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UV-Excimer-Laser Ablation of Polymethylmethacrylate at 248 nm: Characterization of Incubation Sites with Fourier Transform IR- and UV-Spectroscopy

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Abstract. Ultraviolet and Fourier transform infrared (FTIR) spectroscopic experiments with thin films of polymethylmethacrylate (PMMA) are reported. During the incubation with 248 nm excimer laser light or continuous (cw) UV light sources PMMA exhibits a rapidly increasing, broad UV absorption. This is caused by the production of unsaturated species, which are detected in the infrared spectrum of irradiated PMMA films. The spectral data explain the incubation process preceding the ablation of PMMA at 248 nm. Taking advantage of the increased UV absorption, cw light incubated PMMA films can be selectively ablated by standard 308 nm excimer laser pulses.

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Surfaces can be structured by ablation with intense UV laser light [1, 2]. A wide variety of polymers with different penetration depths for UV laser light show for certain fluence ranges high removal rates of material on the order of micrometers per pulse, along with little thermal damage to the edges. Thus the surfaces of many polymers have been patterned with a resolution down to less than one micrometer [3]. While this technique is already applied in industry and surgery, many effects of photoablation still have to be explained and a detailed understanding of the ablation process remains a challenge.

In a wide fluence range polymethylmethacrylate (PMMA) does not start ablation with the first laser pulse, but requires a number of incubation pulses [4, 5] before a steady ablation regime is reached. During these incubation pulses the material is believed to suffer damage in its chemical structure. The etch curve of PMMA (cf. Fig. 2 of [4]) with 248 nm excimer laser pulses shows for higher fluences a leveling off and reaches a saturation plateau, where a further increase in fluence does not yield a significantly higher etch rate. This effect had been attributed to a shielding of the PMMA surface by the ablation plume [5, 6]. Our model calculations [4] showed, however, that this alone could not fully explain the effect. Assuming a dynamic absorption coefficient, depending on the irradiation dosis and the intensity of the laser light, the etch rate and the number of incubation pulses could be predicted quantitatively for the ablation of PMMA with excimer laser pulses of 16 ns duration at 248 nm. This paper will discuss the origin of the increase in absorption due to the irradiation dosis.

Infrared and UV spectra provide valuable information about the excimer laser induced photochemistry of PMMA. In earlier studies [7–11] other researchers have observed an increasing UV absorption upon irradiation of PMMA with a 253.7 nm mercury lamp or 266 nm laser radiation. The increasing UV absorption was attributed mainly to the formation of carbonyl or unsaturated species [10], which, however, were *not* detected in the infrared spectrum.

In the following we shall describe ultraviolet- and infrared-spectroscopic experiments with PMMA, irradiated with light from a 248 nm (16 ns) excimer laser and various continuous light sources. The light intensities range from $\ll 1\ \mathrm{W/cm^2}$ up to about $50\ \mathrm{MW/cm^2}$, which is sufficient to cause ablation. The

results show the origin of the dynamic absorption coefficient of PMMA and can explain the incubation process and the saturation behaviour of the etch rate for high fluence ablation. We shall also describe the ablation of undoped PMMA with 308 nm excimer laser light, taking advantage of the increased UV absorption of incubated PMMA.

1. Experimental

Materials

The experiments were performed with samples, spin coated with commercial PMMA (extra purity kind, Röhm GS 214, density = 1.18 g/cm^3, $\alpha_{248} = 102$ cm^{-1}) from a solution in trichloroethylene. Prior to experiments, the samples were baked at 80°C in vacuo for 48 h to remove solvent traces trapped in the films. Complete evaporation of the solvent was checked in the infrared spectrum. Infrared spectra were obtained from 1.3 μm thin films on aluminum mirrors, ultra violet spectra were recorded from 40 μm thick films on calcium fluoride windows. Ablation at 308 nm was performed on 1.5 μm thin PMMA films on silicon wafers.

