157nm Photoresists: Synthesis of Partially Fluorinated Copolymers of Norbornene (and its derivatives) With Tetrafluoroethylene.

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Introduction

With the increasing need to reduce circuit size and increase processor speed, the semiconductor industry has focused on extending the life of optical lithography using 157nm technology. One of the biggest challenges with 157nm lithography has come in the photoresist. Because many organic compounds are opaque at 157nm, designing transparent photoresists at this wavelength has become a challenging task. Fluorocarbon polymers and compounds were identified as being relatively transparent at 157nm and thus, research efforts have been devoted to incorporating fluorine into bicyclic monomers and polymers.

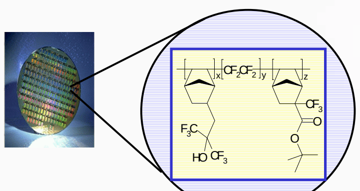


Figure 1. Example Photoresist for 157nm Containing All Four Components.

The resist polymers under investigation contain four components:

1) Norbornene serves as an etch resistant group.
2) Tetrafluoroethylene serves to increase transparency at 157nm.
3) Ester or ether functionality serves as the acid labile group
4) Alcohol functionality serves to increase adhesion and dissolution characteristics

Polymerization

Because of the detonation hazards associated with tetrafluoroethylene, it is transferred under high vacuum and polymerizations are carried out in an oxygen free environment using reactors shown in Figure 2 designed to handle high pressures.

Types of polymerizations tested included:

- Supercritical Carbon Dioxide
- Liquid Carbon Dioxide
- Aqueous Emulsion
- Solution – F113, t-butanol

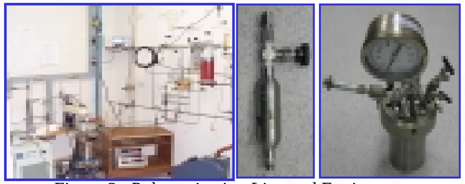
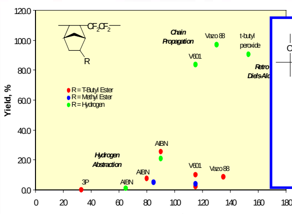
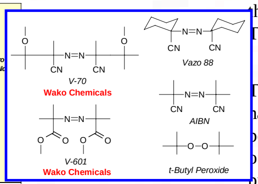


Figure 2. Polymerization Line and Equipment

Effect of Initiators

A study on the effects of temperature on the polymerization showed that the copolymerization of norbornene with tetrafluoroethylene was temperature dependent, Figure 3.

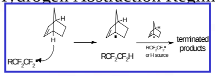


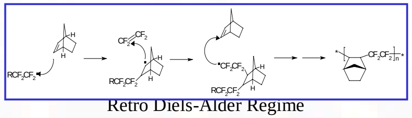


...ene Polymeriztions.

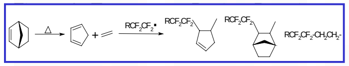
The polymerization was found to have three major regimes as illustrated in in Figure 3. The reactions occurring in each of these regimes, Figure 4, demonstrate the complexity of the polymerization.

Hydrogen Abstraction Regime

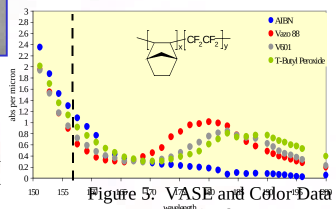




Retro Diels-Alder Regime



The color and transparency of the polymers were found to be initiator dependent, Figure 5. The VASE was run on all polymers unpurified except in the case of Vazo 88 which was purified using chromatography resulting in significant loss of polymer.



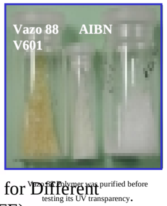
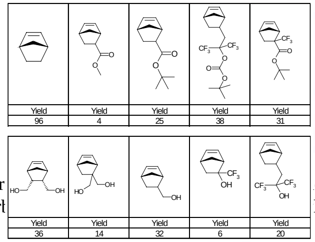


Figure 5. VASE and Color Data for Different Poly(norbornene-co-TFE)

Because of the excellent yield in the polymerization and the quality of the bulk polymer, no purification is needed. Therefore, V601 has become the preferred initiator.

Norbornene Derivatives

The acid labile functionality and the alcohol functionality have caused considerable difficulties in the polymerization process, Figure 6; however, copolymers of these derivatives with tetrafluoroethylene have been produced.



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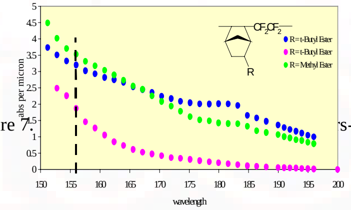

Figure 7. ...s-co-

As seen in Figure 7, the transparency of the ester functionalized polymers are not consistent and the reason for this is not known at this time.

Photoresists

The first series of photoresists based on norbornene esters and tetrafluoroethylene have been prepared and show exceptional UV transparency as illustrated in Figure 8. The unoptimized yield for the polymerization is around 39%.

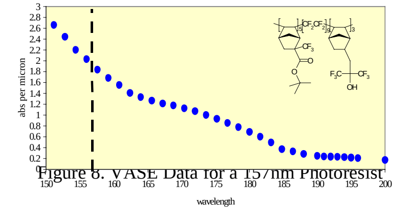

Figure 8. VASE Data for a 157nm Photoresist

Future Work

- Produce more terpolymer resists of varying compositions and use these resists to print.
- Determine the cause for the inconsistent VASE data of the esters.
- Investigate other monomers which may provide better transparency or yield in the polymerization process.

Conclusions

- The polymerization of tetrafluoroethylene with norbornene is a temperature dependent polymerization with optimum yields produced between 115-150°C.
- UV transparency of the polymer seems to be initiator dependent.
- Resists of norbornene/tetrafluoroethylene derivatives show good UV transparency.

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University of Texas