Single Layer Fluoropolymer Resists for 157 nm Lithography

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ABSTRACT

We have developed a family of 157 nm resists that utilize fluorinated terpolymer resins composed of 1) tetrafluoroethylene (TFE), 2) a norbornene fluoroalcohol (NBFOH), and 3) t-butyl acrylate (t-BA). TFE incorporation reduces optical absorbance at 157 nm, while the presence of a norbornene functionalized with hexafluoroisopropanol groups contributes to aqueous base (developer) solubility and etch resistance. The t-butyl acrylate is the acid-catalyzed deprotection switch that provides the necessary contrast for high resolution 157 nm imaging. 157 nm optical absorbances of these resists depend strongly upon the amount of t-BA in the polymers, with the TFE/NBFOH dipolymers (which do not contain t-BA) exhibiting an absorbance lower than $0.6 \ \mu m^{-1}$. The presence of greater amounts of t-BA increases the absorbance, but also enhances the dissolution rate of the polymer after deprotection, yielding higher resist contrast. Formulated resists based upon these fluorinated terpolymer resins have been imaged at International Sematech, using the 157 nm Exitech microstepper with either 0.6 NA or 0.85 NA optics. We have carefully explored the relationship between imaging performance, resist contrast, optical absorbance, and t-BA content of these terpolymer resist resins, and describe those results in this contribution.

Keywords: 157 nm photoresists, fluoropolymers, tetrafluoroethylene, optical absorbance, lithographic performance, etch resistance

1. INTRODUCTION

157 nm lithography is scheduled to be used at the 65 and 45 nm nodes in the ITRS roadmap[1], and will thus be an important factor in maintaining the validity of Moore's Law[2] until at least 2010. Progress developing photoresists for 157 nm lithography has been rapid, with the primary focus being to reduce the optical absorbance of *formulated* resists to less than $A_{157} = 1.0 \ \mu m^{-1}$. Measured values of 157 nm absorbance for resists[3] developed for application at longer wavelengths, such as 248 nm and 193 nm, are far too high for use at 157 nm, except perhaps in the form of ultrathin resist films (~50 nm film thickness). These high resist optical absorptions are primarily due to the high absorptions of the particular polymer resins used in these resists (e.g., polystyrenes or acrylates). Thus, progress toward the development of low absorption 157 nm photoresists has required the development of new, highly transparent resins. It is here that the use of fluoropolymers is very attractive[3].

It has been conclusively shown[4-9] that incorporation of fluorine in polymers very effectively reduces the optical absorbance at 157 nm. This reduction is associated with the high electronegativity of fluorine, which shifts the fundamental absorption edges of polymers to higher energies. In fact, there is an approximate inverse correlation between the fluorine content of polymers and their 157 nm optical absorbance[10], so the first step in designing transparent fluoropolymers is to incorporate as much fluorine as possible. An additional condition necessary to achieve high transparency is that the fluorine be incorporated with some degree of alternation in the polymer backbone to eliminate, or at least minimize, electronic delocalization (conjugation) along the polymer chain[11]. In order to incorporate a large amount of fluorine, with alternation, we have chosen to use TFE as a comonomer in our resins[4,12-14]. Here we report the properties of a family of TFE terpolymer resists with optical absorbance below $1.5 \ \mu m^{-1}$.

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Of course, while 157 nm transparency may be the primary property we must control in designing 157 nm resists, other properties such as aqueous base solubility and etch resistance are also very important. A logical approach to resist development is to first obtain the required optical transparency, and then introduce the additional functional groups necessary to obtain satisfactory aqueous base solubility. Finally, additional polycyclic groups can be introduced to provide enough etch resistance to enable high quality pattern transfer to the substrate when the resist is used at the maximum film thickness permitted by the optical absorbance. For the materials we describe here, this approach was followed to develop a family of terpolymers based upon TFE, NBFOH, and *t*-BA. This terpolymer system provides a relatively simple example of the design of a 157 nm photoresist resin, but nevertheless it clearly illustrates that a systematic approach, based upon a combination of polymer chemistry, polymer charac terization and resist performance, is necessary to successfully optimize the properties required of these new fluorinated copolymer systems.

2. EXPERIMENTAL

2.1 Polymer synthesis

The polymers studied and described in this report are terpolymers composed of TFE, a norbornene fluoroalcohol, and *t*-BA. These polymers were prepared by free radical solution polymerizations using a standard initiator (peroxydicarbonate) and a hydrofluorocarbon solvent[14]. Some polymers were also prepared using a fluorocarbon dimer peroxide (FC-*dp*) initiator to investigate the effect of end groups on polymer absorbance at 157 nm. The basic polymer structure is shown in Figure 1.
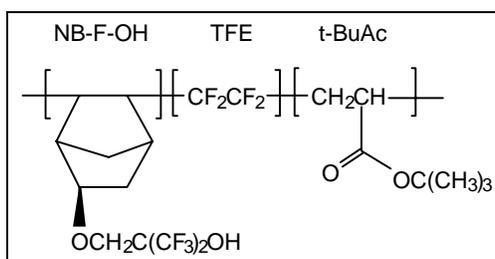

Figure 1. Structure of the TFE/NBFOH/t-BA terpolymer resist resins used in this paper.

Polymer compositions were determined by ^{13}C, ^{19}F and ^{1}H NMR. Polymer molecular weights were measured by Gel Permeation Chromatography, and typical $M_w \sim 10,000$. Polymer glass transition temperatures were determined by DSC and typically were in the 140-150 ºC range.

The NBFOH synthetic route has been published[14]. It is important to note that the NBFOH fluoroalcohol is the pure exo-isomer, and the properties described below for polymers made with that monomer may reflect the presence of that particular stereochemistry.

2.2 Resist formulations

Resists were formulated using standard onium photoacid generators (for example, triphenylsulfonium nonaflate, TPS-Nf), various bases (for example, tetrabutylammonium lactate, TBALac), and standard solvents such as 2-heptanone, PGMEA (propylene glycol methyl ether acetate), or cyclohexanone.

