

Spectroscopic Studies of ArF Laser Photoablation of PMMA

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Abstract. A spectroscopic study has been made of the emission spectra arising from ArF laser initiated photoablation of PMMA samples. This process leads to direct etching of the polymer. The thermal temperature of the CH fragment species in the plume immediately above the ablated site was found to be $\sim 3200 \pm 200$ K. The translational velocity of this species was found to be $\sim 4.2 \times 10^5$ cm/s corresponding to a translational temperature of $\sim 11,000$ K. These results are consistent with a rapid direct bond scission model for ablation.

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Direct etching of polymeric films following exposure to short (~ 20 ns) pulses of 193 nm ArF laser radiation has recently been reported [1]. Since submicrometer patterns can be replicated with remarkably good definition in photoresist materials using this process [2–4], there is an interest to try and improve the technique to a level at which it might replace the wet chemical development methods currently used in photolithography. It has been suggested that this “ablative photodecomposition” occurs as a result of the efficient rapid rupturing of polymeric bonds following absorption of the 6.4 eV photons [1, 5, 6]. The resultant energetic fragment molecules then rapidly ablate from the irradiated sites. However, very little quantitative data has been published which supports this suggestion. On the other hand, using 4 eV photons from an XeCl laser [7], there is evidence to suggest that for some polymer films, dissociation by thermal degradation is the most likely cause for ablation. We now present results of a spectroscopic study of the emission spectra arising from some of the ablated species which

are present in the plume that occurs above the ablation site during ArF laser irradiation of poly-(methyl methacrylate) (PMMA) samples. The results are consistent with previous suggestions [1, 5, 6] that ablation occurs as a result of direct bond scission by the energetic laser photons.

Both cross-linked PMMA¹ positive resists spun on chromium-on-glass substrates and PMMA in bulk form were used in the present study. Radiation at 193 nm from an excimer laser was focussed to an energy fluence of ~ 300 mJ/cm² in ~ 20 ns pulses onto the PMMA samples. When necessary, samples were placed in an evacuable chamber which could be pumped down to $\sim 10^{-2}$ Torr. For time-integrated low resolution studies of the emission spectra from the plume, a Princeton Applied Research (PAR) Model 1225, 0.2 m polychromator was used in conjunction

¹ The cross-linked PMMA resist was poly-(methyl methacrylate-co-methacrylic acid) and poly-(methyl methacrylate-co-methacryloyl chloride)

