TEOS / O_2 MMP-DECR plasma deposition . Growth processes and analytical modeling.

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Abstract

The interaction between the gaseous phase of a DECR plasma using a TEOS and O_2 mixture and a silicon surface has been studied. The growth rate measurements with respect to the different parameters of the discharge (Pressure, Power, TEOS/O_2 ratio) give experimental values which are correlated with a semi-empirical model of growing process. Consequently, a few references are available in the literature about this type of surface chemistry. Then, some assumptions have been made, about the phenomena occuring in the coating process, from experimental data achieved in the DECR reactor, such as: Gaseous phase analysis by mass-spectroscopy. Furthermore, a good agreement between the model and the experimental growth rates has been noted.

Introduction

Plasma reactors are nowadays fully used tools for various surface treatment such as, surface cleaning [1], surface functionalization for adhesion improvement [2], anisotropic etching of silicon wafers for microelectronic applications, thin films growth for passivation, wettability [3], modification or protection against moisture and corrosion. Among the large number of precursors used in Plasma Enhanced Chemical Vapour Deposition (PECVD) organosilicon (Tetraethylorthosilicate (TEOS) or Hexamethyldisiloxane (HMDSO)) are used to synthesize insulating materials in microelectronic devices. The thin films obtained from organosilicon and oxygen mixtures have a chemical composition and dielectric properties very close to those of silica. They can replace advantageously the SiH_4 in situations where requirements for the purity of the carbonless coats are reduced.

Growth processes of dielectric thin films obtained from TEOS and Oxygen plasma are studied and an analytical model is developed. In the first part of this article, the experimental apparatus and the main features of the ECR discharge are presented. The gas phase analysis by mass spectrometry, allows to follow the dissociation of TEOS and oxygen with regard to the microwave power. So, an approximated shape of the evolution of the gas dissociation coefficients with respect to the injected power is proposed. In the second part a growth model is presented. This model use the earlier works of Bourreau [4] and simplified surface reactions balance and is related to the experimental data. A good agreement is found in almost all cases, despite the simplicity of the model and the lack of information about the real nature of the reactions occuring in the overall process.

Experimental

The experimental apparatus, [5], is a cylindrical MMP-DECR reactor. The electromagnetic wave (2,45 Ghz) is launched in the system by height antennas, located inside the reactor in front of each magnet. The center of the reactor is a quasi-neutral region and the electronic density is about 10^{10} cm^{-3}. This is the domain of diffused particles where the coating processes are achieved. In such a reactor experimental conditions are as follow : The residual gas pressure is about 10^{-4} Pa. A thermostatic bath keeps the temperature constant (about 30°C) in the TEOS flask. The TEOS line is also heated to avoid any monomer condensation. A mass spectrometer is settled on reactor with the species extraction aperture standing near the sample holder. The volumic flow rate of the turbo-molecular pump is 170 l/s. The volume of the reactor is 20 10^3 cm^3. The pressure range can be varied from 0.05 Pa to 0.2 Pa and the TEOS/O_2 ratio from 0 to 100%. The microwave power is ranging between 40 and 800 W. The treated samples are intrinsic [100] silicon wafers, 10 cm in diameter. During the treatment the sample is always at floating potential. An annular injector has been used with the aim to improve the uniformity of the coating .

Gazeous phase analysis by Mass spectrometry

Two kinds of plasma have been studied, the first one is a pure TEOS plasma, the second is a pure O_2 one. Figures 1 and 2 give the variations of the peak intensities with respect to the microwave power for TEOS and O_2 respectively. It appears different apparent dissociation rates for both gases. The characteristic peaks of TEOS disappear for a power value close to 100 watts, whereas the peak 32 a.m.u in the oxygen plasma decreases more slowly and remains present up to 800 watts.
Figures 3 and 4 show a limitation of gas dissociation when the initial pressure increases. Indeed, for a power of 200 W, the amount of molecular oxygen dissociated is about 40 % at a pressure of 0.075 Pa and, about 13 % at a pressure of 0.133 Pa. In the case of TEOS, for a power of 100 watts, the monomer is entirely dissociated at a pressure of 0.1 Pa, while a part of 8% remains detectable at a pressure of 0.2 Pa. This phenomena is generally encountered when the collision frequency between electrons and neutral species in plasma is in order of some percent with regard to the microwave frequency, a condition which occurs in the high pressure range. This means that the microwave propagation along the antennas is limited by the absorption in the medium. For pressure above 1 Pa, the plasma cannot expand in the reactor.
For the pure TEOS plasma, if these results give a general knowledge of the gas apparent dissociation rate, they do not give any indication about the real nature of the radical species created.
With the aim to give a relationship between the growth rate and the external parameters of the discharge (i.e. pressure, power, TEOS/O_2 ratio), it is useful to give an expression for the apparent dissociation rate of the both gases (α and β), as a function of the microwave power. A simplified balance of the electron-gas interaction is described by the following equations:

