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Research Article

Characterization of the Chemical Kinetics in an O_2/HMDSO RF Plasma for Material Processing

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Experimental study of the plasma gas phase in low-pressure radiofrequency discharges of oxygen and hexamethyldisiloxane is presented. The plasma phase has been studied by means of optical emission spectroscopy. Mass spectroscopy of the neutral and of the charged species has been performed too, directly sampling the plasma gas phase, by a dedicated spectrometer. We also measured the ion energy distribution. We have studied the influence of the operating conditions on the plasma gas-phase composition which plays a primary role in the formation process of SiO_2 films, which are known for their important applicative uses.

1. Introduction

Plasma-enhanced chemical vapour deposition (PECVD) of silicon oxides is one of the most promising techniques allowing industrial-scale deposition of high-quality, transparent, and thin coatings [1, 2]. SiO_2-like films deposited by plasma polymerisation was first developed for microelectronics. Then, they have been applied also as protective coatings in optoelectronics and packaging [3]. The most favourable option is to use organosilicon compounds as precursor, like hexamethyldisiloxane (HMDSO) mixed with O_2 and/or noble gases. It was found that composition and structure of films change with the deposition conditions [1]. A systematic control of plasma is then needed to obtain films with the desired properties. Better understanding of the chemical kinetics processes happening in the discharge is then mandatory and requires suitable diagnostics to probe directly the plasma gas phase. Previous investigations employed mass spectroscopy (MS), optical emission spectroscopy (OES), and infrared absorption spectroscopy (FT-IR) [1, 4–7]. However, many points are still open, for instance, concerning the role of ions in the gas phase, the deposition and the film growth process [1]. We have investigated O_2/HMDSO plasmas produced by a resonant inductive radiofrequency (RF) plasma source and used to deposit SiO_2-like films on polyethylene terephthalate (PET).

Diagnostics include OES and on-line MS of neutrals and ions from the discharged gas phase. Our mass spectrometer allows to change the electron energy in the ionization source, in order to better identify the parent radical sampled from the plasma. We were able to measure also ion energy spectra. The properties of the film have been studied by attenuated total reflectance infrared (ATR) spectroscopy, electron microscopy, and by contact angle measurements.

2. Experimental Setup and Diagnostics

A scheme of the setup is shown in Figure 1. The plasma source was developed by CCR Technologies Gmbh [8, 9]. It is mounted on the top of a cubic vacuum chamber and consists of a single-turn coil coupled to a RF supply. The coupling of the discharge is enhanced by the presence of a static magnetic field B which allows resonant energy absorption at the electron cyclotron frequency when its value matches the 13.56 MHz of RF supply. A constant flow of O_2 and Ar (or He) is provided, while HMDSO in a sealed bottle is evaporated into the chamber through a micrometer needle valve. Total pressure is measured just before entering into the plasma source and inside the chamber. To keep the desired pressure there, the effective pumping speed is varied by partially closing the gate valve. OES of the discharge is used to gain insight into the excited species produced.

