

# WAVELENGTH-DEPENDENT VACUUM-ULTRAVIOLET PHOTOCHEMICAL EFFECTS AT POLYMER SURFACES

F. Truica-Marasescu and M. R. Wertheimer

Département de Génie Physique et Génie des Matériaux, École Polytechnique, Montréal, Quebec, Canada

## Abstract

The overall aim of our research is to investigate the possible vacuum ultraviolet (VUV) photochemical contribution to various low-pressure plasma processes. Here, we report preliminary results on  $\lambda$ -dependence of the etch rate,  $R$  (in  $\text{ng/min-cm}^2$ ), of poly(methyl-methacrylate) PMMA. Other experiments reported include all-dry patterning of the polymer by VUV etching through metallic masks.

## 1. Introduction

Plasmas are now used extensively for the treatment of polymer surfaces, in modification, etching and deposition operations [1]. Since plasmas comprise a wide variety of energetic particles, both charged (electrons, ions) and neutral (excited molecules, radicals, metastables), and photons, it is *a priori* impossible to identify the main species responsible for a particular change at a polymer surface. Since the pioneering work of Hudis [2], it is known that vacuum ultraviolet (VUV) photons can give rise to an important photochemical contribution during such treatments. This has been amply confirmed, for example, in recent work of Fozza [3], who used a microwave plasma in  $\text{H}_2$  as a broadband ( $\sim 110 \leq \lambda \leq 170 \text{ nm}$ ) VUV light source. Such research has not only a pure scientific interest, but is also motivated by applications in deep-UV lithography and space technologies, for example.

## 2. Technical Details

Extending the work of Fozza [3], we have built an apparatus, shown schematically in Fig. 1, to further investigate VUV irradiation effects on selected polymers, but in which the VUV wavelength,  $\lambda$ , can be judiciously selected among four different commercial VUV sources (r.f. plasma lamps, Resonance Ltd.). These, and their main characteristics are shown summarized in Table I.

In-situ mass change measurements are carried out, as in Fozza's case [3], by using a quartz crystal microbalance (QCM, Phelps Electronics Inc.) with a very thin coating ( $\sim 1 \mu\text{m}$ ) of PMMA (supplied by Polyscience Inc.), uniformly deposited from solution on the active surface of the QCM. The QCM head's center was located at a frontal distance of 15 cm from the  $\text{MgF}_2$  window of the VUV lamp; in the case of photo-etching experiments, the lamp was separated from the sample chamber by a cell with an additional  $\text{MgF}_2$  window, purged by a dry nitrogen flow. During measurements, the QCM's head was cooled with a flow of water at constant temperature ( $25 \pm 1^\circ\text{C}$ ). The experiments were carried out in vacuum ( $< 10^{-5}$  torr), typical duration of treatments being 60min.

Table 1: The VUV lamps used, and their characteristics

Lamp	Wavelength (nm)	Power density* ( $\mu\text{W}/\text{cm}^2$ )	Photon flux ( $\times 10^{12}$ ) ( $\text{ph}/\text{cm}^2/\text{s}$ )
Kr line	123.6	79	50
Xe line	147	279	209
Xe excimer	158-190, 172	61	52
D <sub>2</sub> Ar continuum	110-170	227	205

\* at a frontal distance of 15 cm

For dry-patterning experiments, thin PMMA films ( $\sim 1 \mu\text{m}$ ) were deposited on silicon wafers using spin coating, after which all the samples were baked for 6 h at  $60^\circ\text{C}$  under vacuum. The samples were exposed under vacuum for 120 min, at a frontal distance of 6 cm to the radiation from the Xe line lamp (147 nm,  $1.5 \text{ mW}/\text{cm}^2$ ). A 50-mesh/inch Ni microscope grid with  $445 \mu\text{m}$  square openings was placed in intimate contact with the sample surface. After VUV exposures, the samples were kept under vacuum for another hour, then examined by scanning electron microscopy (SEM, Philips XL 20).

