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AFM study of excimer laser ablation of polythiophene films

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Abstract

Atomic force microscopy (AFM) was used to estimate the etching form on excimer laser ablation of polythiophene films. Electrochemically prepared polythiophene films were irradiated with ArF (193 nm) and KrF (248 nm) excimer lasers through a mask attached to the film. Single pulse irradiation of these lasers created a well-defined periodic structure on the irradiated region. The periodic structure was ascribed to Fresnel diffraction of the incident beam with the edge of the mask and was characteristic of non-fusible polythiophene films. The threshold fluences above which the etching occurs were determined to be approximately 30 and 50 mJ cm^{-2} for the 193 nm and 248 nm lasers respectively. The emission spectra from the plume suggested that the degree of fragmentation was higher for 193 nm irradiation than for 248 nm irradiation at the same fluence. © 1997 Elsevier Science S.A.

Keywords: Atomic force microscopy; Excimer laser ablation; Polythiophene films

1. Introduction

Since Srinivasan and Mayne-Banton [1] reported that the pulsed irradiation of intense ultraviolet (UV) lasers could be used to etch polymer films, laser ablation has been applied to various fields as a new method of processing solid materials. From the viewpoint of spatial resolution and depth control, laser processing with UV lasers is superior to that with a Nd:YAG (1.064 μm) or CO_2 (approximately 10 μm) laser, because UV lasers induce etching with minimal thermal damage. Most studies on UV laser ablation have been concentrated on saturated insulating polymers, such as polymethylmethacrylate (PMMA) [2–6], polyethylene terephthalate (PET) [1,4,7–12] and polyimides (PI) [4,6,8,9,11,13–15]. A few reports have been published on the UV laser ablation of conjugated semiconducting polymers [16–18].

Conducting polymers are promising materials for application in microelectronics as semiconductors or metal-like conductors. The patterning of the conducting polymer at dimensions on the micrometre or submicrometre scale is one of the most important subjects in practical applications. Direct photoetching by UV laser ablation can be used for this purpose. This method is a fast, single, totally dry process compared with conventional lithography [19] and, in principle, can be applied to any type of conducting polymer.

Most studies of laser ablation have used scanning electron microscopy (SEM) to estimate the etching profiles [1–3,6–11,15–18]. Atomic force microscopy (AFM) has a spatial resolution higher than SEM and thus is a powerful tool for estimating the change in the surface morphology caused by laser irradiation. Wefers et al. [20] have performed AFM investigations of the surface structures of PET and observed that the surface roughness increases monotonically with the number of pulses, irrespective of the laser fluence. Phillips et al. [21] have reported the AFM images of periodic line structures produced on a PI film by excimer laser ablation using an interferometric technique. Most of these studies have been

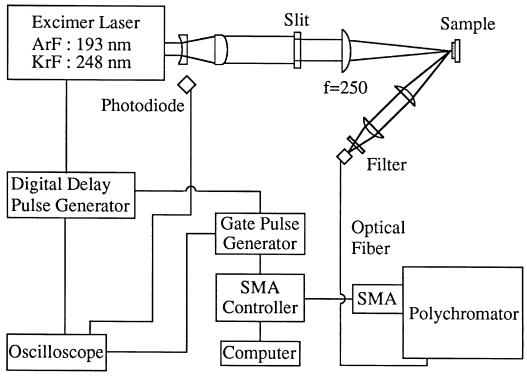

Fig. 1. Schematic diagram of the optical system for measuring the emission spectra of the plume.