2.3 Optical property measurements

We have made vacuum ultraviolet (VUV) transmission measurements using a double-beam McPherson spectrometer equipped with a deuterium lamp. Each resist sample was spin-cast at two different film thicknesses on Si substrates to determine the resist spin curve. The resists were then spin-coated on CaF$_2$ substrates at the appropriate speeds to obtain film thickness from 50 to 200 nm. The transmission spectra of the films were then measured, and the results divided by the transmission of the uncoated CaF$_2$ substrates to obtain the final transmission spectra. The transmission spectra were converted to absorbance spectra by using the relation A_{157} (µm^{-1})=$\log_{10}(1/T)/FT$, where T is the transmittance of the film and FT is the film thickness in microns. Optical absorbance measurements were also performed at International Sematech using vacuum ultraviolet variable angle spectral ellipsometry (Woollam VUVvase). Resist or polymer films

were spin-cast on Si wafers and measured in reflectance. The resulting amplitude and phase data were converted to index of refraction and absorption coefficient data by standard fitting procedures.

2.4 Infrared spectroscopy and deprotection measurements

The infrared measurements were made on a Nicolet Magna-IR 560 Fourier transform infrared (FTIR) spectrometer at International Sematech, or on a Nicolet Nexus 670 FTIR at DuPont. Si wafers, which were polished on both sides and coated on one side with a thin (~100 nm) evaporated Al film, were coated with resist films on the remaining bare Si surfaces (Figure 2). Exposure wavelengths of 157 nm (Exitech stepper at International Sematech) or 193 nm (Micrascan III scanner at International Sematech) were used to generate the photoacid needed for subsequent deprotection.
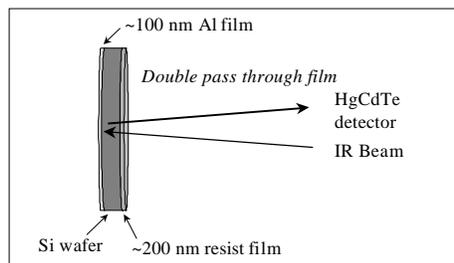

Figure 2. Schematic of the infrared reflectivity measurement of resist films on Si wafers. This technique was used to measure both infrared spectra of resists, and to measure the changes in the spectra as a function of 157 nm or 193 nm exposure.

2.5 157 nm imaging

157 nm imaging was performed at International Sematech using the Exitech stepper equipped with Tropel optics. Images were collected with 0.6 or 0.85 numerical aperture (NA) optics using a binary ($\sigma = 0.7$) or alternating ($\sigma = 0.3$) phase shift mask. Formulated resist films were coated on Si wafers, or in some cases on an organic (Shipley AR-19) or an inorganic (SiON) antireflective coating (ARC), post-apply baked (PAB) at temperatures between 120 ℃ and 150 ℃ for 60 seconds, then imaged on the stepper. After exposure the resist films were post-exposure baked (PEB) at temperatures between 90 ℃ and 150 ℃ for 60 seconds, and then puddle developed using Shipley MF-26A or LDD-26W for 60 seconds. The resulting images were examined using a JEOL JWS 7550 scanning electron microscope (SEM) or a KLA Tencor 8100 XP. Cross-sections were measured at International Sematech using a Hitachi 4500 SEM.

2.6 Etch resistance measurements

Etch resistance was measured at International Sematech. Both polysilicon and silicon oxide etch resistance was measured for a number of terpolymers of TFE, NBFOH and t-BA. The etch conditions utilized Cl_2/HBr chemistry on a TCP etcher for the poly-Si etch, and C_4F_8 chemistry on a Tel Oxide etcher for the SiO_2 etch.

3. OPTICAL ABSORBANCE

3.1 Polymer contribution to 157 nm optical absorbance

Low 157 nm optical absorbance is the primary requirement of resins for 157 nm photoresists. In order to obtain an initial qualitative understanding of how this property is affected by polymer composition we have measured and compared the optical properties of a number of polymers. The results are listed in Table 1.

We believe NB will be a fundamental building block for 157 nm photoresists in order to provide plasma etch resistance. The optical absorbance at 157 nm of a NB homopolymer has been reported[3] to be 6.1 μm^{-1}. However, this absorbance would be prohibitively high for use at 157 nm. We thus began our resin design by measuring the absorbance of an alternating copolymer of TFE and NB, with the hope that TFE incorporation between the NB rings would decrease the optical absorbance. Indeed the data in Table I show exactly that result: the TFE-*alt*-NB dipolymer has an optical

absorbance at 157 nm of 1.3 μm^{-1}. The presence of the alternating, highly electron withdrawing TFE monomers shifts the optical absorbance to significantly higher energies than the NB homopolymer, dramatically lowering the 157 nm absorbance that TFE-*alt*-NB is an excellent copolymer base upon which to build a 157 nm resist resin.

Table 1. 157 nm absorbance values for several polymers illustrating the effect on optical absorbance of TFE incorporation in a norbornene homopolymer, addition of fluoroalcohol groups to the norbornene polycyclic rings, and the incorporation of the ester *t*-BA in a TFE-*alt*-NBFOH copolymer.

Polymer	A_{157} (μm^{-1})
NB homopolymer[3]	6.1
TFE-*alt*-NB	1.3
NBFOH homopolymer	2.0
TFE-*alt*-NBFOH	0.7
TFE/NBFOH/*t*-BA	1.9

The TFE-*alt*-NB copolymer is clearly very hydrophobic, thus requiring the introduction of additional hydrophilic monomers or functional groups to the polymer. For this reason, we next added a hydrophilic fluoroalcohol group (see Figure 1) to the NB polycyclic group to provide some aqueous base solubility, and measured the 157 nm optical absorbance of the resulting TFE-*alt*-NBFOH copolymer (Table I). The absorbance further decreased compared with TFE-*alt*-NB, from 1.3 to 0.7 μm^{-1}, showing that the addition of functional groups containing fluorine to the NB polycyclics also decreases the 157 nm absorbance by shifting the optical transitions to higher energy. *Thus a combination of "in-chain" and "out-of-chain" fluorination appears advantageous to achieve the low 157 nm optical absorbance of $A_{157} < 1.0$ μm^{-1} required for a high performance photoresist.* This conclusion is further substantiated by comparing the optical absorbance of a NBFOH homopolymer, with only "out-of-chain" fluorination, to the TFE-*alt*-NBFOH copolymer (Table 1). The value of 2.0 μm^{-1} for the vinyl addition homopolymer is considerably higher than the copolymer with TFE ("in-chain" fluorination) incorporated.

