Behavior of candidate organic pellicle materials under 157 nm laser irradiation

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ABSTRACT

Transmission loss during irradiation remains the critical limitation for polymer pellicle materials at 157 nm. In this work we establish a framework for calculating the necessary pellicle lifetime as well as a test methodology for evaluating the laser durability of candidate polymer films. We examine the role of key extrinsic environmental variables in determining film lifetime. Oxygen concentration affects pellicle lifetime, but there is not an oxygen level that effectively balances pellicle perforation and cleaning against the onset of photochemical darkening. Neither moisture level nor 172-nm UV lamp pre-cleaning were found to have a significant impact on pellicle lifetime.

1. INTRODUCTION

The introduction of 157 nm as the next optical lithography wavelength has created a need for new polymeric pellicle materials optimized for this wavelength. Materials design and development of ultra transparent fluoropolymers suitable for 157-nm soft pellicle applications has produced a number of promising candidate materials with absorbance below 0.03/µm as is necessary to achieve pellicle transmissions above 95%.[1,2] To date, DuPont has developed 12 families of experimental TeflonAF® (TAFx) materials which have sufficient transparency to produce transmissions above 95%.

For the successful fabrication of 157-nm pellicles from these materials, the fluoropolymers must have appropriate physical properties to permit the spin coating of thin polymer films and their lifting and adhesive mounting to pellicle frames, the processes which produce free standing pellicle membranes of micron scale thickness. Relevant physical properties include molecular weight, glass transition temperature, and mechanical strength and toughness. DuPont has successfully developed a subset of the ultra-transparent TAFx polymer families with these physical properties.

Upon irradiation, these 157-nm pellicle polymers undergo photochemical darkening (PCD), a process whereby their transmission degrades with exposure. As a result of photochemical darkening, the best pellicle lifetimes remain at least 1000 times less than the target. In a companion paper in this conference, DuPont describes their efforts to extend pellicle lifetime through polymer composition and growth (intrinsic variables). Here, we focus on pellicle lifetime requirements, methods for quantifying PCD and the possibility of extending pellicle lifetime through changes in irradiation conditions (extrinsic variables).

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2. PELLICLE LIFETIME REQUIREMENT

We first estimate the laser durability requirement for pellicles under 157-nm irradiation. Such a target is broadly applicable to a variety of reticle protection schemes since it is simply an estimate of the cumulative dose delivered to the pellicle. There is currently a substantial gap between the lifetime of polymeric pellicles at 157 nm, and the lifetime specification previously formulated. The main objective of this section is to revisit the process for deriving the requirement to explicitly enumerate the key variables and assumptions.

2.1 Derivation of Dose Delivered to Pellicle

We first assume that pellicle damage is a linear process, therefore that the correct quantity to specify is cumulative dose. Experiments at MIT Lincoln Laboratory have shown this to be a reasonable assumption, at least over the relatively narrow range of pulse energy that we need to consider. Furthermore, all damage testing is performed around the pulse energy of interest (~0.1 mJ/cm^2/pulse), so we can avoid the uncertainties of accelerating testing.

The simplest method for calculating the total dose at the pellicle is to work backwards from the exposure dose E_w required by the resist at the wafer. The dose E_r transmitted through any clear region in the reticle per exposure is

$$E_r = \frac{E_w}{M^2 T}, \tag{1}$$

where M is the reduction ratio of the projection lens and T is its transmission. To estimate the dose at the pellicle, we make the reasonable assumption that the pellicle is effectively in the far field of the reticle. For a pellicle-reticle separation of 5 mm and a 0.8 NA lens with a 4X reduction ratio, reticle features are blurred over a disc approximately 1 mm in radius (5*0.8/4). If we further assume that the spatial variation of patterns on the reticle is primarily much less than 1 mm (i.e., there is little long range variation in pattern density), the dose delivered to the pellicle per exposure E_p is simply the product of reticle dose (E_r) and the reticle transmission (R):

$$E_p = E_r R. \tag{2}$$

Although light diverges between the reticle and the pellicle, the distance is sufficiently short that the spatial extent of the illuminated region is virtually unchanged, and the decrease in energy density is negligible.

Finally, the total dose transmitted through the pellicle E_t is the product of the dose per exposure with the total number of fields exposed. This amounts to

$$E_t = \frac{FWRE_w}{M^2 T}, \tag{3}$$

where F is the number of fields per wafer, W is the total number of wafers printed before re-pelliclization.

