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Articles

On the Question of Acid Generation upon 157-nm Laser Exposure of Fluorinated Polymers

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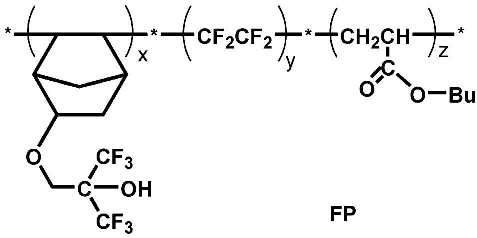
Exposure of thin polymer films to laser excitation at 157 nm leads to surface ablation that in the case of fluorinated polymers is accompanied by the photogeneration of HF, a possible problem in lithographic and imaging applications of these compounds. Fluorescence spectroscopy, fluorescence microscopy and atomic force microscopy have been used to examine the polymer films following laser exposure and to compare fluorinated and nonfluorinated films.

Introduction

The demand for increasingly smaller features in microlithography has been the driving force behind the use of shorter wavelengths. Excimer lasers have proven extremely useful in photolithography and provide common wavelengths at 248, 193, and 157 nm. The last two wavelengths are absorbed by most organic molecules, thus presenting challenges in the selective excitation of specific components of resist formulations, in particular the photoacid generators (PAGs) normally used to create the images. Fluorinated materials are more transparent in the deep-UV region than most other organic materials.[1,2] This makes them attractive as building blocks for polymeric materials that have acceptable optical properties below 200 nm. However, at 157 nm ejection of material cannot be avoided, even at low incident energy doses.[3,4]

Several of the fluorinated polymers developed for deep-UV applications can be viewed as modified Teflon structures where moieties other than tetrafluoroethylene confer the material appropriate adhesion, film-forming, and photochemical properties.[2] Chart 1 shows a representative structure containing some of the common features in these polymers and, in particular, to the material used in this work. Notably, groups derived from hexafluoro-2-propanol are common. In addition, protected carboxylate groups provide the photoswitchable group required for solubility-based imaging.

Chart 1



FP

High energy laser pulses can excite highly fluorinated polymers, potentially leading to polymer degradation products,[4] among them HF, a material of considerable concern given its corrosive properties and the high cost of lithographic equipment. Two recent publications report the formation of acidic species upon 157-nm exposure of fluorinated copolymers, but the identity of the acidic species was not established.[5,6]

This paper explores the chemical and topological consequences of 157-nm laser excitation of films of a fluorinated polymer (FP) with the basic structure of Chart 1. To compare with other polymers, we have used as controls films of ethyl cellulose (EC) and of polymethylsilsesquioxane (PMSSQ). Previous studies reported on ablation and etching using deep-UV and vacuum-UV light irradiation of poly(ethylene terephthalate), poly(methyl methacrylate) (PMMA), and modified PMMA.[7,8] The results we present in this paper have been acquired using a variety of techniques, in particular,

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fluorescence microscopy combined with acid−base and fluoride sensors and AFM imaging. In addition laser-flash photolysis experiments were performed in solution, aimed at understanding the role of hexafluoro-2-propanol moieties in the polymer degradation process.

Experimental Section

Materials. 3-(2-Benzothiazolyl)-7-(diethylamino)coumarin (Coumarin 6, C6, 98%), 7-hydroxy-4-methylcoumarin (Coumarin 4, C4, 97%), imidazole (99%), triisopropylsilyl chloride (TIPSCl, 97%), 2-heptanone (99%), benzyl acetate, 1,4-dimethoxybenzene (1,4-DMB), 1,1,1,3,3,3-hexafluoro-2-propanol (HFP), and ethyl cellulose (EC, 48% ethoxyl content, 100 cP) were purchased from Aldrich and used as received. Polymethylsilsesquioxane (PMSSQ) and the fluorinated polymer (FP) were a kind gift from Rohm & Haas Electronic Materials. The solvents used were chloroform (Omnisolv, from BDH), methanol (Omnisolv, from EM Sciences), acetonitrile (Omnisolv, from EM Sciences), and *N*,*N*-dimethylformamide (DMF, Omnisolv, from BDH). 4-Methyl-7-(triisopropylsilanyloxy)-coumarin (C4TIPS) was prepared by reaction of Coumarin 4 with TIPSCl and imidazole in DMF that was previously dried on activated 4A molecular sieves.[9] The crude product was purified by column chromatography on silica gel using hexane:dichloromethane as eluent. More details about the synthesis, characterization, and selectivity of C4TIPS will be published elsewhere.