It is also necessary to add to the TFE-*alt*-NBFOH copolymer an acid-activated solubility switch. Since the dissolution rate of the dipolymer is low, simply protecting the NBFOH monomer is not a viable option. We have thus added a third monomer to the resin to serve as the solubility switch, and chose for that purpose the well-known ester tertiary butyl acrylate (*t*-BA). As a result of acid deprotection this monomer is converted to acrylic acid, and can thus provide the needed solubility enhancement for our terpolymer system to achieve the rapid dissolution rates required for high resist contrast. The optical absorbance of such a TFE/NBFOH/*t*-BA terpolymer is also listed in Table 1, where it can be seen that the addition of the acrylate component significantly increases the 157 nm optical absorbance. In order to look at this effect more systematically, in Figure 3 we show the 157 nm absorbance values of a series of TFE/NBFOH/*t*-BA
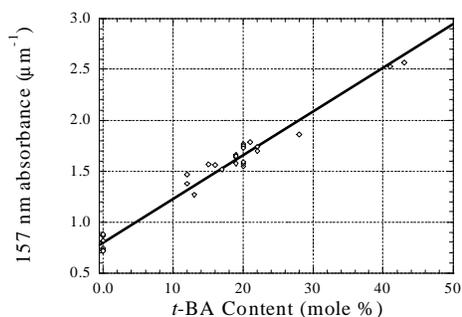

Figure 3. 157 nm absorbance versus mole percent *t*-BA in a series of TFE/NBFOH/*t*-BA terpolymers. The absorbance values were determined by variable angle spectral ellipsometry measurements.

terpolymers that contain various amounts of t-BA. There is an approximately linear increase in absorption with increasing t-BA content, and from these data we deduce that, in order to obtain an optical absorbance of 1.5 μm^{-1} or lower in this system, it is necessary to limit the amount of t-BA to less than 15%.

3.2 Contributions of polymer end groups to 157 nm optical absorbance

An important absorbance contribution that we have also addressed is that of the polymer chain end groups, which are introduced by the free radical initiator used for the polymerization. In the work described in this paper we have used two different initiators: Perkadox® and a fluorocarbon dimer peroxide, FC-dp (Figure 4). The terpolymers whose 157 nm absorbance values are shown in Figure 3 were made exclusively with Perkadox®.
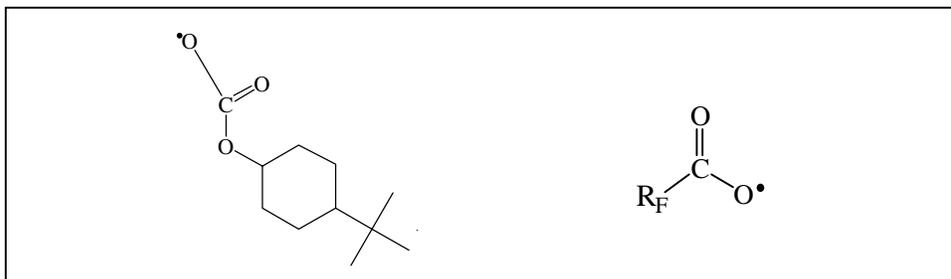

Figure 4. Chemical structures of the free radicals generated from the Perkadox® (left) and FC-dp (right) initiators. The resulting copolymer end groups are equivalent to the entire fragment shown for Perkadox® and the R_F fragment for the fluorocarbon dimer peroxide initiator. The important difference is that the end group left by the Perkadox® initiator contains a highly absorbing carbonyl group.

The end group contribution to the 157 nm optical absorbance can be evaluated by 1) synthesizing a series of polymers of varying molecular weight, but identical monomer composition, and 2) observing the change of 157 nm absorbance with increasing molecular weight. The end group contribution should be more important at low number-average molecular weight (M_n), and gradually vanish with increasing M_n. In Figure 5 we show 157 nm optical absorbance data for a series of terpolymers of different number average molecular weight (M_n) which have been fractionated from a single synthesis run of a $TFE_{31}NBFOH_{45}t$-BA_{24} parent polymer made using the Perkadox® initiator. We have fit a curve to the optical absorbance data which assumes a constant (that is, independent of M_n) term, which is the contribution to optical absorption from the polymer itself, and a second term, that scales inversely with M_n, which we attribute to the end groups. The constant term is equal to 1.74 μm^{-1}, and for an M_n of 5,000 the end groups contribute about 0.3 μm^{-1} to the optical absorbance at 157 nm.
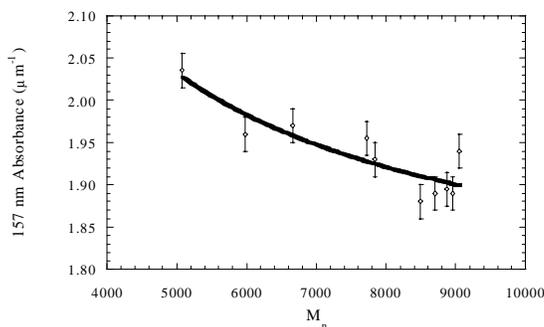

Figure 5. 157 nm optical absorbance versus number average molecular weight (M_n) for a series of fractionated $TFE_{31}NBFOH_{45}t$-BA_{24} terpolymers. The solid curve is a least-squares fit to the function $A(M_n) = C_1 + C_2(1/M_n)$, where the fitting parameters are $C_1 = 1.74$ μm^{-1} and $C_2 = 1481$. C_1 is the intrinsic resin 157 nm absorbance extrapolated to $M_n = \infty$, that is, the absorbance without a contribution due to end groups. The optical absorbance data were determined by transmission measurements (with approximate correction for reflectivity losses).

