Materials Design and Development of Fluoropolymers for Use as Pellicles in 157nm Photolithography

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ABSTRACT

The introduction of 157nm as the next optical lithography wavelength has created a need for new soft (polymeric) or hard (quartz) pellicle materials optimized for this wavelength. Materials design and development of ultra transparent fluoropolymers suitable for 157 nm soft pellicle applications has produced a number of promising candidate materials with absorbances below 0.03/\(\mu\)m as is necessary to achieve pellicle transmissions above 95%. We have developed 12 families of experimental TeflonAF\textsuperscript{®} (TAFx) materials which have sufficient transparency to produce transmissions above 95%.

For the successful fabrication of 157nm pellicles from these materials, the fluoropolymers must have appropriate physical properties to permit the spin coating of thin polymer films and their lifting and adhesive mounting to pellicle frames, the processes which produce free standing pellicle membranes of micron scale thickness. Relevant physical properties include molecular weight, glass transition temperature, and mechanical strength and toughness. We have successfully developed various of the ultra transparent TAFx polymer families with these physical properties.

Upon irradiation these 157nm pellicle polymers undergo photochemical darkening, which reduces the 157nm transmission of the material. Measurements of the photochemical darkening rate allow the estimation of the pellicle lifetime corresponding to a 10% drop in 157nm transmission. Increasing the 157nm lifetime of fluoropolymers involves simultaneous optimization of the materials, the pellicles and the end use. Similar optimization was essential to achieve the desired radiation durability lifetimes for pellicles successfully developed for use with KrF (248nm) and ArF (193nm) lithography.

Keywords: 157 nm lithography, pellicle, fluoropolymer, absorbance, radiation durability, VUV spectroscopy, VUV ellipsometry

1. INTRODUCTION

With the introduction of 157 nm as the next optical lithography wavelength, the need for new pellicle materials optimized for this wavelength has produced much activity in development of ultratransparent fluoropolymers suitable for 157 nm pellicle applications where absorbances below 0.03/\(\mu\)m are necessary to achieve pellicle transmissions above 96 to 98%.

Initial results from MIT Lincoln Labs demonstrated that the commercial fluoropolymers which are used for pellicles at 248 nm and 193nm wavelengths, such as Teflon AF\textsuperscript{®} and Cytop\textsuperscript{®} have no mechanical integrity and rapidly burst under irradiation with 157 nm light. Therefore we have undertaken an extensive program to screen for, and develop, novel fluoropolymer candidates which have the required combination of optical properties, film forming properties, and radiation durability (both mechanical and photochemical) to produce 157 nm pellicles. The 157nm pellicle must be a complete system, and the requirement for minimal outgassing and contamination arising from the pellicle and its materials of construction require that noncontaminating adhesives, as well as pellicle frames and gasket materials, be developed in this program.

To produce an optically transparent, radiation durable 157nm pellicle, the guiding principle is to minimize the optical absorption of all components in the material. In this manner the transparency will be maximized, and potential photochemical avenues for radiation induced photochemical darkening will be minimized. Reduction of all contributions to the optical absorption is important to achieve the desired pellicle radiation durability lifetime.

Photochemical darkening of the pellicles under irradiation determines the useful lifetime of the pellicles. The role of initial absorbance, photochemical darkening rate and potential pellicle lifetimes is also discussed.

2. EXPERIMENTAL AND ANALYTICAL TECHNIQUES

Optical Characterization for 157 nm Pellicle Materials Design

Development of new materials for use in 157nm photolithography involves both VUV spectroscopy and VUV spectroscopic ellipsometry.\textsuperscript{1} This is because the required transparency of the pellicle film is high, and the accuracy of simple
transmission based absorbance/μm measurements is insufficient and also does not supply knowledge of the materials index of refraction needed for pellicle fringe optimization. Instead, ellipsometry based film structure and optical models are required to determine the complex index of refraction and film thickness. Also, the rapid turnaround time possible from absorbance measurements is essential in the materials screening phase, as novel materials are being developed.