General Techniques. The polymer films containing the probes were exposed to radiation at 157 nm using a GSI-Lumonics excimer laser filled with a fluorine mixture (fwhm 12−15 ns). The energy of the beam incident on the polymer films surface varied between 1.1 and 2.8 mJ/(cm^2·shot) with a beam area of ~2 cm^2 and it was measured using a Molectron JD2000 joulemeter radiometer and a Coherent J45LP-MB photon detector. The exposures were carried out under a nitrogen atmosphere. In most of the exposure experiments a contact mask was placed on top of the films during irradiations to obtain a patterned image. The mask used is a grid made from copper and has a regular pattern of hexagons whose centers are 60 μm apart.

For all films used in this paper the thickness was measured using a TFA-11 thin film analyzer from Luzchem Research.

Fluorescence images were recorded using a Leica DMLS fluorescence optical microscope with a 20× objective with a 50-W Hg lamp as a light source and a Leica DFC300 FX camera. Filter cubes E4 (excitation, centered at 436 nm; emission, long pass 470 nm) and M2 (excitation, centered at 546 nm; emission, long pass 590 nm) from Leica were used to monitor the fluorescence of C6 and protonated C6, respectively. An XF02-2 filter cube (excitation, centered at 330 nm; emission, long pass 470 nm) from Omega opticals was used to monitor the fluorescence of C4TIPS. The fluorescence images were acquired using the software Leica IM50 version 4.0 release 117 from Leica Microsystems Imaging Solutions Ltd.

Laser flash photolysis studies in solution were performed with a system similar to that described earlier[10] using 266 nm [the fourth harmonic from a Nd:YAG laser (Surelite)] or 308 nm from a Lumonics Excimer-500 laser; both lasers gave pulses around 7−10 ns in duration. The solutions for laser flash photolysis were contained in 7 × 7 mm cuvettes made of fused silica. Fluorescence measurements in solution were performed with a PTI spectrofluorimeter using 1 × 1 cm quartz cuvettes.

Atomic force microscopy (AFM) studies were done at the National Research Council laboratories in Ottawa. AFM measurements were carried out on a Multimode Nanoscope III atomic force microscope (Digital Instruments, Santa Barbara, CA). The J scanner (120 mm) and 200-mm-long soft cantilevers with integrated pyramidal silicon nitride tips (spring constant of 60 mN/m) were used for all measurements.

Polymer Films for Fluorescence Imaging Experiments. For the fluorescence imaging experiments, the PMSSQ formulations were obtained using a solution of 25 wt % PMSSQ and 75 wt % 2-heptanone as solvent; the films of fluorinated polymer (FP) were prepared using 18 wt % polymer and 82 wt % 2-heptanone, whereas the solutions of ethyl cellulose contained 1 wt % polymer and 99 wt % chloroform.

The content of fluoride sensor (C4TIPS) was 5.0 wt % of dry polymer weight, whereas the content of Coumarin 6 was 0.5 wt % of the dry polymer weight. All films were spin-coated on 1-in. quartz disks for 20 s at different revolutions per minute (rpm): FP at 3000 rpm, ethyl cellulose at 1000 rpm, and PMSSQ at 3500 rpm. A postapplication bake (PAB), to remove the solvent, and a postexposure bake (PEB) were done at 90 °C for 60 s on a hot plate inside an oven, followed by rapid cooling of the films on a metallic surface at room temperature. The PMSSQ films were ~485 nm thick, the FP films ~350 nm, and the ethyl cellulose films ~400 nm thick.

Polymer Films for AFM. The polymer films for AFM were prepared such that the thickness was ~400 nm for all of them. To reach the same thickness for all films, the loadings of the dry polymers were varied: 25 wt % PMSSQ in 2-heptanone, 18 wt % FP in 2-heptanone, and 1 wt % ethyl cellulose in chloroform, respectively. When C6 was introduced in the films, the loading was 0.5 wt % C6 from the dry polymer weight. The films were prepared by spin coating on 0.5-in. glass disks at 3500 rpm for 20 s for PMSSQ, 3000 rpm for 20 s for FP, and 1000 rpm for 20 s in the case of ethyl cellulose. After coating, the films were baked at 90 °C for 60 s and then cooled at room temperature on a metallic surface. Before AFM measurements, the surface was cleaned with an air gun.