We assumed that the carbonyl groups in Perkadox® (see Figure 4), which are transferred to the end groups, were the primary source of optical absorption. Based upon this hypothesis, we identified a different initiator, FC-*dp* (also shown in Figure 4), which would not contribute carbonyls to the end groups. We then synthesized a series of terpolymers using that initiator rather then Perkadox®. The 157 nm optical absorbance of this second series of terpolymers is compared with terpolymers made using Perkadox® in Figure 6. The optical absorbance for terpolymers synthesized using the FC-*dp* initiator is lower by approximately 0.3 μm^{-1} compared with the polymers made with the Perkadox® initiator, which we believe is due to the elimination of the highly absorbing carbonyl groups from the end groups. Since all of these terpolymers had M_n values in the range of 5,000-7,000, these results agree reasonably well with the end group absorbance estimate we made before based upon the fractionated molecular weight series. We have also found that using hydrocarbon peroxydiesters as initiators, rather than fluorocarbon peroxydiesters such as FC-*dp*, also yields polymers which are more transparent than those made using Perkadox®, again implicating the carbonyl group in Perkadox® as the principal source of 157 nm optical absorption in those end groups.
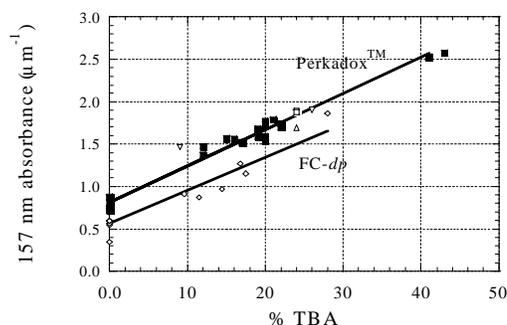

Figure 6. Decrease of 157 nm optical absorbance due to substitution of FC-*dp* end groups for Perkadox® end groups in two similar series of terpolymers (although there is some variation in molecular weights). The FC-*dp* end groups decrease the absorbance by about 0.3 μm^{-1} for these two series of terpolymers.

4. INFRARED SPECTROSCOPY AND DEPROTECTION CHEMISTRY

One can utilize infrared (IR) spectroscopy to observe the end groups in dipolymers, as well as to characterize the deprotection of terpolymers after ultraviolet excitation. In this section we will describe some examples of these IR applications.

4.1 IR spectrum and end group absorbance
In Figure 7 we show the IR spectra of three different TFE/NBFOH/*t*-BA terpolymer films on Si substrates. The various features that can clearly be associated with vibrations of particular chemical groups in the IR spectrum are labeled on the figure. The OH band is broad, suggesting that there is a significant amount of hydrogen bonding in this polymer. One can barely discern a small shoulder on the high-energy side of the OH band (near 3,600 cm^{-1}) that can be attributed to free hydroxyl groups, but most of the OH groups on the NBFOH monomers are clearly participating in hydrogen bonds. This shoulder vanishes with increasing *t*-BA content, suggesting that the C=O group in the acrylate can serve as a hydrogen bond acceptor for the fluoroalcohol[15].

In the case of the TFE-*alt*-NBFOH dipolymers, where there are no intrinsic carbonyl bands from an ester, the Perkadox® end groups can also be readily seen in the IR spectrum via their carbonyl absorption bands. In Figure 8 we show an example of an IR spectrum of a TFE-*alt*-NBFOH dipolymer which was polymerized using Perkadox® as the initiator, compared with the spectrum of a similar dipolymer polymerized with a FC-*dp* free radical initiator. The M_ns of these dipolymers were similar (see caption to Figure 8). Carbonyl vibrations near 1750 cm^{-1} are due to the end groups introduced by the Perkadox™ initiator, and these C=O IR bands are absent for the dipolymer made with the FC-*dp* initiator. The 157 nm optical absorptions of these two dipolymers were also different as a result of elimination of the

additional carbonyl groups from the end groups, with the A_{157} of the Perkadox®-initiated polymer about 0.2-0.3 μm^{-1} higher (Figure 6).
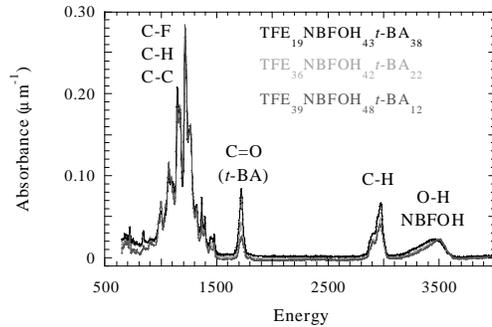

Figure 7. Infrared spectra of three TFE/NBFOH/t-BA terpolymers with different amounts of t-BA coated on Si substrates and measured in reflection. Approximate group frequencies are labeled for the IR bands.
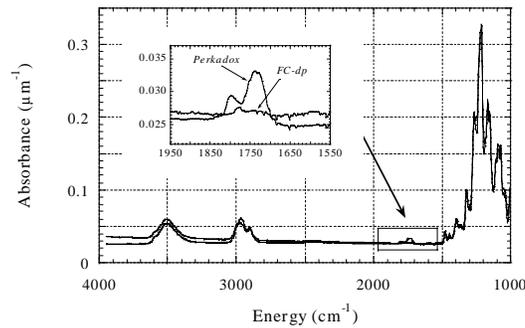

Figure 8. Comparison of infrared spectra of two TFE-alt-NBFOH dipolymers made with a Perkadox® or a FC-dp free radical initiator. The inset shows an expanded view of the spectral region where the C=O vibrations associated with end groups introduced by the Perkadox® initiator is found. The polymer made with the Perkadox® initiator had M_n = 6,000 and M_w = 8300; the polymer made with the FC-dp initiator had M_n = 5200 and M_w = 7100.

4.2 Deprotection chemistry

The deprotection of the t-BA can be observed and quantified by measuring the integrated absorbance of the CH bands (near 3,000 cm^{-1}) before and after exposure to light and subsequent PEB. It is also possible to track the deprotection reaction by monitoring the appearance of absorbance due to the OH groups associated with the acrylic acid, but this absorbance is very broad due to significant amounts of hydrogen bonding, and it overlaps both the OH band due to the NBFOH groups and the CH bands due to the NBFOH and acrylate groups. The presence of these overlapping bands makes quantitative peak area integrations more difficult for the OH than for the CH bands.

