Remote Microwave Plasma Enhanced Chemical Vapour Deposition of SiO₂ Films : Oxygen Plasma Diagnostic

C. Regnier, J. Desmaison, P. Tristant, D. Merle

► To cite this version:

C. Regnier, J. Desmaison, P. Tristant, D. Merle. Remote Microwave Plasma Enhanced Chemical Vapour Deposition of SiO₂ Films : Oxygen Plasma Diagnostic. Journal de Physique IV Proceedings, 1995, 05 (C5), pp.C5-621-C5-628. 10.1051/jphyscol:1995574 . jpa-00253936

HAL Id: jpa-00253936

<https://hal.science/jpa-00253936>

Submitted on 1 Jan 1995

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Remote Microwave Plasma Enhanced Chemical Vapour Deposition of SiO₂ Films: Oxygen Plasma Diagnostic

C. Regnier, J. Desmaison, P. Tristant and D. Merle

Laboratoire des Matériaux Céramiques et Traitements de Surface, URA 320 du CNRS, Université de Limoges, 123 av. Albert Thomas, 87060 Limoges cedex, France

Abstract : Silicon oxide is deposited by remote microwave plasma enhanced chemical vapour deposition (RMPECVD). The silica films are produced by exciting oxygen in a microwave discharge while a mixture of 5% of silane diluted in argon is introduced downstream. In the afterglow, double Langmuir probe measurements and rotational temperatures deduced from optical emission spectroscopy (OES), show that the electron energy is transferred to the gas when the pressure increases (19 - 26 Pa). Therefore the electronic temperature decreases from 22000 to 11000 K and the gas temperature increases from 400 to 500 K. Moreover the microwave power (180 - 480 W) has an influence on the deposition rate and on the quality of SiO₂ coatings (density and etch rate in an HF solution). This effect can be correlated with the increase in the electron density ($0.7 \cdot 10^{10}$ to $3.7 \cdot 10^{10}$ cm⁻³) and of the gas temperature (400 to 460 K).

1. INTRODUCTION

Plasma enhanced chemical vapour deposition (PECVD) is a process developed for the production of coatings over temperature sensitive substrates [1-2]. In this technique, the reaction energy is supplied by plasma excitation instead of thermal activation. Indeed, the energy of the electrons in the discharge corresponds to a temperature of the order of 20000 K. Nevertheless the gas temperature remains in the range of 25-350°C avoiding excessive heating of the substrate.

Two types of reactors are using microwave discharge : direct PECVD and remote PECVD [3]. In the former, the substrate is placed in the plasma where all the process gases are excited. So there is a large variety of chemical and ionic species, and it is quite difficult to distinguish the influence of process parameters on the quality of the coatings. On the contrary, in the latter method the substrate is placed in the afterglow where no high energy electron is present. In addition only some of the gases are subjected to direct plasma excitation while the others are fed downstream. This results in the formation of specific precursor species. Moreover it allows independent control of the flux and the energy of active species and simplification of the reaction pathways.

In-situ optical emission spectroscopy (OES) is one of the best suited tool for the detection in the afterglow [4-6] of radiative species electronically excited. Furthermore, analysis of the emission spectra of diatomic molecules such as N₂ can provide rotational temperature information which are good estimates of the true gas temperature [7-8]. Electrostatic Langmuir probes are also of interest in order to estimate electronic temperatures and densities. But their theory is complex and interpretation of the results must be conducted carefully [9-11].

In this paper, the deposition of silicon oxide by remote microwave plasma enhanced chemical vapour deposition (RMPECVD) is described. The influence of plasma parameters on the deposition of SiO₂ is detailed. Then the effects of pressure and microwave power on the oxygen plasma are studied using Langmuir double probe and OES measurements.

2. EXPERIMENTAL

The plasma reactor and its associated diagnostic equipment is shown schematically in figure 1.

Figure 1 : Experimental set-up

The oxygen plasma is generated in a quartz tube where the microwave power (2.45 GHz) is coupled by means of a rectangular wave guide. The plasma, sustained by a surface wave along the quartz tube, expands in the afterglow region. A mobile short cut and a triple stub tuner provide the impedance matching that minimises the reflected power.

The silane is fed into the deposition chamber through a circular injector located under the glow plasma region and a few centimetres above the substrate. The samples are placed on a substrate-holder which can be RF biasable and heated up to 600°C.

