Optical Observation of Deep Bulk Damage in Amorphous Perfluorocarbon Films Produced by UV Photons Emitted from Low-Pressure Argon Plasma

Takao Ono, Ryo Iizuka, Takanori Akagi, Takashi Funatsu, and Takanori Ichiki

In plasma processing, UV photons generate damage deep in the bulk of transparent materials such as amorphous polymers and glass. In this article, we propose the use of total internal reflection fluorescence microscopy for the nondestructive and highly sensitive detection of UV-induced deep bulk damage and for the first time demonstrate the three-dimensional profiling of UV penetration and optical damage production inside amorphous perfluorocarbon films. Weak fluorescence from damaged molecules, whose original chemical structure was altered through bond breaking and reconstruction, was detected up to several hundred nanometers below the surface after exposure to argon plasma.

Keywords: plasma induced damage, 3D profiling, total internal reflection fluorescence microscopy, amorphous perfluorocarbon, argon plasma

1. Introduction

Since the early days of plasma processing of microelectronic devices, plasma-induced damage has been a critical issue in improving device properties and/or reliability. Soon after the development of reactive ion etching [1,2], plasma-induced damage such as gate oxide breakdown due to charge build-up and lattice defects induced by high-energy ion bombardment were reported [3-5]. When magnetized high-density plasma etchers such as electron cyclotron resonance (ECR) plasma etchers and magnetically enhanced reactive ion etchers (MERIEs) came into practical use in the late 1980s, intensive researches were carried out to overcome the problem of gate oxide breakdown originating from the poor plasma uniformity over a wafer. In the 1990s, the charge build-up at the bottom of finely etched patterns during high-aspect-ratio contact (HARC) etching using high-density plasma caused serious problems in production lines because the distortion of the ion trajectory resulted in the degradation of etching features such as notching effects and etch stops [6-8]. Thus, plasma-induced damage has long been a problem in the history and progress of plasma processing.

As with electrical charge-up and ion bombardment, photons in the UV and especially in the vacuum ultraviolet (VUV) regions emitted from plasma also induce damage on device materials [9-17]. Although the number of reports on UV-induced damage in LSI fabrication is much smaller than those on damage induced by electrical charge-up and ion bombardment, the recent increase in the use of organic materials in electronic devices, e.g., for low-k dielectric barrier and flexible semiconductors, has highlighted the ever-growing importance of the study on UV-induced damage in plasma processing. Compared with other energetic particles in plasma such as ions and electrons, UV photons have a much larger depth of penetration into transparent materials and can induce defects in the bulk region several hundred nanometers below the surface.
In past studies, various analytical methods have been employed for the detection and characterization of plasma-induced damage, including X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and ellipsometry [4,9-14,19,20]. Indeed, these approaches are very useful for studying near-surface damage produced by ion bombardment, but not for detecting very slight damage generated deep in the bulk.

In this article, we report the nondestructive detection of UV-induced damage in the deep bulk of amorphous perfluorocarbon films exposed to argon plasma. Fluorescence originating from damaged molecules with modified chemical structures was detected using total internal reflection fluorescence microscopy (TIRFM) [21,22]. Taking advantage of the extreme sensitivity and high spatial resolution of this technique, three-dimensional profiles of UV penetration and optical damage produced inside amorphous perfluorocarbon polymers were experimentally obtained for the first time.

2. Experimental Methods

Amorphous perfluorocarbon (Asahi Glass Cytop™ CTX-809AP2) films were used as samples. This polymer, synthesized from perfluoro-4-vinyloxy-1-butene via radical polymerization reaction, has high optical transparency, low autofluorescence in the visible and near-UV regions (absorption edge is approximately 170 nm) [23] and a very low refractive index [24], and hence, it is used as polymer optical fibers and antireflection films in display panels [25]. In addition, such excellent optical properties make the amorphous perfluorocarbon an attractive material for biodevices especially for bioimaging or optical biosensing applications [26-30]. In this study, the films were spin-coated on borosilicate glass substrates of 18×18 mm² area and 0.15 mm thickness. The film thickness was varied from 200 to 800 nm by controlling the spin speed. Unless otherwise stated, it was set at 200 nm in this study.