In Figure 9 we show plots of the fraction of deprotection as a function of exposure dose for both 157 nm and 193 nm excitation. It can readily be seen that much higher doses are required to achieve a similar degree of deprotection for 157 nm excitation compared with 193 nm excitation. We believe this difference is primarily associated with the much higher optical absorbance at 157 nm (2.7 μm^{-1}) compared with 193 nm (0.55 μm^{-1}). This hypothesis is supported by comparison of the left and right frames in Figure 9. In the left frame the exposure dose plotted along the x-axis is the dose delivered by the stepper to the *top* of the resist film, while in the right frame it is the dose that reaches the *bottom* of the resist film, and is absorbed by the PAG, that is plotted. The latter quantity is a measure of the local photoacid concentration generated near the Si/resist interface, and is approximately given by

$$[Acid(x)] \sim [PAG(x)] \bullet A_{PAG}(\lambda) \bullet I(x) \bullet QE(\lambda). \tag{1}$$

In Equation (1) the quantities in square brackets are the photogenerated acid and initial photoacid concentrations (in units of molecules cm^{-3}) at the depth x into the film, $A_{PAG}(\lambda)$ is the PAG absorbance at the wavelength λ (units of cm^2/molecule), $QE(\lambda)$ is the PAG quantum efficiency for production of photoacid after absorption of a photon of wavelength λ, and I(x), the light intensity (in photons cm^{-2}) at depth x (units of μm) into the film, is given by the Beer-Lambert law as

$$I(x) = I_0 \bullet 10^{-(A_{resist}(\lambda) \bullet x)} . \tag{2}$$

Here $A_{resist}(\lambda)$ is the resist absorbance, in units of μm^{-1}, at the wavelength λ, and I_0 is the light intensity incident on the film surface. It is interesting that applying this simple scaling for the film transmittance and PAG absorbance is sufficient to bring the two sets of data nearly into agreement (Figure 9, right frame), and we expect that correcting for the Si/resist interface reflectivity would remove most of the small remaining difference. The infrared measurement, which integrates uniformly over the thickness of the film, will be rather sensitive to the slow deprotection near the Si\resist interface, where the attenuated ultraviolet light generates less photoacid. Thus we conclude that the primary difference between the two excitation wavelengths is simply the much higher resist film absorbance at 157 nm, combined with a second, smaller contribution due to the difference in PAG optical absorption at the two wavelengths. *These data demonstrate that there is little, if any, energy transfer from the terpolymer resin to the PAG after 157 nm excitation, and that to a large extent the PAG photochemical processes (as represented by the quantum efficiency, QE, in Equation 1) must be the same after excitation at 157 nm or 193 nm.*

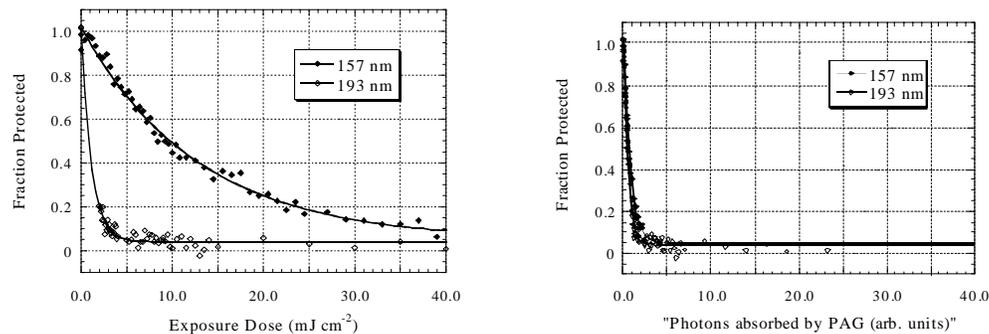Figure 9. Deprotection versus dose data for a TFE$_{19}$NBFOH$_{43}$t-BA$_{38}$ terpolymer formulated with 5 weight % PAG only. Shown is the deprotection versus the dose delivered to the *top* of the film (left frame), and deprotection versus scaled dose transmitted to the *bottom* of the film and absorbed by the PAG (right frame). These data were obtained from infrared measurements, as described in the text. The resist absorption coefficients were 0.55 μm^{-1} at 193 nm and 2.7 μm^{-1} at 157 nm. The PAG absorption coefficients were approximately 0.2 μm^{-1} at 157 nm and 0.5 μm^{-1} at 193 nm. The solid curves are single exponential fits to the data.

IR data such as these can be used to extract reaction parameters for the deprotection chemistry[16]. Uniform illumination, at wavelengths for which the optical absorbance is low, can be used to avoid complications due to acid diffusion, and under those conditions measurements of deprotection with varying PEB temperatures can be used to obtain the activation energy for deprotection. Illumination at highly absorbing wavelengths, which generates significant gradients in the photoacid concentration, can be used to estimate acid diffusion coefficients[17]. On a simpler level, the infrared deprotection data can be compared with resist contrast curves to determine the average degree of deprotection needed to achieve resist solubility in the developer. This information can then be used as an aid in optimization of the resist resins and formulations.

5. TFE TERPOLYMER RESISTS: 157 NM CONTRAST AND IMAGING

A number of the TFE/NBFOH/*t*-BA resins were formulated with PAG and base, as described in Section 2.2 above, and imaged on the 157 nm Exitech stepper at International Sematech. In this section we will briefly discuss the change in resist contrast with decreasing acrylate content, and illustrate the effect of acrylate content on the resist imaging performance.

5.1 Terpolymer resist contrast
In Figure 10 we show the resist contrast curve for a $TFE_{31}NBFOH_{45}t\text{-}BA_{24}$ terpolymer with an optical absorbance of 1.98 μm^{-1}. The resist has a contrast of $\gamma = 3.2$. Also in Figure 10 we show the contrast curve for a $TFE_{43}NBFOH_{47}t\text{-}BA_{10}$ terpolymer resist, i.e. one, which has approximately half the amount of protected acid. The contrast curves look very similar, and in fact the contrast value estimated from this curve is nearly the same as that of the higher *t*-BA content resist.

