Polymers Based on a Novel 1,3-perfluorodioxole for Use as a Soft Polymer Pellicle in 157nm Lithography

Darryl D. DesMarteau, Norman Lu, Paul Zimmerman and Daniel Miller

Department of Chemistry, Clemson University, Clemson, S.C. 29634-0973, USA

International SEMATECH, 27006 Montopolos Drive, Austin, TX 78741, USA

A series of copolymers of tetrafluoroethylene and 4-trifluormethoxy-1,3-perfluorodioxole (TFETFMD) were prepared as well as a homopolymer of the dioxole (TEMD) using various free-radical initiators. The copolymers were characterized by \(^{19}\)F NMR, TGA, DSC and VUV measurements. The transparency at 157nm increased with increasing dioxole content reaching an \(\alpha (\mu m^{\text{-1}}) = 0.76\) for an unoptimized homopolymer of the dioxole prepared with a perfluorinated peroxide initiator. Exposure studies of the dioxole homopolymer at 157 nm indicate rapid formation of carbonyl species and therefore an anticipated short lifetime as a potential polymer pellicle for 157 nm lithography.

Keywords: polymer pellicle, perfluorodioxole, 157 nm lithography

1. Introduction

The goal of utilizing 157nm microlithography as the next major advance in reducing feature size in integrated circuits faces many obstacles. The lack of a suitable soft polymer pellicle material is perhaps the major obstacle and played a role in Intel Corporation's recent decision to bypass 157nm lithography (May 23, 2003).[1] Considerable effort has been made to develop polymer materials for 157nm soft pellicles and some remarkably transparent fluoropolymers have been found.[2] However, none of these materials exhibit reasonable lifetimes under 157nm exposure and none even begin to approach the desired cumulative energy dose of several kJ/cm\(^2\).

Teflon\(^{\circledR}\) AF amorphous fluoropolymers have excellent transparency in the VUV with transparency of the copolymer TFE/2,2-bis(trifluoromethyl)-1,3-perfluorodioxole increasing with higher dioxole content. Teflon\(^{\circledR}\) AF 2400 (89 mol\% dioxole) and Teflon\(^{\circledR}\) AF 1600 (65 mole\% dioxole) have \(\alpha =0.02\) and 0.97 (\(\mu m^{1}\)), respectively. Cytop\(^{\circledR}\), another commercial amorphous fluoropolymer with only one ring oxygen (Figure 1) has \(\alpha = 4.4 (\mu m^{1})\) at 157nm.[2] Assuming that additional oxygen in the polymers might reduce the transparency further, we pursued a high % dioxole copolymer of 4-trifluoromethoxy-1,3-perfluorodioxole [3] with TFE(PTFETFMD) and the homopolymer of the dioxole (TFMD). (Figure 1)

2. Method

2.1 Polymerizations

The polymerization reactions were carried out with TFE/TFMD in Vertrel\(^{\circledR}\) XF and/or CFC 113

Received April 22, 2004
Accepted June 10, 2004
solvent at 65-80°C using a 25mL Parr stainless steel autoclave. TFE pressures ranged from 70-180 psi with monomer ratios TFE/TFMD from 3/1 to 1/10. AIBN, Perkadox® 16N (Akzo Noble), V-601 (Wako) and perfluorodisopropylyl peroxide were used as initiators.[4] V-601 seemed to give the highest polymer yields and most transparent copolymers. Homopolymerizations of TFMD were carried out in a 50 mL glass vessel fitted with a Teflon-glass valve. The perfluorinated peroxide (14.6% in CFC-113) was used as the initiator at 50-60°C. Conversions of TFMD to PTFMD were low with polymer yields near 10%. Molecular weights of the polymers were not determined, but were estimated by viscosity measurements to be less than 10,000.

3. Polymer Characterization
3.1 $^{19}$F NMR

Both the PTFETFMD and PTFMD polymers were soluble in a variety of highly fluorinated
solvents but these interfered with observing the NMR spectra of the polymers. Finally, trifluoromethyl iodide was selected as the solvent because the CF$_3$ resonance (δ = -4.8) of CF$_3$I was far away from the spectral regions of interest δ = -50 to -65 and -105 to -125. The areas of these 2 regions was used to determine the ratio of TFMD/TFE in the copolymers. Figure 2 shows a typical NMR spectrum.

![Figure 2](image1)

Table 1 for a series of PTFETFMD and PTFMD polymers.

A typical TGA scan of a PTFETFMD copolymer is shown in Figure 4. The onset of decomposition in air was near 450° C for the copolymers.

3.3 Photolytic Stability

The stability of PTFMD at 157 nm was evaluated by FTIR spectroscopy. Figure 5 shows the infrared spectrum in 2000-1700 cm$^{-1}$ region as function of 157 nm exposure. The unexposed polymer shows no carbonyl absorptions in the region, but upon exposure carbonyl absorptions quickly appear. These are assigned as indicated in Figure 5.

**Acknowledgments**

The financial support of this research by International SEMATECH (Agreement # 305373-OF) is gratefully acknowledged. We thank Solvay Solexis and Dr. Vito Tortelli for supplying the TFMD monomer.

**References**