Aust. J. Phys., 1996, 49, 1169-80

Kinetic Model of an RF Discharge in Oxygen

X. J. Dai

Plasma Research Laboratory, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia.

Abstract

A kinetic model to assist in understanding the complicated physical and chemical processes occurring in an RF oxygen plasma has been developed. Ten fundamental reaction equations are considered to account for the production and loss processes of the main reactive species. The rate coefficients for the electron impact processes used in the balance equations are calculated using the measured electron energy distribution function. The calculated concentrations of O and O_2^* are compared with experimentally measured values for a range of pressure and RF power. The reasonable agreement between results of the model calculation and the experimental data confirms the validity of the model used.

1. Introduction

The industrial use of plasma oxidation for procedures such as oxidation of semiconductors, photoresist removal in semiconductor devices, and low-temperature ashing is increasing. It is also of special interest in the processing of wool fibre and some polymers, where it can be used to increase the surface energy and thus render the normally hydrophobic surface hydrophilic. A previous paper (Dai *et al.* 1995) has reported the measurement of the concentrations of the main reactive species of interest, namely atomic oxygen O and metastable excited molecular oxygen $O_2(a^1\Delta_g)$, generated by an RF glow discharge in oxygen at pressures (0.005-0.1 mbar) at discharge powers between 50 and 300 W (conditions used during an investigation of plasma processing of wool). To help understand the complicated physical and chemical processes which occur in the plasma, a theoretical model has been developed and used to explain the observed results. The model considers electron collision processes and uses the measured electron concentrations and energy distributions as inputs.

The experimental apparatus and measurement procedure have been described in detail in Dai *et al.* (1995). Fig. 1 shows the essential geometry and the coordinate system used here. The plasma source consists of a glass cylinder, mounted vertically above a continuously pumped stainless steel reaction chamber. As the active species are mainly produced inside the plasma source and then flow into the reaction chamber below, the theoretical model is set up to predict their concentrations inside the plasma source itself using measured values of the electron density and electron energy distribution function. A zero-dimensional (global) model is used, i.e. the rate equations are spatially averaged throughout the plasma source and the temperatures of the neutral particles (O_2, O, O_2^*) are all taken to be equal. Because of the limitations of the experimental equipment, the concentrations of the neutrals could be measured in only one location inside the chamber, 16 cm below the open end of the source, which complicates the comparison between the results of the model and the experimental results. However, since the electron energy distribution inside the source varies little with radius (Dai 1995), and since most of the active species which reach the chamber originate in the source, we should expect the concentration of the neutrals within the chamber to at least follow the same trends as these deduced by modelling

the chamber to at least follow the same *trends* as those deduced by modelling the source plasma. It is also reasonable for us to assume that the active neutrals in the chamber are uniformly distributed, especially in the central region of most interest $[-R_s < (x, y) < R_s]$, where R_s is the radius of the plasma source], since both volume atomic recombination and molecular de-excitation can be neglected at the low pressures used, and the recombination occurs at the walls with low probability (Sabadil and Pfaul 1985; Gousset *et al.* 1989; Donnelly and Rose 1990).



Fig. 1. Geometry of the apparatus and the coordinate system. The plasma source is 300 mm long and 150 mm diameter and the reaction chamber is 650 mm long and 320 mm diameter.

In Section 2, the equations for the most important reactions are described and the fundamental production and loss processes discussed. Reaction rate calculations are presented in Section 3, while Section 4 presents the calculated concentrations of the active species as functions of the experimental parameters. Finally the calculated values of concentrations in the source are compared with the experimental results in the chamber.