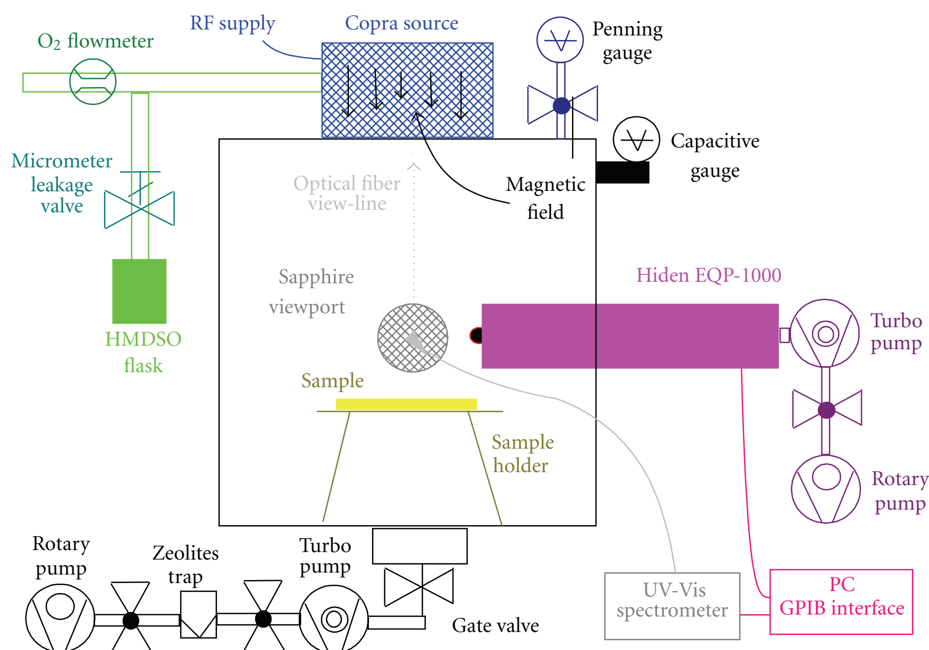

FIGURE 1: The experimental setup with diagnostics.

Measurements of the emission spectra are obtained with a wideband, low-resolution spectrometer. Spectra cover the UV-Vis-NIR range from 200 to 850 nm with a resolution of about 1 nm. Emission line intensity was measured, and atoms and molecules have been identified [10]. An EQP-1000 spectrometer by Hiden [9] allows MS of neutral species. Abundances and energy distribution of ions can be measured too. Ions and molecules enter through an orifice in a hollow tube mounted on a movable feed-through to probe plasma well inside the chamber. A sheath develops between the plasma and the grounded surface surrounding the orifice. Energy spectra are, thus, shifted by a value corresponding to the plasma potential V_p. Besides measuring the shift, the energy spectra were also fitted with a general form of the energy distribution function (EDF) [11, 12]. The following formula is general enough to describe the energy spectra recorded in the experiments

$$f(E) = N \cdot \sqrt{E} \cdot e^{-(1/\alpha)\cdot((E-qV_p)/\varepsilon)^{\alpha}}, \quad (1)$$

where ε is related to the mean energy of the ions, and α is a parameter describing how steep is the high energy tail of the distribution ($\alpha = 1$ is the Maxwellian thermal distribution). From the fitted parameters values, the mean energy could be then easily calculated and compared.

3. Plasma Characterization

Results are shown in Figures 2 to 5. In particular, data refers to discharges at a total pressure $P = 0.42$ Pa, an O_2 flowrate $Q = 10$ sccm and an O_2 to HMDSO partial pressure ratio of 3.8 : 1. This oxygen level is lower than the stechiometric ratio needed to have complete oxidation of HMDSO to SiO_2, CO_2, and water vapour (13 : 1). Data concerning these

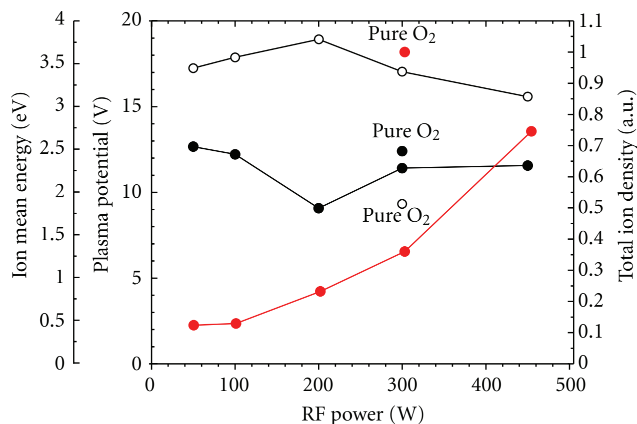

FIGURE 2: Mean ion energy (•) and plasma potential (∘) as a function of the RF power. On the right, in red, is the total plasma density normalized to that measured in a pure oxygen discharge.

experiments are plotted as a function of the RF power. At first we have analysed the charged particle produced in the plasma state. In the whole RF power range, the ion energy spectra are strongly peaked, with exponent α ranging between 3 and 5. The EDFs have high energy tails, nearly Maxwellian but with low population. Results derived from the EDF measurements are shown in Figure 2. Mean ion energies are about 2–2.5 eV, slightly decreasing with power and similar to those measured in pure O_2 discharges. Ion density increases strongly with RF power, but its values are much smaller than in pure O_2. Then HMDSO appears as a strong quenching agent of the discharge, probably because most of the electron energy is released into dissociation of the monomer, rather than contributing to the ionization