Light Sources

The source of 248 nm laser radiation was a Lambda Physik EMG 200 excimer laser, equipped with unstable resonator optics, with the appropriate filling of krypton, fluorine and helium for 248 nm, delivering pulses of 16 ns duration (full width at half maximum; FWHM). 308 nm laser radiation with a pulse width of 17 ns FWHM was taken from a Lambda Physik EMG 103 MSC excimer laser, filled with xenon, hydrogen chloride and neon. To avoid possible effects arising from heating of the sample, the repetition rate was kept below 6 Hz. For both laser sources, the pulse energy was measured with a Laser Precision Corp. energy meter Rj-7200. Energy measurements were averaged over 10 pulses. For all experiments, fluence measurements are within an uncertainty of $\pm 10\%$. Continuous UV light sources were a Fusion Systems F 440 UV lamp, delivering 6 W/cm^2 in the spectral range from 200 to 400 nm, and a Hanau Fluotest chromatography lamp with an output power of $\ll 1$ W/cm^2 at 254 nm.

Procedure

UV-spectra were recorded on a Shimadzu UV-160 UV-Visible Recording Spectrometer. External reflection infrared spectra were obtained on a Nicolet Fourier Transform Infrared Spectrometer, equipped with an external reflection accessory. The infrared beam was incident on the sample mirrors with an angle of 40° to normal incidence. Infrared spectra were recorded in a dry nitrogen atmosphere with a resolution of 4 cm^{-1} and a recording time of 30 scans. For infrared measurements, the excimer laser beam was coupled into the sample compartment of the spectrometer through a quartz window, and samples were irradiated in situ without any movement or exposure to air between irradiation and spectral recordings. The excimer laser beam was expanded by a cylindrical lens and directed at the sample at normal incidence. The fluence was calculated from a measurement of the pulse energy and the beam area on the sample. Typically, an infrared spectrum was recorded every 100 excimer laser pulses. For the UV spectra, samples were handled in air atmosphere, and in turns irradiated and placed in the spectrometer for spectral recording.

Ablation at 308 nm was done in air atmosphere with the set up described in detail [4]. Before ablation, the sample was placed under a contact mask with 200 μm holes and irradiated for 40 s with the fusion systems UV lamp. For the following ablation the contact mask was removed and the sample was scanned in front of the laser beam on an encoder mike controlled translation table. The laser was operated at 5 Hz, and the scanning speed was adjusted, such that every place on the sample received a dose of 20 pulses at 1.2 J/cm^2.

2. Results

The insert of Fig. 1 shows the UV transmission spectra of a 40 μm thick PMMA film after irradiation with varying numbers of excimer laser pulses at 248 nm and a fluence of 40 mJ/cm^2. The sample shows the rise of a broad UV absorption up to wavelengths in the visible region. In Fig. 1 the transmission of the same sample at 248 nm is plotted versus the number of pulses. An exponential like decrease of transmission is observed. After 1000 pulses the sample did not show any macroscopic damage, which might cause scattering, so the decrease in UV transmission has to be attributed to increased *absorption* due to changes in the chemical constitution of the material.

These changes in the chemical structure of PMMA can be observed in the infrared spectrum. In comparison to transmission spectra of PMMA films on KBr or CaF_2 windows, wavenumber shifts of the peak maxima, due to the technique of external reflection [12] were, over the whole infrared spectral range, less than 5 cm^{-1}, and proved to be of minor importance for this work.

Figure 2 shows the FT IR difference spectrum between a 1.3 μm thin PMMA film on an aluminum mirror after 600 pulses of 35 mJ/cm^2 and the same sample before irradiation. The strongest difference in