2.2 Estimate of Lifetime Requirement

Using Eq. (3), we can estimate the total dose that a pellicle must be able to withstand. For the purposes of this analysis, we have used the following rationale to choose the parameters. The number of fields F was estimated at about 150 by assuming a 500 mm^2 field and 300-mm wafers (from the International Technology Roadmap for Semiconductors). Although the reticle transmission can be extremely low for certain layers (e.g., contact), we assumed a relatively bright field reticle with a transmission R of 75% as a reasonable upper bound. We estimated lens transmission T at 30% by assuming a generic optic consisting of 50 surfaces each with 99% transmission, 100 cm of bulk material with an absorption of 0.002/cm (base 10), and two 90% full reflectors. Each lens design will be different, but this approach gives a conservative estimate of lens transmission. A reduction ratio M of 4 was assumed. Resist dose was varied between half and two times the target value of 10 mJ/cm^2, and wafer count was varied from 100 to 10000 (note that these are 300-mm wafers). In Figure 1, we plot total dose as a contour plot of the latter two variables.

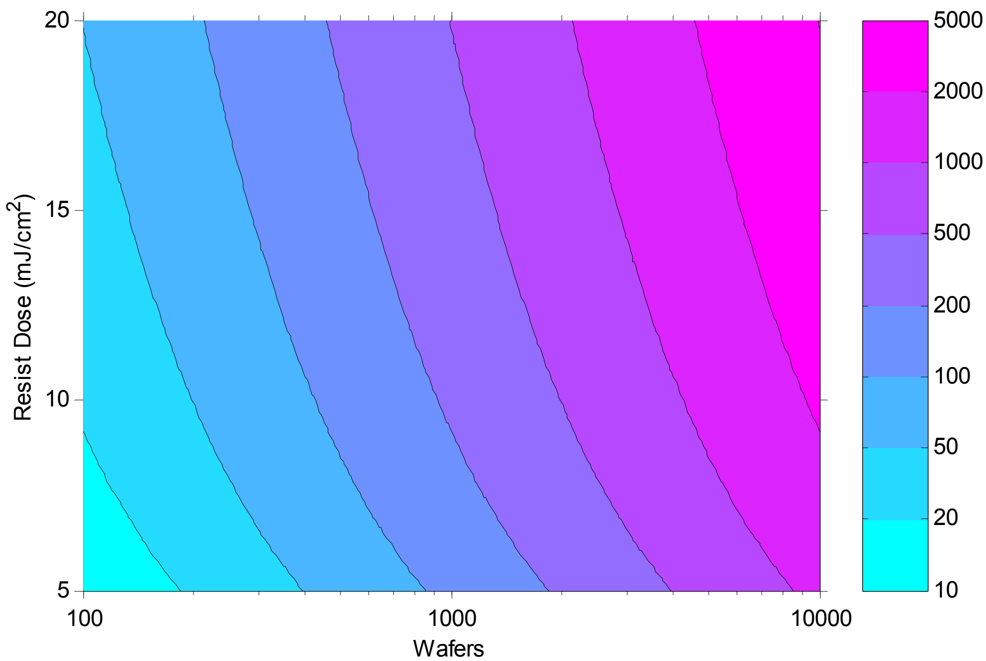

Figure 1: Contour plot illustrating total dose delivered to pellicle (in J/cm^2) as a function of 300-mm wafers processed and resist dose.

The number of wafers that are printed with a given reticle varies substantially between types of products (memory prints many more than microprocessors which in turn prints many more than ASIC). The current target of 5 kJ/cm^2 is in the upper right corner of the chart, corresponding to a conservative estimate of 10,000 wafers and 20 mJ/cm^2 resist dose. For an estimate of 5000 wafers, and a resist dose of 10 mJ/cm^2, we obtain a total dose of 1.2 kJ/cm^2. By dropping the total wafer count to 1000, the required durability drops to just under 250 J/cm^2. Note that these targets vary substantially with input assumptions associated with the product type being printed.

It is also critical to specify the maximum allowable change in transmission over the required lifetime. Targets for previous generations have been 1%. In fact, spatial variation of transmission is of primary concern due to its impact on linewidth control. In practice, this equates to variation with time given the pattern density variation over distance scales greater than the 1-mm radius blur derived above in Section 2.1. For this reason, 1% remains a reasonable target.

3. LASER DURABILITY EXPERIMENTS

3.1 Apparatus

Figure 2 shows a layout of the irradiation chamber for performing pellicle durability testing. Illumination is provided by a 1-kHz 157-nm laser with the beam expanded by a doublet cylindrical lens to obtain a uniform spot approximately 10 mm in diameter. The pulse energy is approximately 0.1 mJ/cm^2/pulse, the nominal fluence for the reticle plane. Insitu transmission measurements are performed by pulse-to-pulse ratiometry using the two pyroelectric detectors as shown. The 172-nm lamp provides 1 mW/cm^2 at the sample and can irradiate the sample simultaneously with the laser. The baseline oxygen concentration of the chamber is approximately 1 ppm at equilibrium. To explore alternate ambients, we constructed a mini-environment around the pellicle with two 157-nm reticle blanks. This permitted us to independently vary oxygen and water concentration in the immediate vicinity of the pellicle.