$$e^- + TEOS \text{ --- } (\alpha) \text{ ---> } [(R\text{-}O)_a Si(O)_{(4-a)}] + (4-a)\,R + e^- \quad \text{with } 0<a<4 \text{ and } R = C_2H_5.$$

$$e^- + O_2 \quad \text{----}(\beta)\text{-----> } 2\,O + e^-$$

α et β are the apparent dissociation rates of TEOS and O_2 respectively.
Simple relations are established between the partial pressure of each active species generated by the discharge and the partial pressure of TEOS or O_2 (P[TEOS] and P[O_2] respectively) firstly injected in the reactor.

$P[(R\text{-}O)_a\ Si(O)_{(4-a)}] = \alpha\ P[TEOS]$; $P[R] = (4-a)\ \alpha\ P[TEOS]$; $P[O] = 2\ \beta\ P[O_2]$.

$P[(R\text{-}O)_a\ Si(O)_{(4-a)}]$ is the partial pressure of the organosilicon radicals $[(R\text{-}O)_aSi(O)_{(4-a)}]$, P[R] is the partial pressure of the carbonyl radicals [R] and P[O] is the partial pressure of atomic oxygen. Empirical laws have been calculated from the mass spectroscopy results to fit the variations of α and β with the microwave power in the range 0-800 W:

$$\alpha = (1 - \exp(-W/30))^4$$

$$\beta = 0.5\ (1 - \exp(-W/400))$$ (W is the microwave power value).

Hence, they have no physical meaning. However, the experiments show they remain valid as the composition of the gas change. As for as the total pressure is concerned the shape of α and β remains the same in a pressure range varying from 0.05 Pa to 0.2 Pa, which is the range of interest in this study.

Analytic model of the growth process

In the following it is assumed that precursors involved in the overall growth process are organosilicon radicals like $[(R\text{-}O)_aSi(O)_{(4-a)}]$, organic groups R like C_2H_5 or CH_3, and atomic oxygen. The partial pressure of each precursor is estimated from the respective apparent dissociation rates of TEOS and oxygen (α and β). Radicals created in the gazeous phase are impinging on the surface, they have there a probability of adsorption and desorption on the site of the surface. The works, carried out by the research team at the IMN [4], are based on the estimation, of the fraction of sites occupied, by organosilicon radicals and atomic oxygen, on the surface. The balance of the organosilicon adsorption, given by these authors is:

$$[(R\text{-}O)_aSi(O)_{(4-a)}] + s \underset{K_{+1}}{\overset{K_{-1}}{\rightleftharpoons}} [(R\text{-}O)_aSi(O)_{(4-a)}]_s$$

Where $[(R\text{-}O)_aSi(O)_{(4-a)}]$ is a free radical in the gazeous phase, s a preferential site of adsorption on the surface, and $[(R\text{-}O)_aSi(O)_{(4-a)}]_s$ a radical adsorbed on this surface. K_{+1} and K_{-1} are respectively the adsorption desorption rates. In a steady state (i.e the fluxes of adsorbed and desorbed radicals per unit of area and time are equal), the balance is written as:

$$K_{+1}\ \alpha\ P_{TEOS}\ \theta_0 = K_{-1}\ \theta_1 \qquad (1)$$

Same equation holds for the different kinds of precursors:

$$2\ K_{+2}\ \beta\ P_{O2}\ \theta_0 = K_{-2}\ \theta_2 \text{ for the atomic oxygen.} \qquad (2)$$

$$K_{+3}\ (4\text{-}a)\ \alpha\ P_{TEOS}\ \theta_0 = K_{-3}\ \theta_3 \text{ for the carbonyl groups} \qquad (3)$$

$\alpha\ P_{TEOS}$, $\beta\ P_{02}$, are the partial pressure of the organosilicon radicals related to the initial pressure of TEOS and of atomic oxygen related to initial pressure of molecular oxygen respectively.

θ_0 is the fraction of free sites on the surface.