Nevertheless, we expect that direct measurements of dissolution rates as a function of dose would show a higher rate for the higher *t*-BA terpolymer when fully deprotected, but the data in these plots only allow one to determine a dissolution rate when that rate is approximately equal to or less than the initial film thickness divided by 60 seconds (the development time), in other words on the order of 30-40 Å/sec. Faster dissolution rates will yield zero film thickness after development, so the true resist contrast can not be measured by this technique, but requires resist dissolution *rate* measurements. We have made such measurements for some terpolymers similar to those described here, and find maximum dissolution rates on the order of 10^3-10^4 Å/sec.
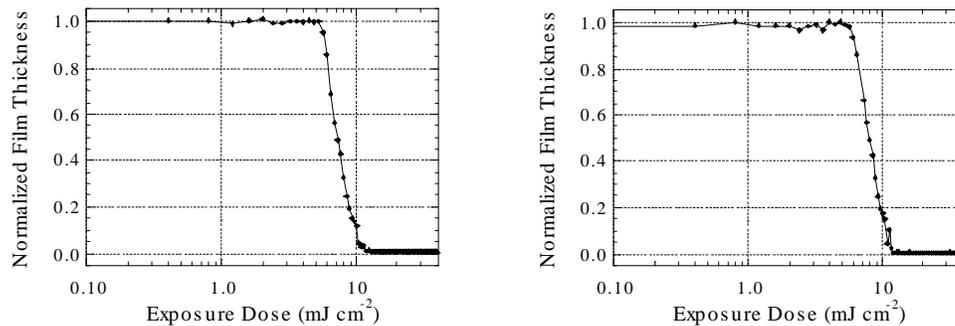

Figure 10. (Left) Contrast curve for a $TFE_{31}NBFOH_{45}t\text{-}BA_{24}$ terpolymer resist formulation, which included 5% PAG and a base (at a concentration of 10 mole % referenced to the PAG), spin-cast on Si. The initial film thickness was 217 nm, and the PEB temperature was 105 °C. The E_0 for this resist is about 10 mJ/cm². (Right) Contrast curve for a $TFE_{43}NBFOH_{47}t\text{-}BA_{10}$ terpolymer resist (same formulation), spin-cast on Si. The initial film thickness was 226 nm and the PEB temperature was 105 °C. The E_0 for this resist is slightly greater than 10 mJ/cm². These two resists have similar contrast ($\gamma \sim 3.2$), as measured by this technique.

5.2 Terpolymer imaging performance
In Figure 11 the imaging performance for a $TFE_{31}NBFOH_{45}t\text{-}BA_{24}$ resist is shown. This resist can image 90 nm 1:1 lines and spaces, although the spaces are not clear to the Si surface (significant amounts of residue appear between the lines), and the lines show appreciable footing. A plausible explanation for this is the high optical absorbance, which prevents sufficient light penetration to the Si surface to provide effective acid deprotection. At higher exposures, the resist near the Si/resist interface can be properly exposed, but the top layers of the resist are then overexposed. This resist might provide better imaging in thinner films, and may in fact be satisfactory if used at a thickness between 100 and 150 nm, but it is too absorbing for use at a thickness near 200 nm.

In Figure 12 we show the imaging performance of a $TFE_{40}NBFOH_{47}t\text{-}BA_{13}$ based resist which has considerably less *t*-BA, leading to lower absorbance. This resist was imaged using the 0.6 NA optics on the Exitech stepper. The decrease in NA should lead to lower resolution through the well-known Rayleigh relation $R = (k_1 \cdot \lambda/NA)$. Nevertheless, the

resist images 50 nm 1:5 lines and spaces with a film thickness of 219 nm. In Figure 13 we show imaging results for a resist with a similar t-BA content (and 157 nm optical absorbance) imaged with the 0.8 NA optics. This resist images 70 nm 1:2 semi-dense lines and spaces, as well as less dense (1:5) lines and spaces as small as 43 nm.
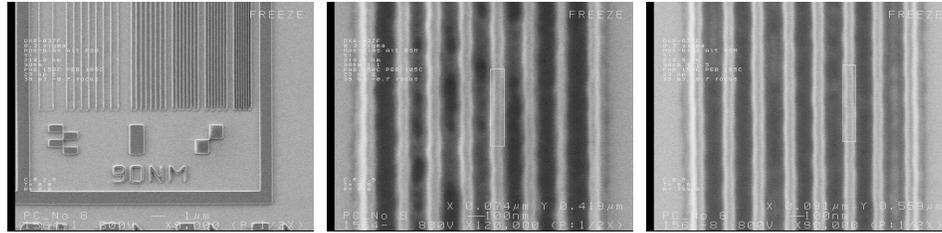

Figure 11. Top-down SEM images of a TFE$_{31}$NBFOH$_{45}$$t$-BA$_{24}$ terpolymer resist formulation spin-cast on Si and exposed at 157 nm using the Exitech stepper at International Sematech equipped with Tropel 0.85 NA optics and an alternating phase shift mask with a partial coherence of $\sigma = 0.3$. The film thickness is 219 nm, and the feature sizes and densities are 90 nm (left), 90 nm 1:1 (center), and 90 nm 1:1.5 (right). The optical absorbance of this resist formulation is 1.98 μm^{-1}.

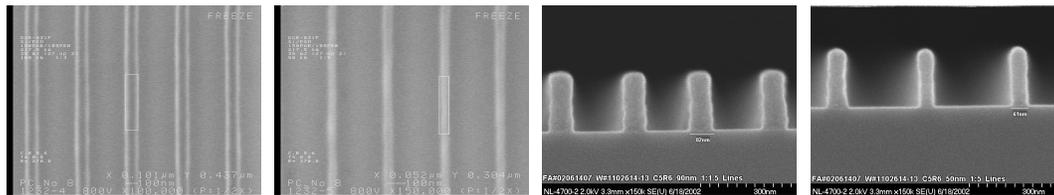Figure 12. Top-down (left two images) and cross-section (right two images) SEM images of a TFE$_{40}$NBFOH$_{47}$$t$-BA$_{13}$ terpolymer resist formulation spin-cast on Si and exposed at 157 nm using the Exitech stepper at International Sematech equipped with Tropel 0.6 NA optics and an alternating phase shift mask with a partial coherence of $\sigma = 0.3$. The film thickness is 219 nm. The feature sizes and densities in the top-down images are 100 nm 1:3 lines and spaces (far left) and 50 nm 1:5 lines and spaces (left center). The cross-sections are 90 nm 1:1.5 lines and spaces (right center), and 50 nm 1:5 lines and spaces (far right). The optical absorbance of this resist formulation is 1.62 μm^{-1}.