Before each run the reactor is evacuated with a turbomolecular pump to a pressure of 10^{-4} Pa. The deposition pressure, measured with a Baratron gauge (precision : 0.1 Pa), is around 20 Pa.

To monitor the afterglow, a 1 meter focal length monochromator (Jobin-Yvon THR 1000), with a 1200 gr/mm grating and a liquid nitrogen cooled Coupled Charged Device (CCD), is connected to the plasma reactor by means of a quartz optical fibre.

To measure the electron temperature and concentration as a function of position in the afterglow, a Langmuir double probe is used. It is made of two platinum wires 0.1 mm in diameter and 2 mm spaced which are 6 mm exposed to the plasma. The probe is protected by a glass/alumina assembly which can be moved radially and longitudinally along the afterglow. A voltage (-40, +40 V) is applied on the two probes and the current is measured through a 10 k Ω resistance. The probe characteristics $I = f(V)$ are automatically recorded by means of digital voltmeters interfaced with a computer.

3. RESULTS AND DISCUSSION

3.1 Parametric study of the SiO₂ deposition

Silica films are produced by exciting oxygen in the microwave discharge while a mixture of 5% of silane in argon is introduced in the afterglow. The typical conditions of deposition are [12] :

- Pressure : 26 Pa,
- O₂ flow rate : 300 sccm,
- 5% SiH₄-Ar flow rate : 300 sccm,
- Microwave power : 380 W,
- Temperature : 350 °C.

The substrates, single crystal silicon wafers, are heated in order to enhance the desorption of by-products and hence to improve the film density [1,2]. Typical deposition rates obtained are about $0.5 \mu\text{m}/\text{min}$.

For each experiment the substrate is weighed before and after deposition. The thickness is obtained with a profilometer after a step being etched in a P-etch solution ($\text{HF} : \text{HNO}_3 : \text{H}_2\text{O} ; 1.5 : 1 : 30$) [13]. Density and etch rate are also deduced with 10 % of accuracy.

The effects of the pressure and of the microwave power are studied by changing separately the value of these parameters while the others are maintained to the values described before.

3.1.1 Effect of the pressure

The deposition rate is weakly dependent on the pressure (fig. 2). But the density is improved and reaches the value of 2.2 which is the theoretical density for amorphous silica. This indicates that the deposited mass increases with pressure.

No significant variation of the etch rate can be observed. The values remain almost constant ($12 \text{ \AA}/\text{s}$), and indicate that the coatings are of good quality [14].

3.1.2 Effect of the microwave power

The deposition rate increases with the microwave power and at the same time no strong variation of the density of the films can be observed (fig. 3). In addition, for a low value of the microwave power, the etch rate is very high. This is consistent with the low value of the density for this point. Indeed it is well known that chemical etch rate in an HF solution is a good indicator of the quality of the films. The value of $11 \text{ \AA}/\text{s}$ obtained for 380 W is a good result compared with the etch rate of thermal SiO_2 which is $2 \text{ \AA}/\text{s}$ [13].

Figure 2 : Thickness, density and etch rate versus pressure

Figure 3 : Thickness, density and etch rate versus microwave power

3.2 Langmuir double probe measurements

3.2.1 Probe theory and limitation

The principle of electrostatic probes is based upon the fact that a conductor immersed in a plasma collects a current I that depends on its applied voltage V [15]. A Langmuir double probe consists of two single probes similar in shape and size biased one with respect to the other. Hence it is a "non perturbing system" that does not need any reference electrode, $I = f(V)$ is the double probe characteristic (DPC) where I represents the sum of ionic and electronic currents.

The study of the DPC is complex, so simple geometric shape (such as cylindrical one) must be chosen. Furthermore, one had to make sure that the basic hypotheses of the Langmuir theory [16] are verified :

- the plasma is assumed to be infinite, homogeneous and quasi neutral in the absence of the probe,
- electrons and ions have Maxwellian velocity distributions with $T_e \gg T_i$,
- the mean free paths of electrons λ_e and ions λ_i are large compared to the characteristic length of the system,
- each charged particle hitting the probe is absorbed and doesn't react with it,
- the region in front of the probe surface, where the plasma parameters deviates from their values in the undisturbed plasma, is confined to a space charge sheath with a well defined boundary. Outside this boundary the space potential is constant,
- the sheath thickness is small compared to the lateral dimension of the probe.