2. Principal Species and Their Reaction Equations

While some attempts (e.g. Ichikawa et al. 1989; Laska et al. 1979; Masek and Laska 1980) have been made to model the whole plasma production process for DC discharges, such an approach is far too ambitious and unnecessarily complicated for our purpose. Since this work is predominantly interested in explaining how the reactive species useful for oxidising, O and O_2^* , are generated, the model has concentrated on the relevant dissociation, ionisation and excitation processes which control their formation and loss, starting from a given initial neutral gas filling and using the experimentally measured relationship of the plasma parameters, i.e. charge density and electron energy distribution, to the applied RF power and pressure. The following ten fundamental reaction equations are considered here to describe the production and loss processes of the main species which occur in our plasma:

$$O_2 + e \xrightarrow{K_i} O_2^+ + 2e, \qquad O_2 + e \xrightarrow{K_e} O_2^* + e, \qquad (1,2)$$

$$O_2 + e \xrightarrow{K_d} 2O + e, \qquad O_2 + e \xrightarrow{K_{da}} O + O^-, \qquad (3,4)$$

$$O_2^+ + e \xrightarrow{K_{r_1}} 2O, \qquad O_2^* + e \xrightarrow{K_{r_2}} 2O + e, \qquad (5,6)$$

$$O_2^* + e \xrightarrow{K_{r3}} O_2 + e, \qquad O + O^- \xrightarrow{K_{r4}} O_2 + e, \qquad (7,8)$$

$$O + O + \operatorname{wall} \xrightarrow{K_{w1}} O_2, \qquad O_2^+ + \operatorname{wall} \xrightarrow{K_{w2}} O_2, \qquad (9, 10)$$

where $K_i, K_e, K_d, K_{da}, K_{r1}, K_{r2}, K_{r3}, K_{r4}, K_{w1}$ and K_{w2} are the corresponding reaction rate coefficients.

In the case of atomic oxygen, our experimental results in the chamber showed a high concentration with fractional dissociation, $N[O]/2N[O_2]$, as high as 40% in the optimum pressure range (Dai *et al.* 1995; Dai 1995). Such a high concentration suggests that the atomic oxygen results not only from the direct electron collision dissociation process (3), but also from subsequent dissociation of O_2^+ and O_2^+ both of which are in a higher energy state than O_2 and thus are more easily dissociated by electron collisions (5) and (6). The main loss mechanism for the atomic oxygen is assumed to be by recombination at the walls (9), since gas phase recombination can be neglected in the low pressure range investigated (Glockler and Lind 1939). The loss of O by the detachment reaction (8) can also be neglected since the reaction rate $(3 \cdot 0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1})$ is much smaller than the wall recombination rate (see Section 3).

Although the measured concentration of metastable excited molecular oxygen O_2^* is about one order of magnitude lower than that of atomic oxygen O, it has been suggested that O_2^* might be a useful and selective reagent in some surface reactions (Foner and Hudson 1956). The O_2^* is produced mainly by collisional excitation (2) and is lost principally through electron induced vibrational dissociation into atomic oxygen (6) and by super-elastic collisions with electrons to the ground state (7).

We assume that at our pressures the predominant positive ions in the oxygen discharges are O_2^+ . The O_2^+ is produced mainly by direct ionisation (1), and lost by electron collisional dissociation (5) and by neutralisation at the walls

(10). The values of the positive ion density used in the calculation of the kinetic equations are taken from the experimental data.

Because oxygen is electronegative, it can form negative ions $(O_2^- \text{ and } O^-)$ either by direct attachment or by dissociative attachment (Dreicer 1960), although experimentally we were unable to identify their presence in our plasma. The former process requires a three-body collision involving an electron and two oxygen molecules, which produces an O_2^- ion with the second molecule carrying away the attachment energy. However, the rate for the three-body process is very small (Pace and Lacombe 1978) at our low pressures and the process is therefore neglected. In contrast, dissociative attachment is a two-body process leading to the formation of an O^- ion and an oxygen atom. Charles and Boswell (1995) using an energy selective mass spectrometer observed that the predominant negative ions in an RF oxygen discharge in a similar apparatus to ours are O^- . Therefore, dissociative attachment from the ground state has been considered to be the main source of negative ions (4). Their principal loss mechanism is by collisional detachment with atoms (8).



Fig. 2. Electron energy distribution function in the source.

3. Calculation of Reaction Rates

Provided the relevant cross sections are known, all the reaction rates for the electron collision processes (1)-(8) described above can be calculated through the following integration:

$$K_j = \int_0^\infty \sqrt{(E/2m)} \sigma_j(E) f(E) dE , \qquad (11)$$

where E is the electron energy, f(E) is the electron energy distribution function (EEDF), and $\sigma_j(E)$ is the appropriate cross section. The EEDF in our plasma has been measured in detail using a Langmuir probe as described in Dai (1995). Fig. 2 shows a typical electron energy distribution function obtained in the source.