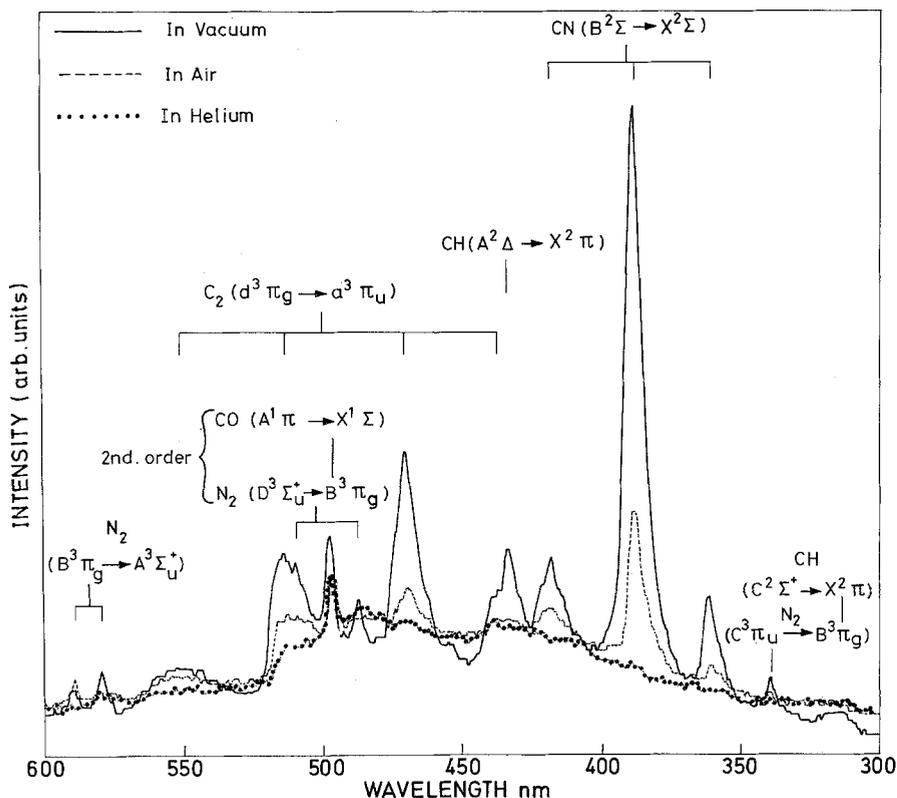


Fig. 1. Survey spectra of the emission between 300–600 nm following irradiation of PMMA resist in air, vacuum, and He (1 atm) environments

with a PAR OMA2 optical multichannel analyser with a Model 1420 diode array detector. In higher-resolution work a Model 1254 vidicon detector was used with a Rank Hilger Monospek 1 m spectrometer. For time and spatially resolved studies of the spectra at various wavelengths, different parts of the plume were sampled by moving the PMMA substrates on micrometer translators relative to the vertical entrance slit of a 0.5 m-Jarrell-Ash spectrometer and an EMI 9783QR (S5 response) photomultiplier combination. In Fig. 1 we show survey spectra of the emission from the plume directly above the ablation site in air, vacuum and He (1 atm) environments. The most prominent bands in the region 300–600 nm are due to transitions arising from diatomic molecules. In particular, the CN B-X transition at 389 nm, C₂ Swan, CH A-X transition at 431 nm, CO Fourth Positive, and N₂ First and Second Positive band systems are the most readily recognisable and are characteristic features of low temperature flames [8, 9].

It can be seen in Fig. 1, that for many bands the emission appears stronger in the nominal vacuum environment than in air. Since the gas collision frequency is lower for the vacuum case we might expect the plume to have a much greater extent than in air at 1 atm pressure. We observed this to be the case. The emission in front of the substrate in the vacuum case was found to extend to completely fill the vacuum

vessel (~25 cm in front of the substrate). Thus the apparent increase in the intensity of the emission for the vacuum environment shown in Fig. 1 is most likely due to an increase in the size of the emission source. Although there should be very few nitrogen atoms in our PMMA substrates, the presence of strong emission on the CN violet transition is probably due to the creation of this species by photochemically induced reactions of the ablated species with the surrounding air—even in the nominal vacuum case, the background concentration of air is sufficient to make these bands appear stronger because in this case the source was so much larger. Further evidence for this explanation of the relative intensities of the bands is also shown in Fig. 1 by observing the spectra obtained in a helium environment. In this case the vacuum cell was filled and evacuated with helium several times and then filled to a pressure of 1 atm with helium so that the background concentration of air should be very small. Although we observed that the visual extent of the plume was roughly the same as that observed in air, as can be seen in Fig. 1, the intensity of all of the bands is greatly reduced. In particular, no evidence of emission from CN could be observed.

To measure the temperature of the plume, immediately above the ablated site, we studied the (0, 0), (1, 1), and (2, 2) bands of the CH(A²Δ → X²Π) transition at 431.4 nm in a vacuum environment using higher