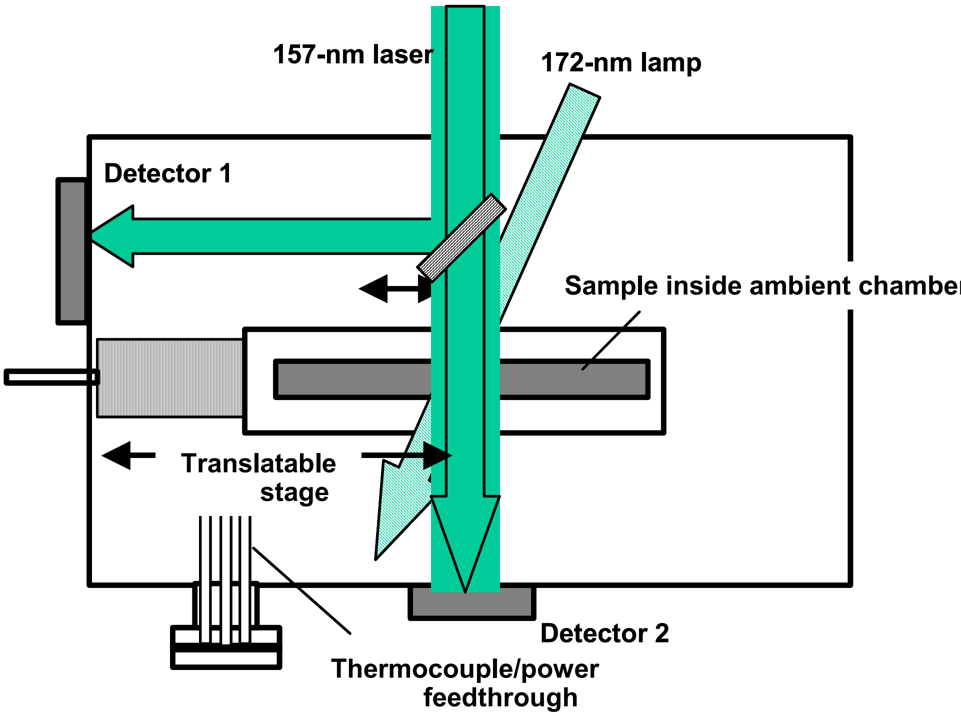

Figure 2: Schematic of pellicle laser irradiation chamber.

3.2 Photochemical Darkening

Upon irradiation the candidate pellicle polymers undergo photochemical darkening (PCD) which reduces the 157-nm transmission of the material. PCD can be considered as arising from the absorption of the high energy 157-nm photons in the pellicle membrane, with this absorbed energy producing absorbing chromophores. PCD has been reported in the literature for many materials including both polytetrafluoroethylene and TeflonAF®. [3]

The PCD process can be considered as a nucleation and growth process, in which the first step is the absorption of 157-nm photons by some pre-existing absorption site (a PCD nucleation site or nuclei) in the pellicle which upon absorption leads to formation of some transient excited state, which upon decay results in final absorbing species. This final PCD absorbing species can lead to absorption of subsequent 157-nm photons, and we enter a regime of growth in the absorption in the material.

In a nucleation and growth process, the first line of attack is to reduce the initial number of absorbed 157nm photons in the material (the nuclei), which produce and initiate the photochemical darkening. With a reduction in the initial absorption we are reducing the number of nuclei that start off the PCD pathway. The second avenue is to modify the growth rate of the darkening. In this paper, we focus on extrinsic factors which may decrease either the nucleation or growth rate for photochemical darkening, thereby extending pellicle lifetime.

3.3 Double Exponential Fits to Photochemical Darkening Data

An example of laser irradiation data is shown in Figure 3. In the figure on the left, insitu 157-nm transmission is plotted as a function of accumulated dose. Since the thickness of the films being tested varied between 0.5 - 3 µm, to facilitate comparison of different films we converted transmission to absorbance per micron. In many of the samples, photochemical darkening was preceded by a slight gain in transmission. This appears similar to "cleaning" effects observed on substrates or coatings where hydrocarbon contamination is removed during initial irradiation. Since the effect appeared to be independent from PCD, we chose to fit the experimental data with a double-exponential curve of the following form:

$$A_{Induced} = A_0 + A_1 e^{-\frac{Dose}{T_1}} + A_2 e^{\frac{Dose}{T_2}} \quad (4)$$

with the 5 fit parameters are A_0, A_1, A_2, T_1 and T_2. The second term represents the "cleaning" effect (A_1 is negative), while the third is PCD, which grows exponentially as outlined by the simple model above. A_0 is a small, arbitrary fit parameter to account for slight uncertainty in selecting zero absorbance.

