Quasi Steady-State Measurements of Sub 1-minute Vacuum Outgassing Rates & Application to EUV Photoresists

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1 Introduction

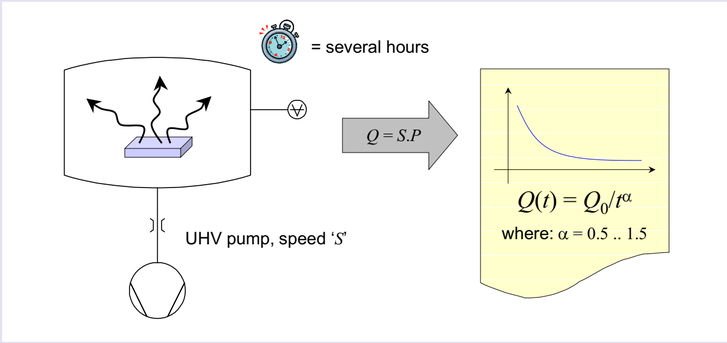
Low short-term (<< 1 hour) outgassing (particularly of water and hydrocarbon species) will be an important property of photoresist materials for EUV lithography, where tight control of these contaminants is required to preserve the life of costly multilayer mirrors. This is particularly true of stimulated outgassing since, when exposed to EUV, the outgassed species are by definition in line-of-sight to the optics. The need for suppression of these contaminants greatly influences the design of production EUV tools.

Measurements of outgassing after several hours under vacuum may not be reliable for predicting behaviour (particularly of stimulated outgassing) in the short-term. Assessing resists in a way that is applicable to the situation of a wafer in the 'wafer stage' of a tool (where the wafer may only have been under vacuum for a matter of minutes) presents some previously un-addressed technical challenges. BOC Edwards has developed a novel approach to the measurement of short-term outgassing rates, in which samples are transferred in a few seconds from atmosphere (or a controlled environment at atmospheric pressure) to UHV pressures, and the measurement of outgassing is conducted under conditions of near-constant total pressure. At these pressures residual gas analysis (RGA) techniques can be used to 'fingerprint' the outgassed species.

Initially we have measured outgassing rates of carbon-steel, to characterise the method against other measurements of outgassing - the results are presented here. The method can be simply extended to measure stimulated outgassing of candidate EUV photoresist compositions..

2 Traditional Measurement of Outgassing - The Throughput method

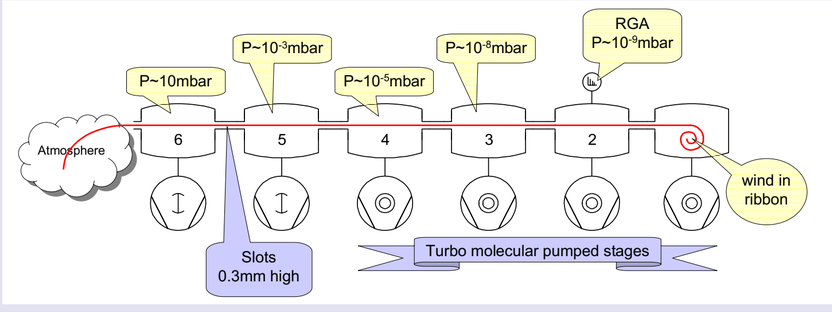
- A chamber containing the sample is pumped by a UHV pump of a known speed (S), then pressure (P) is recorded as a function of time, typically between 1 and 100 hours.



- The outgassing rate Q(t) is calculated from Q = pump speed x pressure.
- Fundamental surface physics shows that the pressure (and hence outgassing rate) can be expected to closely follow $Q(t) = Q_0/t^{\alpha}$.
- Clearly NOT VALID for short times, since $Q \rightarrow \infty$ as $t \rightarrow 0$.