Sample preparation

Polymer films were prepared by spinning from solution onto various substrates. For VUV spectroscopy, CaF₂ substrates from Corning² were used, while for VUV ellipsometry the samples were pellicle membranes. Film thicknesses were measured using a Filmetrics³ F20 thin film measurement system.

Vacuum Ultraviolet Spectroscopy

VUV spectroscopy including both transmission and reflectance measurements has become an established technique for electronic structure studies of large band-gap, insulating materials such as polysilanes⁴ and fluoropolymers. The details of the VUV-LPLS spectrophotometer have been discussed previously.⁵ The spectrophotometer utilizes a laser plasma light source (LPLS),⁶ and a 1 meter monochromator with Al/MgF₂ and iridium coated optics. The energy range of this windowless instrument is 1.7 to 44 eV (700 to 28 nm), which extends beyond the air-cutoff of 6 eV and the window-cutoff of 10 eV. The resolution of the instrument is 0.2 to 0.6 nm, which corresponds to 16 meV resolution at 10 eV and 200 meV resolution at 35 eV.

A Perkin Elmer Lambda 9 spectrophotometer, with transmission and reflectance attachments and using xenon and deuterium lamps, was used to cover the UV/vis/NIR spectral regions. The wavelength (energy) resolution is 2 nm (40 meV) at 5.0 eV. Transmission was measured over the complete energy range of the instrument to check the accuracy of the VUV transmission spectra. The results agreed well with the data from the VUV spectrophotometers. Data were spliced together in the overlapping wavelength region using a multiplicative scaling factor on the VUV transmission to bring it into agreement with the UV/vis results.

Absorbance/μm From Transmission Based Vacuum Ultraviolet Spectroscopy

Once the transmission spectra of the substrate and the film coated on that substrate are determined, the film transmission and optical density can be determined using Equation 1 and Equation 2 respectively. The absorbance/μm (A/μm) is then determined by dividing the optical density by the film thickness, as shown in Equation 3. The optical absorbance/μm reported here are base 10.

\[
\text{Equation 1.} \quad T_\text{film} = 100 \frac{T_\text{sample}}{T_\text{substrate}}
\]

\[
\text{Equation 2.} \quad \text{O.D.}_{\text{film}} = \log_{10} \frac{100}{T_\text{film}}
\]

\[
\text{Equation 3.} \quad A_{\text{film}} (\mu m^{-1}) = A / \mu m = \frac{\log_{10} \left| \frac{T_\text{substrate}}{T_\text{sample}} \right|}{t_\text{film}}
\]

Vacuum Ultraviolet Spectroscopic Ellipsometry

The variable angle spectroscopic ellipsometry measurements were taken on the Woollam Co.⁷ VUV-VASE™ Model VU-302.⁸ It covers the wavelength range from 142 nm to 1700 nm with an angle range from 15° to 90°. It is based on a rotating analyzer VASE® instrument, which covers the UV-Visible-NIR spectral range. It incorporates a computer controlled MgF₂ Berek waveplate as a compensator to improve the ellipsometric Δ measurement accuracy. The introduction of a retardating element also allows the ellipsometer to distinguish unpolarized light. This was found to improve results when dealing with thicker films, because it allowed a careful treatment of non-idealities such as instrument bandwidth and sample non-uniformity. The entire system is purged with dry nitrogen gas to avoid absorption of VUV light by ambient oxygen and water vapor. Light from both the deuterium lamp and the xenon lamp passes through a double-chamber Czerny-Turner type monochromator to provide wavelength selection and stray-light rejection. Computer-controlled slit widths can adjust the bandwidth to insure adequate spectral resolution of optical features in the data such as the closely spaced fringes, which arise in very thick films. A photomultiplier tube is utilized for signal detection in the ultraviolet. A stacked Si/InGaAs photodiode detector is used for longer wavelengths.
Optical Properties from Vacuum Ultraviolet Spectroscopic Ellipsometry of Pellicles

We use a pellicle made of the fluoropolymer TAFx3P-10517 as an example of the ellipsometric analysis. The ellipsometry (Figure 1) and transmission (Figure 2) data taken on the pellicle membrane were "fit" to an optical model (Figure 3) of the pellicle to determine the pellicle membrane thickness, roughness and thickness non-uniformity and the complex refractive index (Equation 4). We chose the Tauc-Lorentz model for these films, which remains Kramers-Kronig consistent and helps describe the onset of film absorption.