The dots are experimental data and the solid line is the curve of best fit to the function $f(E) = a\sqrt{E}\exp(-bE^c)$ (Rundle *et al.* 1973). It is very interesting to note that the measured EEDF is intermediate between the Maxwellian and Druyvesteyn distributions (see Fig. 3).



Fig. 3. Comparison of the measured EEDF with Maxwellian and Druyvesteyn functions in the source.

Only four of the cross sections needed, corresponding to ionisation (1) (Rapp and Englander-Golden 1965), excitation (2) (Luft 1975), dissociation (3) (Konishi *et al.* 1970), and dissociative attachment (4) (Rapp and Briglia 1965), are available in the literature, and they are reproduced in Fig. 4. For these processes the reaction coefficients (K_i, K_e, K_d, K_{da}) were obtained by numerical integration of (11). Notice that the cross section for the dissociative attachment of O₂ is much smaller than those for its ionisation and dissociation and that direct dissociation is the main process for producing O in the electron energy range of interest. As we could not find the cross sections corresponding to equations (5)–(8) in the literature, the reaction coefficients $(K_{r1}, K_{r2}, K_{r3}, K_{r4})$ have been taken directly from the references shown, in which a Maxwellian distribution has been assumed. Table 1 lists the reaction coefficients used in this model.

When the mean free path (λ) of O is smaller than the source radius R_s , K_{w1} is obtained by

$$K_{w1} \approx \frac{1}{\tau_a} \,, \tag{12}$$

where τ_a is the confinement time of the atomic oxygen, which can be derived from (Delcroix 1968)

$$\tau_a = \frac{\Lambda^2}{D} = \Lambda^2 \frac{M_a \nu_a}{k_B T_a} \,, \tag{13}$$



Fig. 4. Cross sections for ionisation, dissociation excitation, and dissociative attachment as a function of the electron energy of oxygen.

Table	1.	Reaction	coefficients
-------	----	----------	--------------

Reaction	Reaction coefficient $(cm^3 s^{-1})$	Reference
(1) (2) (3) (4) (5) (6) (7) (8)	$\begin{split} K_i &= 2 \cdot 0 \times 10^{-9} \\ K_e &= 4 \cdot 87 \times 10^{-10} \\ K_d &= 9 \cdot 0 \times 10^{-9} \\ K_{da} &= 3 \cdot 9 \times 10^{-11} \\ K_{r1} &= 2 \cdot 0 \times 10^{-7} \\ K_{r2} &= 1 \cdot 5 \times 10^{-9} \\ K_{r3} &= 1 \cdot 4 \times 10^{-9} \\ K_{r4} &= 3 \cdot 0 \times 10^{-10} \end{split}$	This work This work This work Wills <i>et al.</i> (1970) Fournier (1983) Masek <i>et al.</i> (1978) Fehsenfeld <i>et al.</i> (1966)

where T_a is the temperature of the atoms of mass M_a (here assuming $T_a = T_g$), $\nu_a = v_a/\lambda$, $v_a = \sqrt{8kT_a/\pi M_a}$ is the mean thermal velocity of the oxygen atoms, and Λ is the diffusion length. For a cylindrical system, Λ is given by (Brown 1966)

$$\frac{1}{\Lambda^2} = \frac{2 \cdot 405}{R_s}^2 + \frac{\pi}{L}^2, \tag{14}$$

where L is the length of the source tube.

If $\lambda \geq R_s$, K_{w1} is calculated using the relation (Frimer 1985)

$$K_{w1} = \frac{\gamma v_a}{2R_s} \,, \tag{15}$$

where γ is the surface recombination coefficient of oxygen atoms at the source wall (Pyrex glass). The value of γ ($\simeq 5 \times 10^{-3}$) is taken from experiments described by Gousset *et al.* (1989), which used the same material for the discharge tube as ours. From equation (15), we have $K_{w1} = 24 \text{ s}^{-1}$.

