

Diagnosics and insights on PECVD for gas-barrier coatings*

Mariadriana Creatore[‡], Fabio Palumbo, and Riccardo d'Agostino

Università degli Studi, Dipartimento di Chimica, CNR, Centro di Studi per la Chimica dei Plasmi (now Istituto di Metodologie Inorganiche e Plasmi), via Orabona 4, 70124 Bari, Italy

Abstract: In this work, we report on our last results concerning the polyethyleneterephthalate barrier performance optimization as a function of the chemistry of the SiO_x coating, deposited by means of hexamethyldisiloxane/oxygen-fed plasmas ignited in an RF capacitively coupled parallel plates reactor. The influence of the gas feed composition and power on the plasma phase/coating chemistry and on the O₂ gas transmission rate has been investigated. The plasma phase has been studied by means of Fourier transform infrared absorption (FT-IR) and optical emission spectroscopies (OES), and the results have been coupled to the film chemistry investigated by means of FT-IR spectroscopy. These techniques show excellent potentialities in the correlation of the plasma phase and film chemistries with the barrier properties of the SiO_x-coated polymer, especially when a very good barrier level is required.

INTRODUCTION

Flexible commodity polymers have widely overcome the use of glass and pewter as they show properties such as resistance to cracking, low weight, printability, and sealability. However, the major concern is about their poor gas barrier performance, which ranges from hundreds to thousands cm³/m² day atm (in the case of noncondensable gases), depending on the polymer thickness and chemical structure. SiO_x coatings provide superior barrier performance with respect to all plastic-composite materials, besides reducing environmental concerns, as they are recyclable. Moreover, they are currently substituting Al-coated polymers, because they are transparent and microwaveable. Plasma-enhanced chemical vapor deposition (PECVD) appears to be the most suitable candidate for SiO₂-like film deposition on lab- and large-scale reactors, with respect to other deposition techniques, as evaporation and sputtering. Organosilicon-fed plasmas constitute *a priori* a complex system, and although a huge literature has been produced on this topic, still there is the need for identifying the main deposition precursors, defining their production pathways and understanding the deposition mechanism. This would eventually lead to an easier control of the SiO_x film chemistry and to a more immediate process scaling up to industrial reactors.

EXPERIMENTAL AND RESULTS

The deposition process and the investigation of the plasma phase of hexamethyldisiloxane (HMDSO)/O₂ gas mixtures were carried out in a stainless steel reactor [1] with a parallel plate configuration (the lower substrate-holder electrode can be connected to the ground or be RF-driven; the upper

*Lecture presented at the 15th International Symposium on Plasma Chemistry, Orléans, France, 9–13 July 2001. Other presentations are presented in this issue, pp. 317–492.

[‡]Corresponding author; present address: Eindhoven University of Technology, Department of Applied Physics, Eindhoven, The Netherlands

electrode is always RF-driven). The plasma phase investigation was performed by means of FT-IR and OES techniques. The plasma-emitted radiation was sampled through a sapphire window mounted on the reactor by means of a quartz optical fiber and analyzed by a Jobin-Yvon HR 320 spectrometer. The actinometric approach was carried out by adding an Ar/He (in the ratio of 3/7) mixture to the gas feed, in the amount of 5 % with respect to the total flow rate. The infrared absorption of the gas and plasma phase was monitored by means of a Bruker IR Fourier Equinox 55 spectrometer, utilized also for the *ex situ* deposited film chemistry investigation. SiO_x films were deposited onto 12- μ m RNK12 Mitsubishi polyethyleneterephthalate (PET) films for performing O₂ transmission measurements (OTR) carried out at 23 °C and 50 % humidity.

Effect of the gas feed composition

Figure 1 shows the CO ($B^1\Sigma-A^1\Pi$, 519.8 nm), CO₂⁺ ($A^2\Sigma^+-X^2\Pi$, 288.3 nm) and O ($3s^3S^0-3p^3P$, 844.6 nm) actinometrically corrected emission trends, as a function of the O₂/HMDSO flow rate ratio. The CO and CO₂ density trends as a function of the gas feed composition can be explained with the conversion of CO to CO₂, as the oxygen content increases. For O₂/HMDSO higher than 19, also CO₂ decreases because the monomer source diminishes with the dilution. It can be concluded that in the considered experimental conditions the maximum efficiency in the conversion of carbon moieties in CO₂ is obtained for an O₂/HMDSO ratio between 9 and 19. This can turn useful for choosing the gas feed composition for the deposition of SiO₂-like films characterized by a low carbon content, potentially suitable in the packaging field. In Fig. 2, the infrared spectra of the deposited films have been reported as a function of the O₂/HMDSO ratio, together with the bonds attribution [2,3]. It can be observed that the films contain carbon for O₂/monomer ratio lower than 9. This is in agreement (within the detection limit of the FT-IR technique) with the results found by investigating the plasma phase (Fig. 1): at low O₂/HMDSO ratio, the film chemistry can be referred to as SiC_xH_yO_z. As the O₂-to-monomer ratio increases, the higher oxidation efficiency leads to an increased inorganic character of the deposited film, defined as SiO₂-like. The permeability to O₂ (data not reported here) decreases as the coating is characterized by an increasing inorganic character. The OTR values range from the virgin PET one (124 cm³/m² day atm), obtained at O₂/HMDSO equal to 2, to 0.3–0.6 cm³/m² day atm,