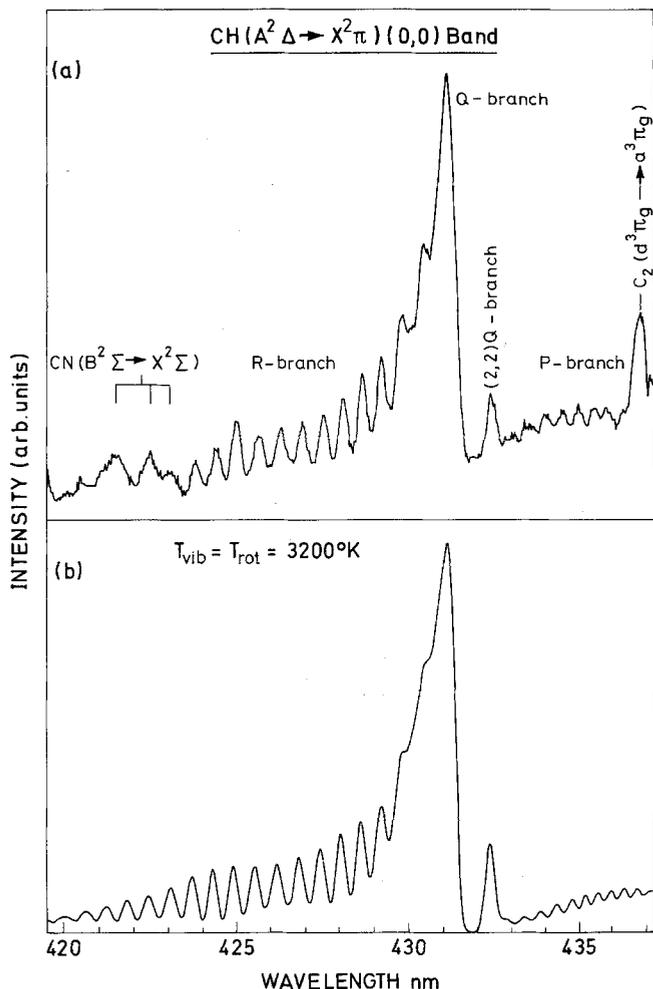


Fig. 2a and b. $\text{CH}(A^2\Delta \rightarrow X^2\Pi)$ band emission at 431 nm. (a) Time integrated spectrum in vacuum environment. Note that bands due to CN and C_2 slightly interfere with the CH band. (b) Computer generated spectra with $T_{\text{vib}} = T_{\text{rot}} = 3200 \pm 200$ K and a resolution of 0.3 nm

resolution, as shown in Fig. 2a. CH was chosen for detailed study since its large rotational constants make its band structure readily rotationally resolvable and its $(A^2\Delta \rightarrow X^2\Pi)$ transition is spectroscopically well characterised. Furthermore, this species is one of the most likely to be produced as a direct product of the photoablation process rather than by any subsequent chemical reaction. Using appropriate line strengths for this transition [10], it is possible to generate a computer fit to the band by adjusting the vibrational and rotational temperatures. The best fit is shown in Fig. 2b and corresponds to vibrational and rotational temperatures being in equilibrium at 3200 ± 200 K. Because of the rapid thermalisation rates between rotational and thermal motion we may then conclude that the thermal temperature above the ablation zone is also 3200 K. From measurements of the etch depth

[3, 6] and the specific heat of PMMA, we calculate that the maximum temperature obtainable when all of the laser energy is absorbed in the ablated region is only ~ 1900 K. It thus appears that the higher temperature which exists in the plume is a result of exothermic photochemical reactions, such as bond scission, produced by the laser photons.

To study the translational motion of some of the species present in the ablation region, we used a 15 cm focal length lens to image (one to one) the horizontal plume onto the vertical entrance slits (width $\sim 10 \mu\text{m}$) of the spectrometer and then translated the substrate. The time resolved emissions from the $\text{CH}(A^2\Delta)$, $\text{C}_2(d^3\Pi_g)$, and $\text{CN}(B^2\Sigma)$ states were studied as a function of distance from the substrate. Oscilloscope traces of the $\text{CH}(A^2\Delta)$ 431 nm emission recorded at increasing distances in front of the substrate are shown in Fig. 3a-d. In Fig. 3 we show measurements taken from these traces of the time to the peak of the CH emission as a function of distance from the substrate. Provided that the quenching rates for CH are insensitive to position, then the slope of this curve provides an estimate of the translational velocity v , with which CH is moving after leaving the irradiated site. At the surface of the PMMA, we find from Fig. 3, that the velocity away from the substrate, $v_0 \approx 4.2 \times 10^5$ cm/s for $\text{CH}(A^2\Delta)$. If the mean speed of the flow $v_0 \approx \sqrt{8RT/\pi M}$ then this speed corresponds to a translational temperature of $\sim 11,000$ K. In supersonic expansions we expect the translational temperature to be higher than the thermal temperature [11] in agreement with our observations. By monitoring the time resolved emissions from the $\text{C}_2(d^3\Pi_g)$ and $\text{CN}(B^2\Sigma)$ states, in a similar manner we have measured initial translational velocities for these fragments of $\sim 2.0 \times 10^5$ cm/s and 5.1×10^5 cm/s, respectively.