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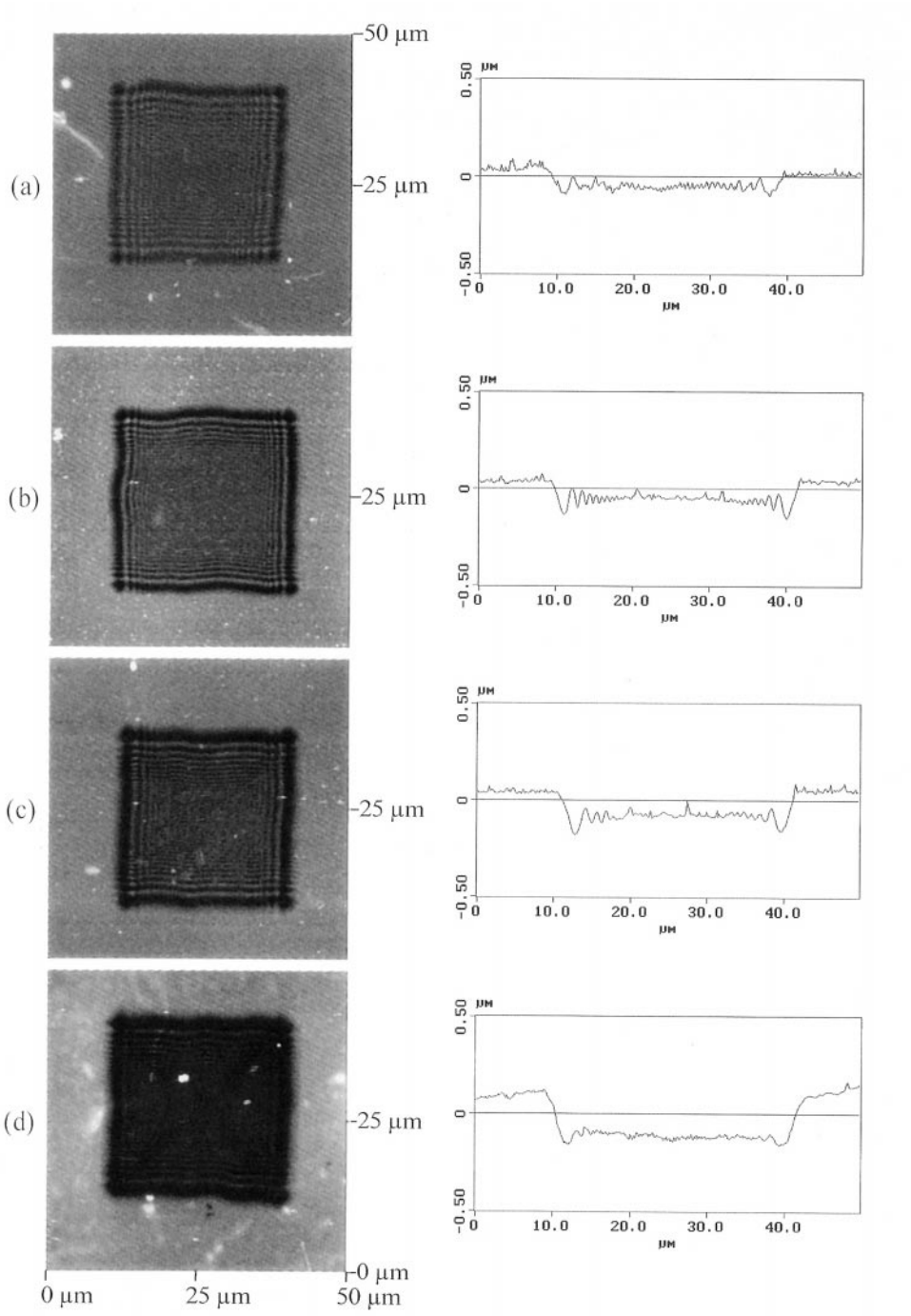

Fig. 2. AFM images and their cross-sectional profiles of PT surfaces for 193 nm irradiation with a single pulse at various fluences: (a) 0.10 J cm^{-2}; (b) 0.20 J cm^{-2}; (c) 0.30 J cm^{-2}; (d) 1.0 J cm^{-2}.

made on a surface irradiated with many laser pulses. Successive irradiation of lasers sometimes causes melting or carbonization of polymers and alters the nature of the surface. Thus in order to gain essential information on the laser ablation of polymers, it is important to probe the change in the surface structures caused by single pulse irradiation with a high resolution using AFM.

In this work, we examined the etching profiles of polythiophene (PT) films irradiated with ArF (193 nm) and KrF (248 nm) excimer lasers using AFM. We also measured the emission spectra from the plume to analyse the decomposed products on ablation.