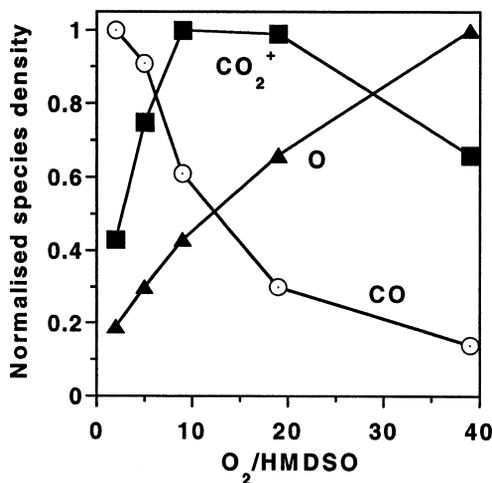


Fig. 1 O, CO, and CO₂⁺ normalized densities as a function of the O₂-to-HMDSO flow ratio. 100 mTorr, 100 W (upper electrode), and 50 W (lower electrode).

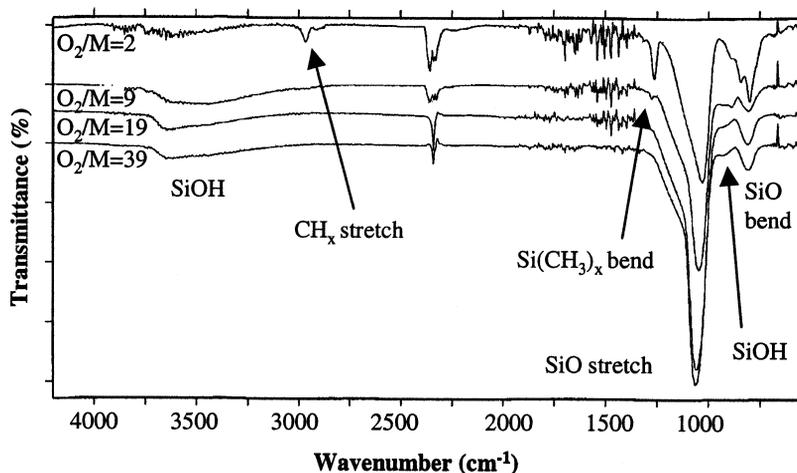


Fig. 2 FT-IR spectra of plasma-deposited SiO_x films as a function of the O_2 -to-HMDSO flow ratio. 100 mTorr, 100 W upper electrode, 50 W lower electrode.

for high dilution conditions. Carbon is known from literature to negatively affect the barrier properties of the deposited layer, and our results agree with the previous ones [4].

Effect of the RF power

The effect of the power on the plasma process has been studied by feeding the discharge with an oxygen-rich mixture ($\text{O}_2/\text{HMDSO} = 19$), in order to have a high oxidation efficiency. Figure 3 shows the infrared spectra of the HMDSO/ O_2 -fed plasmas [1,5] at different power conditions. CO and CO_2 integrals (data not reported here) increase as a function of the power and reach a plateau for power values higher than 200 W. Therefore, in these experimental conditions, the maximum oxidation efficiency can be achieved in this power range. Broad absorption bands appear in the regions of 3270, 1070, and

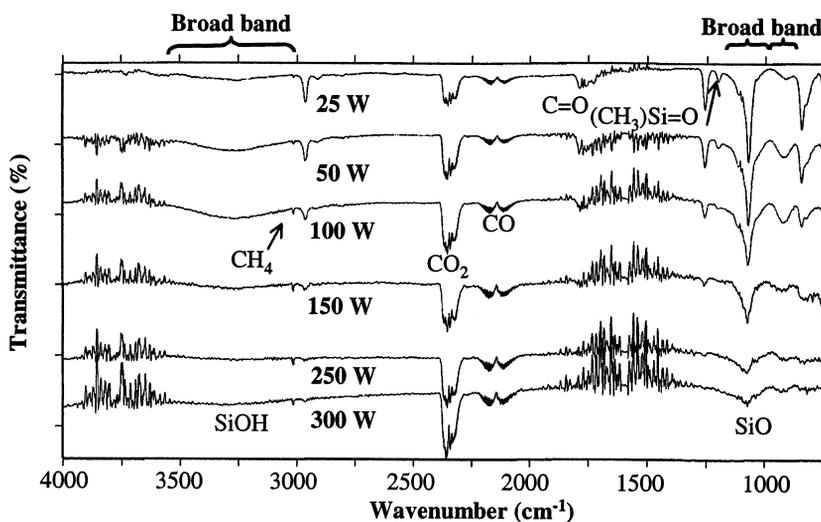


Fig. 3 FT-IR transmittance spectra of HMDSO/ O_2 plasmas as a function of the RF power. 100 mTorr, HMDSO flow rate 1 sccm, O_2 flow rate 19 sccm.