θ_1, θ_2, θ_3 are the fraction of sites occupied by adsorbed organosilicon radicals, adsorbed atomic oxygen and carbonyl groups respectively.
$K_{+2,-2}$ and $K_{+3,-3}$ are the coefficients of adsorption (+) desorption (-) of atomic oxygen and carbonyl groups on the surface respectively.
On the surface, the balance between the free sites and the sites occupied by the miscellaneous precursors is written:

$$1 = \theta_0 + \theta_1 + \theta_2 + \theta_3 \qquad (4)$$

It must be noted that the relations of adsorption have a similitude with the BET one (Brunauer, Emmet, and Teller) [6] . Among the different possibilities of surface reaction, the followings have been selected to describe the growing process.

$$[(R\text{-}O)_aSi(O)_{(4-a)}]_s + [(R\text{-}O)_aSi(O)_{(4-a)}]_s \text{ ------}(k_1)\text{----------> Film} \quad (5)$$

$$[(R\text{-}O)_aSi(O)_{(4-a)}]_s + [R]_s \text{ ---------}(k_2)\text{--------> Film} \quad (6)$$

$$(k_3) \begin{cases} [(R\text{-}O)_aSi(O)_{(4-a)}]_s + O \text{ ----------> } R\text{-}O^{\nearrow} + [(R\text{-}O)_bSi(O)_{(4-b)}] \\ [R]_s + O \text{ ----------> } R\text{-}O^{\nearrow} \end{cases} \qquad (7)$$

k_1, k_2, k_3 are coefficients related to the reaction rate on the surface for the three chemical reactions. The symbol $R\text{-}O^{\nearrow}$ represents a group created by the combination of an atomic oxygen and a carbonyl group (R= C_2H_5 or CH_3) which desorbs from the surface. In equation (7), indexes a and b characterize the ablation by atomic oxygen of a carbonyl group on any organosilicon group adsorbed on the surface. Then the growth rate is written as the addition of the different reaction rates between the sites occupied by the different reactants.

$$V_d = k_1 \theta_1^2 + k_2\theta_1\theta_2 - k_3 \theta_3(\theta_1+\theta_2) \qquad (8)$$

The combination of equations (1,2,3,4,8) leads to the analytical expression of the growth rate Vd with respect to the external parameters of the discharge (i.e the initial pressure, the gas mixture ratio, the microwave power):

$$V_d = \frac{\left\{ (k_1K_1^2+(4-a)k_2K_1K_3)(\alpha P_{[TEOS]})^2 \right\} - \left\{ k_3K_2((4-a)K_3+K_1)2\alpha\beta P_{[TEOS]}P_{[O_2]} \right\}}{\left\{ (1+K_1+(4-a)K_3)\alpha P_{[TEOS]} + 2K_2\beta P_{[O_2]} \right\}^2}$$

In this expression the terms K_1, K_2, K_3 are the ratio between the coefficients of adsorption and desorption, previously written in the equations (1,2,3). For example $K_1 = K_{+1}/K_{-1}$ No direct access to the numeric values is available for the different coefficients of the equation, nevertheless, from this expression, a numeric relation has been assessed which allows to fit the experimental data. The partial pressure of TEOS and O_2 can be written as a function of the total pressure and the expression (9) becomes with the empirical numeric coefficients:

$$Vd = 12 \times 10^5 \frac{[(1.5\alpha^2(1-C_o)^2)-(0.34\ \alpha\beta\ (1-C_o)\ C_o)]}{[\frac{1}{P_{total}}+12\alpha\ (1-C_o)+28\ \beta C_o]^2} \qquad \text{with } C_0 = \frac{P_{[O_2]}}{P_{[TEOS]}+P_{[O_2]}}$$

Comparison of the model with the experimental results

The three studied external parameters are then included in this expression. In fact, this expression is only related to a specific reactor with a given flow rate. Although many simplifying assumption have been made, figures 5, 6, 7 show a good agreement, between the computed and the experimental values. Figure 5 shows the decrease of the growth rate, with respect to the increase of the oxygen content in the gas mixture, but with a power of 100 watts and a pressure of 0.1 Pa. The experiment shows growth rates slightly weaker than the computed one. This underestimation is reproduced for pure TEOS plasma (with a microwave power of 100 W). Then, when the power is 100 watts, the model overestimate the growth rate. On the contrary, when the power is about 400 watts (figure 6), the model seems to underestimate it. In fact, the coefficient of adsorption of the organosilicon precursors has been fixed, indepentenly of the power level. The model takes into account a slight difference of the total apparent dissociation of TEOS in the both cases of power, but does not predict any enhancement of the reactivity of these radicals with surface, when the power increases. As previously seen, the gazeous phase evolves when the power raises and then, more and more radicals seem to be produced, and a stronger dissociation of the initial monomers seems to occur. The change of nature, of the organosilicon precursors implied in the coating process, is probably a way of explanation of the growth rate raise experimentally observed. In figure 7 the model and the experimental data exhibit a maximum for a power close to 100W. This behaviour can be explained by considering that the apparent dissociation rate of TEOS is not the same of the oxygen one. In the low power range, the oxygen weakly dissociated does not strongly etch the growing film. As the power increases the production rate of atomic oxygen increases and from 100 W etching becomes efficient enough to lower the growth rate. Nevertheless, the model curve is smoother than the experimental one.