Results

Acid Detection. Acid detection in polymer films was carried out using Coumarin 6 as a sensor and employing the same approach as in earlier contributions.[11,12] In these systems the dye is added in very small amounts, typically 0.5 wt % of the polymer weight. While C6 absorbs at 157 nm, at the concentrations used its absorbance is relatively small compared with that of other components, including the polymer itself. The absorbance and fluorescence of neutral and protonated Coumarin 6 in polymethyl methacrylate (PMMA) are shown in Figure 1. Solutions containing 15 wt % PMMA, 85 wt % MPK (methyl propyl ketone), 3 wt % triphenylsulfonium triflate as PAG, and 0.5 wt % Coumarin 6 were spin-coated on 1-in. quartz disks at 3000

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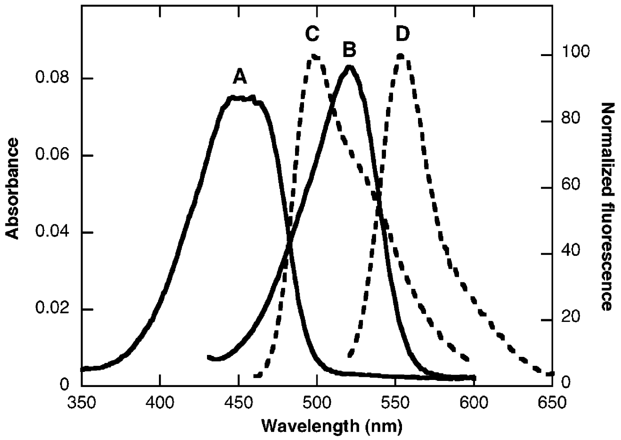


Figure 1. Absorbance (A and B) and fluorescence (C and D) of neutral (A and C) and monoprotonated (B and D) Coumarin 6 in a PMMA film. Excitation wavelengths were 450 nm for the neutral Coumarin 6 and 510 nm for the protonated Coumarin 6.

Table 1. Digital Color Intensity for the Main Features in Figure 2

sample	color	unexposed[a] (line)	exposed[a] (center of grid)
FP A	green	64.0	50.3
FP B	red	5.3	42.0
ethyl cellulose A	green	93.5	61.3
ethyl cellulose B	red	3.3	44.3
PMSSQ A	green	84	58.3
PMSSQ B	red	2.3	23.8

[a] Arbitrary units.

rpm for 20 s. The films were baked in the oven for 60 s prior to exposure to ensure complete removal of the solvent, and after exposure to ensure complete protonation of Coumarin 6, they were cooled immediately on a metallic surface at room temperature. The exposure was done in the HTG exposure unit at 254 nm for 20 s and the same film was used for absorbance and fluorescence measurements. During exposure and absorbance and fluorescence measurements, the film was at room temperature. The molar absorption coefficient for neutral Coumarin 6 (C6), previously reported, is 5.4 × 10^4 L mol^{-1} cm^{-1}.[13] An exact determination of the molar absorption coefficient for protonated Coumarin 6 (C6H+) is complicated by the multiple equilibria involved; however, from the plot in Figure 1, we estimate a value of ≥5.9 × 10^4 L mol^{-1} cm^{-1} at 520 nm, where the equality would apply if the unprotonated and diprotonated forms were totally absent. Attempts to monitor the acid formation and dependence of the production of HF as a function of incident dose at 157 nm in the absence of PAG by recording fluorescence spectra characteristic to C6H+ were difficult due to weak emissions. Exposure to high-energy doses leads to destruction of Coumarin 6. Fluorescence microscopy proved more sensitive (vide infra).

The amounts of polymer, solvent, and probe used for fluorescence microscopy imaging and AFM experiments are reported in the experimental part of this paper.

The films were examined by fluorescence microscopy. Representative images obtained using the fluorinated polymer in samples doped with C6 are illustrated in Figure 2, using a mask with 60 μm hexagonal patterns. This figure illustrates both positive and negative patterns obtained from the same film by changing the excitation and detection wavelengths in the microscope. This provides unequivocal evidence for acid formation, with exposures of ~10 mJ/cm^2 or higher. For comparison, with our current imaging facilities, ~1 mJ/cm^2 is enough to get good feature definition when a PAG is used. For illustration purposes, the images of Figure 2 were obtained with 42.0 mJ/cm^2. Table 1 gives the intensity green and red in Figure 2 measured with a digital color meter in the exposed and unexposed areas for each image. For the

