

A Model of the Chemical Processes Occurring in CF_4/O_2 Discharges Used in Plasma Etching

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A model has been developed in an attempt to explain the chemistry which occurs in plasmas produced in mixtures of CF_4 and O_2 . Emphasis is placed on gas-phase free radical reactions, and the predictions of the model are compared with experimental results. Dissociation rates following electron impact are deduced mainly from experimental observations although relative dissociation rates have been calculated. An important assumption of the model is that CF_2 can be produced as a primary dissociation product following electron impact. Furthermore, this process is favored over that producing CF_3 by more than a factor of 2. Experimental evidence is presented to support this assumption. Although the model agrees well with experiment on the total amount of fluorine produced, some discrepancy exists between the predicted and measured values of $[\text{F}_2]$. It is suggested that the higher concentrations detected in the experiments resulted from recombination of F atoms in the sampling region. The agreement for concentrations of CO_2 , CO, and COF_2 is generally better than a factor of 2 over a wide range of experimental conditions.

KEY WORDS: Plasma etching; gas-phase reactions; modelling.

1. INTRODUCTION

Plasma etching represents an important step in the fabrication of semiconductor devices for the microelectronics industry. Nevertheless the rapid progress which has been evident in this area has been based largely on an empirical approach. This is because the multitude of complex processes which occur in the plasma environment make it very difficult to develop a model which can predict or explain the observed results for a given set of conditions. It is evident that, for further rapid development of etching technology, the fully empirical approach will have to give way to more sophisticated methods based upon at least a partial understanding of the processes involved. Attempts to develop quantitative models must focus on

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two complicated aspects of the plasma process, namely processes occurring in the gas phase and those occurring at the gas–solid interface. Clearly these are strongly coupled regions of interaction, but this somewhat arbitrary separation can provide some insight into the possible mechanisms of the overall process. For example, a reasonable model for the gas-phase chemistry will be able to predict the chemical identity of the active species which arrive at the gas–surface interface. With this knowledge, one is then in a better position to begin to consider how these identified species interact with the surface.

In the gas phase one is confronted with a particularly complicated set of conditions which can lead to a diverse range of reactions. Furthermore, important parameters such as the electron number density and energy distribution are poorly defined and, even if they were well known, dependent parameters such as the rates and pathways of molecular dissociation resulting from electron impact are not. One aspect of the gas-phase processes about which there is considerable uncertainty is the free radical chemistry. In particular one needs to know which are the important reactions, how the rates of these reactions vary with gas number density, gas composition and temperature, and what role these variations play in controlling the identity of the species arriving at the surface.

Recent publications from this laboratory^(1–4) have reported measurements of the rate coefficients for gas-phase free radical reactions which are believed to occur in plasma etching. In this study we consider in more detail the implications of some of those measurements for the chemistry of plasmas of mixtures of CF_4 with O_2 . In particular a reaction set is developed using the best available reaction rate coefficients—either estimated or measured—and the predictions derived from this reaction set are compared with available measurements of the gas-phase composition downstream of the plasma. In an accompanying work⁽⁵⁾ the relevant parts of the model are applied to plasmas of pure CF_4 and the results again compared with experimental findings.

The most detailed experimental information concerning stable products detected downstream of a CF_4/O_2 plasma can be found in the work of Smolinsky and Flamm.⁽⁶⁾ In that work, mixtures of CF_4/O_2 at a total gas number density of $1.6 \times 10^{16} \text{ cm}^{-3}$ (0.5 torr) flowing in a 1.9 cm i.d. alumina tube were excited by a 49 W 13.56 MHz discharge extending over 5 cm of the tube length. Sampling of the effluent from the discharge was by mass spectrometry with the inlet pinhole located 15 cm downstream from where the discharge commenced. The residence time could be varied by changing the pumping speed, while the pressure was maintained by increasing or decreasing the incoming flow rates. Experimental results were reported for nominal discharge residence times of 7, 20, and 99 ms.

Perhaps the most notable feature of the results at each of these residence times was the dependence of [COF₂] and [CO₂] on the mole percent of O₂ in the feed gas. In all cases [COF₂] was much higher than [CO₂] at low mole percent O₂ while for high mole percent O₂, CO₂ became the dominant product. In a recent publication⁽³⁾ we have speculated that reactions of COF may provide a partial explanation for these observations. It was proposed that, under conditions of low [O], COF would be converted mainly to COF₂ whereas at higher [O], COF would be converted mainly to CO₂. The mechanisms controlling the production of COF₂ and CO₂ in these plasmas must clearly be an important part of any model developed to explain the chemistry.

In the next section details of the development and structure of the model are given. This is followed in Section 3 by a detailed comparison of the predictions of this model with experimental results obtained by Smolinsky and Flamm.

2. DEVELOPMENT OF THE MODEL

Apart from the free radical chemistry the most uncertain aspects in the formulation of the model are: (a) the electron impact dissociation rates for molecules and radicals in the plasma, (b) the branching ratios for these dissociations, particularly for CF₄, and (c) the influence of walls on the chemistry by providing a significant sink for radicals. Each of these aspects will be considered in turn.

2.1. Dissociation Rates

In principle these can be derived by estimating the electron number density and the electron energy distribution and combining these estimates with what is known of the electron impact dissociation cross-sections of the species concerned. We have made such estimates for CF₄, O₂, and CO₂ and the results of our calculations are given in Appendix 1. Because of the number of approximations employed in these calculations we would not expect them to be accurate to better than an order of magnitude.