### 3. Results and Discussion

From spectroscopic measurements, performed using a NIST-calibrated VUV/visible spectrophotometer (Acton Research Corp. VM 502, nominal resolution 0.4 nm), the power density and spectral distributions of our light sources have been established with care. These results, corrected for sample position, are presented in Fig. 2.

PMMA, well known as a photo-degradable polymer, has long been used for UV lithography [3, 4]. Its absorption spectrum is shown in Fig.3 [5]. Previous experiments have clearly shown that the photo-etching mechanism of PMMA strongly depends on the wavelength,  $\lambda$ , of the incident radiation. Absorption of photons with  $\lambda < 160 \text{ nm}$  leads to the scission of the main chain via C-C, C-H bond breakage, while longer-wavelength  $\lambda$  can produce Norrish type I reactions followed by the scission of the main chain, or photolysis of side groups with hetero-atoms [6, 7].

Figure 4 shows the PMMA mass loss as a function of time, when exposed to VUV radiation from each of the four lamps. The etch rate,  $R$ , is defined as follows:

$$R = \frac{\Delta M_{\text{tot}}}{tS}, \quad (1)$$

where  $\Delta M_{\text{tot}}$  is the total mass loss during the exposure,  $t$  is the duration of exposure, and  $S$  is the film area. Measured  $R$  values for each of the lamps we used are presented in Table 2. When discussing the QCM results, one must of course take into account the absorption coefficient of PMMA (Fig. 3) which presents three distinct regions:  $115 < \lambda < 125 \text{ nm}$ , which displays the highest absorption, compared with the spectral regions  $125 < \lambda < 170 \text{ nm}$  and  $170 < \lambda < 300 \text{ nm}$ . [3, 6, 8]. Because of these stronger absorptions of PMMA at 123.6 nm and at 147 nm, a high etch rate is expected for the Xe and Kr line lamps. Since the power density also plays an important role in the photo-etch process, a higher  $R$  is expected from the Xe

lamp. Indeed, PMMA exhibits a very similar optical density for those two wavelengths, but the power density of the Xe line lamp is almost 3.5 times greater than that of its Kr counterpart (see Table 1). It is therefore not surprising that  $R(\text{Xe}) > R(\text{Kr})$ . Now, the Xe excimer lamp presents a broad spectrum centred at 172 nm, where PMMA's absorption is less (Fig. 3). This, combined with the lower power density of this excimer lamp, leads to the observed lower  $R$  values.

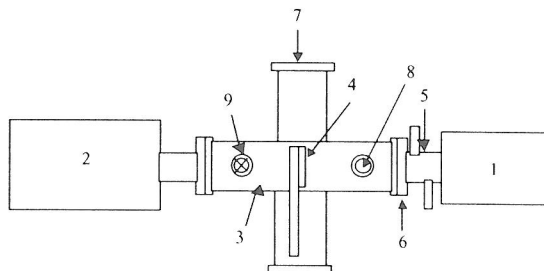


Fig.1 Experimental setup: 1 - VUV lamp, 2 -VUV monochromator (or detector), 3 - stainless steel vacuum chamber, 4 - sample holder (or QCM) with sample, 5- flowing  $\text{N}_2$  purge cell, 6 -  $\text{MgF}_2$  window, 7 - turbomolecular pump, 8 - pressure gauge, 9 - gas inlet

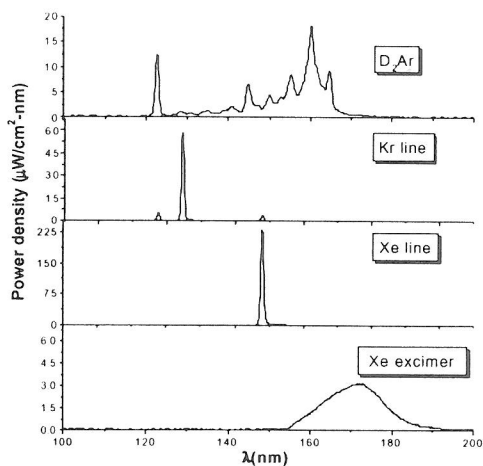


Fig.2 Power density and spectral distribution of the radiation from the four VUV sources, measured at the sample position