In the plasma exposure experiment, we employed an in-house-made plasma reactor comprising a plasma source with a single-turn antenna wound around a 100-mm-diameter quartz bell jar, a stainless steel diffusion chamber and a turbomolecular pump for the exhaust system. A water-cooled sample stage was set downstream, 95 mm from an rf antenna. The 13.56 MHz rf power, total pressure, and sample temperature were kept at 40 W, 4 Pa, and below 323 K, respectively. The positive ion saturation current was measured to be 1.4 mA/cm² under these conditions.

To examine the effect of VUV photons from argon plasma on damage deep in the bulk, some of the samples were covered with a 1-mm-thick synthetic quartz window with high transparency over a wide wavelength range from 170 nm to 2.6 μm without absorption bands (Shin-Etsu Quartz Products SUPRASIL-P30), as shown in Fig. 1.

![Fig. 1. 200-nm-thick amorphous perfluorocarbon films were exposed to argon plasma. (i) A polymer film was directly exposed to argon plasma. (ii) The quartz window prevented exposure to VUV photons of a wavelength shorter than 170 nm.](image-url)

Figure 2 shows a schematic of the experimental setup used for damage detection in the plasma-treated polymer films. Using an objective-lens-type TIRFM, the rear surface of the polymer film was illuminated with an evanescent light field, which is generated by the total reflection at the polymer/glass interface. The excitation volume was typically restricted within 100-200 nm in the direction perpendicular to the focal plane, and hence, ultrahigh signal-to-noise ratio was realized. The TIRFM system comprised an inverted fluorescence microscope (Olympus IX-71), an objective lens of 1.45 numerical aperture (Olympus UApo 150×OTIRF), a 488 nm laser source (Coherent Sapphire 488 LP-75-P), a 520/35-nm band-pass emission filter (Semrock FF01-520/35-25) and an electron multiplying charge-coupled device (EMCCD) camera (Hamamatsu Photonics C9100-13). In addition, a spectral imaging unit (Applied Spectral Imaging SpectraCube) was used to measure the fluorescence spectra of the samples. In the spectral imaging experiment, a 488 nm notch filter (Semrock NF03-488E-2) was used instead of an emission filter.
Fig. 2. Schematic illustration of UV-induced damage detection using objective-lens-type TIRFM. The rear surface of the polymer film was illuminated with an evanescent light field propagating along the glass/polymer interface. An arrow labeled \( l \) represents the origin and the positive direction for distance from the top surface as mentioned in Fig. 5. Fluorescence signals emitted from damaged molecules were recorded using a highly sensitive EMCCD camera.

3. Results and Discussion

Perfluorocarbon films directly exposed to argon plasma exhibited stronger fluorescence than the nonexposed control, which indicates the generation of optically active damage during the plasma treatment. As shown in Fig. 3, the average fluorescence intensity from the films increased linearly with an increase in plasma exposure time up to approximately 300 s and then showed saturation before decreasing. Similar results were also observed when fluorescence was excited with light of different wavelengths i.e., 532 nm and 635 nm, as reported elsewhere [31]. We found that the linear increase in intensity is observed for a longer exposure time when the energy of excitation light becomes higher. This implies that the saturation phenomenon is not due to the saturation of the number of generated fluorophores, i.e., optically active damage, but is due to concentration quenching effect. From these results, the fluorescence intensity is considered to be proportional to the amount of plasma-induced damage and is expected to give a relative measure of plasma-induced damage as long as concentration quenching does not occur.