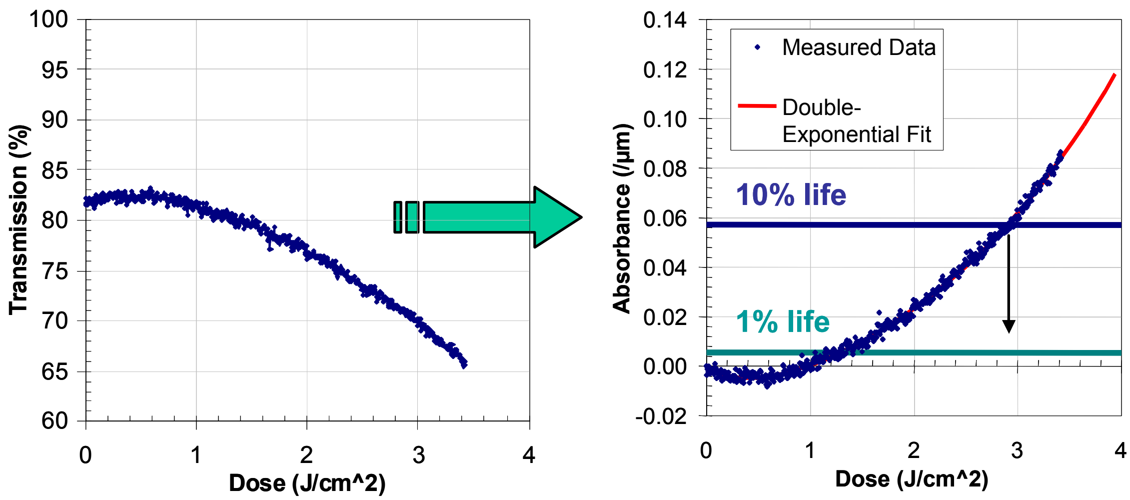

Figure 3: Example of pellicle laser irradiation data. Induced absorbance was calculated from insitu transmission. Lifetime can be read directly from this chart.

The double-exponential fit was applied to reduce the noise in calculating polymer lifetime. For the purposes of this study, lifetime has been defined as a 10% transmission drop from an original value of a 0.8-micron thick freestanding polymer film (i.e., absorbance of 0.057 /µm). To decouple initial cleaning from PCD, we attempted to extract a PCD rate constant (e.g., T_2) from the fit. This turned out to be a less stable proxy for lifetime than the 10% measure, so here we state all results in terms of the latter.

All new samples were tested in a standard dry environment with a nominal oxygen concentration of 1 ppm. To give a sense of the data obtained from different polymer formulations, we have plotted 10%-lifetime in Figure 4. Feedback from this lifetime data was incorporated into the design of future polymers. The impact of oxygen and other variables is discussed in the next section.

4. IMPACT OF KEY EXTRINSIC ENVIRONMENTAL VARIABLES

4.1 Oxygen Concentration

Previous experiments have shown that oxygen concentration is a factor affecting pellicle lifetime. Low levels of oxygen (<10 ppm) generally show little or no initial "cleaning", and relatively rapid onset of photochemical darkening (PCD). Conversely, at high levels of oxygen (~1000 ppm), the pellicle typically exhibits a short cleaning phase, followed by a gradual decay and then relatively flat transmission ending with perforation of the pellicle. We hypothesized that there may be an opportunity to balance the two processes so that flat transmission was achieved without a perforation forming.

We irradiated three TAFx3P pellicles at different oxygen concentrations (130, 370 and 940 ppm). Transmission versus dose is plotted in Figure 5. The trends noted above were observed, but there did not appear to be a middle ground as hypothesized. Both of the higher oxygen samples perforated at approximately 4 J/cm^2, while the 130-ppm sample did not. The PCD rate of the middle sample was somewhat lower than for the sample at the lowest concentration, however, it is unlikely that an intermediate level would yield a substantially different PCD rate, nor would it plateau without perforation.

