

Actinometry for understanding PECVD of thin films from O₂/HMDSO plasmas

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We applied actinometry for the calculation of dissociation degree in oxygen CCP discharges used for the deposition from O₂/HMDSO plasmas. Dissociation degree exhibited a slight increase with increasing r.f. power and maximum of 20 % for 5 Pa of oxygen. This relatively high value was not enough for deposition of SiO₂-like films because the HMDSO percentage in the feed was too high at this low oxygen partial pressure. Rapid decrease of dissociation degree to 2–4 % for higher oxygen flow rates, i. e. higher pressures resulted in still insufficient oxidation of film precursors.

1. Introduction

Organosilicon-oxygen mixtures can be used for plasma enhanced chemical vapor deposition (PECVD) of inorganic silicon oxide films (SiO_x) as reported many times for tetraethoxysiloxane (TEOS) as well as for hexamethyldisiloxane (HMDSO) compounds. Decreasing high percentage of oxygen in the organosilicon-oxygen feed the inorganic character of the deposits can be changed to more organic as shown for example by Valée *et al.* [1]. The films prepared without any oxidizing gas, i. e., from pure monomer or with addition of an inert gas like argon, are then often referred as plasma polymers due to their high organic content [2].

2. Experimental

In this paper we discuss the role of oxygen radicals and ion bombardment on the deposition of thin films under various conditions in 13.56 MHz low pressure glow discharges from oxygen/HMDSO feed with different concentrations of HMDSO. The experiments were carried out in a capacitively coupled (CCP) stainless steel parallel plate reactor. The bottom electrode, 420 mm in diameter, was r.f. powered and due to an asymmetric coupling and different mobility of electrons and ions the negative self-bias was superimposed over the r.f. voltage. The bottom electrode was used as a substrate holder in order to allow an ion bombardment of the growing films. Gases were fed into the chamber through an upper grounded showerhead electrode. The distance between the electrodes was 55 mm. R.f. power was in the range

50–450 W. For the deposition, the HMDSO reactant with fixed flow rates of 2 or 4 sccm (Q_{HMDSO}) were used. The oxygen flow rate varied from 0 to 98 sccm (Q_{O_2}). Thus a HMDSO percentage in the feed ($\chi = Q_{\text{HMDSO}}/(Q_{\text{HMDSO}} + Q_{\text{O}_2})$) from 4.8 to 100 % was achieved. Corresponding total pressure in the reaction chamber prior to the deposition was in the range 1.2–53 Pa.

Discharges in oxygen/HMDSO and pure oxygen were studied by optical emission spectroscopy using a Jobin Yvon TRIAX 550 spectrometer. Actinometry method described below was applied to assess dissociation degree, i. e., oxygen radical concentration. Electron energy distribution function in the CCP reactor with similar electrode configuration and power density was determined by Langmuir probe measurements using r.f. compensated probe from Scientific Systems Ltd.

3. Results and Discussion

3.1 Film deposition

The optical and mechanical properties as well as the atomic composition and chemical structure of the deposited films were investigated in detail in the previous paper [3]. According to the film mechanical properties we can divide the depositions roughly into three groups, (i) deposition of films in HMDSO-rich discharges ($\chi = 16.7\text{--}100\%$), (ii) deposition in intermediate conditions and (iii) deposition in oxygen-rich discharges ($\chi = 4.8\text{--}6.7\%$). Films from the first group exhibited compressive intrinsic stress, especially at the high power, i. e., high d.c. self-bias and besides SiO_x, SiH, SiOH and OH contained high amount of organic groups

such as SiCH_x and CH_x . The percentage of carbon and hydrogen in the films were in the range 10–17 at. % and 42–65 at. %, respectively. Refractive index was higher than tabulated for SiO_2 and the films exhibited absorption in the ultraviolet/visible range. Polymer character of the films was confirmed by low hardness, low elastic modulus and viscoelasto-plastic behavior.