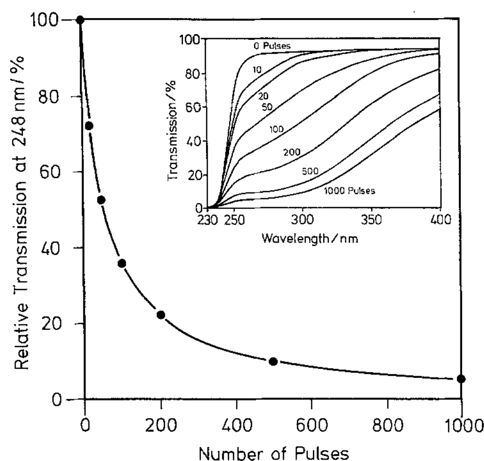

Fig. 1. Transmission of a 40 μm thick PMMA film at 248 nm as a function of excimer laser irradiation dose at 248 nm with a fluence of 40 mJ/cm^2. After 1000 pulses, the transmission has dropped to less than 6% of its initial value. Insert: The UV spectrum of the same sample exhibits a broad absorption for wavelengths up to the visible

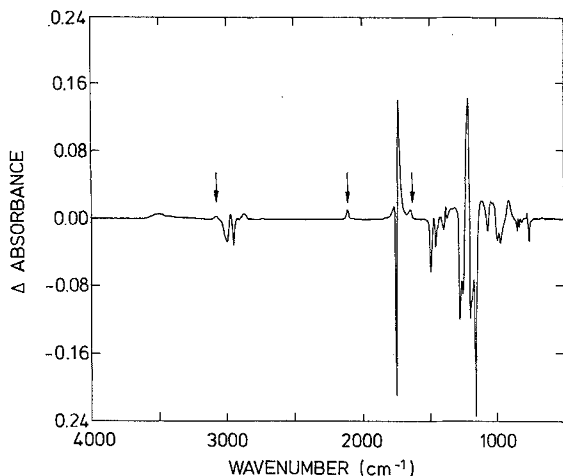

Fig. 2. FT IR difference spectrum between a 1.3 μm thin PMMA film on an aluminum mirror after exposure to 600 excimer laser pulses of 35 mJ/cm^2 at 248 nm and the same sample before irradiation. Unsaturated species, which absorb at longer UV wavelengths than PMMA itself, can be identified by their bands at 3078, 2104, and 1643 cm^{-1} (see arrows), and a shift in the wavenumber of the characteristic ester absorptions is observed

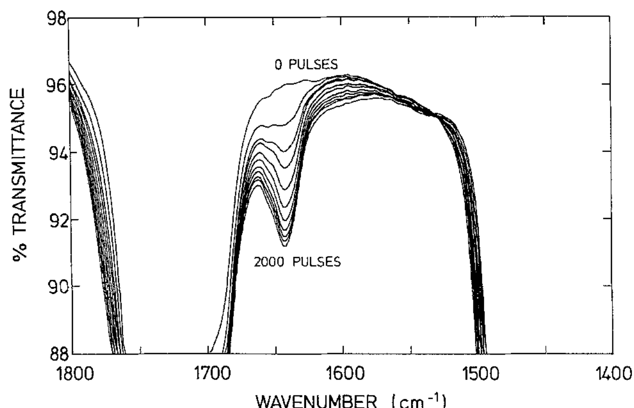

Fig. 3. FT IR spectrum of PMMA in the 1600 cm^{-1} region as a function of the number of excimer laser pulses at 248 nm. Up to 2000 pulses, a peak, typical for C=C double bonds, grows in and reaches a photostationary equilibrium for higher pulse numbers

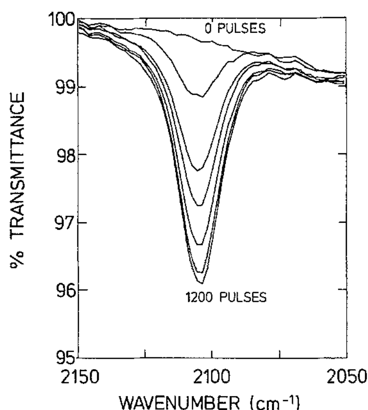

Fig. 4. FT IR spectrum of PMMA in the wavenumber region typical for the absorption of cumulated double bonds or triple bonds. A peak at 2104 cm^{-1} grows in, which is most likely due to the formation of carbon monoxide, which is trapped in the PMMA film