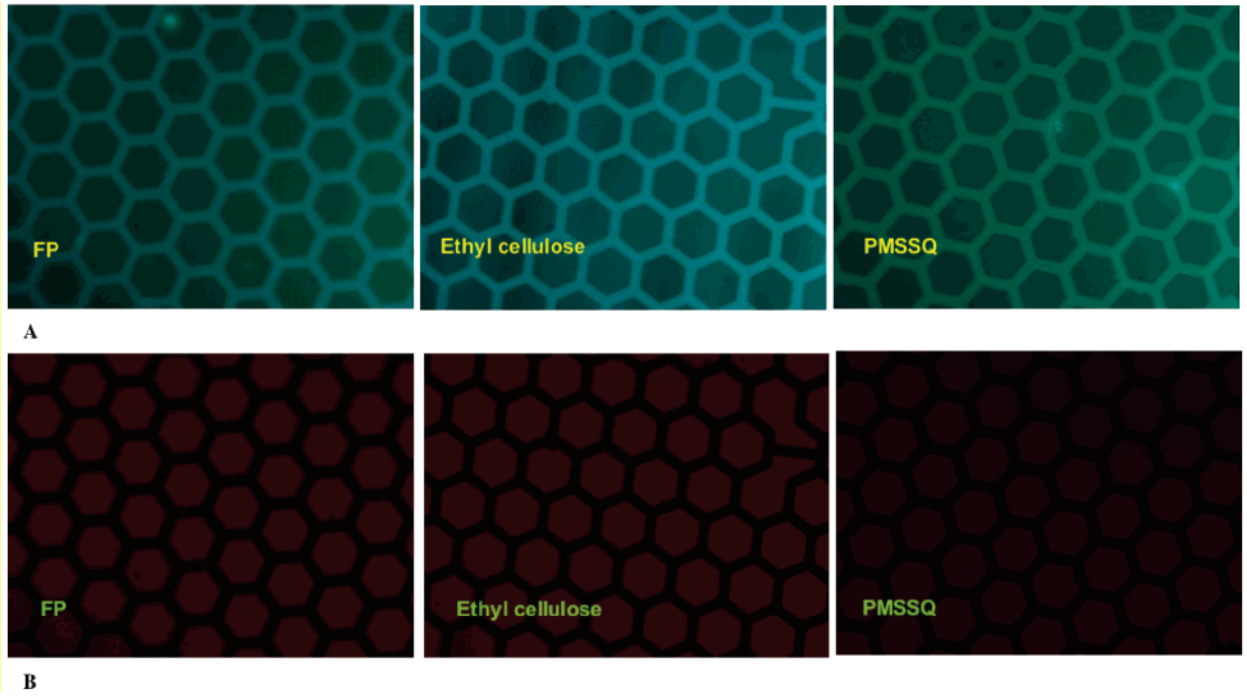
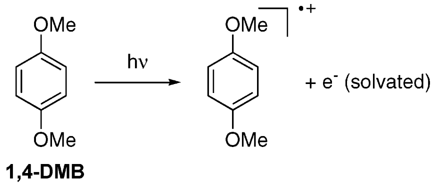


Figure 2. Fluorescence images of the polymers containing the fluorescent acid probe C6 (0.5 wt %) after 157-nm laser exposure through the mask, obtained with the (A) E4 filter and (B) M2 filter. The 157-nm irradiation was delivered in 30 shots and amounts to a total dose of 42 mJ/cm^2. The films' thicknesses: FP, 350 nm; ethyl cellulose, 400 nm; and PMSSQ, 485 nm. The green fluorescence corresponds to C6 in the neutral form and the red fluorescence corresponds to the protonated form.

Scheme 1



images obtained with filter E4, it should be noted that the change in blue intensity, not reported, follows the change in green intensity.

Laser Flash Photolysis in Solution. One of the possible processes induced by 157-nm laser irradiation is electron photoejection (vide infra). To test for the ability of some of the moieties included in the polymer to trap electrons, we carried out laser flash photolysis experiments in which the electrons were produced by photoejection from 1,4-DMB in methanol by laser irradiation at 266 nm, according to Scheme 1.

The radical cation of 1,4-DMB can be readily identified by its characteristic absorption at ∼430 nm,[14] while the solvated electron shows a broad band absorption at 600−700 nm. This absorption is readily quenched by N_2O, which serves as a diagnostic for the electron signal. Figure 3 shows the spectra of the solvated electron obtained following laser flash photolysis of 1,4-DMB under N_2 and N_2O atmospheres.

The rate constant for the scavenging of solvated electrons by hexafluoro-2-propanol (HFP) was determined by monitoring the decay of the solvated electron in methanol at 650 nm in the presence of varying concentrations of HFP as shown in Figure 4A.