Since the penetration depth of low-energy ions or radicals are known to be limited to near-surface layers, deep bulk damages observed in Fig. 3 is attributed to photons from the argon plasma [32]. To confirm the origin of damages, effect of VUV photons from the plasma was investigated by covering the sample surface with a quartz window in the plasma exposure experiment. Figure 4 shows the fluorescence spectra of the amorphous perfluorocarbon films exposed to argon plasma with no cover (i) and with a synthetic quartz window (ii). The fluorescence spectrum of the sample exposed directly to the plasma showed a single broad peak ranging from approximately 500 to 700 nm, while no clear fluorescence peaks were detected from the sample prepared with a synthetic quartz window. Although emission spectrum of low-pressure argon plasma contains many peaks that are dominated by atomic Ar lines in the blue light region (due to 4s-5p transitions) and in the red/near-infrared spectral region (due to 4s-4p transitions) [33,34], few emission lines are emitted in UV and VUV region; resonance lines at 104.8 nm (ArI, \( 1s_0-1s_2 \)) and 106.7 nm (ArI, \( 1s_0-1s_4 \)) [10,11,14,16,34-36]. Photon energies of these VUV emission lines are high enough (11.8 and 11.6 eV) to cause breakage of C-C, C-O and C-F bonds.
bonds in the perfluorocarbon polymer, whose bond energies are 3.60, 3.64 and 4.57 eV, respectively [37].

In most cases, the bond breakage is followed by cross-linking and/or recombination between dangling bonds and radicals [38]. It is difficult to identify the structures of resulting damaged molecules from the fluorescence spectra, but we assume some rigid-structured fluorophores having \( \pi \)-conjugated systems may have formed as often seen in the fluorescent molecules that absorb visible light [39,40]. In addition, the broad fluorescence peak is considered to reflect the broad heterogeneity of their chemical structures and consequent electronic energy states. Furthermore, to check the influence of small contamination of other elements from the apparatus or atmosphere in our experiment, we also conducted control experiments where amorphous perfluorocarbon films were exposed directly to oxygen and nitrogen plasmas generated using the same plasma apparatus. Since we did not observe any fluorescent damages in these experiments, we concluded that the VUV light responsible for the damage production is emitted from Ar and not from contaminant species.

Finally, we attempted the depth profiling of plasma-induced damage using TIRFM. The spatial distribution of UV damage induced during plasma processing is important since it has a large effect on the property degradation and reliability problem in microdevice fabrication. As shown in Fig. 5(a), TIRFM images were systematically obtained from the sample films with different thicknesses. By evaluating the fluorescence intensity of these images, the relative density of UV-induced damage at different distance from the top surface was obtained and is plotted in Fig. 5(b). The damage density exhibits an exponential decrease with the distance \( l \), which is consistent with the expected exponential decay of the penetrating VUV flux.

![Fluorescence spectra](image)

**Fig. 4.** Fluorescence spectra of the perfluorocarbon films with 200 nm thickness exposed to argon plasma. (i) and (ii) correspond to those in Fig. 1. The plasma exposure time was 240 s for both samples.

![Depth profile](image)

**Fig. 5.** (a) Fluorescence images of damaged amorphous perfluorocarbon films with different thicknesses. Images are stacked along the depth from the top surface. Scale bar: 10 \( \mu \)m. (b) Depth profile of plasma-induced damage in perfluorocarbon film. The fluorescence intensity decreased exponentially with increasing depth. The plasma exposure time was set at 240 s, when concentration quenching did not occur in the bulk region deeper than 200 nm. The fluorescence intensity was measured from approximately \( 4.9 \times 10^5 \) pixels in 26-\( \mu \)m diameter area and averaged over the five areas after subtracting the background signal intensity. Error bars represent one standard deviation from the mean of total \( 2.5 \times 10^5 \) pixels. Dotted part of the fitting curve was extrapolated. The power of the 488 nm excitation light was 0.62 mW. The shutter speed and EM gain of the EMCCD camera were 200 ms and 240, respectively.
The decay constant $\alpha$ corresponds to the optical absorption coefficient at the wavelength of which VUV damages the polymer.