Films deposited in the intermediate conditions had hardness below 5 GPa and were stress-free, especially for low r.f. power. Intrinsic stress in the films changed its character to the tensile one for the films deposited in oxygen-rich discharges. The film properties, such as refractive index, extinction coefficient and hardness, approached the properties of SiO_2 but the films still contained some hydrocarbon impurities. The atomic percentage of carbon and hydrogen for our lowest HMDSO concentration $\chi = 4.8$ % were in the range 5–8 and 20–40 at. %, respectively. This is a different result compared to the deposition from inductively coupled O_2 /HMDSO or O_2 /TEOS plasmas where pure SiO_2 -like films were obtained for $\chi = 10$ % [4]. Furthermore, we compared our oxygen-rich deposits ($\chi = 2$ %, $Q_{\text{HMDSO}} = 2$ sccm, r.f. power of 300 W) with the films from the inductively coupled plasma (ICP) and found their optical and mechanical properties quite different [5]. The ICP film deposited with the same χ and r.f. power had its refractive index higher than tabulated SiO_2 whereas our CCP films exhibited values lower or close to SiO_2 . Comparison of the mechanical properties revealed even more interesting differences. The ICP films exhibited compressive stress and hardness higher than SiO_2 . The hardness of the CCP films depended on the r.f. power, i. e., self-bias on the substrate electrode. A tensile stress was found in the high hardness CCP films.

It is obvious that oxygen radicals play a key role in the deposition of SiO_2 -like films from oxygen/organosilicon plasmas. They are involved in dissociative reaction with monomer, oxidation of organic plasma species and surface oxidation reactions with adsorbed precursors. Raupp *et al.* [6] and Stout *et al.* [7] suggested that the oxygen atom flux was a limiting step for their deposition of SiO_2 films from the O_2 /TEOS CCP discharges. Therefore, we assumed that the major difference between the CCP and ICP deposition processes discussed above was a concentration of oxygen radicals. In order to prove this hypothesis and also to understand the changes of atomic composition for different χ we measure the concentration

of oxygen radicals [O] in our experimental conditions by actinometry.

3.2 Actinometry

Within the actinometric method intensities of two emission lines, one of the monitored species and the other of the reference ones, are divided in order to calculate the specie density. According to the suggestion in Refs. [8, 9] we used the oxygen emission line at 844.6 nm ($3p^3P \rightarrow 3s^3S$ transition) and argon at 750.4 nm ($2p_1 \rightarrow 1s_2$ transition) as the actinometer for determination of [O]. Ratio between argon and oxygen concentrations in the gas feed was kept as low as 0.01-0.03. It is assumed that the corresponding excited states are populated from the ground states by an electron impact. Additionally, the dissociative excitation of oxygen has to play a minor role and the calculations are simplified neglecting a non-radiative de-excitation by quenching.

The emission intensity I_{ij}^X of a transition $X_i^* \rightarrow X_j^* + h\nu_{ij}$ normalized to a plasma volume is

$$I_{ij}^X = [X_i^*] h\nu_{ij} A_{ij} \quad (1)$$

where A_{ij} is Einstein transition probability of spontaneous emission, $h\nu_{ij}$ is the energy of each light quantum and $[X_i^*]$ is the concentration of excited species X_i^* . The concentration $[X_i^*]$ can be determined from an excitation/de-excitation balance equation. Neglecting the quenching we can write for the concentration of oxygen and argon excited species

$$\begin{aligned} [\text{Ar}_{p_1}^*] &= n_e \frac{[\text{Ar}]k_{\text{exc}}^{\text{Ar}}}{\sum_j A_{ij}^{\text{Ar}}} \quad (2) \\ [\text{O}_{3P}^*] &= n_e \frac{([\text{O}]k_{\text{exc}}^{\text{O}} + [\text{O}_2]k_{\text{diss}}^{\text{O}})}{\sum_j A_{ij}^{\text{O}}} \end{aligned}$$

where [Ar], [O] and $[\text{O}_2]$ are the concentrations of argon, atomic and molecular oxygen in plasma, respectively, $k_{\text{exc}}^{\text{Ar}}$, $k_{\text{exc}}^{\text{O}}$ and $k_{\text{diss}}^{\text{O}}$ are the rate constants for direct excitations to $\text{Ar}(p_1)$, $\text{O}(^3P)$ and dissociative excitation of $\text{O}(^3P)$, respectively, $\sum_j A_{ij}^{\text{Ar},\text{O}}$ represent the sums of all radiative de-excitation processes for $\text{Ar}(p_1)$ or $\text{O}(^3P)$ and n_e is the density of electrons. Thus, the electron density is excluded from considerations calculating the ratio of oxygen-to-argon emission line intensities $I_{\text{O}}/I_{\text{Ar}}$. This is the principle of actinometric

