrum, the flexible bellows was isolated from vacuum and shaken so that the glass ampoule shattered *in situ*. A series of evacuation steps ensured complete removal of any inert gas left in the ampoule. The sample vapor was then allowed to charge the measurement cell up to a setpoint pressure at which point a full spectrum was recorded. Spectra were measured at a scan rate of 50 Å/minute from 200 nm to 130 nm. The photomultiplier detector was scanned at a rate of 2000 Hz. Each data point reported in the spectra is an average of 2000 scans, effectively quantizing the spectral data to 0.083 nm interval averages

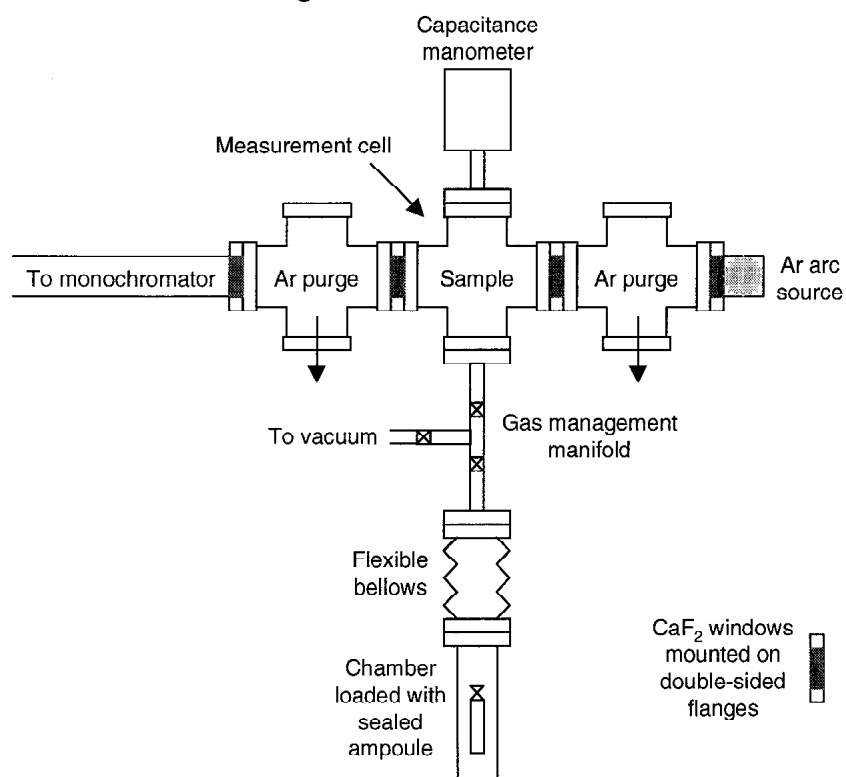


Figure 5: Gas cell for spectroscopic measurements

This procedure was used to record the spectra of a variety of structures including octane and 1,1,1-trifluoro-2-trifluoromethyl-2-propanol (TTP), the spectra of which are shown in figure 6. These data show that the hexafluoroisopropanol unit is very transparent at 157 nm.