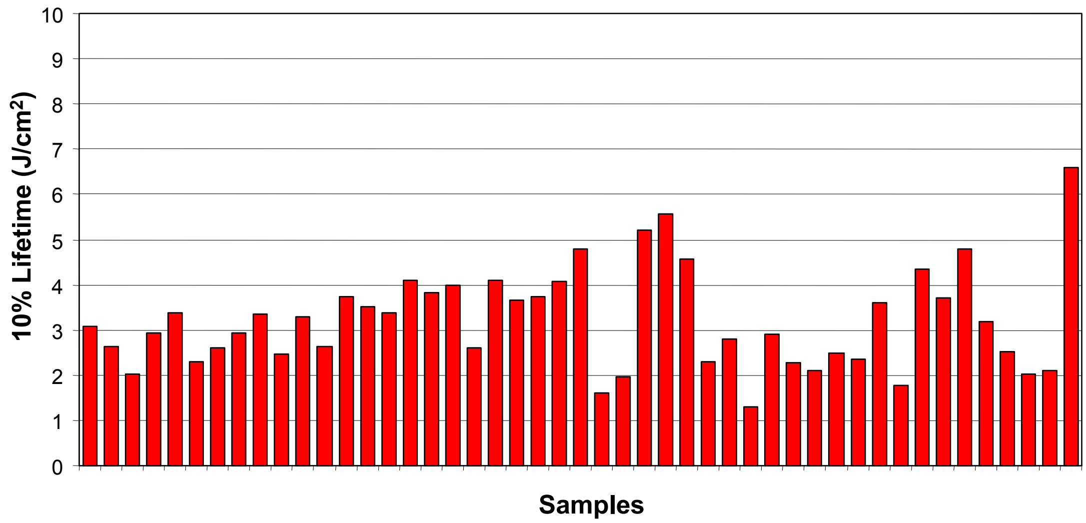

Figure 4: 10%-lifetime of pellicle material samples tested.

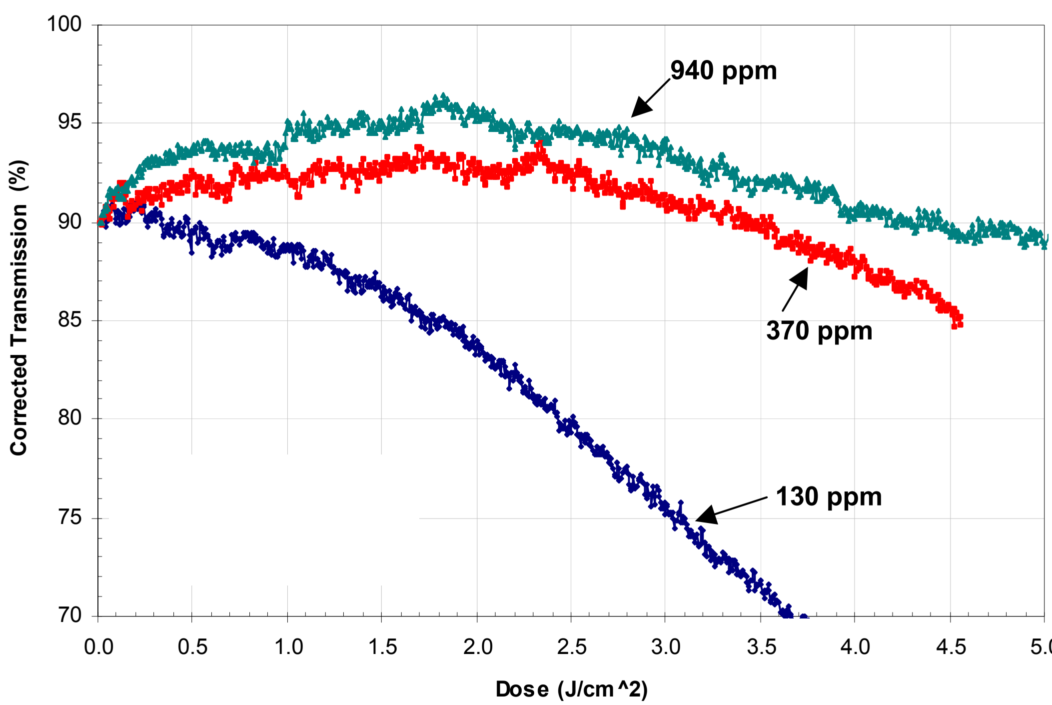

Figure 5: Impact of varying ambient oxygen concentration on pellicle lifetime.

Another possibility we investigated was whether it was possible to perform the initial irradiation in an oxygen ambient thereby performing an initial cleaning step, followed by irradiation in a low oxygen ambient. We hypothesized that by reducing the absorption in the initial phase, the PCD process would be slowed. Figure 6 shows the results of this experiment again with TAFx3P pellicles. In both cases, oxygen flow was initially set for a concentration of approximately 400 ppm. In the case of the "varying O_2" trace, oxygen was shut off once a dose of 2.5 J/cm^2 had been delivered, and the chamber was given time to purge down to an oxygen concentration below 30 ppm. The two conditions show negligible difference, so we conclude that changing oxygen concentration in the middle of the run had no impact on PCD, and by inference, that the cleaning phase and PCD phase are largely independent processes. We also examined this hypothesis at higher levels of oxygen and reached the same conclusion.