To determine the electronic temperature from the DPC, Polman [17] compared two methods (Burrows, Johnson and Malter). He showed that agreement between the results of the two methods is reasonably good considering 10 % uncertainty. We have chosen Burrows' method because it appears to be more insensitive to the way of extrapolation of the DPC. Observing that there is only one inflection point in the DPC (fig. 4), Burrows [18] demonstrated that electronic temperature T_e could be calculated using the following expression :

$$\frac{k \cdot T_e}{e} = \frac{(I_{+1s} + I_{+2s}) - 0.85(S_1 \cdot \Delta V_1 + S_2 \cdot \Delta V_2)}{4 \left(\frac{dI_d}{dV_d} \right)_i - (S_1 + S_2)}$$

where :

- I_{+1s} and I_{+2s} are the ionic currents at saturation,
- ΔV_1 and ΔV_2 are the potential variations required to decrease to zero the electron current from the value in the inflection point of the DPC,
- S_1 and S_2 are equal to the slopes of the saturation currents,
- $\left(\frac{dI_d}{dV_d} \right)_i$ is the derivative of the curve in the inflection point,
- the subscript 1 and 2 refer to the two probes.

Figure 4 : Typical double probe characteristic (DPC)

According to Kagan and Perel [17], the electronic density n_e is obtained from the ionic current at the inflection point of the DPC, by a linear extrapolation of the saturation current so that :

$$I_i = c \cdot e \cdot n_e \cdot A_s \left(\frac{2 \cdot k \cdot T_e}{m_i} \right)^{1/2}$$

where :

- c is a constant that depends on T_e / T_i ($0.29 < c < 0.37$ for a cylindrical probe),
- m_i is the O_2^+ mass,
- A_s is the area of the sheath surface, often taken equal to the probe area.

3.2.2 Probe results

A typical DPC obtained with our Langmuir double probe is shown figure 4. The symmetry of this curve indicates that the probes used during the experiments are nearly equal in size and shape, and that they are located at positions where the plasma parameters are approximately equal. Consequently the hypotheses made in the previous paragraph are verified and the measurements accuracy is estimated to 10 %.

Let us determine the influence of the main parameters of the plasma when it is created using typical deposition conditions (see § 3.1), with the probe situated at 8 cm below the wave guide.

Figure 5 : Electronic density and temperature versus pressure

Figure 6 : Electronic density and temperature versus microwave power

Figure 7 : Electronic density and temperature versus wave guide to probe distance

3.2.2.1 Effect of the pressure : When the pressure increases, the mean free path of the plasma species decreases. The length of the plasma is reduced and the probe collects less electrons. By extension the electronic density decreases from $15 \cdot 10^{10}$ to $0.5 \cdot 10^{10} \text{ cm}^{-3}$ (fig. 5). On the other hand, the energy transfer being improved, the electronic temperature is lowered (from 22000 K to 11000 K). The electrons are progressively thermalized.

3.2.2.2 Effect of the microwave power : When the microwave power increases from 180 to 480 W, the electronic density increases linearly from $0.7 \cdot 10^{10}$ to $3.7 \cdot 10^{10} \text{ cm}^{-3}$ (fig. 6). This indicates that the microwave energy transfer is efficient. The microwaves are directly responsible for the creation of high energy electrons in the discharge. However, the electronic temperature remains rather constant. It shows that an increase in microwave power increases the number of electrons without significantly changing their energy represented by their temperature [19].

3.2.2.3 Effect of the distance between the wave guide and the probe : A longitudinal study of the oxygen plasma (fig. 7) indicates that when the distance increases from 1 to 12.5 cm, the electronic density decreases from $9 \cdot 10^{11}$ to $0.7 \cdot 10^{10} \text{ cm}^{-3}$. In fact the electronic density decreases from a maximum into the

wave guide to a value below which the surface wave does not propagate. This critical density n_{ec} can be obtained with the expression :

$$\omega_p = \left(\frac{e^2 \cdot n_{ec}}{m_e \cdot \epsilon_0} \right)^{1/2} = \omega (1 + \epsilon_\gamma)^{1/2}$$

where :

- ω_p is the plasma pulsation,
- ω is the microwave pulsation,
- ϵ_γ is the permittivity of the quartz tube equal to 3.8.

At a frequency of 2.45 GHz, the value of n_{ec} is $3.6 \cdot 10^{11} \text{ cm}^{-3}$. This value is obtained in our experimental conditions for a distance of 5 cm down to the wave guide. Below this distance, we can consider that the probe is in close post-discharge. Finally it can be seen in figure 7 that as the plasma expands in the afterglow, the electron are thermalized so their temperature decreases linearly.