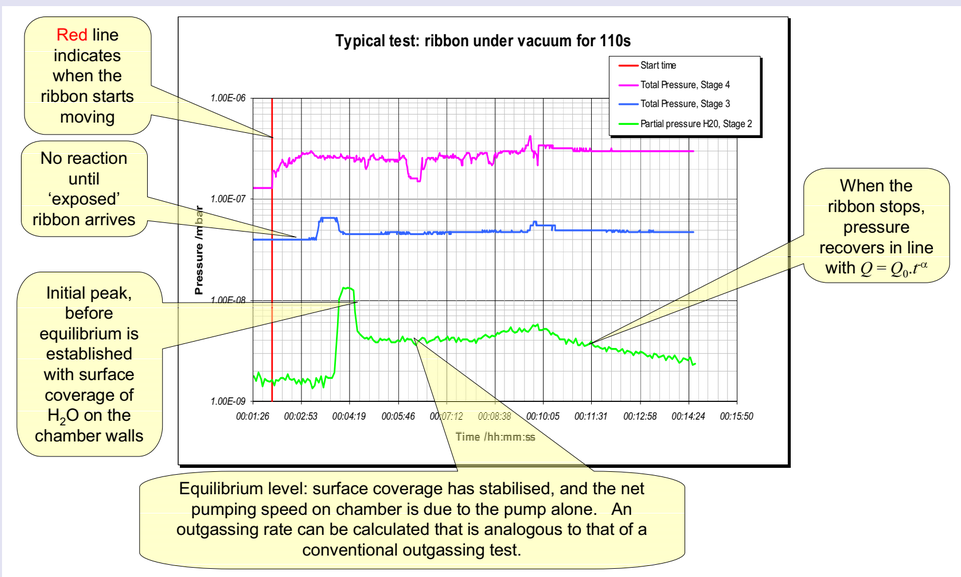
3 Experimental Outline

- Fine metal ribbon (shown in red) 15mm x 0.15mm is drawn at constant speed through a series of chambers separated by thin slots, 0.3mm high.
- Appropriately sized pumping at each stage ensures a pressure reduction from one stage to the next.
- An OUTGASSING MEASUREMENT is made in STAGE 2, using a residual gas analyser (RGA) and ionisation gauge, together with a knowledge of the pumping speed.
- The time taken for a section of ribbon to reach the chamber (and be measured) can be varied by varying the 'rate of winding'. Times from ~20s up to several minutes can be measured.



4 Results Part I

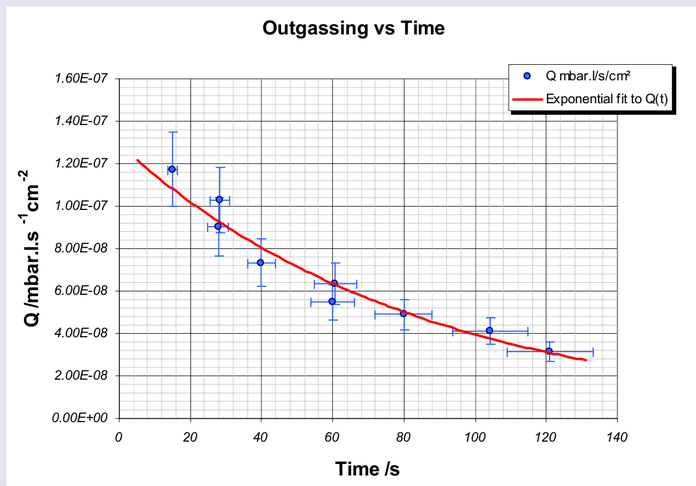
The graph below shows a typical trace of the WATER VAPOUR partial pressure (18 amu on the RGA) as a function of time, as well as the pressure in Stages 4 and 3.



5 Results Part II

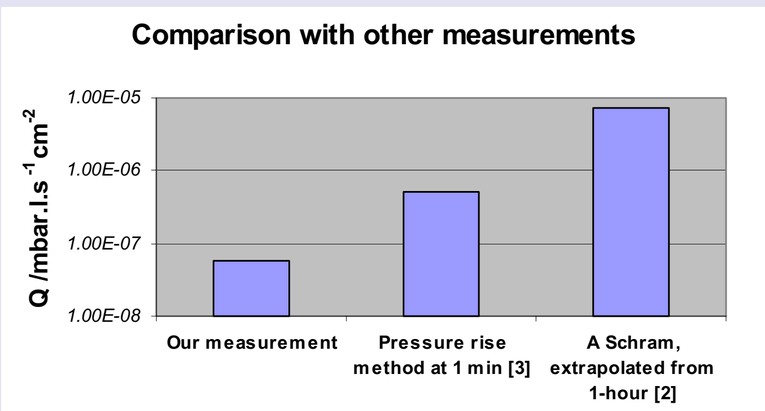
By measuring outgassing at different ribbon speeds, it is possible to assess the uncertainties, and explore how the outgassing rate is varying with time under vacuum.

- Uncertainties of <15% are achievable using this method.
- Results indicate that in the short term, outgassing vs. time may follow an exponential relationship, with a finite value at t = 0, Q(0) ~ 1.2×10^{-7} mbar.l.s^{-1}cm^{-2}.



6 Conclusions

These results can be compared with accepted measurements of outgassing from carbon-steel obtained by the 'throughput method', which are widely published in the vacuum science literature.



- Measurements made by two short-term methods indicate that outgassing measurements made by the throughput method (after several hours) and extrapolated back to ~ minutes, are an overestimate by a factor of 10-100.

7 Future Work

In the coming months, the extension of this work is two-fold:

- Theoretical study to develop a first-principles model of short-term outgassing:
  1. What is the applicability of the non-equilibrium adsorption isotherm (Langmuir, Temkin etc.) to the surface coverage after only short periods under vacuum?
  2. What is the influence of residence times for different molecules?
  3. What is the role of re-adsorption on the measured outgassing rate in the short-term?
- By working closely with our partners, modification of the existing apparatus to enable characterisation of stimulated outgassing from photoresist on exposure to EUV.

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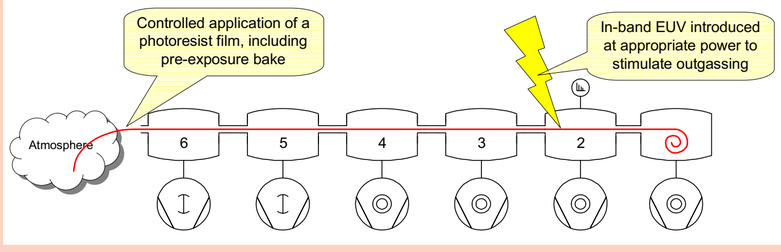

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