Kinetic Model of RF Discharge

Although λ is a little smaller than R_s in the pressure range of interest $(5 \times 10^{-2} - 10^{-1} \text{ mbar})$, the value of K_{w1} changes little from the value obtained from (15). In order to simplify the calculation of the rate equations, we take the value of $K_{w1} = 24 \text{ s}^{-1}$.

The positive ion recombination rate coefficient at the wall K_{w2} is calculated from the relation (Lee *et al.* 1993)

$$K_{w2} = \frac{2V_{B,O_2^+}(R_s^2 h_L + R_s L h_R)}{R_s^2 L}, \qquad (16)$$

where $V_{B,O_2^+} = \sqrt{kT_e/M_i}$ is the Bohm velocity for O_2^+ ions, with M_i the mass of the O_2^+ ion. The coefficients h_L and h_R are respectively (Lieberman and Lichtenberg 1994)

$$h_L = N_{s,axial} / N_i = 0.86 / \sqrt{3.0 + 2L/\lambda_i} , \qquad (17)$$

$$h_R = N_{s,radial}/N_i = 0.8/\sqrt{4.0 + R_s/\lambda_i}, \qquad (18)$$

where $N_{s,axial}$ and $N_{s,radial}$ are local values of sheath-edge ion densities in the axial and radial directions respectively, and λ_i is the mean free path between the collisions of O_2^+ and O_2 . The values of K_{w2} are between $5 \cdot 8 \times 10^4$ and $3 \cdot 1 \times 10^4$ s⁻¹ for the pressure range 0.005 to 0.1 mb.

4. Rate Equations, Results of Calculation and Comparison with Experiments

(4a) Rate Equations

0.37

The concentrations of the main species can be calculated by solving the rate equations. To complete the rate equations for the reactions (1)–(10), we must include the flow in our apparatus between the plasma source and the reaction chamber. In order to simplify the rate equations, the flow terms are considered only for the atomic oxygen because its measured concentration is much higher than other species. We consider two flow terms in this calculation, from the source to the chamber and vice versa. The coefficients A and B in equation (19) are taken as flow rate coefficients which are determined by the thermal velocity of the particle as well as by the geometry of the source and the chamber. At room temperature, the values of A and B in our conditions are 15.37 and 36 s⁻¹ respectively. Under those assumptions described in the Introduction, the rate equations for the main species in the plasma, from the expressions given earlier, can be written as

$$\frac{\partial N_1}{\partial t} = 2K_d N_2 N_e + K_{da} N_2 N_e + 2K_{r1} N_i N_e + 2K_{r2} N_m N_e + B N_{1c} - K_{r4} N_1 N_n - K_{w1} N_1 - A N_1 , \qquad (19)$$

$$\frac{\partial N_2}{\partial t} = K_{r3} N_m N_e + K_{r4} N_1 N_n + \frac{1}{2} K_{w1} N_1 + K_{w2} N_i - (K_i + K_e + K_d + K_{da}) N_2 N_e , \qquad (20)$$

$$\frac{\partial N_m}{\partial t} = K_e N_2 N_e - K_{r2} N_m N_e - K_{r3} N_m N_e , \qquad (21)$$

$$\frac{\partial N_n}{\partial t} = K_{da} N_2 N_e - K_{r4} N_1 N_n \,, \tag{22}$$

where AN_1 and BN_{1c} describe respectively the flow from the source to the chamber and vice versa. Here N_{1c} is the experimentally measured atomic oxygen concentration in the chamber. No equation for N_i is required since this is taken as measured. The other symbols in the above equations designate the respective particle number densities as shown in Table 2.

Table 2. Symbols for the respective particle

number densities			
Species	Symbol		
Electron	Ne		
O_2^+	N_i		
0	N_1		
O2	N_2		
O_2^*	N_m		
O ⁻	N_n		
Total neutral density	No		

In addition, two other conditions must be met, namely those of charge neutrality and of mass conservation:

$$N_i = N_e + N_n \,, \tag{23}$$

$$N_0 \simeq N_2 + N_m + \frac{1}{2}N_1 \,, \tag{24}$$

where N_0 is the total number density of the particles and $N_0 = p/k_B T_g$, and where p is the filling gas pressure and T_g the gas temperature. In (24), N_i and N_n are neglected since their densities ($\sim 10^8 - 10^{10} \text{ cm}^{-3}$) are much much lower than the neutrals ($\sim 10^{14} - 10^{16} \text{ cm}^{-3}$).