the spectra is observed for the absorption bands of the ester carboxyl group. At 1740 cm^{-1} (C=O stretch) and 1149 cm^{-1} (C–O stretch) a decrease in absorption is observed, while at 1732 cm^{-1} and 1212 cm^{-1} peaks grow in. These absorptions are still typical for an ester functional group, which however is situated in a different chemical environment. The most interesting changes in the spectra are the bands, which grow in at 3078 cm^{-1}, 2104 cm^{-1}, and 1643 cm^{-1} (see arrows, Fig. 2). Infrared absorptions at 1643 cm^{-1} (C=C stretch) *and* 3078 cm^{-1} (C=C–H stretch) are typical for unsaturated aliphatic compounds. For symmetry reasons the transition moment of these groups can be small and therefore cause weak absorption (like in the spectrum of methylmethacrylate, the monomer of PMMA), still their absorption bands are clearly observed in the IR-spectra of PMMA, irradiated at 248 nm. Figure 3 shows the infrared spectrum in the 1600 cm^{-1} region as a function of the irradiation dosis. Up to 2000 pulses, the 1643 cm^{-1} peak grows in and reaches an equilibrium for higher numbers of pulses. The effect is identical for the 3078 cm^{-1} band, however the signals are small, which is due to the weak absorption of the C=C–H group. Figure 4 shows the infrared absorption in the 2100 cm^{-1} area, which corresponds to cumulated double bonds or triple bonds. Again, the formation of a new absorption band at 2104 cm^{-1} is observed, which reaches a stationary intensity after 1200 pulses. Finally, an additional broad absorption at 3500 cm^{-1} can be seen, which correlates

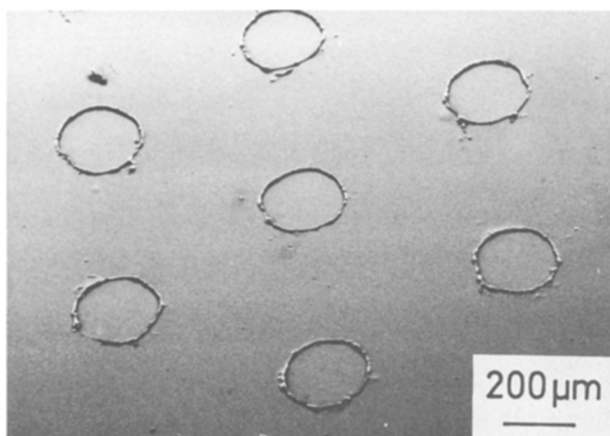

Fig. 5. Scanning electron micrograph of a silicon wafer, spin coated with 1.5 µm of PMMA, after incubation with continuous UV light under a contact mask with 200 µm holes, followed by ablation with 308 nm excimer laser pulses of 17 ns duration. The incubated circles are etched away selectively, while the non-incubated material remains unaffected, although the laser fluence was homogeneous over the *whole* sample

to an O–H stretch. Due to the overall degradation and possible loss of material, most signals of PMMA suffer a loss in intensity. Minor changes in the fingerprint region cannot be interpreted unambiguously.

The spectral changes in PMMA after exposure to UV light are virtually independent of the intensity of the incident light. All spectra in this paper are from PMMA samples irradiated with 248 nm excimer laser light in the fluence range from 35 to 40 mJ/cm^2. However, qualitatively the same spectral changes were induced by exposure of PMMA to 248 nm radiation of higher fluences. Furthermore, PMMA, exposed for 5 s to the continuous light of a Fusion Systems UV lamp (200–400 nm), or for 26 h to the light from a chromatography lamp (254 nm), also exhibits virtually the same characteristic changes in its spectra.

As a consequence of the increased absorption over the whole UV range, it becomes possible to ablate PMMA with standard 308 nm excimer laser pulses. Figure 5 shows a silicon wafer, spin coated with 1.5 µm PMMA, after 40 s exposure under a contact mask to the light of a fusion systems UV lamp, followed by ablation with 20 pulses of 1.2 J/cm^2 at 308 nm. The circles, which had been exposed to the UV lamp, are etched away selectively, while the area, previously covered by the mask, remains unaffected by the excimer laser light, even though the laser fluence was homogeneous over the whole sample.