From the slope of the plot in Figure 4A we obtain a rate constant for electron scavenging by HFP of 3.6×10^{10} M^{-1} s^{-1}, or essentially diffusion controlled. Given the presence of ester groups in the polymer, we also tested the reactivity of benzyl acetate (Figure 4B) and obtained a rate constant of 2.9×10^8 M^{-1} s^{-1}. The modest value is in line with other trapping rate constants for esters.[15] Following reaction, the radical anion is expected to cleave to acetate and benzyl radical.[16]

Fluoride Detection. Detection of fluoride in aqueous systems is straightforward, either with specific sensors or simply using fluoride electrodes.[17] This is not the case in thin films that contain only trace amounts of fluoride and where diffusion is severely restricted. We have been working on the development of several fluorescent sensors capable of operating under typical thin film lithographic conditions. While these sensors are not yet fully characterized in terms of their specificity for fluoride, it is clear that in our films no other halide can be formed. Control experiments with PMSSQ and ethyl cellulose films under comparable conditions were negative, as expected.

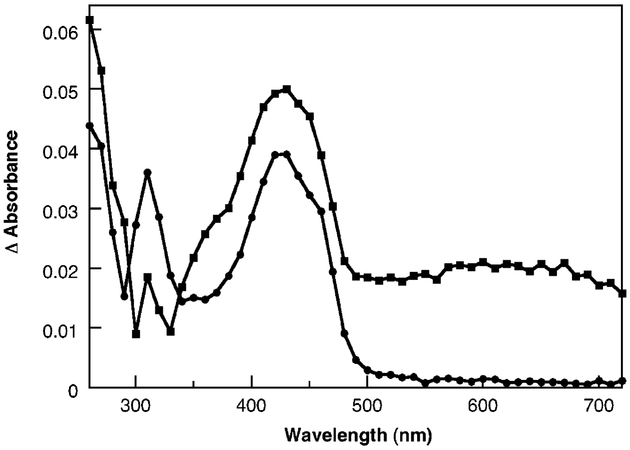


Figure 3. Laser flash photolysis spectra with 266 nm of 0.66 mM 1,4-DMB in methanol, deaerated with N_2 (■), 0.32 μs after the laser pulse, and N_2O (●), 0.24 μs after the laser pulse.

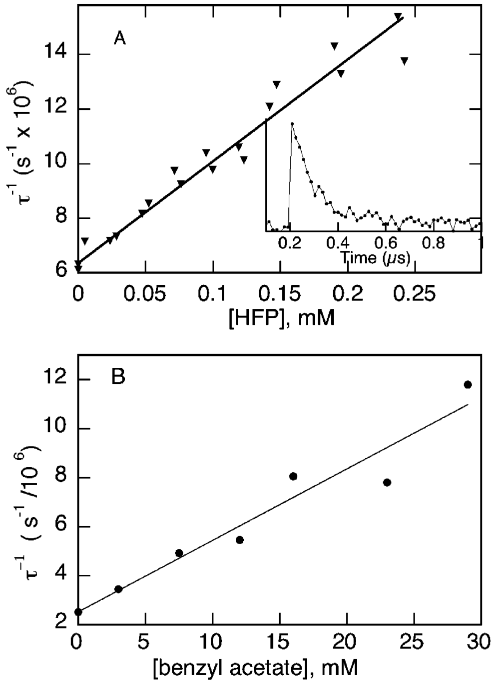
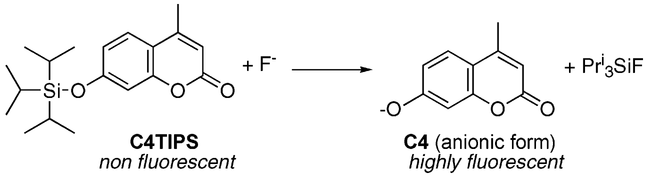


Figure 4. (A) Plot of decay pseudo-first-order rate constants obtained by laser flash photolysis of 1.9 mM 1,4-DMB in methanol in the presence of varying concentrations of HFP with 266-nm laser excitation; inset shows representative kinetic decay trace at 650 nm from which rates were derived. (B) Plot of pseudo-first-order rate constants determined by laser flash photolysis of 0.3 mM 1,4-DMB in methanol against benzyl acetate concentration.