In a steady state $\partial/\partial t = 0$, the above rate equations reduce to

$$2K_d N_2 N_e + K_{da} N_2 N_e + 2K_{r1} N_i N_e + 2K_{r2} N_m N_e + B N_{1c}$$
$$-K_{r4} N_1 N_n - K_{w1} N_1 - A N_1 = 0, \qquad (25)$$

$$K_{r3}N_mN_e + K_{r4}N_1N_n + \frac{1}{2}K_{w1}N_1 + K_{w2}N_i$$
$$-(K_i + K_e + K_d + K_{da})N_2N_e = 0, \qquad (26)$$

$$K_e N_2 N_e - K_{r2} N_m N_e - K_{r3} N_m N_e = 0, \qquad (27)$$

$$K_{da}N_2N_e - K_{r4}N_1N_n = 0, (28)$$

The computer software 'Mathematica' was used to solve these equations and calculate the concentrations of O, O_2^* , O_2 , O^- and e.



Fig. 5. Comparison with the experimental data of the calculated concentration of (a) atomic oxygen and (b) metastable molecular oxygen in the source as a function of pressure in the chamber.

(4b) Results and Comparison with Experiments

The effects of pressure in the chamber on the concentrations of atomic oxygen in the source as derived from the model calculations are compared with the experimental data in Fig. 5*a*. They clearly show the same general trend. From the rate balance equations, it can be seen that O is produced by several reaction routes. The concentration of atomic oxygen depends not only on N_e and $N[O_2]$ but also on $N[O_2^+]$ and $N[O_2^*]$. As we know, within the pressure range used, N_e and $N[O_2^+]$ decrease while $N[O_2]$ and $N[O_2^*]$ increase as the pressure increases. This results in a peak value in N[O] within the pressure range investigated. It also provides a means to choose the optimum experimental parameters for the plasma processing. A similar comparison for metastable molecular oxygen is shown in Fig. 5b. The values from the model calculation and the experimental data also show the same general trend. However, from Fig. 5 it can be seen that the values calculated in the source and the ones measured in the chamber diverge at higher pressure. As low pressure has been assumed in the model calculation, the agreement between theory and experiment at lower pressure should be better than at higher pressure in both figures for a valid comparison.



Fig. 6. Comparison of the calculated atomic oxygen concentration as a function of pressure using our measured EEDF with that for a Maxwellian distribution.



Fig. 7. Comparison with the experimental data of the calculated atomic oxygen concentration in the source as a function of the charged particle density in the chamber.

It is interesting to compare the concentration of atomic oxygen as a function of pressure derived from the model calculations using our measured electron energy distribution function and that resulting from a Maxwellian distribution with the same mean energy. As shown in Fig. 6, there is only a small difference between them. Thus, although the different EEDF lead to different individual reaction rates, overall these result in only a minor effect on the computed atomic oxygen density.

Fig. 7 shows the effects of the charged particle density on the concentration of atomic oxygen as calculated by the model, compared with the experimental data. The trend is the same in both cases: N[O] increases for ion densities up to about 5×10^9 cm⁻³ (corresponding to 100 W RF power), while increasing the ion densities by using higher RF powers has little effect. This saturation is a consequence of the near complete oxygen dissociation in the discharge. The ratio of $N[O]/2N[O_2]$ indicates that about 80% of the oxygen *in the source* is dissociated at higher powers when p = 0.03 mbar, which indicates that only low RF power is needed to produce a high concentration of atomic oxygen.