Equation 4. \( \tilde{n} = n + ik \)

Pellicle membranes with thicknesses on the order of 1 \( \mu \)m were studied. This produced increased sensitivity to optical absorption and the extinction coefficient in the film due to the increased path length of light through the material. These pellicle membranes exhibit both roughness and thickness non-uniformity. They are also more susceptible to the effects of finite spectrometer bandwidth. Both non-uniformity and finite-bandwidth can depolarize the measurement beam, and ellipsometers that include a retardation element are capable of measuring the resulting \% depolarization. We quantify these non-ideal effects and model their behavior during analysis of the experimental data. The thickness non-uniformity for this pellicle was 2.8\%, the roughness was 0.4 nm and the light bandwidth was 1nm.

Once the extinction coefficient \( k \) has been determined, the optical absorption parameters \( \alpha \) and \( A \) can be determined using Equation 5. The absorption coefficient, \( \alpha \) is calculated on a natural logarithm basis while the absorbance per \( \mu \)m, \( A \), is determined from the base 10 logarithm of the optical density given in Equation 2, therefore a value of \( \ln(10) \) or 2.302585 is introduced into Equation 5 and Equation 6. Both \( k \) and \( \alpha \) are inherent optical properties of the material, while the absorbance/\( \mu \)m is based only on transmission measurements, and thus neglects effects arising from the index mismatch between the film and substrate, thin film (or Fresnel) interference effects, and film non-uniformity effects. Values of absorbance/\( \mu \)m and \( k \) particular for 157nm are given in Equation 7.

Equation 5. \( k = \frac{\alpha \lambda}{4\pi} = \ln(10) \frac{A \lambda}{4\pi} = 2.302585 \frac{A \lambda}{4\pi} \)

Equation 6. \( \alpha = 2.302585 \ A \)

Equation 7. \( \text{Abs.}(157nm) = 34.761 \ k(157nm) \)

Figure 1. The experimental ellipsometric parameters \( \Psi \) (upper figure) and \( \Delta \) (lower figure) and the fitted results from the optical model are shown for a pellicle made from TAFx3P-10517.

Figure 2. The transmission of a TAFx3P-10517 pellicle and the fitted results from the optical model.

Figure 3. Optical model of the TAFx3P-10517 Pellicle.
3. MATERIALS SYNTHESIS FOR 157NM PELLICLES

The optical absorbance/µm of two commercial amorphous fluoropolymers such as TeflonAF® and Cytop® is shown in Figure 5. The 157nm transmission of a pellicle membrane of this TeflonAF® would be ~45% while Cytop® would have a 157nm transmission of 2.5%. These fluoropolymers have been shown to become perforated rapidly under 157nm laser irradiation, with physical lifetimes on the order of a joule. For commercial TeflonAF® we estimate that the pellicle lifetime for a 10% drop in 157nm transmission would be on the order of 0.001 Joules.

Therefore we have pursued the development of novel fluoropolymers with substantially less optical absorption at 157nm. Using an optical absorbance of 0.3/µm as the criteria for identifying candidate materials for use as 157nm pellicles, we have found twelve novel fluoropolymers families. Table 1 lists these pellicle polymers and Figure 6 shows the optical absorbance of these polymers.

Table 1. Optical Absorbance of experimental TeflonAF® polymer families.