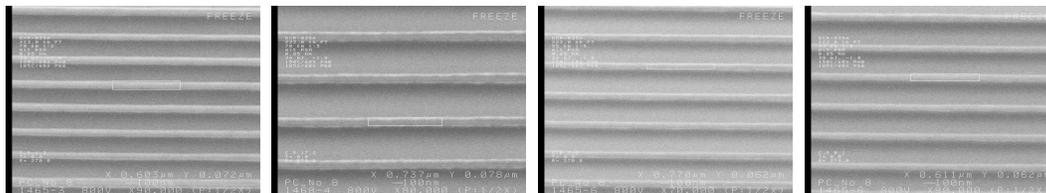Figure 13. Top-down SEM images of a TFE$_{39}$NBFOH$_{48}$$t$-BA$_{12}$ terpolymer resist formulation spin-cast on Si and exposed at 157 nm using the Exitech stepper at International Sematech equipped with Tropel 0.85 NA optics and an alternating phase shift mask with a partial coherence of $\sigma = 0.3$. The film thickness is 224 nm. The feature sizes and densities are (from left to right) 70 nm 1:2, 70 nm 1:5, 55 nm 1:5, and 43 nm 1:5 lines and spaces. The optical absorbance of this resist formulation is 1.70 μm^{-1}.

In Figure 14 we show the imaging performance of a TFE$_{43}$NBFOH$_{49}$$t$-BA$_8$ resist with a low optical absorbance of 1.27 μm^{-1}. Despite the low t-BA content, the resist can image 90 nm 1:1.5 lines and spaces. These results illustrate the remarkably wide compositional range over which these TFE terpolymers are capable of sub-100 nm imaging. However, as the t-BA content is further reduced, the resist contrast, as characterized by the values of R$_{min}$ and R$_{max}$ (the fully protected and fully deprotected dissolution rates, respectively), and not the less informative type of contrast measurement shown in Figure 10, becomes insufficient for high-resolution imaging.
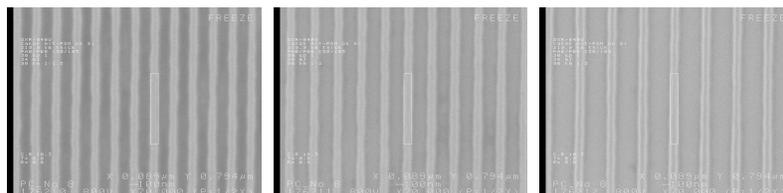
Figure 14. Top-down SEM images of a $TFE_{43}NBFOH_{49}t\text{-}BA_8$ terpolymer resist formulation spin-cast on Si and exposed at 157 nm using the Exitech stepper at International Sematech equipped with Tropel 0.85 NA optics and an alternating phase shift mask with a partial coherence of $\sigma = 0.3$. The film thickness is 224 nm. The feature sizes and densities are 90 nm 1:1.5, 90 nm 1:2, and 90 nm 1:3 lines and spaces. The optical absorbance of this resist formulation is 1.27 μm^{-1}.

6. PLASMA ETCH RESISTANCE

The etch resistance of these terpolymers is an important property for evaluating their potential use as 157 nm resist resins. We have made etch resistance measurements, using standard International Sematech etch conditions (see Section 2.6), for a number of these materials. Some of the data and conclusions have been presented elsewhere[4]. In Table 2 we list the etch rates for several materials to illustrate the general trends we observe in fluorinated polymer resins. The lowest etch rates are seen for TFE/NB dipolymers, where values equal to or less than those of APEX-E show that incorporating large amounts of TFE in the polymer backbone does not have a strongly deleterious effect on the poly-Si or oxide etch resistance. The most important effect we have discovered is that the incorporation of the fluoroalcohol moiety on the NB ring system dramatically increases the poly-Si etch rate. The oxide etch resistance also increases with addition of fluoroalcohol groups, but not as rapidly as the poly-Si etch rate. We have reported[4] that other fluoroalcohol moieties can provide etch resistance better than the one described here, but they do not necessarily provide equivalent imaging performance and may not polymerize as efficiently with TFE.

Table 2. Etch rates, relative to APEX-E, for two dipolymers that contain TFE, and one homopolymer that does not contain TFE.

Polymer	**Poly-Si**	**Oxide**
TFE/NB	0.59	1.076
TFE/NBFOH	1.30	1.19
NBFOH	1.18	1.34

As shown in Figure 19, the *poly*-Si and oxide etch rates for the terpolymers vary from 1.0-1.6 times the rate for APEX-E, with no clear emerging trend with increasing *t*-BA content. Although these results might seem to limit the use of these terpolymers for 157 nm lithography, where thin resist films are required, it is possible to significantly decrease these etch rates by using different fluoroalcohol moieties, incorporating carbon-rich groups in the polymers (but low 157 nm optical absorbance must be maintained), or perhaps by adjusting the etch chemistries to enhance the selectivity of fluoropolymers with respect to these substrates. It will be interesting to see which of these approaches is taken in the future.
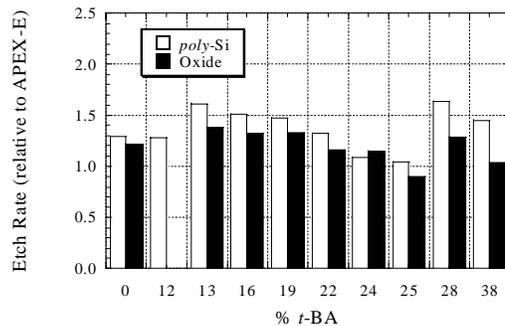
Figure 15. Poly-Si and SiO$_2$ (oxide) etch rates relative to APEX-E for various TFE/NBFOH/t-BA terpolymers with different amounts of t-BA measured at International Sematech under the conditions described in Section 2.6.

7. CONCLUSIONS

We have described the properties of a 157 nm photoresist resin platform, based upon copolymers of TFE with a norbornene fluoroalcohol and t-butyl acrylate, which provides high quality imaging over a wide composition range, and illustrates many features important in the design of highly fluorinated 157 nm resist resins. Resists incorporating these resins exhibit optical absorbance below 1.5 μm^{-1}, limited by the amount of t-BA needed for good dissolution, and can image with sub-100 nm resolution in thick (~200 nm) films. This polymer platform should be viewed as a DuPont TFE Version I 157 nm resist resin, and we believe that, by appropriate modifications, fundamental properties such as optical transparency, dissolution rate, imaging behavior, and plasma etch resistance can be further improved.