3.3 Rotational temperature

When the energetic difference between rotational levels of a same vibration electronic state are weak (10^{-2} eV) and close to the translation energy of the molecules, the exchanges between rotation molecules and translation molecules are fast and efficient. So a rotational temperature can be defined corresponding to a statistical distribution of the rotational energy level and this rotational temperature can be estimated to the true gas temperature [21].

3.3.1 Formalism of the calculation

The intensity of each transition of the rotational distribution taking place between the upper state with a kinetic momentum J and a rotational energy F_J , and the lower state with a kinetic momentum J' is obtained by [21] :

$$I_{JJ'} = C \cdot S_{JJ'} \cdot \exp\left(\frac{-F_J \cdot h \cdot c}{k \cdot T_{rot}}\right)$$

$$\text{with } F_J = B_{v=0} \cdot J(J+1) + D_{v=0} \cdot J^2(J+1)^2$$

where :

- $S_{JJ'}$ is the Höln-London factor representing the transition probability,
- $B_{v=0}$ and $D_{v=0}$ are the rotational constants of the upper state of vibrational momentum $v = 0$.

Therefore the slope of the plot $\ln\left(\frac{I_{JJ'}}{S_{JJ'}}\right)$ against F_J is equal to $-\frac{hc}{kT_{rot}}$.

3.3.2 Rotational temperature in O_2 discharge

The measurement of T_{rot} in our discharge is obtained from the atmospheric band corresponding to the transition $O_2(b^1\Sigma_g^+, v=0 \rightarrow X^3\Sigma_g^-, v=0)$ recorded between 758 and 770 nm.

This molecular band is emitted with sufficient intensity so that the spectral resolution (0,03 nm) of our experimental set-up allows us to distinguish the fine structure of this band (fig. 8). Finally the calculation of T_{rot} is achieved using the $^P P$ and $^P Q$ branches of the rotational distribution identified on the recorded spectra of figure 8. For the $^P P$ and $^P Q$ branches, $S_{JJ'}$ are respectively given by [20] :

$$S_{JJ'} = 0.5(J+0.75) \text{ and } S_{JJ'} = 0.5(J+1)$$

Otherwise, for this band, the values of $B_{v=0}$ and $D_{v=0}$ are given by :

$$B_{v=0} = 1.39138 \text{ cm}^{-1} \text{ and } D_{v=0} = 5.486 \cdot 10^{-6} \text{ cm}^{-1}$$

Figure 8 : Rotational distribution of $b^1\Sigma_g^+$ state measured in our oxygen discharge with a typical plot of $\text{Ln}\left(\frac{I_{JJ'}}{S_{JJ'}}\right) = f(F_J)$

Figure 9 : Gas temperature versus pressure and microwave power

3.3.3 Results

The measurements are done in the afterglow, just above the injector. The plasma is created using typical deposition conditions (see § 3.1). Figure 8 shows a typical plot of $\text{Ln}\left(\frac{I_{JJ'}}{S_{JJ'}}\right) = f(F_J)$. The regression coefficient of this straight line is about 0.995, measurements accuracy is estimated to 5 %.

3.3.3.1 Effect of the pressure : When the pressure increases, the number of collisions between different plasma species increases. So the energy exchanges between "hot particles" (the electrons) and "cold species" (the gas molecules) are improved. Hence the electrons energy is transferred to the gas and its temperature increases (Fig. 9). This fact is confirmed by the previous decrease observed for the electronic temperature.

3.3.3.2 Effect of the microwave power : The gas temperature increases linearly with the microwave power (Fig. 9). This is not a surprising result because as the power transferred to the gas increases, its temperature follows the same variation. But at this point of the study, we cannot know whether the microwave power transfer more energy with or without changing the length of the discharge.

3.4 Comparison of the results

Concerning the increase in the electronic density with the microwave power, Zellagui [20] has explained that it is due to an extension of the plasma. In fact, in the wave guide, the plasma absorbs more energy per unit of length. However, the composition of the discharge end does not vary much but its position is moved farther below. So because our diagnostic location is fixed, the part of the plasma analysed has got more energy. That is the reason why the electronic density and the gas temperature increase. Finally due to a good energy transfer, the microwave power enhances the coating deposition rate. This result is confirmed by the poor properties obtained for silica film deposited at low power (180 W).