method. Finally, we can write

$$\frac{I_O}{I_{Ar}} = \frac{\lambda_{750} A_{844}^O \sum_j A_{ij}^{Ar}}{\lambda_{844} A_{750}^{Ar} \sum_j A_{ij}^O} \left(\frac{k_{exc}^O[O]}{k_{exc}^{Ar}[Ar]} + \frac{k_{diss}^O[O_2]}{k_{exc}^{Ar}[Ar]} \right) \quad (3)$$

where the intensity ratio has to be corrected for an optical response of the measurement system. The rate coefficients k_ν^X ($X = Ar, O$ and $\nu = exc, diss$) can be expressed as

$$k_\nu^X = \sqrt{\frac{2}{m}} \int_0^\infty \sqrt{E} \sigma_\nu^X(E) f(E) dE \quad (4)$$

where $\sigma_\nu^X(E)$ are collision cross sections for excitation or dissociative excitation of argon and oxygen as function of electron energy E , m is the electron mass and $f(E)$ is a spherically symmetric electron energy distribution function (EEDF). Assuming Maxwell distribution the EEDF can be written as

$$f(E) = \frac{4\pi}{m} \sqrt{\frac{2}{m}} \left(\frac{m}{2\pi k_B T} \right)^{3/2} \sqrt{E} e^{-E/k_B T} \quad (5)$$

where k_B is Boltzmann's constant and T is the electron temperature.

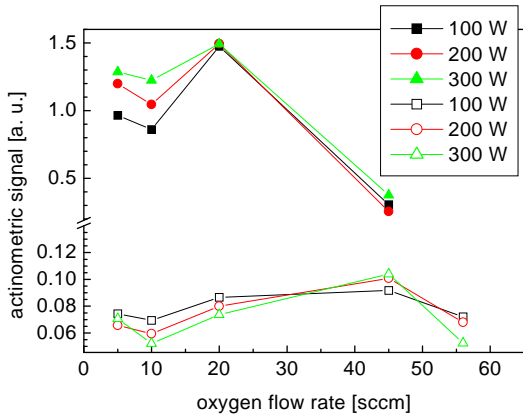


Figure 1. Actinometric signal given by Eq. (6) in pure oxygen (solid symbols) and oxygen/HMDSO (open symbols) plasmas.

In order to calculate the concentration of oxygen atoms in the plasma, i. e., the dissociation degree $\alpha_d = [O]/[O_2]_{feed}$ we have to couple Eq. (3) with the mass conservation law between oxygen molecules in the gas feed and oxygen atoms and molecules in the plasma. Similar as in Ref. [10] we obtain following relation between so called actinometric signal on the left side and α_d and rate constants on the right side of the equation:

$$\frac{1}{C} \left| \frac{[Ar]}{[O_2]} \right|_{feed} \frac{I_O}{I_{Ar}} = \frac{k_{diss}^O}{k_{exc}^{Ar}} + \alpha_d \left(2 \frac{k_{exc}^O}{k_{exc}^{Ar}} - \frac{k_{diss}^O}{k_{exc}^{Ar}} \right) \quad (6)$$

where the constant C , according to Eq. (3), contains the corrections on different wavelengths of the emission lines used and on the Einstein transition probabilities. The actinometric signal measured in pure oxygen and oxygen/HMDSO discharges in dependence on oxygen flow rate and r.f. power is shown in Fig. 1. We can see that its value is much lower in O₂/HMDSO than pure O₂ which can be caused by high depletion of oxygen radicals in oxidation reactions but also de-excitation of excited atomic oxygen by quenching. In pure oxygen and low flow rates, i. e. low pressures, the signal exhibited a certain increase with the r.f. power. This trend can be expected from a simple view of increased energy delivered into the discharge. However, this effect almost diminishes for higher flow rates. Granier *et al.* [10] reported almost linear increase of the actinometric signal with the power for the ICP discharge but the influence of the power in the CCP mode was not quite distinguishing. It is interesting to notice that the actinometric signal rapidly decreases with increased flow rate from the maximum value at 20 sccm. We think that these results are necessary to clarify by more experimental points.