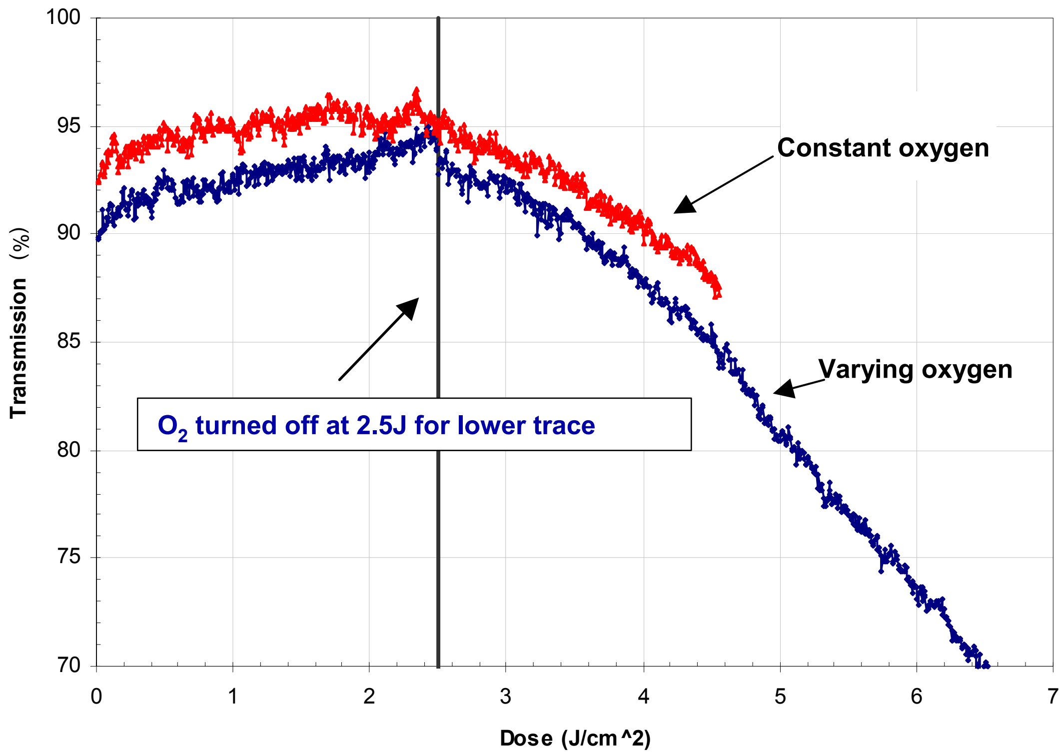

Figure 6: Impact of varying oxygen concentration over time on pellicle lifetime.

Finally, we examined the events leading to catastrophic failure of the pellicles in a high oxygen ambient. As is shown in Figure 7, in the vicinity of 5 J/cm^2, the pellicles showed an inflection point in transmission followed by a plateau, or a slowly oscillating transmission. Closer inspection of the pellicle during irradiation showed that the inflection point was in fact when perforation first started. Perforation evolved from a slit to a round hole at a variable rate depending on the sample. We explain the plateau as a combination of 100% transmission in the center of the hole, with a near opaque region around the periphery where the pellicle has gathered up. The subsequent slow increase in transmission corresponds to a slow enlargement of the hole. In some cases (e.g., sample #2 in Figure 7), this process is combined with PCD yielding continued decay, followed by a rise. This explanation is supported by the observation that polymer on CaF_2 samples do not show a plateau in transmission under irradiation in high concentrations of oxygen.