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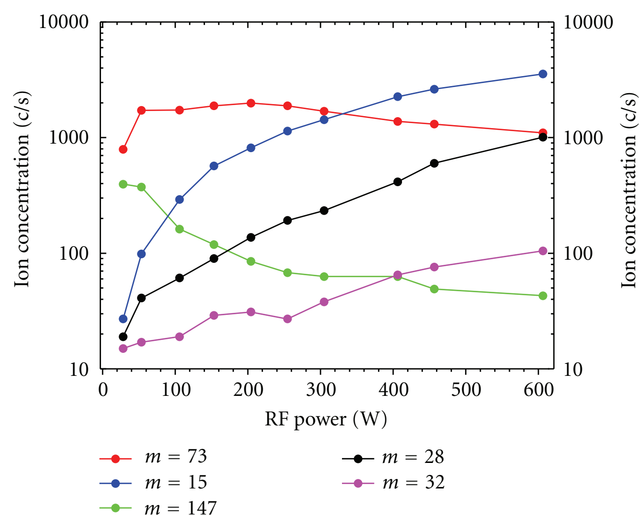

FIGURE 3: Concentration of a few major ionic species as a function of the RF power.

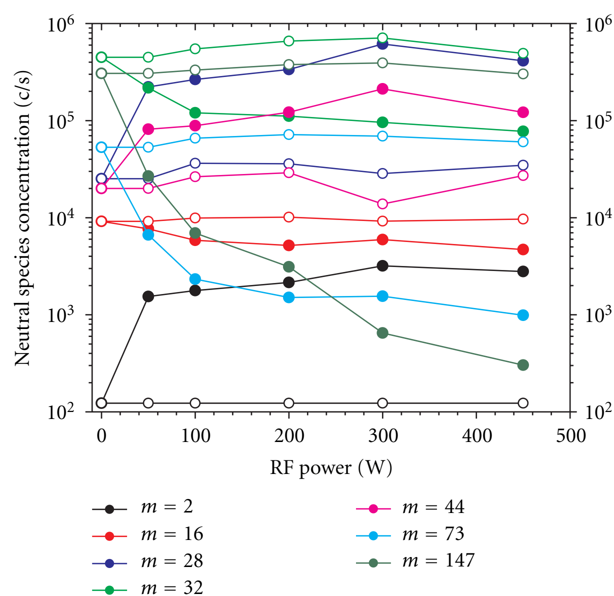

FIGURE 4: Neutral species concentration in the gas phase as a function of the RF power. Data could be compared when the discharge is ignited (• plasma on) or not (∘ plasma off).

processes sustaining plasma. The plasma potential is about 18 V, independent from the power. This is almost double than in pure O_2 and in Ar/HMDSO plasmas. Thus, if the film is grown on a grounded sample holder, ions are accelerated in the sheath up to energies of tens of eV, high enough to break all kinds of chemical bonds and induce radical formation at the surface of the growing film.

The measured ion mean energies correspond to the same range of electron temperatures, since ion energy distribution builds up in the presheath region, according to the Bohm criterion [13]. Electron impact ionization of HMDSO at such low energies mainly produces ions with the removal of a methyl group, that is, at a mass of 147 amu [6, 7]. From data shown in Figure 3, it could be seen that their concentration steadily declines. This is consistent with a strong dissociation level of HMDSO at high power, removing the source of this ion. The trend of the $Si(CH_3)_3^+$ ion (73 amu), which is formed from HMDSO after breaking of a Si–O bond, is similar. It reaches quickly a plateau and then declines, indicating a decrease of heavy fragments in the gas phase. Light ion density keeps increasing with power instead. This happens for CH_3^+ (15 amu) and for 28 amu ion. The latter grows almost exponentially in the whole RF power range. Its identity is not sure, since it could be CO^+ or Si^+, after complete dissociation/oxidation of HMDSO but also it could come from ionization of N_2, C_2H_4, or other hydrocarbons. The detection of strong emission lines from CO, with a similar trend with power, and the weak signals of CH, C_2, and Si from OES, favours the first hypothesis. O_2^+ increases too but it is always minor. Other peaks at odd masses like 27, 29, 31, 43, 45, and 59 can be assigned to (oxidated) carbon compound ions, while no peak was observed for masses larger than 150.

This indicates that polymerization and clusterization of HMDSO fragments proceeds slowly, if not at all, in the plasma gas phase.

Neutral species have been detected too, and we have compared the signal with and without plasma in Figure 4 [1, 6]. HMDSO (147 amu peak) disappears almost completely from the plasma, reducing by three orders of magnitude. In the actual operating conditions of the experiments the device works under the so called well-mixed reactor regime [14, 15]. Then in the main chamber the gas phase is mixed by diffusion before being evacuated by the pumping flow. This was also checked by varying the sampling position of our MS orifice. So our results confirm that already at the of 50 W more than 90% of HMDSO flow is actually dissociated before reaching the substrate holder where deposition occurs.