An alternative approach for the estimation of dissociation rates is suggested by the results of Fig. 7 of Smolinsky and Flamm. The percent conversions of both CF₄ and O₂ are plotted as functions of both composition and discharge residence time. At the longest residence time, 99 ms (equivalent to a flow rate of 5 sccm), it is seen that for 80% O₂, the CF₄ is 82% converted to products. At this particular [O₂] it would be expected that reactions between O and CF₄ dissociation products (CF₃ and CF₂) would dominate and that reactions between CF₃ or CF₂ and F to reform

CF_4 would be unimportant. From the reported percent conversion it can be concluded that the phenomenological rate coefficient for dissociation is of the order of 20 s^{-1} .

One can arrive at an estimate of the dissociation rate coefficient for O_2 using arguments similar to those outlined above for CF_4 . Thus in Fig. 7 of Smolinsky and Flamm it can be seen that for a gas composition of 18% O_2 , 76% of the O_2 is converted to products. If it is assumed that the $[\text{O}]$ is kept so low by reaction with radicals derived from CF_4 that combination to reform O_2 downstream may be ignored, then these figures again result in a value of about 20 s^{-1} for the first-order dissociation rate coefficient for O_2 . From these observations we make the simplifying assumption that the dissociation rate for all species is 20 s^{-1} throughout the entire range of conditions considered in this study unless more quantitative information is available.

2.2. Branching Ratio for CF_4 Dissociation

No quantitative experimental evidence exists from which the breakdown pathways for CF_4 , following electron impact, can be deduced. Obviously CF_3 formed by electron impact on CF_4 can dissociate further following subsequent electron impact. However, because CF_3 reacts rapidly with neutral species under the conditions discussed here, electron impact of CF_3 is a negligible source of CF_2 . However, CF_2 can be produced rapidly following the initial electron impact on CF_4 . This can occur through the production of CF_3 in an excited state which then undergoes a rapid dissociation to produce CF_2 . In this regard we note that Flamm⁽³¹⁾ postulated a short-lived state of CF_3 which dissociates, after a transition to a repulsive state, into $\text{CF}_2 + \text{F}$. These observations were made in a radiofrequency discharge and support the suggestion that CF_2 can be looked upon as a direct product of electron impact of CF_4 on the time scale appropriate to collisions in the plasma etching environment.

The branching ratio forms an important component of any model designed to describe these plasma processes. Earlier studies from this laboratory demonstrate that, in O atom rich environments, CF_3 reacts to produce COF_2 while CF_2 produces CO_2 and CO .^(1,3) This information may be used to obtain an estimate of the relative rates for dissociation of CF_4 to produce CF_3 and CF_2 from the results in Fig. 8 of the work of Smolinsky and Flamm. In part c of that diagram the results obtained at high mole % O_2 and short discharge residence times indicate that $[\text{COF}_2]$, $[\text{CO}_2]$, and $[\text{CO}]$ are all roughly equal. Assuming that under these conditions COF_2 arises predominantly from CF_3 while CO_2 and CO are derived from CF_2 , the results imply that the primary dissociation of CF_4 favors the production of CF_2 by about a factor of 2.

In view of the importance of this branching ratio and the uncertainty in the estimate given above, it was decided to make a more direct determination which was again based upon product analysis in an oxygen-rich environment. Such a determination will be accurate provided that:

- (i) the degree of dissociation of products by electron impact is negligible,
- (ii) $[O] \gg [F]$, $[CF_2]$, or $[CF_3]$ so that CF₂ and CF₃ react only with oxygen atoms, and
- (iii) sufficient time is allowed downstream of the discharge so that CF₂ and CF₃ are consumed completely.

Experiments were performed using the gas flow reactor described previously.⁽¹⁻⁴⁾ Mixtures of CF₄ with O₂ in helium were passed through a microwave discharge. Typically the $[O_2]$ was $1.6 \times 10^{15} \text{ cm}^{-3}$ and the $[CF_4]$ 10^{13} cm^{-3} . The residence time in the discharge was 1 ms, which resulted in 5% dissociation of O₂ and 7% dissociation of CF₄, although the amount of dissociation depended on the discharge power employed. The $[O]$ was $> 10^{14} \text{ cm}^{-3}$ and typically > 200 times the combined initial concentrations of CF₃ and CF₂. Given the rate coefficients for reactions of CF₃ and CF₂ with O atoms, the pseudo-first-order loss rates for CF₃ and CF₂ with O would be $> 3.1 \times 10^3$ and $1.8 \times 10^3 \text{ s}^{-1}$ respectively. Assuming that the first-order dissociation rates for CF₃ and CF₂ are comparable to those for CF₄ and O₂, then, under these experimental conditions, a negligible fraction of the radicals produced in the primary dissociation step is subjected to further electron impact dissociation.

The sensitivity of the instrument for CO and for CO₂ was determined using known flows of the pure gases while that for COF₂ was obtained by allowing CF₃ produced by reaction of F atoms with CF₃H to react with excess O atoms. The $[COF_2]$ produced was equated with the measured change in $[O]$. These experiments resulted in a value of (2.5 ± 1.0) for the ratio of the primary dissociation rate for CF₂ production relative to that for CF₃ production. In subsequent treatment of the dissociation of CF₄ by electron impact it has been assumed that $(CF_3 + F)$ and $(CF_2 + 2F)$ are the dissociation routes. The processes producing CF₂ are viewed as consecutive unimolecular dissociations of CF₄ and CF₃ rather than a direct process which yields CF₂ + F₂. This view is taken mainly because, in experiments using the flow reactor, the $[F_2]$ detected was $< 1\%$ of the $[F]$.

It is important to note that the experiments of Smolinsky and Flamm were carried out in a radiofrequency discharge whereas those described here used a microwave discharge to produce the free radicals. Clearly, one would expect that the electron energy distribution would be quite different in these two cases but, nevertheless, both provide strong evidence for the production of CF₂ by very fast processes following electron impact on CF₄.

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