2. Experimental details

2.1. Film preparation

PT films were prepared on indium-tin-oxide-coated glass plates (ITO electrodes) by constant current electrochemical

polymerization at 5 mA cm^{-2} in nitrobenzene solutions containing thiophene (0.1 mol dm^{-3}) and tetra-*n*-butylammonium perchlorate (0.025 mol dm^{-3}) in N_2 atmosphere at 5 °C. The film thickness was controlled by the time of electrolysis. Films, 0.3 and 0.5 μm thick, were used for the AFM and emission spectroscopic measurements respectively. The films were immersed in distilled water for 24 h and then converted to the undoped state as confirmed by UV–visible absorption spectroscopy. The absorption coefficients at 193 nm and 248 nm were 9.2×10^4 and 4.6×10^4 cm^{-1} respectively. The films were peeled off the ITO electrodes in distilled water and transferred onto quartz plates. The films were then dried at 80 °C for 5 h in vacuum. The surfaces of the PT films were very clean and flat with a roughness within 6 nm as estimated by AFM.

2.2. Laser irradiation

Laser irradiation was carried out using an excimer laser system, LEXTRA50 (Lambda Physik), operated at 193 nm (ArF) and 248 nm (KrF). The pulse durations were 17 and 23 ns (FWHM) for the 193 nm and 248 nm lasers respectively. The laser beam was homogenized with a combination of cylindrical lenses and passed through an aperture to obtain a region of uniform intensity. The output power of the lasers was monitored with a power meter (LPA 100, Lambda Physik). The PT films on the quartz plates were placed perpendicularly to the laser beam and irradiated through a mask placed on the films. The mask used was a nickel mesh with 30 μm × 30 μm square apertures.

2.3. Measurements

AFM images of the irradiated surfaces were observed with a NanoScope III (Digital Instruments). The atomic force microscope was operated in contact mode using cantilevers (NP, Digital Instruments). The emission spectrum of the plume generated by laser irradiation of the PT films was measured using the optical system shown in Fig. 1. The emission from the plume was collected with an optical fibre through a UV cut-off filter (UV-31, Toshiba) over 3 ms at various fluences, without spatial resolution, and was analysed with a spectral multichannel analyser (SMA) (DIDA-512, Princeton Instruments). Because the emission was collected at an angle of 45° to the PT surface, all the emitting species were measured irrespective of the distance from the surface. All the experiments were carried out in air at ambient temperature.

3. Results and discussion

3.1. AFM observations

When a PT film was irradiated with a single pulse of the 193 nm laser at a fluence of 0.10 J cm^{-2}, much debris was observed on the surface. The amount of debris decreased as the fluence increased. At the same fluence, 248 nm irradiation produced more debris than 193 nm irradiation. The fluence and wavelength dependence of the amount of debris can be attributed to the different decomposition processes, as described below. Because this debris prevented the smooth movement of the cantilever, the AFM images of the PT films irradiated at low fluences were noisy. However, the debris could be removed by rinsing the surface with acetone.

Fig. 2(a)–(d) show the AFM images and their cross-sectional profiles of PT films irradiated with the 193 nm laser at various fluences. A well-defined periodic structure was created in the irradiated region. The periodic structure decreases in amplitude and increases in frequency towards the interior. This periodic structure is ascribed to Fresnel diffraction of the laser beam at the edge of the aperture, which was confirmed by comparison with the computer simulation of a three-dimensional Fresnel diffraction pattern calculated by Mathematica (Fig. 3). The diffraction-induced periodic structure (DIPS) was also observed on PT films irradiated with the 248 nm laser (Fig. 4). The minimum top-to-top distances of these periodic structures were 0.4 μm and 0.5 μm for the 193 nm and 248 nm lasers respectively. These values may correspond to the maximum resolution of the micropatterning of PT films by these lasers. The etch depth increased consistently with increasing fluence. When the film was irradiated with the 248 nm laser at a fluence above 1.0 J cm^{-2}, the irradiated region completely penetrated the substrate (Fig. 4(d)).

