Pressure-dependence of Radical Densities in Low Pressure Ranges in Plasma Processing

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Investigation of the radical density in terms of the pressure gives us some valuable information on the plasma and surface kinetics, as shown in our previous work for fluorocarbon discharges.¹ There, we found that the radical density depends on the pressure (p) in such a way that p/(the density) is linearly proportional to p^2 . From this finding we could evaluate kinetics parameters, such as reactive sticking coefficient and recombination rate constant. Downward deviations from this linear dependence however were observed at low pressures for some plasma systems. This downward deviation is mostly attributed to the decrease in the dissociation degree (ε) with p. We shortly handle this in this work, in order to refine the previous model, and eventually to apply to various gas discharges.

When the *j*-th chemical species (its density = n_j), e.g. CF₂ radicals in a fluorocarbon discharge, is generated by electron-induced dissociation of feed gas molecules, ε is given by

$$\varepsilon = \frac{P_W}{P_W + \chi^{-1}} \tag{1}$$

with $\chi = \eta \tau_0$, the dissociation efficiency of feed gas molecules (τ_0 = the residence time of feed gas molecules in the reactor). The parameter η relates the rate constant *k* of the dissociation reaction with the electron density n_e to the discharge power P_W , as $kn_e \equiv \eta P_W$.²

The χ depends on *p* through the dependence of $n_{\rm e}$ (and $T_{\rm e}$, the electron temperature) on p,^{3,4,5} and $\tau_0 \propto p$ from the ideal gas law. An example plot for the dependence χ on *p* is shown in Fig. 1: the values of χ (solid line) scale with *p* for CHF₃ electron cyclotron resonance plasmas.⁶ As shown in this figure, however, the value of ε is not very sensitive to the pressure change, while the variation of χ is apparent. In this case $p/n_{\rm j}$ is linearly proportional to p^2 , as discussed in detail in our previous work.¹

On the contrary to this trend, it was found for some plasmas that the values of $1/\chi$ is roughly linearly proportional to p, as exemplified for an oxygen RF discharge in Fig. 2.⁷ This seems to be the case where the pressure is enough low so that the gas temperature is very sensitive to the variation of the pressure. In this regime, ε decreases apparently, and we must take into account this. The previous formulation for the density of the *j*-th species then modifies to

$$n_j \approx \frac{aqp}{C_j \left(1 + \chi^{-1} P_W^{-1}\right)} \tag{2}$$

where *a* is the number of the *j*-th species generated per dissociation reaction, *q* is the flow rate of feed gas, and C_j is a pressure-independent parameter.¹ If $1/\chi$ is roughly linearly proportional to *p*, p/n_j would be linearly proportional to *p*, not to p^2 , at low pressure ranges. Fig. 3 shows an example, which meets this expectation. The densities of F atoms measured for various fluorocarbon discharges⁸ increases with *p* very rapidly to saturation. The manner of this behavior is neatly described as a linear dependence of p/n_j on *p*, as apparent in Fig. 3.



Fig. 1 Variations of χ and ε as a function of *p* for CHF₃ electron cyclotron resonance plasma (M=CHF₃). The values of ε were given by Takahashi et al.⁶



Fig. 2 Variations of χ and ε in terms of p in O₂ RF plasmas. Data were extracted from Kearns et al.⁷



Fig. 3 Pressure dependence of F atom density as a function of *p* measured in C_5F_8 , CHF₃, C_4H_8 and CF₄ inductively coupled plasmas.⁸

References

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