The relatively high thermal and translational temperatures measured in this experiment show that exothermic direct bond scission reactions by the 193 nm photons are responsible for the dynamics of the small fragments which occur in the plume above the ablation site. However, from other work [12], we know that the laser photon/monomer ratio which is necessary to ablate a $\sim 1 \mu\text{m}$ layer of PMMA at 193 nm is only ~ 0.1 . This implies that initially in the ablation zone relatively large molecules in their monomeric or polymeric form are produced. These molecules do not appear to contribute to the emission spectra observed in Fig. 1. It is possible that the photodissociation processes responsible for creating the emission in the plume are separate and subsequent to the breaking of the polymeric bonds which cause ablation, although it is much more likely that direct bond scission by the uv photons is also responsible for the breaking of the

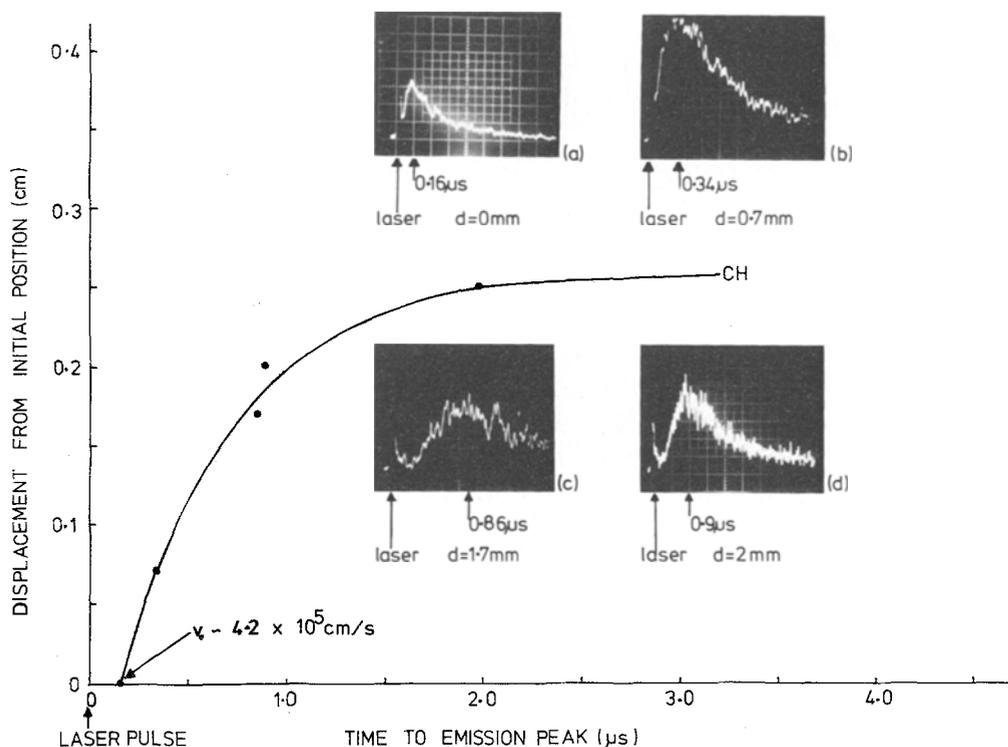


Fig. 3a-d. Displacement from the PMMA substrate vs the time delay between the laser pulse and the peak in the emission from the $\text{CH}(A^2\Delta \rightarrow X^2\Pi)$ band at 431 nm. Spectra recorded in an air environment. Oscilloscope traces of the $\text{CH}(A^2\Delta)$ 431 nm emission as a function of position in front of the substrate are shown in (a)-(d). The horizontal scales were $0.2 \mu\text{s}/\text{div}$ for (a)-(c), and $0.5 \mu\text{s}/\text{div}$ for (d)

relatively weak polymeric bonds. The rapid rupturing of these bonds causes a rapid increase in pressure at the ablation site which then leads to the highly energetic fragments which we observe in the plume.

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