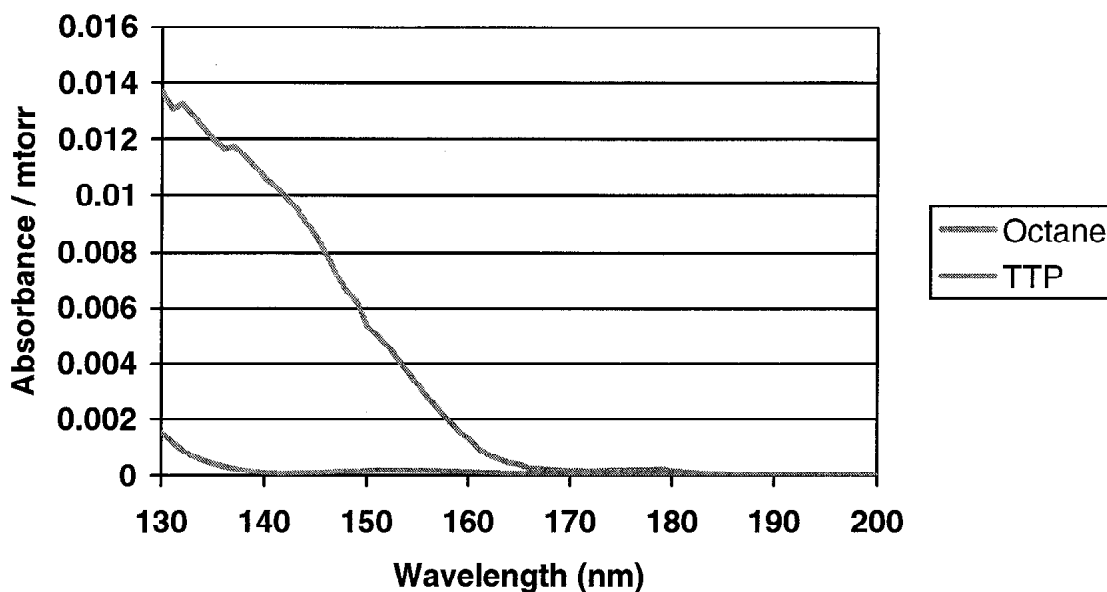


Figure 6: Gas-phase absorbance spectra illustrating the low absorbance of 1,1,1-trifluoro-2-trifluoromethyl-2-propanol (TTP) relative to n-octane

It should be noted that inductively stabilized base soluble groups have been previously utilized in photoresists. The use of a hexafluoroisopropanol functionality first appeared in a DUV photoresist formulation³. The researchers prepared both polystyrene-based matrix polymers and dissolution inhibitors containing these groups and demonstrated base solubility. This same functional group has also recently been incorporated into an alicyclic polysulfone matrix polymer for use as a 193 nm photoresist⁴. The successful utilization of this functional group in earlier photoresist polymers combined with its high transparency at 157 nm make it an ideal candidate for imparting base solubility to 157 nm photoresist designs.

Protecting group unit

Most of the common protecting groups found in current photoresists, such as *tert*-butyl carbonates or *tert*-butyl esters, are not ideal 157 nm photoresist materials since they contain highly absorbing carbonyl groups. Ether or acetal protecting groups on the other hand contain no carbonyls and currently are probably the best choice from a transparency standpoint. Concerns have been raised over potential outgassing problems stemming from the use of acetals in DUV photoresists. These concerns will have to be addressed before acetals can be used successfully in a complete 157 nm photoresist.

Previous photoresists based upon hexafluoroisopropanol functionalities for base solubility were based on *tert*-butyl carbonate protecting groups. To insure that hexafluoroisopropanol groups can function effectively in combination with acetal protecting groups, a model polymer was prepared for lithographic evaluation. The norbornene hexafluoroisopropanol monomer shown in the figure below was prepared according to a literature⁴ procedure. After protection with an acetal group, the monomer was copolymerized with maleic anhydride to create a polymer suitable for imaging experiments at 193 nm as shown in figure 7. Since this evaluation is designed to determine the compatibility of these two functional groups, the ultimate resolution is unimportant. Instead, the results were scrutinized for behavior that might indicate an incompatibility such as scumming between the features, swelling, or an

abnormally high imaging dose requirement. This prototype photoresist gave no indications of incompatibilities during the imaging experiments. Based upon the results shown in figure 8, we are confident that the combination of hexafluoroisopropanol acid groups and acetal protecting groups offers a viable combination for use in 157 nm photoresists.