Scheme 2



The sensor used is shown in Scheme 2. Note that fluoride causes the release of the triisopropylsilanyl protecting group. Coumarin 4, which is highly fluorescent,[18] becomes practically nonfluorescent upon protection of the 7-hydroxy group with the triisopropylsilanyl group. The fluorescence switch

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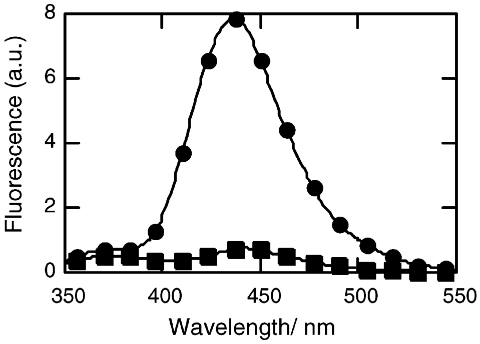

Figure 5. Emission spectra of Coumarin 4 (●) and C4TIPS (■), 5×10^{-5} M in acetonitrile. Excitation wavelength was 340 nm, with a 10 × 10 mm quartz cell.

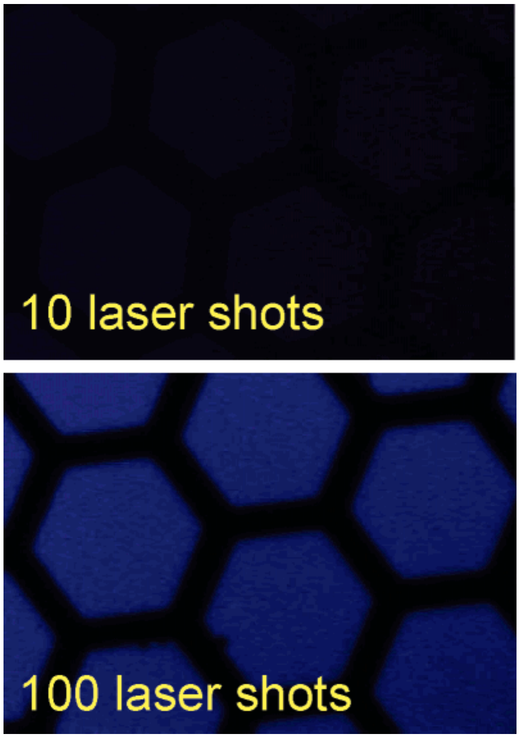

Figure 6. Fluorescence images of a FP film (350 nm thick) containing the "prefluorescent" probe C4TIPS (5 wt %) after 157-nm laser exposure through the mask. The 157-nm dose per laser shot is ~2.2 mJ/cm^2. The fluorescence microscope filter used was XF02-2. The blue regions correspond to the fluoride-activated release of the fluorescent sensor.

based on deprotection of the 7 hydroxyl position has been used to monitor acid formation in films when the protecting group is *tert*-butoxycarbonyl (tBoc).[19]

The emission spectra in acetonitrile solution of C4TIPS, the protected silylated form, and of C4, the unprotected coumarin, are shown in Figure 5.

Exposure of films of fluorinated polymers containing C4TIPS as a fluoride sensor at 157 nm through a mask leads to the fluorescence images of Figure 6, where the release of the fluorescent Coumarin 4 is revealed by its blue fluorescence in the exposed areas. The increase in blue color intensity in the exposed areas relative to those unexposed, as measured with the digital color meter, is 195% after 10 shots and 765% after 100 shots.

Topographical Studies. Films exposed at 157 nm were also examined by AFM to determine the effect of laser exposure on the topography of the film. The results for the FP and a film of EC with C6 are shown in Figure 7. The topography also reveals LIPS (laser-induced periodic structures), as can be seen in Figure 7, a phenomenon that has already been reported in several types of materials exposed to laser irradiation.[20, 21]

We believe that the loss of material is due to laser ablation, a process that has been known for over 20 years.[7] The ablated depth following 157-nm laser excitation observed under comparable conditions of exposure was 17.4 nm for PMSSQ, 66.0 nm for EC, and 33.8 nm for FP. The total dose delivered with 200 laser pulses was 460 mJ/cm^2. The average ablation observed is not linear with the dose delivered to the film. The depth was measured as the difference between the unexposed regions and the center of the exposed hexagon. The ablated depth (typically ~30 nm) in FP represents less than 10% of the total film thickness (typically 400 nm). The ablated depth is slightly bigger when the dye Coumarin 6 is present. Thickness measurements done with Luzchem TFA-11 thin film analyzer showed that there is a larger film loss at the beginning of the irradiation and a plateau is reached. Higher incident doses do not lead to enhanced ablation.