3. Discussion

The UV spectrum of irradiated PMMA shows a steep increase in absorption over a wide range of wavelengths, up to the visible. After 1000 pulses, the transmission at 248 nm has dropped to less than 6% of its initial value, a fact, which indicates significant changes in the chemical constitution of the material. Due to the broadness of the UV absorption however, an assignment to a specific transition is not possible.

More detailed information about the chemical changes can be obtained from the infrared spectra. The most important effect is the formation of unsaturated species, which can be clearly identified by their absorption at 3078 cm^{-1} and 1643 cm^{-1}. They also reveal their presence by a strong fluorescence [13] of PMMA under excimer laser irradiation, which arises with a growing number of pulses. Unsaturated compounds are known to absorb at longer UV wavelengths than their saturated derivatives. Furthermore, a growing absorption band at 2104 cm^{-1} indicates the presence of triple or cumulated double bonds, of which the latter are known [14] to absorb at longer UV wavelengths than unirradiated PMMA. The band at 2104 cm^{-1} cannot be assigned unambiguously from the IR-spectrum alone. Most likely, carbon monoxide is formed, but also ketene has been postulated as a photoproduct of PMMA before [11].

The shift in the wavenumber of *both* ester absorption bands is in contrast to the observations of earlier workers [11] who reported a carbonyl shift and only a *decrease* of the C–O stretch upon irradiation of PMMA with 266 nm laser light. Clearly, in our experiments a different type of ester is formed in the photolysis of PMMA, although it would be speculative to assign a structure from these UV and infrared spectra alone.

The main gaseous product in the ablation of PMMA with 248 nm radiation is methyl formate, which can be unambiguously identified by its infrared spectrum, and has also been observed by others in the mass spectrum of the ablation products [15]. Methyl formate is also produced upon irradiation of PMMA at fluences below the ablation threshold. Therefore, it is likely, that the new ester bands in irradiated PMMA are due to methyl formate, which is split off the main chain under the formation of double bonds [Ref. 16, Fig. 3] and is trapped in the film.

A weak absorption at 3500 cm^{-1} shows the presence of free OH groups, which generally display a strong absorption signal at this wavenumber. Methanol is a known side product in the photolysis of organic methyl esters [17]. The photolysis of the ester chromophore goes along with a general chemical degradation of the polymer and therefore lowers its mechanical stability.

An important observation is, that the requirement for an incubation of PMMA is light with significant absorption (i.e. $\lambda < \approx 270$ nm), not light of an intensity above a certain threshold. Even prolonged exposure to

308 nm excimer laser radiation does not incubate PMMA, but at the wavelengths, covered by our experiments (<254 nm), we observe virtually no dependence of the spectral changes on the incident light intensity. This result is in contrast to the approach of recent models [4, 5], assuming a flux threshold (absorbed photons per unit volume *and* unit time), which has to be exceeded, before any photochemistry is induced. Although this approach can describe the ns etching behaviour of PMMA at 248 nm *quantitatively*, the flux threshold has to be considered as a fit parameter, rather than a physical fact.

With the above spectroscopic results the *incubation process of PMMA* at 248 nm can be explained. During the first incubation pulses the transmission of the UV light decreases dramatically, a fact, which results in a concentration of the pulse energy in the layers closest to the surface. At the same time, this material is photochemically degraded and the mechanical stability is reduced. After several incubation pulses, this *self doping* leads to the start of material removal. The remaining material in the etch pit has not reached the ablation condition, however is already incubated, so that the ablation process can reach a steady state regime [cf. Ref. 4, Fig. 6].

The ablation at high fluences is also affected by an increased UV absorption coefficient of incubated material. The pulse energy is concentrated in the upper material layers which receive more energy than necessary for ablation, but at the same time shield the material deeper in the sample [4].