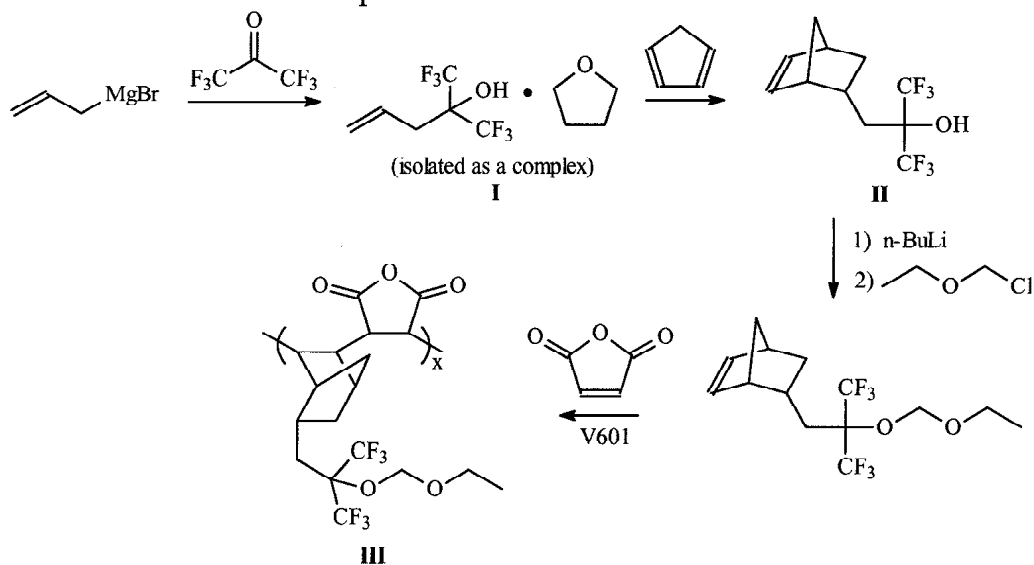


Figure 7: Synthesis of model polymer III to test the combination of hexafluoroisopropanol base-soluble group and acetal protecting group.

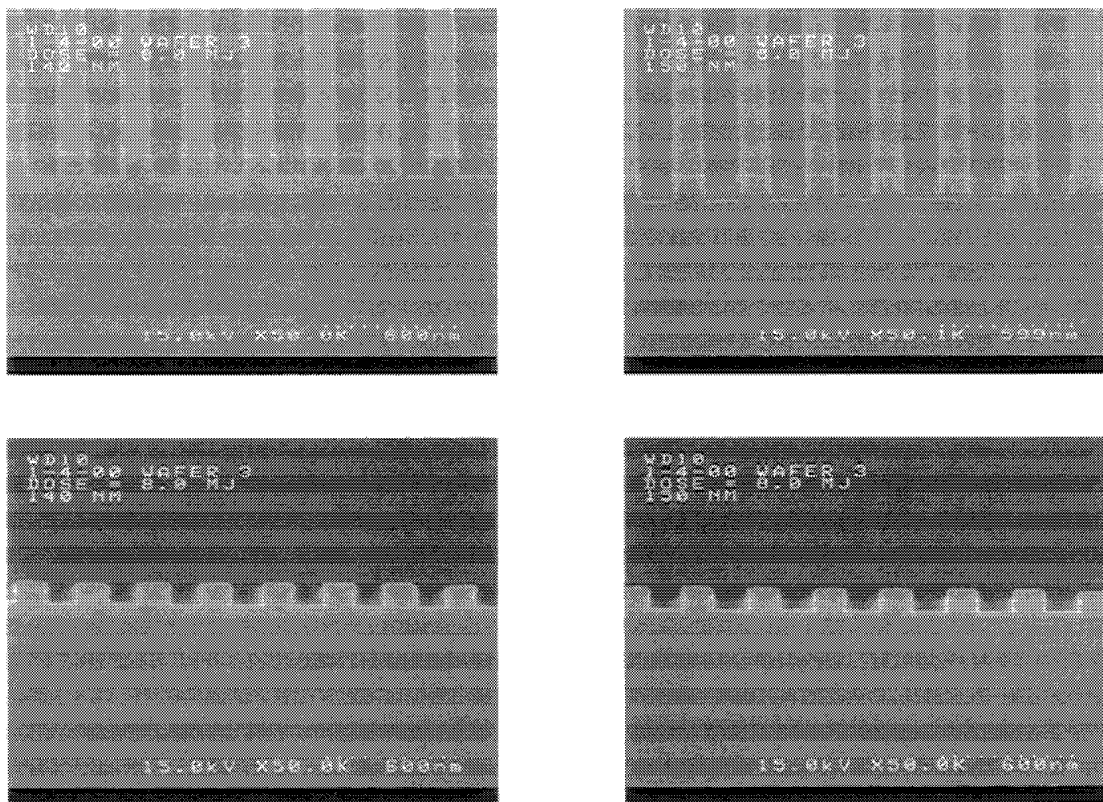


Figure 8: Results from imaging experiments using polymer III at an exposure wavelength of 193 nm. Film thickness = 160 nm, Exposure dose = 8.0 mJ / cm². Features are equal line / space pairs with sizes of (left) 140 nm and (right) 150 nm.