At higher-power level dissociation is virtually complete.

A less pronounced trend is observed by the 73 amu peak, a typical fragment of HMDSO, which could also be produced by heavier fragment of that monomer. Molecular and atomic oxygen decrease in the plasma reaching a constant concentration at power larger than 100 W. They are likely to be consumed in the oxidation of carbon compounds and of silicon ones. In particular, the absence of a significant increase in the atomic oxygen level warrants the high reactivity of plasma discharges, since it proves that O atoms react quickly in the gas phase without accumulation. Indeed in pure oxygen discharges atomic oxygen level increases with the power level, thanks to the dissociation by plasma electrons. The oxygen trend is related to the large increase observed for peaks at 2, 28, and 44 amu. The first is likely due to the formation of hydrogen. The other two can be assigned, respectively, to CO or Si and to CO_2 or SiO. They could receive contribution also from (oxidated) carbon compounds. Again OES results support prevalence of carbon monoxide over silicon. As happens for ions, no peak was observed for masses larger than 165 up to 1000 amu (at the sensitivity level of the spectrometer, 10 ppm). This confirms that the polymerization of HMDSO does not occur in gas phase, at least under our conditions [1].

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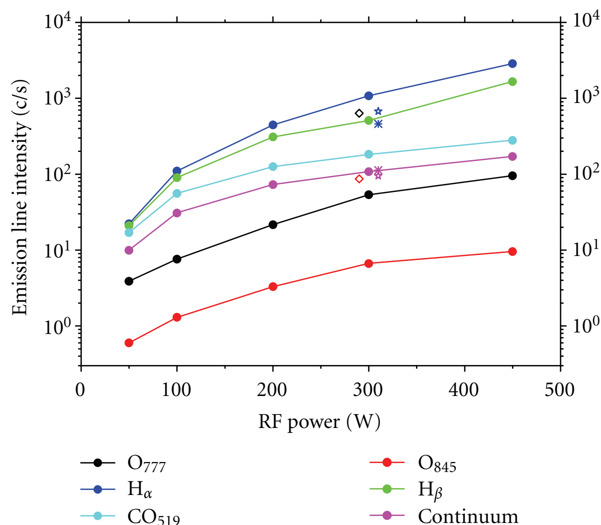

Figure 5: Emission line intensity as a function of the RF power. Data from pure O_2 (diamond) and HMDSO mixed with Ar (asterisk) and He (star) plasmas are shown for comparison.

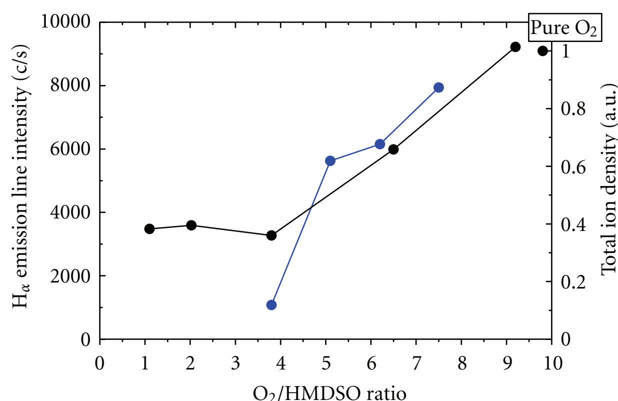

Figure 6: On the left scale is the H_α emission line intensity (blue) in the discharge as a function of the O_2/HMDSO ratio. On the right scale is the total plasma density normalized to that measured in a pure oxygen discharge.

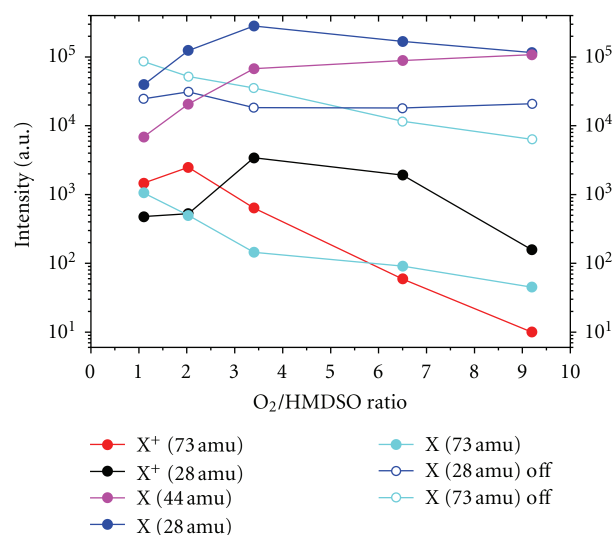

Figure 7: Major ion and neutral species concentration in the gas phase as a function of the O_2/HMDSO ratio (• plasma on, ∘ plasma off).