The etch results with the D<sub>2</sub>Ar lamp are at first quite unexpected and difficult to explain. This powerful lamp has a VUV spectral distribution very similar to that of a hydrogen plasma, exhibiting the molecular Lyman and Werner bands, and the first line of the atomic Lyman series [3].

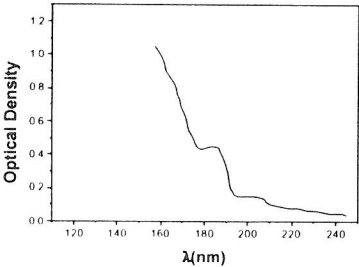


Fig. 3 Absorption coefficient of PMMA

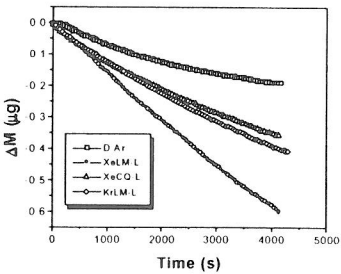


Fig. 4 QCM response for different lamps

Table 2 PMMA etch rate for the different lamps

Lamp	R (ng/min-cm <sup>2</sup> )
D <sub>2</sub> Ar	0.054
Xe excimer	0.104
Kr Line	0.115
Xe Line	0.177

Since the PMMA absorbs differently throughout this spectral region, one may expect photons with  $\lambda > 160$  nm (which represent almost 40 % of the total radiation intensity) to penetrate more deeply into the sample. This gives rise to radical formation well beneath the surface, which have a low probability of diffusing to the surface because of the limited free volume and chain mobility (PMMA is glassy at room temperature). Due to their high chemical reactivity, the free radicals will recombine with each other to form a crosslinked sublayer. The R value of this crosslinked material decreases and eventually becomes very small. Another interesting observation in Fig. 4 is that the etching curves present a non-linear time-evolution, which is more obvious for the case of broad-band spectral lamps (D<sub>2</sub>Ar, Xe excimer). The time-resolved mass loss for each lamp can be fitted with an exponential function:

$$M(t) = M_{res} + A \exp(-kt), \tag{2}$$

where M<sub>res</sub> corresponds to the limit of the etching process, and A and k are constants which depend on  $\lambda$ , radiation intensity, and type of polymer. Assuming a simple exponential absorption in PMMA, the *density of energy*, D absorbed at depth z below the sample surface for a particular  $\lambda$  is given by:[8-9]

$$D(z,t) = \alpha I \exp(-\alpha z), \tag{3}$$

where  $\alpha(\lambda)$  is the absorption coefficient of PMMA for that  $\lambda$ , and  $I$  is the incident *energy flux*. We may assume next that the etch rate,  $R$ , is proportional to the power deposited per unit volume [9]:

$$R \equiv \frac{dM}{dt} = [\Phi D(z, t)]^n, \quad (4)$$

where  $n$  is a constant, and  $\Phi$ , the bond breaking efficiency, is a function of  $\lambda$ . Substituting for  $D(z, t)$ , we find:

$$R = (\alpha I \Phi)^n \exp(-n\alpha z(t)) \quad (5)$$

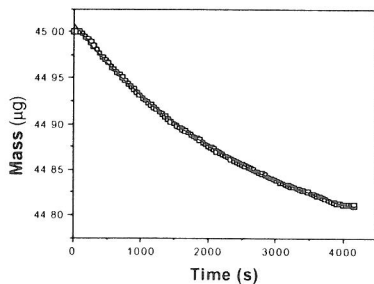


Fig. 5 Mass loss *versus* irradiation time for the D<sub>2</sub>Ar lamp; the continuous line is a fit of the exponential function, eq. (5)