Langmuir double probe and rotational temperature measurements have allowed us to verify that an increase in the pressure reduces the total length of the plasma. As a result of the numerous collisions, the electronic temperature and density decrease while the gas temperature increases. Concerning the effect of the pressure on the deposition reaction, it is difficult to conclude at this point of the study. Indeed when

the pressure increases the energy of the electrons is transferred to the gas. But it would be interesting to gain a better understanding of the gas composition.

4. CONCLUSION

This paper shows the strong influence of the microwave power on the excitation of the oxygen plasma and as a result on the deposition kinetics and quality of the silica films deposited in a RMPECVD reactor. Moreover, double Langmuir probe and rotational temperature measurements have allowed us to determine that the electron energy is transferred to the gas as the pressure increases. Further study will concern the modelling of the gas phase composition of an oxygen plasma and its coupling with a microwave field.

ACKNOWLEDGEMENTS

The authors wish to thank Pr G. Gousset (L.P.G.P. Orsay, France) and Dr J. L. Jauberteau and M. J. Cinelli (L.M.C.T.S. Limoges, France) for helpful discussions concerning respectively, the oxygen plasma and the use of Langmuir probes.

REFERENCES

- [1] H. Del Puppo, T. Sindzingre, L. Peccoud, J. Desmaison, *J. Phys. IV* **3** (1991) C2421-C2428
- [2] H. Del Puppo, J. Desmaison, L. Peccoud, *J. Phys. IV* **3** (1993) 241-246
- [3] G. Lucovsky, D. V. Tsu, R. A. Rudder, J. Markunas, *Thin film process II* (editor J. L. Vossen, W. Kern, Academic press inc., San Diego, 1991) pp 565-619
- [4] M. Ducrepin, J. Dike, R. B. Siegel, V. Tarnovsky, K. Becker, *J. Appl. Phys.* **73**(11) (1993) 7203-7206
- [5] D. V. Tsu, G. N. Parsons, G. Lucovsky, M. W. Watkins, *J. Vac. Sci. Technol. A* **7**(3) (1989) 1115-1123
- [6] A. Banerjee, T. DebRoy, *J. Vac. Sci. Technol. A* **10**(6) (1992) 3395-3400
- [7] T. A. Cleland, D. W. Hess, *J. Appl. Phys.* **64**(3) (1988) 1068-1077
- [8] M. Touzeau, M. Vialle, A. Zellagui, G. Gousset, M. Lefebvre, M. Péalat, *J. Phys. D, Appl. Phys.* **24** (1991) 41-47
- [9] M. J. Kushner, *J. Appl. Phys.* **53**(4) (1982) 2939-2946
- [10] Ta-Chin Wei, J. Phillips, *J. Appl. Phys.* **74**(2) (1993) 825-831
- [11] L. J. Overzet, M. B. Hopkins, *J. Appl. Phys.* **74**(7) (1993) 4323-4330
- [12] C. Tixier, C. Regnier, J. Desmaison, D. Merle, J. F. Goujoud, "Remote microwave plasma enhanced chemical vapour deposition : application to silicon dioxide and diamond like carbon layers", *Ceramic films and coatings*, Sheffield 19-20 december 1994, British ceramic proceedings (Institute of materials, London, 1995), in press
- [13] S. K. Ray, C. K. Maiti, S. K. Lahiri, N. B. Chakraborti, *Semicond. Sci. Technol.* **5** (1990) 33-56
- [14] T. V. Herak, T. T. Chau, D. J. Thomson, S. R. Meija, D. A. Buchanan, K. C. Kao, *J. Appl. Phys.* **65**(6) (1989) 2457-2463
- [15] P. M. Chung, L. Talbot, K. J. Touryan, *Electric probes in stationary and flowing plasmas* (Springer-Verlag, Berlin ; Heidelberg ; New-York, 1975)
- [16] W. Lochte-Holtgreven, *Plasma diagnostics* (North-Holland Publishing Company, Amsterdam, 1968) pp. 171-177 ; 668-731
- [17] J. Polman, *Physica* **34** (1967) 317-324
- [18] K. M. Burrows, *Australian J. Phys.* **15** (1962) 162-168
- [19] P. Brassen, F. J. M. J. Maessen, *Spectrochimica Acta* **29B** (1974) 203-210
- [20] A. Zellagui, PhD Thesis, Université Paris-Sud, (1991)
- [21] R. Safari, PhD Thesis, Université Paris-Sud, (1992)