Discussion

Fluorinated polymers have become frequent choices for lithographic processes in the vacuum ultraviolet region, reflecting their excellent optical properties. While not completely transparent, highly fluorinated macromolecules transmit more light than essentially all other organic materials. However, lithographic polymers are required to have other characteristics beyond transparency, and as a result the optical properties of highly fluorinated polymers are somewhat compromised in order to achieve adequate adhesion and good film-forming properties and to introduce a solubility switch. Chart 1 shows an example of how the basic poly(tetrafluoroethylene) structure is modified in order to meet these requirements.

From the point of view of thin film topography, both AFM and fluorescence microscopy studies show that surface damage takes place upon laser exposure, including ablative damage and the formation of LIPS, a phenomenon that has been characterized before in a variety of films.[20,22] Interestingly, in our AFM images we do not detect particles ejected from one ablated area into another; we speculate that any such particles would probably have a stronger absorption than the initial polymer and would be loosely placed on the surface where light absorption from subsequent laser pulses would tend to clean any debris. The depth of ablative damage

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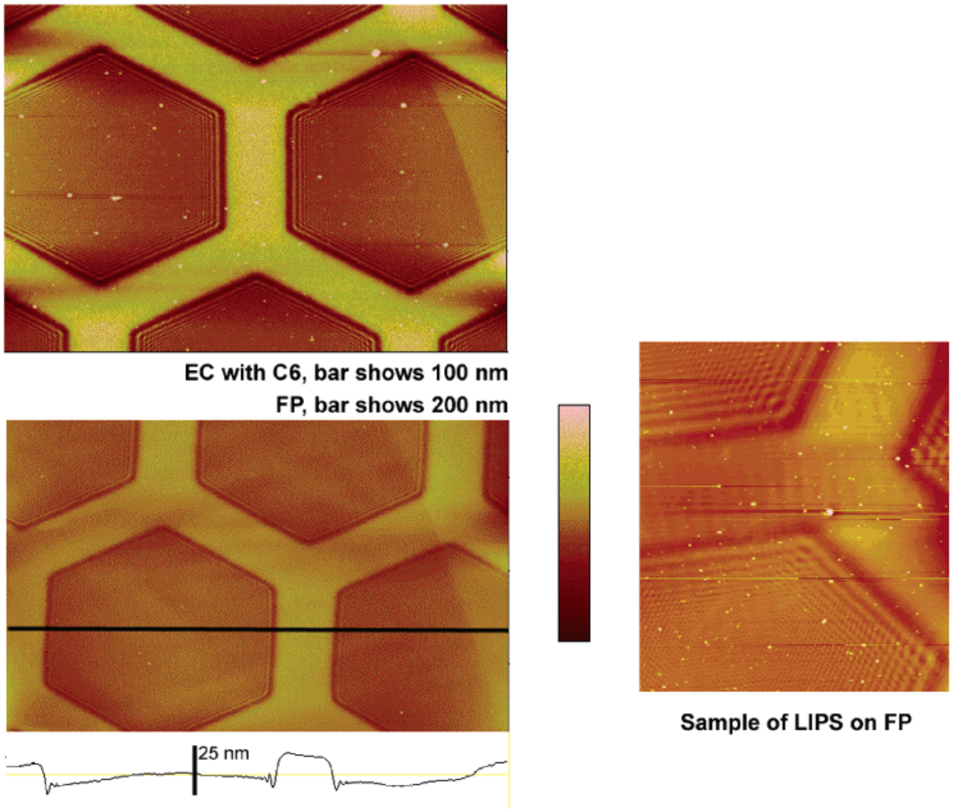

Figure 7. AFM images of EC doped film with C6 and of a FP film; the distance between hexagons is 65 μm (center-to-center). The image on the right shows LIPS formation on the FP film. The line graph at the bottom left shows a depth profile corresponding to the figure immediately above.

is larger in our control films of EC (66 nm) than in the case of FP and PMSSQ and larger in the case of FP (33.8 nm) compared to PMSSQ (17.4 nm). This is reasonable in view of the higher 157-nm absorption of polymers rich in C−H, C═O, and C−OH groups.[23] In accordance with this explanation, fluorinated polymers containing a dye indicator (such as Coumarin 6) undergo slightly more ablative damage than the pure polymer, as determined by AFM profiling. Water, which is strongly absorbing at 157 nm,[24] may also play a role in ethyl cellulose films (vide infra).