In order to clarify the effect of the molecular structure on the DIPS, we conducted microphotoetching of PMMA as a saturated polymer using the same laser irradiation system. With 193 nm laser irradiation, the irradiated surfaces of the PMMA films were irregular and the DIPS was not observed except at the fringe of the irradiated region. This result indicates that PMMA is fused by heat via photothermal conversion. On the other hand, the observation of DIPS indicates

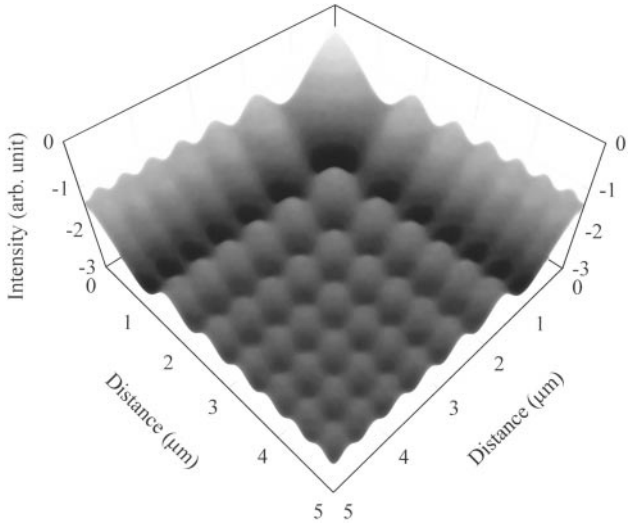

Fig. 3. Three-dimensional Fresnel diffraction pattern of a quarter (5 μm × 5 μm) of the irradiated region including a corner.