5. Summary

A kinetic model which describes the plasma chemical reactions occurring in an RF induced oxygen discharge has been successfully developed. It has been shown that the production of the principal oxidising reactive species can be adequately described by a relatively small number (ten) of fundamental production and loss processes. Although the results of the model calculation are strictly limited to the discharge itself, while the measurements can only be made at a location at some distance away from the discharge, both results show the same trend. The dominant process for producing atomic oxygen is shown to be that of direct dissociation by electron impact. The model calculations reproduce several features of the observations: for example, the maximum in the atomic oxygen concentration which occurs at a pressure of about 0.05 mbar; the linear dependence of the concentration of metastable molecular oxygen with gas pressure; and the saturation of the atomic oxygen concentration at high RF power. The model provides a means to optimise the experimental parameters for plasma processing and should assist in the design of treatment equipment.

Acknowledgments

The author is grateful to Dr A. Perry for his many very useful and helpful discussions; to Professor S. M. Hamberger for his guidance and very helpful comments; to Dr I. J. Donnelly of the Australian Nuclear Science and Technology Organisation and Dr C. Lee of the University of California at Berkeley for valuable discussions. This research was funded by the Australian Wool Research and Promotion Organisation (now the International Wool Secretariat).

References

Brown, S. C. (1966). 'Introduction to Electrical Discharges in Gases' (John Wiley: New York).
Charles, C., and Boswell, R. W. (1995). J. Vac. Sci. Technol. A 13, 2067.
Dai, X. J. (1995). Ph.D. Thesis, Australian National University.
Dai, X. J., Hamberger, S. M., and Bean, R. A. (1995). Aust. J. Phys. 48, 939-51.
Delcroix, J. L. (1968). 'Plasma Physics', Vol. 2 (John Wiley: New York).

- Donnelly, I. J., and Rose, E. K. (1990). Aust. J. Phys. 43, 45.
- Dreicer, H. (1960). Phys. Rev. 117, 343.
- Fehsenfeld, F. C., Ferguson, E. E., and Schmeltekopf, A. L. (1966). J. Chem. Phys. 45, 1844.
- Foner, S. N., and Hudson, R. L. (1956). J. Chem. Phys. 25, 601.
- Fournier, G. (1983). 'Reactive dans les Plasmas' (Paris).
- Frimer, A. A. (1985). 'Singlet Oxygen', Vol. 1 (CRC Press: Boca Raton, Fla.).
- Glockler, G., and Lind, S. C. (1939). 'The Electrochemistry of Gases and other Dielectrics' (John Wiley: New York).
- Gousset, G., Touzeau, M., Vialle, M., and Ferreira, C. M. (1989). Plasma Chem. Plasma Proc. 9, 189–206.
- Ichikawa, Y., Wu, R. L. C., and Kaneda, T. (1989). J. Appl. Phys. 67, 108.
- Konishi, A., Wakiya, K., Yamamoto, M., and Suzuki, H. (1970). J. Phys. Soc. Jpn 29, 526.
- Laska, L., Masek, K., and Ruzicka, T. (1979). Czech. J. Phys. B 29, 498.
- Lee, C., Vahedi, V., and Lieberman, M. A. (1993). Proc. Conf. on Gaseous Electronics, Montreal.
- Lieberman, M. A., and Lichtenberg, A. J. (1994). 'Principles of Plasma Discharges and Materials Processing' (John Wiley: New York).
- Luft, P. E. (1975). JILA Information Center Rep. No. 14, University of Colorado, Boulder.
- Masek, K., and Laska, L. (1980). Czech. J. Phys. B 30, 805.
- Masek, K., Laska, L., and Ruzzcka, T. (1978). Czech. J. Phys. B 28, 1321-34.
- Pace, P., and Lacombe, M. (1978). IEEE J. Quant. Elect. QE-14, 263-74.
- Rapp, D., and Briglia, D. D. (1965). J. Chem. Phys. 43,1480-9.
- Rapp, D., and Englander-Golden, P. (1965). J. Chem. Phys. 43, 1464-79.
- Rundle, H. W., Clark, D. R., and Deckers, J. M. (1973). Can. J. Phys. 51, 144.
- Sabadil, H., and Pfau, S. (1985). Plasma Chem. Plasma Proc. 5, 67.
- Wills, C., Boyd, A., Young, M., and Armstrong, D. (1970). Can. J. Chem. 48, 1505-14.

Manuscript received 2 February, accepted 6 June 1996