Spectra of the light emitted from the discharge show a broad continuum peaking at about 500 nm, with a rich structure of lines, mainly identified as due to the vibrational excitation levels of CO. However, the most intense line is usually the H_α line at 656.3 nm. Emission from O_2 and O_2^+ is not noticeable apart in pure oxygen, while atomic oxygen lines in the near infrared are detected (see Figure 5). Their intensity is, however, greatly reduced in the presence of HMDSO, again indicating that O is actively involved in the oxidation process. Search for atomic emission lines from C, Si, and their ions was unsuccessful. Also absent are the characteristic features due to CH and C_2 emission typically of methane plasmas [14]. This indicates that oxidation of carbon compounds proceeds quickly in our discharged gas phase. OES of HMDSO diluted in Ar or He plasmas shows that H_α intensity is greatly reduced, while the continuum is almost constant, as could be grasped from Figure 5. This indicates a reduced capability in HMDSO dissociation by plasmas containing noble gases compared to oxygen. The expected result is then a larger retention of organic groups in the film deposited from such plasmas [1].

Then we have performed experiments at a fixed-power level where oxygen flow was varied. In this way, we are effectively changing the O_2/HMDSO ratio, in order to ensure more complete oxidation level. Gate valve opening was regulated to have approximately the same pressure in the vacuum chamber, about 0.5 Pa. Results from the plasma diagnostics are shown in Figures 6 and 7. Both plasma density and H_α emission increase as HMDSO gets more diluted in oxygen. As for the former, at O_2/HMDSO = 9.2 plasma density reaches almost the same value of pure oxygen discharges. At such level of dilution HMDSO no longer affects the ionization degree of the discharge. Atomic hydrogen emission could be detected only when O_2/HMDSO is larger than 3, despite that total ion density is almost the same. This is true for the whole light emission spectra, indicating a generalized decrease of electron density in pure or HMDSO dominated discharges. At higher dilution, H_α, intensity rises steadily. The increase appears even bigger than the ion density one, and it largely overcompensates for the decrease in the total hydrogen abundance at higher dilution.

The concentration of a few ionic and neutral species is displayed in Figure 7. The trend of both the ion and the neutral species at 28 and 73 amu is opposite. The former grows reaching a maximum at O_2/HMDSO = 3.8 and then decreases, while the latter steadily declines with dilution. The 28 amu peak is more sensible to oxygen content, indicating that it controls the oxidation level of the HMDSO. At higher dilution, its concentration declines. The low level of the $Si(CH_3)_3$ radical (73 amu) in the discharge gas phase, two orders of magnitude lower, shows the high degree of

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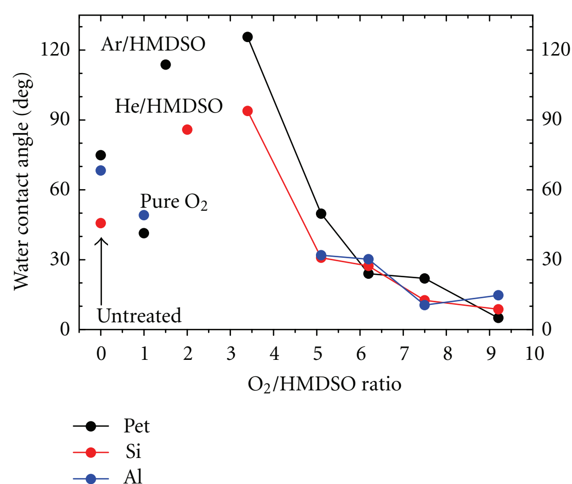

Figure 8: Water contact angle measured on different plasma-treated substrate samples as a function of the O_2/HMDSO ratio ($W = 300$ W, $P = 0.4$ Pa, and $T = 15'$).