Conclusion

The total dissociation of TEOS molecules appears at very low microwave power (100 W), when molecular oxygen is always detected at high power (800 W). The simple empirical model developped to describe the growth process is going on the assumption that only three types of radicals are preponderant : organosilicon radicals, ethyl and methyl groups and atomic oxygen. A balance occurs between the growth due to the recombination of organic and organosilicon groups and the chemical etching by atomic oxygen. It must be noted that the model does not take into acount the temperature changes of the substrates, these being treated at floating potential.

References

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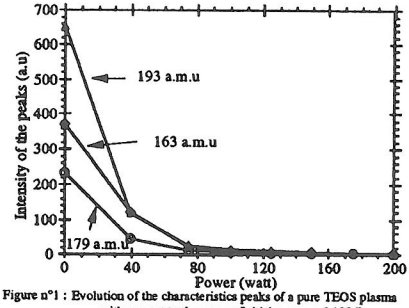

Figure n°1 : Evolution of the characteristics peaks of a pure TEOS plasma with respect to the power. Initial pressure 0.133 Pa.

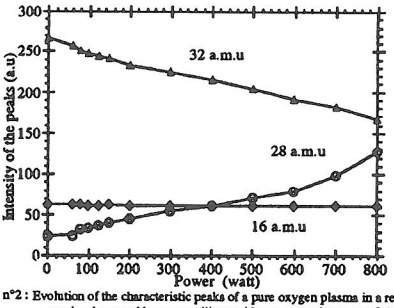

Figure n°2 : Evolution of the characteristic peaks of a pure oxygen plasma in a reactor previously coated by organosilicon with respect to the power. Initial pressure 0.133 Pa

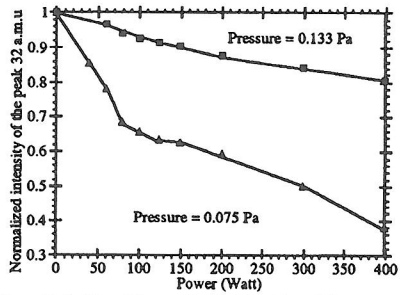

Figure n°3 : Evolution of the normalized intensity of the peak 32 a.m.u with respect to the power, at two different initial pressures in a pure oxygen plasma.

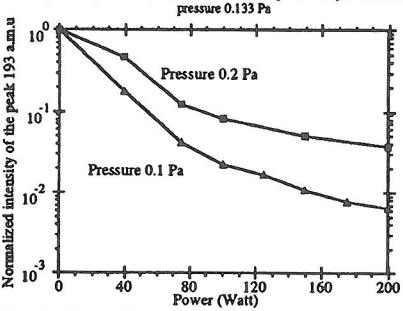

Figure n° 4 : Evolution of the normalized intensity of the peak 193 a.m.u with respect to the power, at two different initial pressures in a pure TEOS plasma

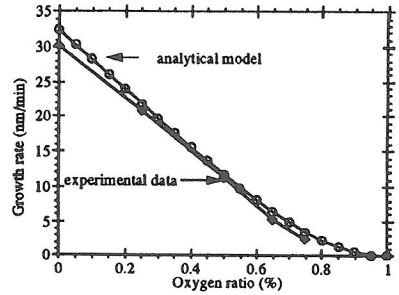

Figure n° 5 : Evolution of the growth rate with respect to the initial ratio of oxygen. Initial pressure 0.1 Pa. Power 100 watts.

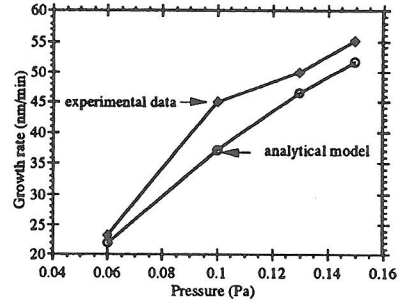

Figure n° 6 : Evolution of the growth rate with respect to the initial pressure in a pure TEOS plasma. Power 400 watts.

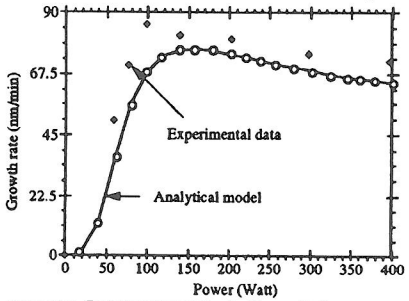

Figure n° 7 : Evolution of the growth rate with respect to the power. 50% O2-50% TEOS. Initial total pressure = 0.066 Pa.