<table>
<thead>
<tr>
<th>Polymer Family</th>
<th>Abs./micron</th>
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</thead>
<tbody>
<tr>
<td>TAFx24P</td>
<td>0.007</td>
</tr>
<tr>
<td>TAFx27P</td>
<td>0.008</td>
</tr>
<tr>
<td>TAFx3P</td>
<td>0.009</td>
</tr>
<tr>
<td>TAFx1P</td>
<td>0.012</td>
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<td>TAFx2P</td>
<td>0.014</td>
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<tr>
<td>TAFx4P</td>
<td>0.015</td>
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<tr>
<td>TAFx5P</td>
<td>0.016</td>
</tr>
<tr>
<td>TAFx7P</td>
<td>0.016</td>
</tr>
<tr>
<td>TAFx20P</td>
<td>0.028</td>
</tr>
<tr>
<td>TAFx6P</td>
<td>0.03</td>
</tr>
<tr>
<td>TAFx28P</td>
<td>0.03</td>
</tr>
<tr>
<td>TAFx21P</td>
<td></td>
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</tbody>
</table>

Figure 7. Film mounted on frame using adhesive.

Figure 4. Optical constants determined from optical modeling of ellipsometry and transmission of the TAFx3P-10517 Pellicle.

Figure 5. Spectral VUV absorbance of a commercial Teflon AF® and a Cytop® polymers.

Figure 6. Spectral VUV absorbance of experimental Teflon AF® polymers with absorbances below 0.03/µm.
4. 157NM PELLICLE AND FRAME ADHESIVES

The development of a viable 157nm pellicle requires a total system design, in which the important role of the adhesives is considered from the beginning. Figure 7 shows a soft pellicle in which a pellicle adhesive is used to attach the pellicle membrane to the frame and a pellicle gasket is used to attach the pellicle frame to the photomask. We have developed pellicle and frame adhesives for use in 157nm pellicles which have the required mechanical performance and also have low optical absorbances to minimize the impact of outgassing on the pellicle and photomask transmission.

5. MATERIALS AND PELLICLE OPTIMIZATION –

The development of 157nm pellicles involves the simultaneous optimization of the pellicle materials and the end use application. The fundamental materials properties of interest for this application are the optical absorption and radiation durability, the polymer molecular weight and spinning solution viscosity required for good membrane formation and the levels of organic, inorganic and particulate contaminants. The important pellicle properties to be optimized are the physical parameters of the thin film membrane, such as the thickness, which produced the tuned etalon fringes in the optical behavior of the membrane. In addition, the degree of surface roughness and thickness non-uniformity must be optimized. In addition the pellicle adhesive and frame gasket, pellicle mounting and purging must be optimized for the application. The end use and environmental aspects of the 157nm pellicle application must also be carefully considered and controlled. For example, it is known that adsorbed oxygen, water, and adsorbed hydrocarbons can reduce the 157nm transmission. Also recent results show the positive role that can be played by active cleaning processes such as 157nm laser cleaning or lamp cleaning.

Teflon AF® x 2P and 3P Pellicles

From ellipsometric analysis of a TAFx2P-10520 pellicle, we find the 157nm transmission of this pellicle is ~ 86%. This pellicle had a membrane thickness of 1.67 µm. For a pellicle of this polymer with a membrane thickness of 0.8 µm, the 157nm transmission increases to~ 92.5 % as shown in Figure 8.

The pellicle thickness directly effects the transmission at the lithographic wavelength. In addition, these pellicles have not had their thicknesses optimized so as to place a etalon fringe peak maximum exactly at 157nm. There we will report the approximate 157nm transmission as the average of the fringe peak maxima above and below 157nm.

Teflon AF® x 3P Pellicles

The fundamental absorption of the polymeric material is another property which directly determines the 157nm pellicle transmission. The optical absorption coefficient ( in units of 1/cm base e) is shown in Figure 9 for both the TAFx2P-10520 pellicle and the variant of another fluoropolymer TAFx3P-10517. This polymer has a much lower 157nm absorption coefficient, and therefore should produce a pellicle with higher 157nm transmission. This is the pellicle analyzed in detail in Section 2, and the 157nm transmission increases for TAFx3P-10517 to a value of 95% as shown in Figure 2.