At 308 nm, PMMA is virtually transparent and therefore only accessible to ablation, when doped with highly absorbing organic dyes [18, 19], or with ultrashort excimer laser pulses, taking advantage of two-photon absorption [4, 20–22]. Undoped PMMA, however, remains unaffected by 308 nm standard excimer laser pulses up to high fluences. Upon irradiation with continuous UV light of a wavelength of 254 nm or shorter, PMMA dopes itself with highly absorbing unsaturated compounds and thus can be ablated with 308 nm excimer laser pulses of 17 ns duration. The selective ablation of only the incubated spots, leaving the non incubated area unaffected, is demonstrated for the first time with the patterning of a PMMA film on a silicon wafer (Fig. 5).

4. Conclusion

The incubation process of PMMA preceding 248 nm excimer laser ablation can be monitored by its UV and infrared spectra. After 1000 excimer laser pulses of about 35 mJ/cm^2 the UV transmission of a 40 μm thin PMMA sample at 248 nm is reduced to less than 6% of its initial due to the formation of unsaturated species, which can be clearly identified in the infrared spectrum. These are known to absorb at wavelengths in the ultraviolet, longer than those of non-irradiated PMMA. Thus, the incubation of PMMA with 248 nm laser radiation can be explained as a process, causing both enhanced UV absorption and reduced mechanical stability of the irradiated material.

The leveling of the etch curve at high fluences can be understood by an increased UV absorption of the upper material layers, which absorb more energy than necessary for ablation and, at the same time, shield the material deeper in the sample.

Taking advantage of the increased UV absorption of incubation sites, the ablation of undoped PMMA with standard 308 nm excimer laser pulses becomes possible. Lamp incubated PMMA is laser etched away selectively, leaving the non-incubated material unaffected.

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References

1. Y. Kawamura, K. Toyoda, S. Namba: Appl. Phys. Lett. **40**, 374 (1982); J. Appl. Phys. **53**, 6489 (1982)
2. R. Srinivasan, V. Mayne-Banton: Appl. Phys. Lett. **41**, 576 (1982)
3. M. Rothschild, D.J. Ehrlich: J. Vac. Sci. Technol. B **5**, 389 (1987)
4. S. Küper, M. Stuke: Appl. Phys. B **44**, 199 (1987)
5. E. Sutcliffe, R. Srinivasan: J. Appl. Phys. **60**, 3315 (1986)
6. G. Koren: Appl. Phys. Lett. **50**, 1030 (1987)
7. A.R. Shultz: J. Phys. Chem. **65**, 967 (1961)
8. R.B. Fox, L.B. Isaacs, S. Stokes: J. Polymer Sci. A **1**, 1079 (1963)
9. J.R. MacCallum, C.K. Schoff: Trans. Faraday Soc. **67**, 2383 (1971)
10. K. Morimoto, S. Suzuki: J. Appl. Polym. Sci. **16**, 2947 (1972)
11. A. Gupta, R. Liang, F.D. Tsay, J. Moacanin: Macromolecules **13**, 1696 (1980)
12. D. Allara, A. Baca, C.A. Pryde: Macromolecules **11**, 1215 (1978)
13. H. Kobsa: Dupont, personal communication
14. C.N.R. Rao: In: *Ultra-Violet and Visible Spectroscopy, Chemical Applications*, 3rd edn. (Butterworths 1975) p. 57
15. R.C. Estler, N.S. Nogar: Appl. Phys. Lett. **49**, 1175 (1986)
16. R. Larciprete, M. Stuke: Appl. Phys. B **42**, 181 (1987)
17. J.G. Calvert, J.N. Pitts, Jr.: In: *Photochemistry* (Wiley, New York 1966) p. 435
18. T.J. Chuang, H. Hiraoka, A. Mödl: Appl. Phys. A **45**, 277 (1988)
19. R. Srinivasan, B. Braren: Appl. Phys. A **45**, 289 (1988)
20. R. Srinivasan, E. Sutcliffe, B. Braren: Appl. Phys. Lett. **51**, 1285 (1987)
21. S. Küper, M. Stuke: Proceedings "Intl. Conf. on Microlithography", ME '88, Vienna (1988)
22. S. Küper, M. Stuke: Appl. Phys. Lett. **54**, 4 (1989)