ACKNOWLEDGMENTS

REFERENCES

1. International Sematech 2002 Roadmap.
2. M. Lundstrom, "Moore's Law Forever?", Science **299**, 210 (2003).
3. R.R. Kunz, T.M. Bloomstein, D.E. Hardy, R.B. Goodman, D.K. Downs, and J.E. Curtin, "Outlook for 157 nm Resist Design", Proc. SPIE **3678**, 13-23 (1999).
4. M.K. Crawford, A.E. Feiring, J. Feldman, R.H. French, M. Periyasamy, F.L. Schadt, R.J. Smalley, F.C. Zumsteg, R.R. Kunz, V. Rao, L. Liao, and S.M. Holl, "New Materials for 157 nm Photoresists: Characterization and Properties", Proc. SPIE **3999**, 357-364 (2000); M.K. Crawford, A.E. Feiring, J. Feldman, R.H. French, V.A. Petrov, F.L. Schadt, R.J. Smalley, and F.C. Zumsteg, "157 nm Imaging Using Thick Single Layer Resists", Proc. SPIE **4345**, 428-438 (2001); M.K. Crawford, W.B. Farnham, A.E. Feiring, J. Feldman, R.H. French, K.W. Leffew, V.A. Petrov, F.L. Schadt, and F.C. Zumsteg, "Fluoropolymers for 157 nm Lithography: Performance of Single Layer Resists", J. Photopolymer Science and Technol. **15**, 677-687 (2002).
5. H. Ito, G.M. Wallraff, N. Fendar, P.J. Brock, W.D. Hinsberg, A. Mahorowala, C.E. Larson, H.D. Truong, G. Breyta, and R.D. Allen, "Development of 157 nm positive resists", J. Vac. Sci. Technol. B **19**, 2678-2684 (2001); H. Ito, G.M. Wallraff, P. Brock, N. Fender, H. Truong, G. Breyta, DC. Miller, M.H. Sherwood, and R.D. Allen, "Polymer design for 157 nm chemically amplified resists", Proc. SPIE **4345**, 273-284 (2001).

6. K. Patterson, M. Yamachika, R. Hung, C. Brodsky, S. Yamada, M. Somervell, B. Osborn, D. Hall, G. Dukovic, J. Byers, W. Conley, and C.G. Willson, "Polymers for 157 nm Photoresist Applications: A Progress Report", Proc. SPIE **3999**, 365-374 (2001).

7. M. Toriumi, S. Ishikawa, S. Miyoshi, T. Naito, T. Yamazaki, M. Watanabe, and T. Itani, "Resists materials for 157 nm lithography", Proc. SPIE **4345**, 371-378 (2001); M. Toriumi, N. Shida, H. Watanabe, T. Yamazaki, S. Ishikawa, and T. Itani, "Fluoropolymer Resists for 157-nm Lithography", Proc. SPIE **4690**, 191-199 (2002); S. Kodama, I. Kaneko, Y. Takebe, S. Okada, Y. Kawaguchi, N. Shida, S. Ishikawa, M. Toriumi, and T. Itani, "Synthesis of Novel Fluoropolymer for 157 nm Photoresists by Cyclo-polymerization", Proc. SPIE **4690**, 76-83 (2002).

8. D. Schmaljohann, Y.C. Bae, G.L. Weibel, A.H. Hamad, and C.K. Ober, "Design Strategies for 157 nmSingle-Layer Photoresists: Lithographic Evaluation of a Poly(α-trifluoromethyl vinyl alcohol) Copolymer", Proc. SPIE **3999**, 330-334 (2000).

9. T.H. Fedynyshyn, R.R. Kunz, R.F. Sinta, M. Sworin, W.A. Mowers, R.B. Goodman, and S.P. Doran, "High Resolution Fluorocarbon Based Resist for 157-nm Lithography", Proc. SPIE **4345**, 296-307 (2001).

10. T. Itani, M. Toriumi, T. Naito, S. Ishikawa, S. Miyoshi, T. Yamazaki, and M. Watanabe, J. Vac. Sci. Technol. B**19**, 2705-2708 (2001).

11. R.H. French, R.C. Wheland, W. Qui, M.F. Lemon, E. Zhang, J. Gordon, V.A. Petrov, V.F. Cherstkov, and N.I. Delaygina, "Novel Hydrofluorocarbon Polymers for use as Pellicles in 157 nm Semiconductor Photolithography: Fundamentals of Transparency", J. Fluorine Chem., in press.

12. R.H. French, J. Feldman, F.C. Zumsteg, M.K. Crawford, A.E. Feiring, V.A. Petrov, F.L. Schadt, and R.C. Wheland, "Progress in Materials Development for 157 nm Photolithography: Photoresists and Pellicles", Semiconductor FabTech **14**, 167 (2001).

13. G. Taylor, C.B. Xu, G. Teng, J. Leonard, C. Szmanda, W. Lawrence, S. Nur, K. Brown, and A. Stephen, "Factors influencing the properties of fluoropolymer-based resists for 157 nm lithography", Proc. SPIE **4690**, 51-57 (2002).

14. A.E. Feiring, M.K. Crawford, W.B. Farnham, J. Feldman, R.H. French, K.W. Leffew, V.A. Petrov, F.L. Schadt, R.C. Wheland, and F.C. Zumsteg, "Design of very transparent fluoropolymer resists for semiconductor manufacture at 157 nm", J. Fluorine Chem., in press.

15. K.S. Guigley, A.E. Feiring, P.C. Painter, and M.M. Coleman, "Infrared Studies of Polymer Blends Containing a Copolymer of Tetrafluoroethylene and a Hexafluoroisopropanol Substituted Vinyl Ether", J. Macromol. Sci. Physics B**41**, 207 (2002).

16. G.M. Wallraf, J. Opitz, W. Hinsberg, and F. Houle, "Reactivity and Kinetic Parameters of UVIIHS", Proc. SPIE **3049**, 492-500 (1997).

17. G.M. Wallraf, W.D. Hinsberg, F.A. Houle, M. Morrison, C.E. Larson, M. Sanchez, J. Hoffnagle, P.J. Brock, and G. Breyta, "Experimental Method for Quantifying Acid Diffusion in Chemically Amplified Resists", Proc. SPIE **3678**, 138-148 (1999).