930 cm^{-1} : although we cannot neglect the presence of particulate within the plasma phase, we believe that the main contribution to these broad bands comes from deposition precursors. These absorption bands falling in the above-mentioned ranges correspond to SiOH stretch, SiO stretch, and SiOH bend modes, respectively.

The IR spectra of the plasma-deposited films (not reported here) at different power conditions have shown the presence of carbon within the film only for power values lower than 50 W. The SiOH-related bands (OH stretch and SiO bend at 3450 and 930 cm^{-1} , respectively, visible also in Fig. 2) decrease as a function of the power, until they are not detected anymore for 250–300 W. This trend can be explained as it follows: the power appears to favor a more inorganic character of the film (SiO_2 -like) and likely promotes the condensation of vicinal silanol groups, to form Si–O–Si bridges (with loss of water). The plasma chemical composition in terms of the ratio of SiOH and SiO_x band integrals, $\text{SiOH}/\text{SiO}_x^{(\text{plasma})}$, has been evaluated and reported in Fig. 4, along with the $\text{SiOH}/\text{SiO}_x^{(\text{film})}$ ratio related to the chemical surface composition. It has been found that the surface chemistry reflects the plasma chemistry in terms of abundance of silanol groups with respect to SiO in silica environment, for power higher than 100 W. For lower power condition, no agreement was found between the plasma phase and the surface, likely because of the contribution of Si–C containing species to the plasma phase $\text{SiOH}/\text{SiO}_x^{(\text{plasma})}$ integral ratio, not accounted for in the analogous film ratio. The OTR dependence from the discharge power (Fig. 4) correlates with the above mentioned ratios at high O_2 -to-HMDSO ratios (poor-carbon films), thus, suggesting that a further optimization in order to obtain SiO_2 -like layers, passes through the efficiency of the plasma power in reducing the SiOH density, likely inducing the deposition of more dense film and potentially more suitable for gas-diffusion barrier applications.

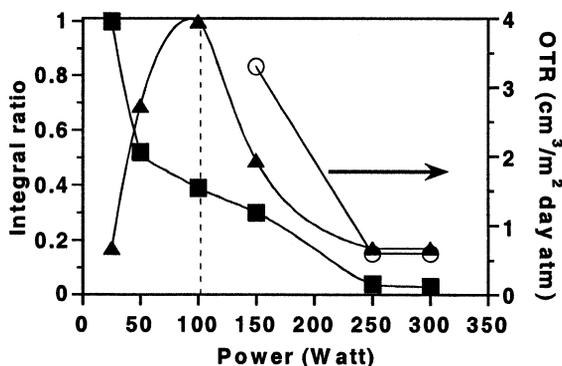


Fig. 4 Effect of the delivered power on the IR integral ratio SiOH/SiO of the deposited film (■) and the plasma phase species (▲) and corresponding OTR values (○). 100 mTorr, HMDSO flow rate 1 sccm, O_2 flow rate 19 sccm.

CONCLUSIONS

HMDSO/ O_2 -fed RF glow discharges have been ignited in order to deposit SiO_2 -like films. The external parameters taken into consideration have been the feed gas composition and the power input. The plasma phase study has highlighted the suitable feed gas composition ($\text{O}_2/\text{HMDSO} = 19$) for the deposition of carbon-poor films, in our experimental conditions. Moreover, the study of the effect of the plasma power at high dilution conditions has led to increase the inorganic character of the films at higher power input, by simultaneously decreasing the SiOH coating density. The detection of silanol groups in the plasma phase can lead to an *in situ* process control of the deposition by means of FTIR

technique, performed at high dilution of the monomer source in O₂, when a very high barrier performance is expected.

REFERENCES

1. M. Creatore, F. Palumbo, R. d'Agostino, P. Fayet. *Surf. Coat. Technol.* **142–144**, 163 (2001).
2. A. Goulet, C. Charles, P. Garcia, G. Turban. *J. Appl. Phys.* **74**, 6876 (1993).
3. K. Aumaille, C. Vallee, A. Granier, A. Goulet, F. Gaboriau. *Thin Solid Films* **359**, 188 (2000).
4. R. Lamendola, P. Favia, F. Palumbo, R. d'Agostino. *Eur. Phys. J. Appl. Phys.* **4**, 65 (1998).
5. D. Magni, Ch. Deschenaux, Ch. Hollenstein, M. Creatore, P. Fayet. *J. Phys. D: Appl. Phys.* **34** (1), 87 (2001).