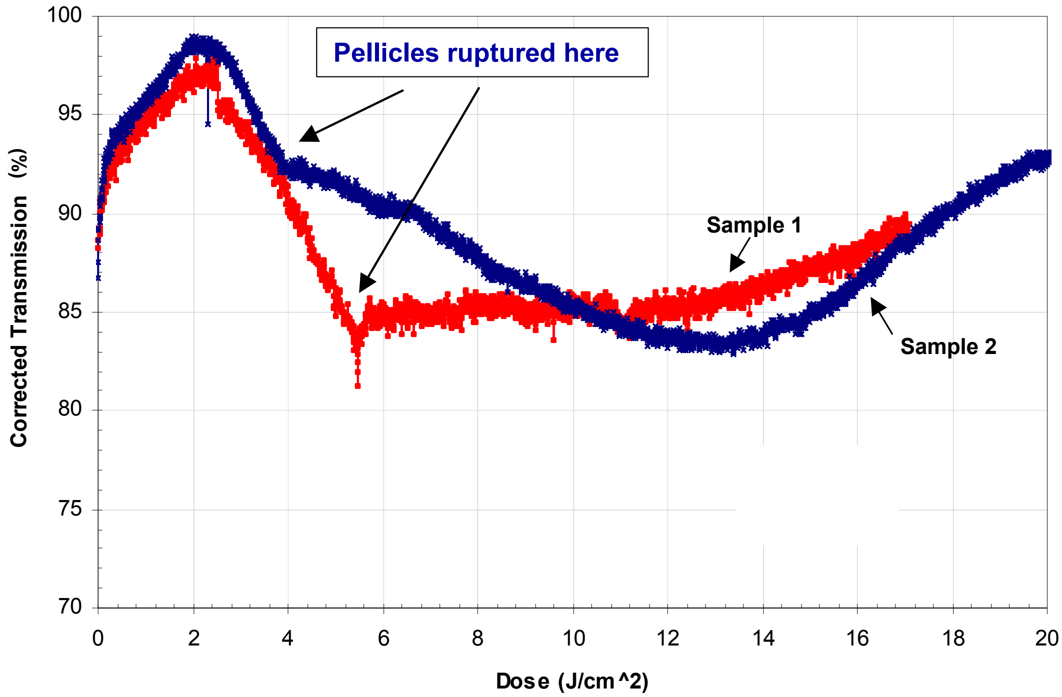

Figure 7: Pellicle laser durability at a high oxygen concentration (1000 ppm).

4.2 UV Lamp Cleaning

Earlier results have shown that pre-irradiation with a 172-nm lamp improves transmission through cleaning of surface contaminants. We have installed an Ushio UER-20H lamp in the chamber to permit investigation of lamp cleaning effects insitu without removing the pellicle prior to irradiation. The lamp provides approximately 1 mW/cm^2 of 172-nm irradiance at the sample. Figure 8 shows the results of an experiment to examine the difference between no lamp cleaning and about 3 J/cm^2 (60 minutes) of lamp pre-clean. The samples were both type TAFx3P polymer on CaF_2. We observed a negligible difference between the two cases. A parallel experiment was performed at elevated oxygen levels (300 ppm). Lifetime was extended, but by a similar amount as might be expected with oxygen and no lamp cleaning. The PCD rate after 2.5 J/cm^2 appeared to be about the same as the low oxygen case. We conclude that lamp cleaning at this dose has no impact for both oxygen levels.

To further investigate the amount of lamp cleaning that can be tolerated prior to damaging the pellicle, we irradiated a polymer on CaF_2 sample at 172 nm, and made periodic transmission measurements at 157 nm. The result obtained in a 300 ppm oxygen ambient is shown in Figure 8. The trend of initial cleaning followed by degradation is similar to that at 157 nm, but with a much higher dose. From this, we expect that a dose of approximately 10 J/cm^2 would be more appropriate for lamp pre-cleaning of this sample (compared with 3 J/cm^2 described above), and that doses up to 20 J/cm^2 could be tolerated prior to significantly damaging the pellicle.

There are several possible explanations for the difference in dose necessary to damage the pellicle at 172 nm versus 157nm. The most likely is the wavelength: the pellicle is substantially more absorptive at 157 nm, and hence damages that much more quickly. Alternate possibilities include duty cycle of the source and peak power.

A similar experiment was performed to examine degradation of a polymer on CaF_2 sample by 172-nm lamp irradiation at low oxygen concentration. 157-nm transmission measurements were only taken at the start and end of the 50 J/cm^2 (16 hours) run, and in contrast to the oxygen ambient results, showed a substantial drop from 75% to 40% transmission. This is roughly in line with previous results.

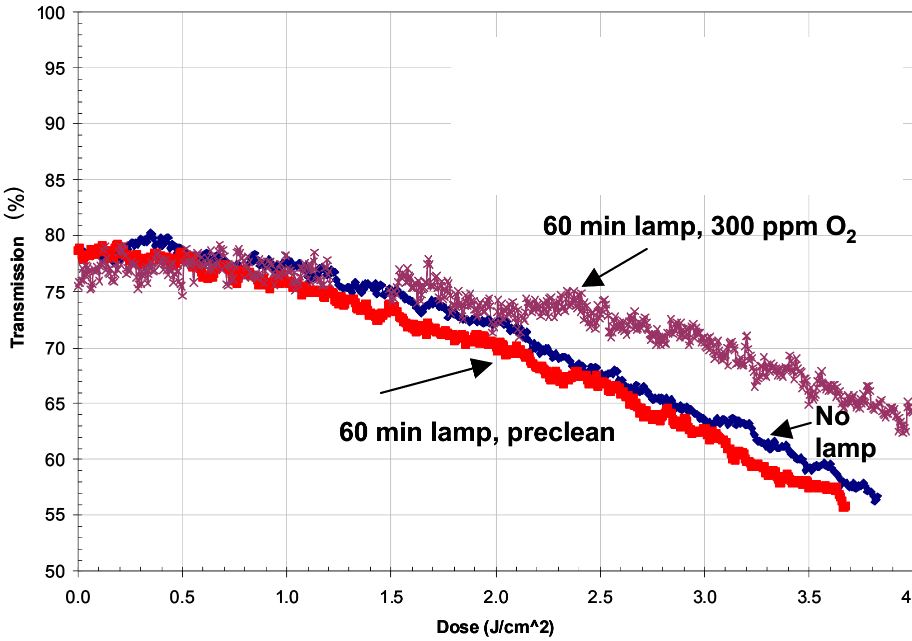

Figure 8: Effect of 172-nm lamp pre-cleaning.