Etch resistant subunit

In i-line and DUV materials, aromatic groups offer the high carbon content required to provide adequate dry etch resistance. Aromatic groups were found to be too strongly absorbing to allow for their incorporation in 193 nm materials. Instead, alicyclic groups, offering high degrees of unsaturation by virtue of numerous rings in their structures, were introduced to replace the aromatic rings. We are pursuing the use of alicyclics in the design of 157 nm photoresist materials. However, in this case, strategically placed electron-withdrawing groups will be necessary to minimize the absorbance contribution from these alicyclic structures.

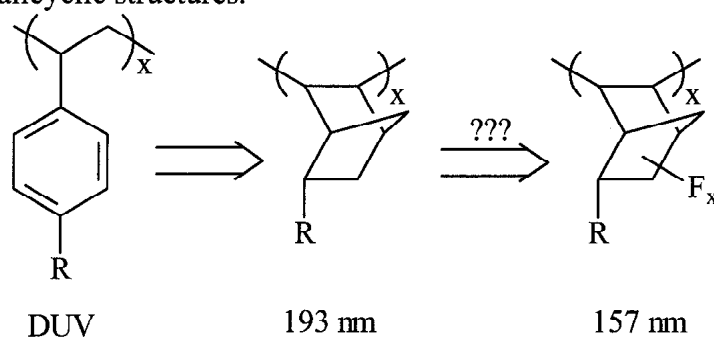


Figure 9: Transition of etch resistant subunits from aromatic groups in DUV resists, to alicyclic groups in 193 nm resists. In the transition to 157 nm, partially fluorinated alicyclic systems present a promising solution.

To gain a better understanding of the effect that fluorination exerts on these materials, a systematic replacement of hydrogen atoms with fluorine has been undertaken for a norbornene skeleton to measure the effect upon the absorbance at 157 nm. Based upon gas-phase measurements of these materials, we hope to discover where and to what level fluorine should be placed into this system to maximize its effect upon the absorbance.

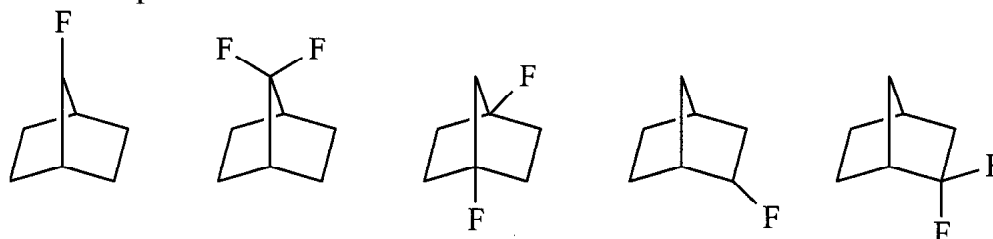


Figure 10: Structures being prepared to study the influence of fluorine position on VUV absorbance

The gas phase absorbance studies may have also provided us with an unexpected source of etch resistance. The data from a series of fluorinated benzene systems indicates that increased fluorination causes a blue shift of the absorbance peak towards 157 nm, and actually increases the absorbance at this wavelength. On the other hand, spectra from fluorinated phenols indicate that increasing fluorination causes a decrease the intensity of absorbance throughout the VUV region. Fluorinated phenols are of interest as they not only provide etch resistance but might also be a second base-soluble group for 157 nm resist designs. Continuing studies are underway surveying many additional substituted aromatics to gain a better understanding of the role that these materials may be able to play in 157 nm resist designs.