Testing for acid formation using low levels of Coumarin 6 as a fluorescent indicator shows unequivocally that 157-nm laser irradiation of fluorinated polymer films leads to acid generation. We previously reported acid formation following exposure at 157 nm of photoresists containing photoacid generators (PAGs).[12] For resist formulations containing PAGs it is enough to deliver 1−2 mJ/cm^2 to notice abundant acid formation, whereas in the case of the FP the dose at which we notice acid formation is ∼10 mJ/cm^2, or slightly below, and the amount of acid is very small compared to the previous reports,[12] where acid was detected at 2.3 mJ/cm^2 in the presence of PAG, even with significantly less sensitive imaging capabilities than those currently available in our laboratory. In other words the acid formed in our previous report originates from the PAG, the absorbance of which at 157 nm is much higher than that of the fluorinated polymer, and not from the polymer matrix, as is the case in the present work.[23] Control experiments with PMSSQ show a very weak fluorescence from protonated Coumarin 6. This is not surprising, since PMSSQ is thought to have the lowest absorbance at 157 nm and consequently it is expected to suffer less photochemical damage at 157 compared to EC and FP. It has the highest thickness, ∼485 nm; however, it shows the least ablation and the lowest emission intensity characteristic to protonated Coumarin 6. EC and FP show approximately the same intensity of emission characteristic to protonated Coumarin 6 (see Figure 2). We note that the absorbance of EC at 157 nm is much higher than that of FP (a polymer especially designed so that its absorbance at 157 nm is low), and consequently, there are more photons absorbed that could generate acid in EC.[23] The second aspect is related to the film thickness, EC films are approximately 50 nm thicker than the FP films. These two factors indicate that FP is a better acid generator than EC. Under different fluorescence excitation and emission conditions in the fluorescence microscope, it is possible to detect negative and positive images from the same film; as pointed out in earlier contributions, this is an important test.[12] While negative images could be obtained by destroying the dye, positive images with the correct spectral response can only result from dye protonation. The emission of neutral Coumarin 6 is stronger in the unexposed regions (see Figure 2A, top). In the exposed regions part of Coumarin 6 is protonated and it emits at a different wavelength, in the red, not green. The film loss in the exposed regions has to be taken into consideration as well, since the amount of dye has decreased after ablation. Further, part of the Coumarin 6 may have been destroyed during irradiation.

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Independent experiments using C4TIPS, the fluoride sensor of Scheme 2, reveal the formation of fluoride upon exposure of the fluorinated films. We emphasize that this sensor is not fully characterized in terms of its specificity to fluoride, and it is possible that it also responds to other halides; however, under the conditions of our experiment, no other halide can be formed, and the positive test of Figure 6 is attributed to the formation of fluoride.

Given the independent confirmation of the formation of acid and of fluoride, it seems reasonable to conclude that the 157-nm laser irradiation of fluorinated lithographic polymers leads to the production of low levels of hydrogen fluoride. It is unlikely for HF to be formed in a concerted process, given the structure of the polymer. We speculate that a possible mechanism may involve electron photoejection, most likely from nonfluorinated moieties in the polymer, followed by deprotonation at the ionization site, thus forming the acid. The most likely mechanism for fluoride release involves capture of the electron by hexafluoro-2-propanol or $-CF_2CF_2-$ groups within the polymer, given that they are much better electron traps than ester groups. Our solution time-resolved experiments (see Figure 4) show that these groups are at least 2 orders of magnitude more reactive toward electrons than esters group, the other moiety present as part of the solubility switch.

The idea that photoionization does not involve the fluorinated groups, but rather the C$-$H rich parts of the molecule, or conceivably carbonyl groups, is consistent with studies of the absorption properties of fluorinated materials that demonstrate that even small levels of hydrocarbons are enough to make them the dominant chromophore at 157 nm.[5,25] It has also been shown[24] that water is strongly absorbing at 157 nm, but in addition, it undergoes photodecomposition with high quantum efficiency; however, water solubility in highly fluorinated materials is extremely small, and even the presence of hydrophilic groups (hexafluoro-2-propanol and esters) is unlikely to retain much water, particularly considering that films are baked at 90 °C before exposure. It is possible that traces of water also contribute to the higher ablation depths in the case of the more hydrophilic, nonfluorinated control polymers.

In conclusion, 157-nm laser exposure of thin films of fluorinated lithographic polymers leads to some ablative damage, with accompanying formation of LIPS and release of hydrogen fluoride; the latter is likely to be initiated by electron photoejection from nonfluorinated moieties in the polymer.

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