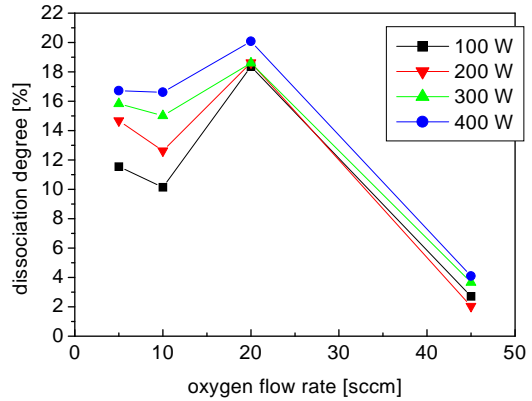


Figure 2. Dependence of dissociation degree in pure O₂ on the oxygen flow rate and r.f. power given in the figure legend. The pressure changed from 1 to 27 Pa.

Combining Eqs. (4), (5) and (6) we can see that the electron temperature must be known for the calculation of dissociation degree. Since it was not possible to measure the EEDF directly in the "deposition" reactor we carried out these measurements in another, 13.56 MHz capacitively coupled, plasma reactor with a similar geometry ("diagnostics" reactor). In this reactor, the distance between two electrodes, 100 mm in diameter, was

also 55 mm. Therefore, comparing the electrode areas we concluded that the r.f. power range 50–450 W in the "deposition" reactor matches the range 5–25 W used in the "diagnostics" one. Assuming the Maxwell distribution for simplicity we found that the electron temperature is approximately 3 eV and did not change within the discussed r.f. power range. Taking into account this temperature and the cross section data published in Refs. [11, 12, 13] we calculated the necessary rate constants using Eqs. (4) and (5). Resulting values for $k_{\text{exc}}^{\text{O}}/k_{\text{exc}}^{\text{Ar}}$ and $k_{\text{diss}}^{\text{O}}/k_{\text{exc}}^{\text{Ar}}$, appearing in Eq. (6), are 3.8 and 0.1, respectively. The dissociation degree is then plotted in Fig. 2. Its values for low flow rates seems to be quite high but we would like to notice that the low partial pressure of oxygen results in the low concentration of oxygen atoms (see Fig. 3). Thus, polymer-like films were deposited under these conditions ($\chi \geq 17\%$). Rapid decrease of α_d for the high oxygen flow rates, on the other hand, resulted in the deposition of the films with remaining carbon impurities.

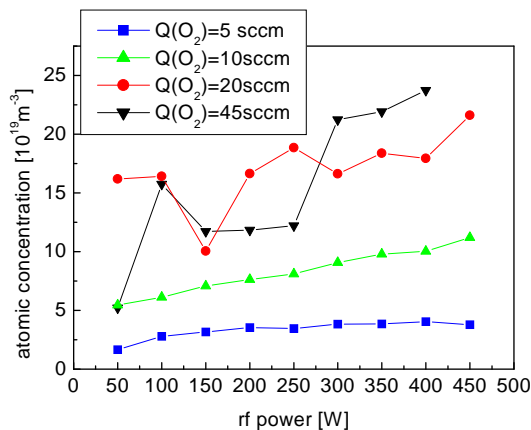


Figure 3. Concentration of oxygen radicals as a function of r.f. power for different oxygen flow rates, i. e., oxygen partial pressure.

4. Conclusion

Actinometric method is very useful and simple tool for understanding the deposition process in O₂/HMDSO discharges where oxygen atoms play a key role in oxidation reactions. We see a high depletion of oxygen emission line when HMDSO is added to the gas feed. The dissociation degree α_d in pure O₂ exhibited a slight increase with increasing r.f. power and more complicated functional dependence on the oxygen flow rate Q_{O_2} , i. e., pressure. The α_d reached about 20 % for

5 Pa ($Q_{\text{O}_2} = 20$ sccm) and then rapidly decreased to 2–4 % for 27 Pa ($Q_{\text{O}_2} = 45$ sccm). The low α_d for high pressures is then probably the reason why pure SiO₂-like films were not deposited at the high dilution of HMDSO in oxygen.

Acknowledgments

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