Here, we comment on the spatial resolution of the present measurement. In the illumination setup of TIRFM, fluorescence is locally excited near the glass/polymer interface because the evanescent wave decays exponentially in the vertical direction with decay constant $d$ expressed by Eq. (1).

$$d = \frac{\lambda}{4\pi} \left( n_{\text{glass}}^2 \sin^2 \theta_m - n_{\text{cytop}}^2 \right)^{1/2} \quad (1)$$

Here, $n$ is the refractive index of glass or amorphous perfluorocarbon ($n_{\text{glass}}=1.52$, $n_{\text{cytop}}=1.34$) and $\theta_m$ is the incidence angle of excitation light (64-67º). When the wavelength $\lambda$ is 488 nm, $d$ is within 96-146 nm. On the other hand, the spatial resolution in the horizontal direction is 219 nm according to the Rayleigh criterion. Hence, the resolution in both vertical and horizontal directions is approximately 200 nm in this study. Herein the incident angle of excitation light was restricted by the numerical aperture of the objective lens. Shorter penetration length up to 54 nm can be attained if one uses the prism-type TIRFM instead of the objective-lens-type TIRFM as the former allows larger incident angle approaching 90º [21].

4. Conclusion

The optical detection of UV-induced damage deep in the bulk of amorphous perfluorocarbon was studied using TIRFM. After the exposure to low-pressure argon plasma, the fluorescence from the damaged polymer increased linearly with the plasma exposure time until the concentration quenching effect occurred. Using the fluorescence intensity as a measure of the amount of damage, the depth profile of UV-induced damage in the polymer film was obtained. It is a useful approach for studying UV-induced damage during plasma processes. Although low autofluorescence of the material is a necessary condition for the practical use of the present method, it can be applied to various transparent materials in principle, and is a useful approach for studying UV-induced damage during plasma processes. Moreover, it is expected that the knowledge obtained in this study is potentially applicable to the in situ monitoring of VUV emission during plasma processes.
23. R. H. French, R. C. Wheland, W. Qiu, M. F. Lemon, E. Zhang, J. Gordon, V. A. Petrov, V. F. Cherstkov and N. I. Delaygina, *J. Fluor. Chem.* 122 (2003) 63.
24. Asahi Glass Co., Ltd., CYTOPT™ Tech. Data 1 (2007).
25. K. Yamamoto and G. Ogawa, *J. Fluor. Chem.* 126 (2005) 1403.
26. T. Ono, T. Akagi and T. Ichiki, *J. Appl. Phys.* 105 (2009) 013314.
27. T. Ono, T. Akagi and T. Ichiki, *J. Photopolym. Sci. Technol.* 22 (2009) 683.
28. S. H. Kim, S. Iwai, S. Araki, S. Sakakihara, R. Iino and H. Noji, *Lab Chip* 12 (2012) 4986.
29. K. Obata, K. Sugioaka, N. Shimazawa and K. Midorikawa, *Appl. Phys. A* 84 (2006) 251.
30. L.-J. Cheng, M.-T. Kao, E. Meyhöfer and L. J. Guo, *Small* 1 (2005) 409.
31. T. Ono, R. Iizuka, T. Akagi, T. Funatsu and T. Ichiki, *Trans. Mater. Res. Soc. Jpn.* 36(4) (2011) 553.
32. G. S. Oehrlein, *Mater. Sci. Eng.* B4 (1989) 441.
33. F. M. Phelps III, “MIT Wavelength Tables, Vol.2”, The MIT Press, Cambridge (1982).
34. T. Czerwiec and D. B. Graves, *J. Phys. D* 37 (2004) 2827.
35. H. Ren, G. A. Antonelli, Y. Nishi and J. L. Shohet, *J. Appl. Phys.* 108 (2010) 094110.
36. J. W. Carr and M. W. Blades, *Spectrochim. Acta* 39B (1984) 567.
37. D. O’Hagan, *Chem. Soc. Rev.* 37 (2008) 308.
38. E. M. Liston, L. Martinu and M. R. Wertheimer, *J. Adhesion Sci. Technol.* 7 (1993) 1091.
39. A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem. Int. Ed.* 37 (1998) 402.
40. Y. Matsubara, A. Kimura, Y. Yamaguchi and Z. Yoshida, *Org. Lett.* 10 (2008) 5541.