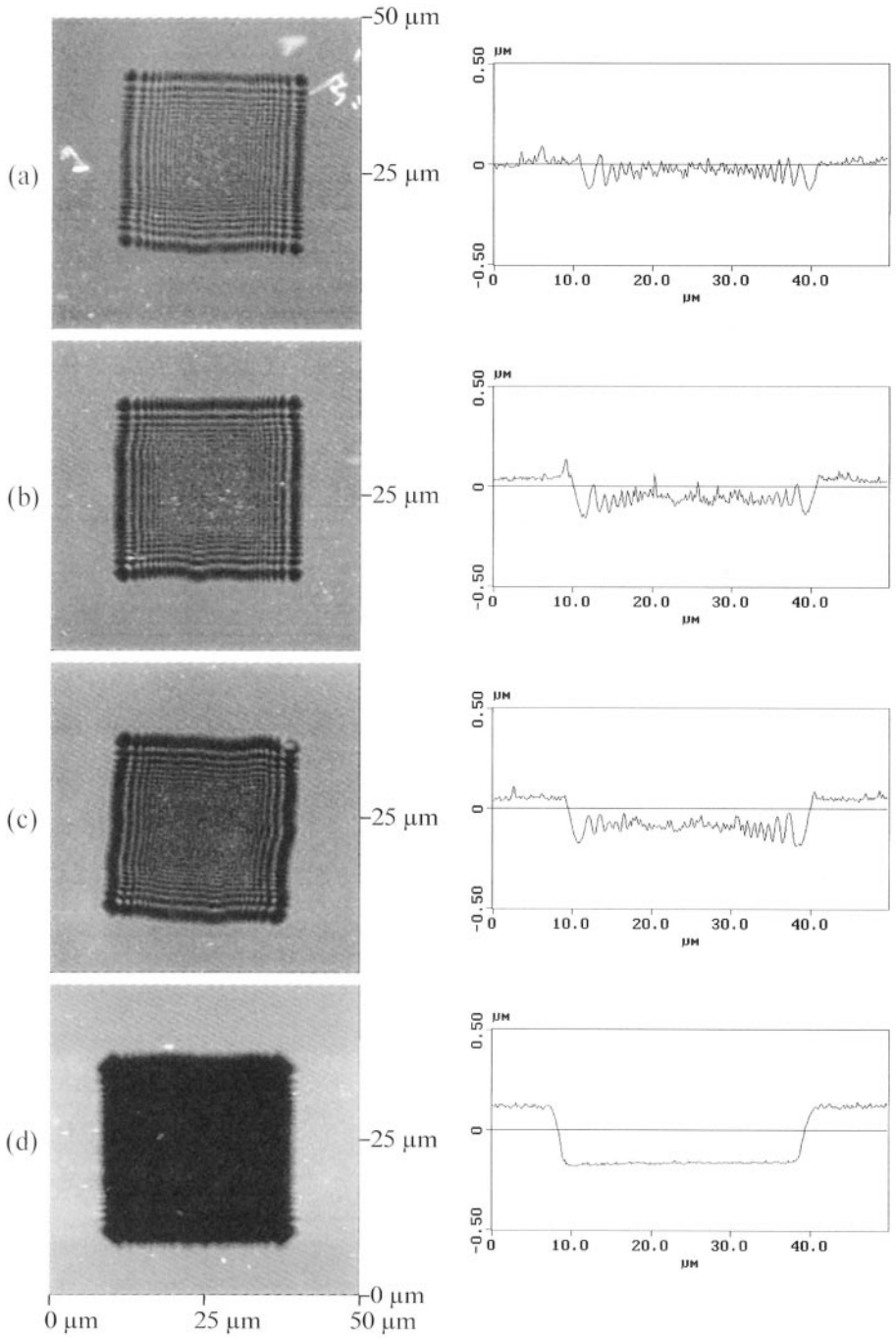

Fig. 4. AFM images and their cross-sectional profiles of PT surfaces for 248 nm irradiation with a single pulse at various fluences: (a) 0.10 J cm^{-2}; (b) 0.20 J cm^{-2}; (c) 0.30 J cm^{-2}; (d) 1.0 J cm^{-2}.

that the PT bonds are decomposed to highly volatile molecular fragments by direct photochemical bond cleavage rather than rapid heating by a photothermal process.

3.2. Etch depth vs. fluence relationship

Fig. 5 shows plots of the etching rate (etch depth per pulse) against the logarithm of the fluence for 193 nm and 248 nm irradiation. The linear relationships are in good agreement with the well-known relationship between the etching rate (d) and the fluence (F) based on Beer's law

$$d = \frac{1}{\alpha_{\text{eff}}} \log\left(\frac{F}{F_{\text{th}}}\right) \quad (1)$$

where α_{eff} is the effective absorption coefficient and F_{th} is the threshold fluence for the etching to occur. By extrapolation to the abscissa, the threshold fluences were estimated to be approximately 30 and 50 mJ cm^{-2} for the 193 nm and 248 nm lasers respectively. From the slopes, the α_{eff} values were found to be 8.5×10^4 and 5.3×10^4 cm^{-1} for the 193 nm and 248 nm lasers respectively. These values were close to the

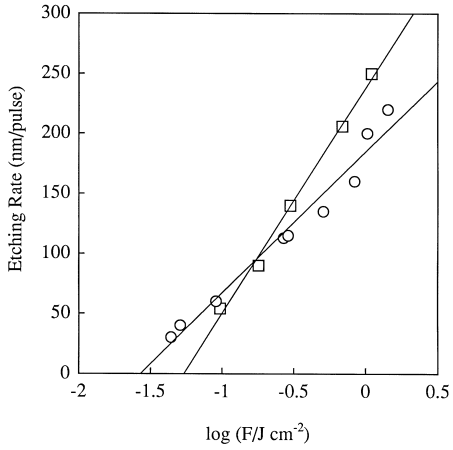

Fig. 5. Plots of the etching rate against the logarithm of the fluence for 193 nm (○) and 248 nm (□) laser irradiation.

absorption coefficients of the PT films at each laser wavelength.

The threshold value for the 193 nm laser was smaller than that for the 248 nm laser because of the difference in their absorption coefficients. The absorbed energies per unit volume $\alpha_{\text{eff}}F_{\text{th}}$ for the 193 nm and 248 nm lasers were 2.3×10^3 and 2.9×10^3 J cm^{-3} respectively. More effective bond scission occurred with the 193 nm laser than with the 248 nm laser. When polymers have a high absorption coefficient at the laser wavelength, they couple efficiently with the incident laser light. Thus effective etching will occur at a small laser fluence. On the other hand, when polymers have a small absorption coefficient at the laser wavelength, they couple less efficiently with the incident light. However, the light penetrates more deeply into the material. This means that the etching rate for 248 nm laser irradiation will rapidly increase against log F compared with that for 193 nm laser irradiation.