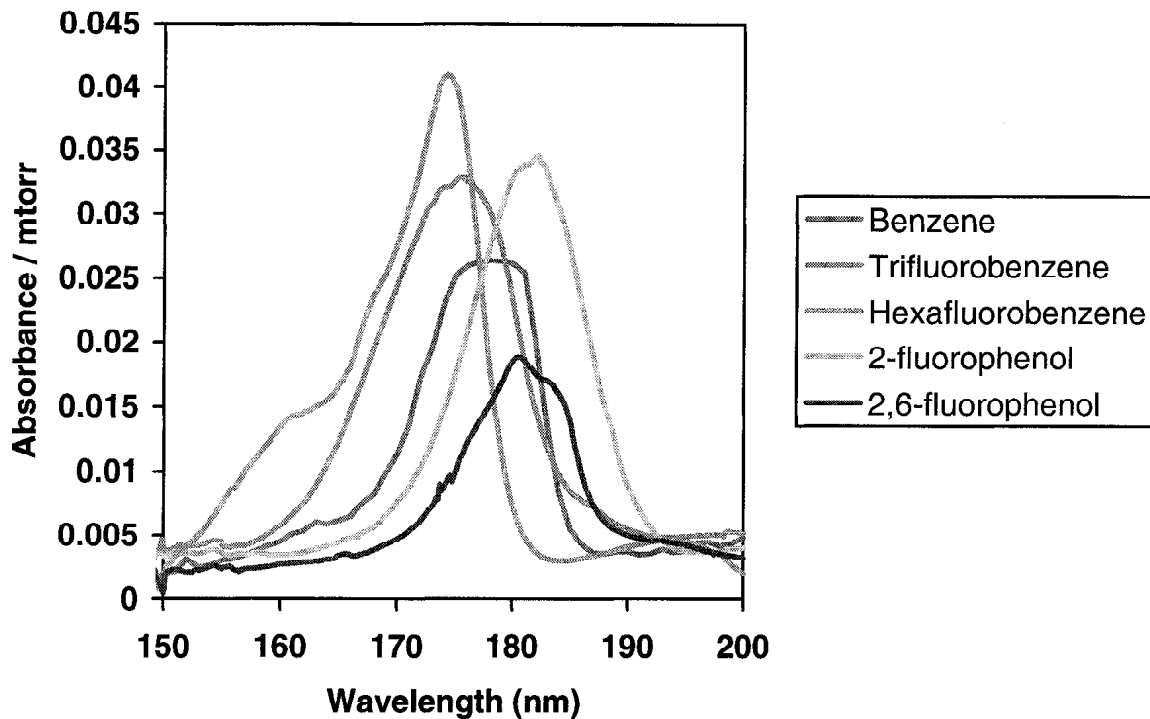


Figure 11: Gas phase spectra of fluorinated aromatic compounds

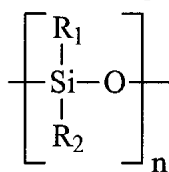
Backbone subunit

The backbone subunit is responsible for tethering the monomer units together and providing the basic mechanical properties for the bulk polymer. The simplest and most common backbone structures based on methylene units are found in photoresist materials such as styrenes and acrylates. Unfortunately, the simplest analog, polyethylene, which is comprised exclusively of methylene units, is reported to absorb strongly in the VUV spectral region⁵. Recent polymer data¹ and the gas-phase measurements on alkanes have verified this finding. An important trend uncovered in the course of the polymer absorbance studies¹ indicates that the transparency of polyethylene at 157 nm can be greatly improved through the use of appropriately placed electron-withdrawing groups such as oxygen and fluorine atoms. Another important finding from these studies is that silicon-based polymers such as siloxanes and silesquioxanes offer high transparency at 157 nm. This information provides the basis for initial designs of the 157 nm backbone. Our group is pursuing designs based upon both of these backbone types.