At the same time note that TAFx3P-10517 exhibits an absorption peak centered at ~ 190 nm. This undesirable absorption has been removed in the TAFx3P-10515 polymer as is shown in Figure 10. The transmission of a pellicle made from TAFx3P-10515 is shown in Figure 11, and one can see that the 157nm transmission is only ~ 92%. This low 157nm transmission is not a function of pellicle thickness; this pellicle membrane is 0.77 µm thick.
The low 157 nm transmission arises from the thickness nonuniformity in this pellicle. Thickness nonuniformity characteristically produces tuned etalon fringes whose amplitude damp as one approaches shorter wavelengths as is shown in Figure 12. One can consider this effect as corresponding to the superposition of pellicles with varying thicknesses, in which the peak fringe transmission is reduced due to the lower transmission of an adjacent area of the membrane with a different thickness and therefore a different wavelength for the fringe maxima.

This effect of thickness nonuniformity is different from the effect arising from surface roughness. Roughness leads to a damping of the pellicle fringes at all wavelengths.

Reducing the thickness nonuniformity in a TAFx3P-10515 pellicle will produce a pellicle with a 157nm transmission of ~ 97%.

6. PHOTOCHEMICAL DARKENING (PCD) AND PELLICLE LIFETIME

Upon irradiation these 157nm pellicle polymers undergo photochemical darkening, which reduces the 157nm transmission of the material. PCD can be considered as arising from the absorption of the high energy 157nm photons in the pellicle membrane, with this absorbed energy producing absorbing chromophores. PCD has been reported in the literature for many materials including both polytetrafluoroethylene and TeflonAF.

The PCD process can be considered as a nucleation and growth process, in which the first step is the absorption of 157nm photons by some pre-existing absorption site (a PCD nucleation site or nuclei) in the pellicle which upon absorption leads to formation of some transient excited state formation which upon decay results in some final absorbing species. This final PCD absorbing species can lead to absorption of subsequent 157nm photons, and we enter a regime of growth in the absorption in the material.

In a nucleation and growth process, the first line of attack is to reduce the initial number of absorbed 157nm photons in the material (the nuclei), which produce and initiate the photochemical darkening. With a reduction in the initial absorption we are reducing the number of nuclei that start off the PCD pathway. The second avenue is to modify the growth rate of the darkening.

We focus on reducing all of the intrinsic and extrinsic absorptions in the polymers as the way of decreasing the nucleation rate for PCD. The reduction of initial absorption has been shown to lead to decreases in the photochemical darkening rate. Approaches to reducing the growth rate of PCD are also being pursued. Reductions in the PCD nucleation rate and the PCD growth rate lead to increases in the 157nm radiation durability lifetime.

Photochemical Darkening

Measurement of the 157nm transmission of a sample as a function of irradiation dose allows one to dynamically follow the photochemical darkening process. This time dependent data is essential to understanding and developing kinetic
models of the photochemical darkening process. The PCD measurement allows us to accurately measure and analyze the transient photochemical darkening, in terms of the PCD rate, in units of induced absorbance / µm / joule.

To review how this is done, let us consider the results for a sample of TAFx3P-1083. Using in situ power meters to determine the 157nm transmission of the sample under irradiation, the decrease in the transmission is determined as a function of increasing dose, as shown in Figure 13. In phase I of photochemical darkening, an initial transient increase in transmission is observed. This is followed in phase II by a plateau in the 157nm transmission. Phase III then corresponds to darkening and a reduction in the 157nm transmission. The initiation and plateau phases correspond to the initiation phase of the photochemical darkening. Once the transmission is decreasing, then using the known thickness of the sample we can determine the absorbance of the sample, and by subtracting the initial absorbance, we can plot, in Figure 14, the induced absorption versus increasing dose.

To determine the PCDi rate of the phase III darkening, we determine the induced absorption rate, i.e. the linear increase in the induced absorption for a given incident dose, starting after the phase II plateau. This procedure is used to determine the PCDi rate in units of induced absorption/µm/J. This corresponds to a linear model for the phase III darkening in the material.