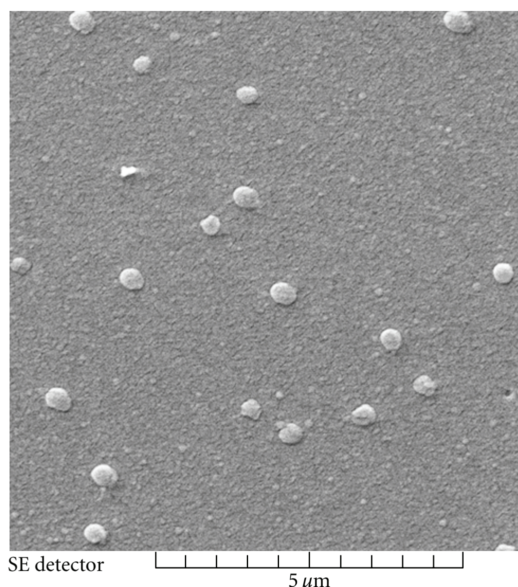

Figure 9: SEM image of the film deposited on silicon ($W = 300$ W, $P = 0.4$ Pa, O_2/HMDSO = 7.5, and $T = 15'$).

dissociation of HMDSO reached at such RF power even at the lowest dilution, while the 44 amu peak increases. All these observations are consistent with a picture where more complete dissociation and oxidation is favoured by higher HMDSO dilution in oxygen. Then a marked increase towards a pure SiO_2 composition of the deposited film can be anticipated at high dilution.

4. Deposited Film Characterization

Film deposition has been performed on 12 μm PET sheets exposed to plasma. Small samples of aluminium foils, Si wafers, and KBr tablets have been exposed too.

They have been employed mainly for evaluation of film properties purposes. Some analysis and characterization of the deposited film was already published [16–18]. Treatments of 15 minutes have been done at a fixed RF power of 300 W, high enough to completely dissociate HMDSO, as discussed above. Oxidation of the film precursors is the plasma state depends on the O_2/HMDSO ratio as discussed above. Although not complete, as it could be deduced from Figure 7, it appears to be sufficient to obtain a low carbon contamination in the film already at ratios above 5. The low carbon content of the film at high dilution is confirmed by ATR spectra recorded for the KBr samples [16]. They show only the typical Si–O–Si bands: the rocking, the bending, and the asymmetric stretching modes (450, 800, and 1000–1150 cm^{-1}). The CH_x stretching bands at 2900–2960 cm^{-1}, the Si–CH_3 rocking vibration band at 840 cm^{-1}, and the CH_3 symmetric bending in Si–CH_3 band at 1260 cm^{-1} do not appear in ATR spectra at high HMDSO dilution, indicating a high SiO_2-like character of the deposit. This correlates fairly well with the increasing hydrophilic nature of the deposited film, displayed in Figure 8.

On the contrary, when carbon compounds oxidation is not complete, many organic groups are embedded in the film, giving a hydrophobic character to the surface [6]. A similar result is obtained when deposition is performed from a plasma of HMDSO mixed with noble gases, like argon and helium. The deposited film is generally more hydrophilic than the original surface as well as the surface oxidated by a pure oxygen plasma treatment.

A SEM image of the film deposited at high dilution is shown in Figure 9. Here, the substrate was a silicon wafer just to have a nicely flat surface. A rather uniform film is obtained with a few micrometer dust particles scattered on the surface.

5. Conclusions

An experimental study of the plasma gas phase produced in a O_2/HMDSO mixture by a resonant inductively coupled radiofrequency plasma source has been performed. Strong dissociation of HMDSO is obtained at large RF power, exceeding 100 W, and high dilution. Ion mean energy was measured to be about 2 eV, while the plasma potential reached tens of volts. Application of the source to the treatment of PET results in the deposition of a highly inorganic SiO_2 film, with very low water contact angle of a few tens of degrees, when oxygen-to-HMDSO ratio is larger than 7. Preliminary measurements of the water vapour transmission rate show a decrease from 23 of untreated PET to 5.5 g/m^2/day at an O_2/HMDSO ratio of 7.5, which appears encouraging even if not yet comparable with results reported in the literature [17, 19]. Chemical kinetics in the gas phase of O_2/HMDSO plasmas largely controls the deposited film composition and characteristics. Suitable diagnostics of the gas phase then allows to have a clue linking the operating conditions with the characteristics of the deposition process. In particular, on-line mass spectroscopy of the plasma gas phase allows to identify all the radicals involved in the film growth and to monitor their concentration as a function of the operating parameters.

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