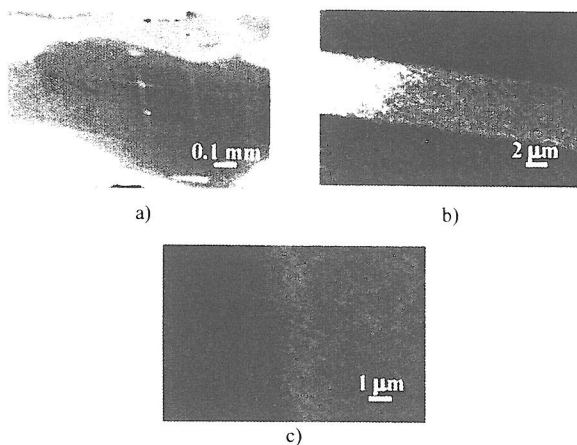


Fig. 6 SEM Images (various magnifications) of PMMA on Si after irradiation through a metallic mask (electron microscope grid)

This simple model takes into account only bond breakage by monochromatic radiation ( $\lambda$ ), and it neglects other processes like crosslinking, diffusion of free radicals, and others. Nevertheless, this so-called “attenuated light model” allows us to explain exponential evolutions of the mass losses observed in Fig. 4. In Fig. 5, we show a fit of eq. (5) for the particular case of the topmost curve in Fig. 4, corresponding to PMMA irradiation with the D<sub>2</sub>Ar lamp; very good agreement is noted, in spite of the simplifying assumptions leading to eq. (5).

Figure 6 shows SEM images of etched patterns on a PMMA surface (see section 2), where portions masked by the metal grid can be clearly discerned. Figure 6 c) suggests even further smoothing of the exposed surface after the VUV treatment, an observation made also by Fozza [3] following VUV exposure of polyethylene.

#### 4. Conclusions

In these preliminary results, we have demonstrated VUV wavelength-dependent dry etching and surface modification of PMMA, using incoherent radiation. The surface etch rate,  $R$ , depends on  $\lambda$  through the polymer's absorption coefficient,  $\alpha(\lambda)$ . Smoothing of the polymer surface is also observed after the VUV treatments. These interesting characteristics may be useful in a variety of technical applications, for example, microfabrication.

#### 5. Acknowledgements

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#### 6. Reference

- [1]:M. R. Wertheimer, L. Martinu, J. E. Klemberg-Sapieha, G. Czeremuszkin, in K.L. Mittal and A. Pizzi (Eds): “Adhesion Promotion Techniques”, Marcel Dekker Inc., New York (1999), p 139
- [2]:M. Hudis, J. Appl. Polym. Sci. 16, 2397 (1972)
- [3]:A.C. Fozza, J.E. Klemberg-Sapieha, M.R. Wertheimer, Plasmas and Polymers 4, 183, (1999)
- [4]:Y. Mimura, T. Ohkubo, T. Takeuchi, K. Sekikawa, Japan. J. Appl. Phys. 29, 2572 (1990)
- [5]: S. Onari, J. Phys.Soc. Jap. 26/2, 500, (1969)
- [6]:J. F. Rabek, “Photodegradation of Polymers. Physical Characteristics and Applications“, Springer-Verlag, Berlin (1996)
- [7]:V. E. Skurat, Y. I. Dorofeev, Angew. Makromol. Chem. 216, 205, (1994)
- [8]:V. N. Vasilets, L. A. Tikhomirov, A. N. Ponomarev, Khimiya Vysokikh Energii, 15/2, 147, (1981)
- [9]:I. E. Ferincz, Cs. Toth, J. F. Young, J. Vac. Sci. Technol. B 15/4, 828, (1997)