4.3 Moisture level

Water strongly absorbs at 157 nm, so we suspected that reducing the water content of the pellicle film may reduce absorption. The experiment did not have any means for actively drying a pellicle insitu, however, we attempted to dry a pellicle by purging it overnight in the dry nitrogen environment of the exposure chamber. No change in laser durability was observed.

To investigate this more thoroughly, we increased the moisture level of the ambient by bubbling the incoming purge gas through a cooled water cell. This raised the moisture level to a partial pressure of 4 Torr. We performed irradiation experiments on TAFx3P pellicles for high and low levels of moisture content in a low oxygen environment (i.e., less than 10 ppm). The results shown in Figure 9 demonstrate that there was negligible impact despite a large change in the local moisture content. The experiment was repeated for polymer on CaF_2 with similar results.

There is a slight possibility that the pellicle was already saturated with water, so increasing the moisture level did not make any difference to the water content of the pellicle. We believe this is unlikely due our lack of success in passively drying the pellicle. This could be investigated further by installing an infrared lamp for aggressively drying a pellicle before irradiation.

5. CONCLUSIONS

Polymer pellicles remain the most desirable reticle protection solution for 157-nm lithography, however the best demonstrated lifetime to date falls roughly three orders of magnitude short of the goal. We have established a test methodology for evaluating the laser durability of candidate polymer films and have examined the role of key extrinsic environmental variables in determining film lifetime. Oxygen concentration indeed has an impact on pellicle lifetime, but there does not appear to be an intermediate oxygen level that effectively balances pellicle perforation and cleaning against the onset of photochemical darkening. Furthermore, at realistic levels of oxygen (<100 ppm), oxygen primarily modulates the degree of initial cleaning rather than the photochemical darkening process itself. Conversely, at elevated levels of oxygen, relatively rapid perforation of the pellicle is observed. Neither moisture level nor lamp pre-cleaning were found to have a significant impact on pellicle lifetime.

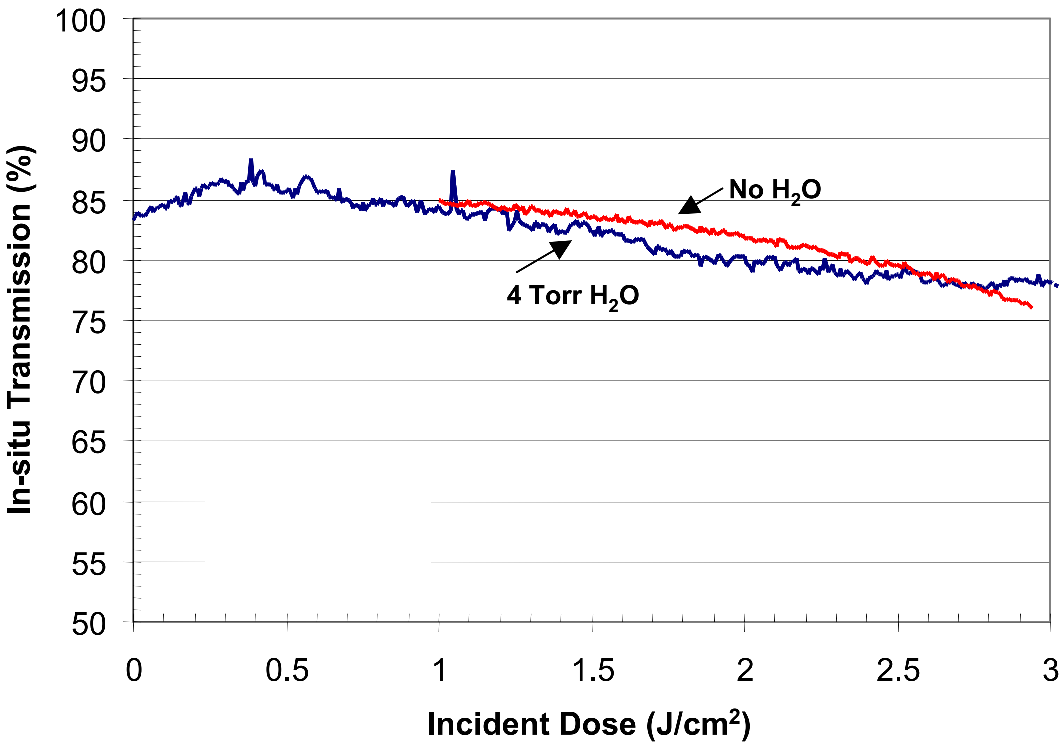

Figure 9: Comparison of pellicle laser durability in high versus low moisture content ambients.

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