Siloxane Materials

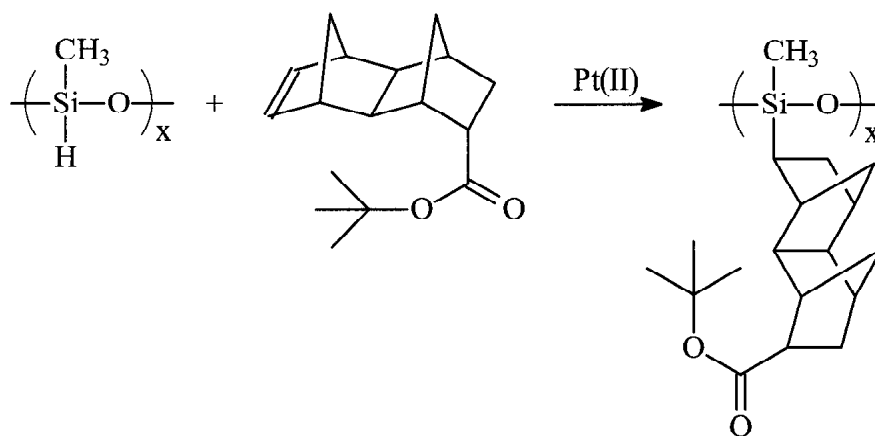
Although siloxanes are promising from a transparency standpoint, their characteristic mechanical properties make the creation of siloxane-based photoresists a significant challenge. The most significant issue with these materials is consistently low Tg's that make them ideal for other uses such as transfer fluids and vacuum pump oils. On the other hand, the low Tg's of siloxanes are ill-suited for photoresist applications. To overcome this shortcoming, recent studies have been directed towards increasing the Tg of these materials. The table below shows common siloxanes and their respective Tg⁶.

Table 1: Literature values for Tg of common siloxanes



R ₁	R ₂	Tg (°C)
CH ₃	H	-138
CH ₃	CH ₃	-125
CH ₃	Phenyl	-90 to -75
CH ₃	CH ₃ CH ₂	-135
CH ₃	CH ₃ CH ₂ CH ₂	-120
CH ₃	CF ₃ CH ₂ CH ₂	-70
Phenyl	Phenyl	50 to 100

Since alicyclic monomers are likely to be utilized for providing etch resistnace in 157 nm resists, various tetracyclo[4.4.1^{2,5}.1^{7,10}.0]dodec-3-ene derivatives have been hydrosilylated onto poly(methylhydridosiloxane) under Pt(II) catalysis to measure the effect on Tg. These molecules, as expected, impart a significant increase in the Tg of the resulting polymers.



Mw	Mn	Tg (°C)	A (mm ⁻¹) @157 nm
34,400	11,900	90	6

Figure 12: Example siloxane polymer prepared by hydrosilylation of a cycloolefinic unit onto an existing poly(hydridosiloxane)

Conclusions

The basic information required to design 157 nm photoresists is beginning to emerge. However, there is still a large amount of fundamental materials research to be done before a single layer system with the requisite combination of etch resistance and transparency can be produced. Our approach to the design of these materials consists of identifying and synthesizing molecular subunits, each capable of providing a vital property to the final polymer. Perhaps the most difficult aspect, transparency at 157

nm, must be considered in the design of all subunits. For the backbone, siloxanes and fluorinated carbon-based materials have been shown by others to offer the highest level of transparency at 157 nm and are being actively pursued by our research group. The etch resistance for these materials is likely to come from partially fluorinated alicyclic components. We are in the process of determining the most effective fluorination patterns to achieve improved transparency at 157 nm. Recent gas phase VUV spectra have shown that fluorination alone actually increases the absorbance of benzene at 157 nm. However, the use of alternative functional groups such as hydroxyls, in combination with fluorination, leads to decreased absorbance and might allow appropriately functionalized aromatic groups to be used in 157 nm photoresist designs for etch resistance. Hexafluoropropanol derivatives have been shown previously by others to present sufficient base solubility for use in photoresist materials. In addition, gas phase VUV studies have shown this functional group to be extremely transparent at 157 nm. Acetals and ethers present the most promising candidates for a protecting groups, and the combination of acetal protecting group and hexafluoropropanol base-soluble group was shown to be capable of producing a functional photoresist. There is much that must be accomplished in record time to develop a single layer 157 nm photoresist platform, but the rate of progress is very promising.

References

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