3.3. Emission spectra

In order to obtain information on the fluence and wavelength dependence of the decomposed products, the emission from the plume was analysed spectroscopically. Fig. 6(a) shows the emission spectra of the plume from 193 nm laser irradiation at various fluences. At low fluences, such as 0.14 J cm^{-2}, the dominant emission was the fluorescence of PT [22,23]. In the fluence region of 0.62–1.8 J cm^{-2}, several emission bands appeared. These emission bands were assigned to radical species as follows: 388 and 422 nm, CN violet system ($B^2\Sigma-X^2\Sigma$); 437, 474, 517 and 564 nm, C_2 Swan system ($A^3\Pi_g-X'^3\Pi_u$); 588 nm, unknown [24]. The band at 588 nm was assigned to N_2 emission [16,25]. However, this band has also been observed in He atmosphere [26]. The prominence of C_2 at 468 nm was assigned to the high pressure bands of the Swan system [24]. The spectra at fluences above 3.0 J cm^{-2} exhibited a broad band around 420 nm and a narrow band from CN. The broad band was assigned to the bremsstrahlung and/or recombination emissions [27], although the peak wavelength did not shift relative to the

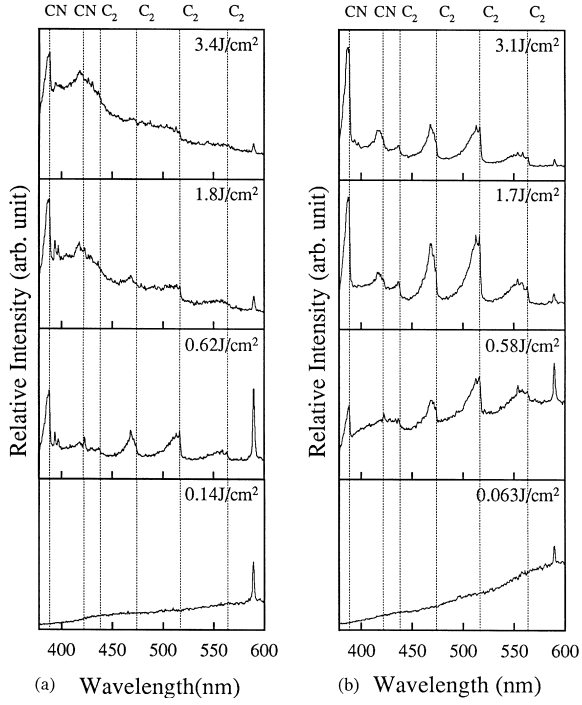

Fig. 6. Fluence dependence of the emission spectra for the ablation of PT films by the 193 nm (a) and 248 nm (b) lasers.

fluence. From the fluence dependence of the emission spectra, it is suggested that the degree of fragmentation increases with increasing fluence. This is supported by the fact that the amount of debris decreases with increasing fluence. In the emission spectra for 248 nm irradiation (Fig. 6(b)), the intensity of the broad band around 420 nm was lower than that for 193 nm irradiation, even at high fluences, suggesting that the degree of fragmentation for 248 nm laser irradiation is lower than that for 193 nm laser irradiation. This also agrees with the greater abundance of debris with 248 nm irradiation than with 193 nm irradiation.

4. Conclusions

AFM is a powerful tool for investigating the excimer laser ablation of PT films. AFM enabled the etching rate on a submicrometre scale to be determined and the threshold fluence for ablation with a single pulse to be estimated. A well-defined DIPS is characteristic of non-fusible PT films. The minimum top-to-top distance on a submicrometre scale shows the potential resolution of the micropatterning of PT films by excimer laser ablation. The threshold fluences were determined to be approximately 30 and 50 mJ cm^{-2} for the 193 and 248 nm lasers respectively, and the etching rate vs. fluence relationship was governed by the absorption coefficient of the film. These are important factors for the practical application of excimer laser ablation to the micropatterning of PT films. The degree of fragmentation is higher for 193 nm irradiation than for 248 nm irradiation as supported by the amount of debris and the emission spectra.

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