The induced absorption versus incident dose for 4 different TAFx polymers are shown in Figure 15. The linear PCDi rates, fitted to the phase III darkening, are given in Table 2.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>PCDi Rate Abs./µm Joule</th>
<th>10% ΔT Linear Lifetime (Joules)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAFx2P-1078</td>
<td>0.022</td>
<td>2.7</td>
</tr>
<tr>
<td>TAFx3P-1083</td>
<td>0.016</td>
<td>3.7</td>
</tr>
<tr>
<td>TAFx3P-1401</td>
<td>0.018</td>
<td>3.2</td>
</tr>
<tr>
<td>TAFx3P-1402</td>
<td>0.010</td>
<td>5.8</td>
</tr>
</tbody>
</table>

**Pellicle Lifetime**

The pellicle lifetime, given in Joules, can be estimated from the photochemical darkening (PCDi) rate, given in Induced Absorbance/ µm / Joule, and the transmission change over the lifetime, ΔT. During the pellicle lifetime, the 157nm radiation leads to induced absorption, which will decrease the pellicle transmission. At the point where the transmission drop corresponds to ΔT, the lifetime has been exceeded. The lifetime is therefore calculated as given in Equation 8.

**Figure 13. In situ 157nm transmission measurements for a TAFx3P-1083 polymer.**

**Figure 14. Calculated induced absorption versus dose for a TAFx3P-1083 polymer.**

**Figure 15. Calculated induced absorption versus dose for four different TAFx2P and TAFx3P polymers.**
Upon irradiation by 157nm radiation, previously developed commercial fluoropolymers, such as Teflon AF® (A = 0.43/μm) or Cytop (A = 1.9/μm), are ablated and the membranes physically thin to bursting. These polymers are perforated after a 157nm dose of on the order of a Joule. The 157nm lifetime, for a 10% transmission drop, of a commercial Teflon AF® or Cytop® polymer therefore can be estimated to be on the order of millijoules dose, even though this very short lifetime has not been experimentally measured.

The experimental Teflon AF®x materials developed to date in this program have much lower optical absorbances (A < 0.03/μm) than any previous fluoropolymers. The newly developed experimental Teflon AF®x materials discussed here exhibit much greater mechanical and physical integrity under irradiation. Still the experimental Teflon AF®x materials do undergo photochemical darkening (PCD), which leads to a decrease in the initially high 157nm transmission of these materials under 157nm irradiation. We have found a correlation between the PCD rate and the initial absorbance, and that materials with lower absorbance also have lower rates of photochemical darkening.

These results are demonstrated in Table 2 where the TAFx2P has the highest absorbance and the shortest lifetime and the TAFx3P-1402 has the lowest absorbance and longest lifetime. The variations in the physical properties of these materials are comparable to those discussed for the pellicles in Section 5 and represent successive improvements in the materials properties. These changes lead to an increase of the 10% ΔT Linear Lifetime increasing from 2.7 to 5.8 Joules.

7. CONCLUSIONS

The introduction of 157nm as the next optical lithography wavelength has created a need for new soft (polymeric) or hard (quartz) pellicle materials optimized for this wavelength. Materials design and development of ultra transparent fluoropolymers suitable for 157 nm soft pellicle applications has produced a number of promising candidate materials with absorbances below 0.03/μm as is necessary to achieve pellicle transmissions above 95%. We have developed 12 families of experimental TeflonAF® (TAFx) materials which have sufficient transparency to produce transmissions above 95%.

For the successful fabrication of 157nm pellicles from these materials, the fluoropolymers must have appropriate physical properties to permit the spin coating of thin polymer films and their lifting and adhesive mounting to pellicle frames, the processes which produce free standing pellicle membranes of micron scale thickness. Relevant physical properties include molecular weight, glass transition temperature, and mechanical strength and toughness. We have successfully developed various of the ultra transparent TAFx polymer families with these physical properties.

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9. REFERENCES
