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Process control of organosilicon plasmas for barrier film preparations

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Abstract: Hexamethyldisiloxane-oxygen and hexamethyldisilazane-oxygen rf plasmas have been used for deposition of organosilicon and SiO_2-like thin films with high barrier properties. Plasma phase has been investigated by Actinometric Optical Emission Spectroscopy; X-Ray Photoelectron Spectroscopy and Infrared Spectroscopy have been used for films surface and bulk composition. A semi-quantitative model of deposition has been assumed which accounts for the deposition kinetics and film composition. A practical process control parameter has been developed by actinometry, able to monitor film composition and O_2 and H_2O vapour permeability.

INTRODUCTION

In the last few years a great deal of work has been produced in the field of Plasma Enhanced Chemical Vapour Deposition (PECVD) of organosilicon compounds (ref. 1-8). The first target of these studies was the production of SiO_2-like films devoted to microelectronics applications. However, beyond their dielectric properties plasma-deposited SiO_2-like materials are characterised by other very important properties such as good hardness, resistance to chemicals and abrasion, optical transparency, good biocompatibility and low gases permeability (ref. 9,10). Such properties make thin films of these materials suitable for a great number of applications ranging from the production of anti scratch coatings for ophthalmic lenses protection to barrier films for food and pharmaceutical packaging. Although SiO_2-like thin films can be deposited from silane-containing feeds, the use of organosilicon monomers is by far preferred because of their cheapness and ease to handle. A great number of safer monomers are utilised both in the field of organosilicon thin film deposition research and industrial production.

In our work both hexamethyldisiloxane (HMDSO)-oxygen and hexamethyldisilazane (HMDSN)-oxygen mixtures have been utilised, under high plasma power density condition, i.e. high monomer fragmentation condition, in a parallel plate reactor. The results here reported are related to both monomers and in particular, the profiles of actinometers, of fragments relative concentrations produced in plasma, and the material composition as a function of O_2-to monomer ratio are very similar and almost independent of which monomer is used. The films have been deposited on silicon and on 12 μm thick polyethilenterephtalate (PET) substrates. X-Ray Photoelectron Spectroscopy (XPS) analyses have been employed for investigations of surface film composition; the O_2 and H_2O vapour (WV) permeability of 500 Å thick siloxane films has been evaluated by means of a MOCOM permeameter. The diagnostic of principal fragments produced in the plasma phase has been performed by means of Actinometric Optical Emission Spectroscopy (AOES).

The most important target of this work is the development of an *in situ* monitoring and control of the deposition process as well as of the material composition and barrier properties. From this point of view AOES was a very useful tool in providing an important practical parameter, i.e. the CH radical density in plasma phase, which has been found to be correlated both to the organic character and to the gas diffusion properties of deposited films. Both the material and the gas phase diagnostics allowed to set the basis of the first "semi-quantitative" mechanism of deposition of siloxane films, accounting for material composition and deposition rate (ref. 11-18).

GAS PHASE AND MATERIAL DIAGNOSTIC

Before analysing the actinometric results, some considerations on the technique are needed. AOES can be considered only to give semi-quantitative information on the trends of emitting species in the plasma phase, on the other hand, actinometry is the only technique which gives such a large number of observables and of information on important fragments produced in the plasma and eventually involved

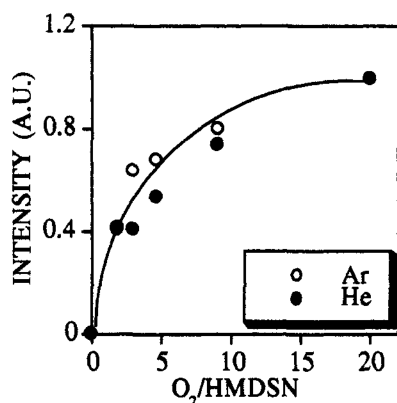

Fig. 1 Normalised emission intensities of the actinometers as a function of feed composition.

in the deposition process. From this point of view, AOES has been successfully utilised in several works, and revealed to be extremely useful to propose simplified kinetics mechanisms accounting for the microscopic processes and pointing out to the role played by various precursors. In this work, besides the study regarding the deposition mechanism, much attention has been focused on the use of the Actinometry as a tool able to *in situ* control both the deposition process and the thin film composition and gas transmission properties. We have utilised the technique with two actinometers, Ar and He characterised by very different excitation threshold energy, 13.5 eV for Ar, and 23.0 eV for He. This approach, although can not rule out the effects produced by excitation channels others than direct electron impact from ground state, acts as a sort of check test for the applicability of actinometry for those species whose excitation thresholds are far from that of the actinometers. Whenever the emission trends of the two actinometers are coincident as a function of plasma parameters, the emission of the detected species divided by the actinometer emission can be assumed representative of the species concentration trends in the ground state.

In Fig. 1 the relative emission intensities of the two gases are plotted as a function of the O_2-to-HMDSO ratio in the feed, very similar profiles have been obtained when O_2-HMDSN containing feeds have been utilised.

It is evident from the Fig. 1 that the emission intensities of both species follow the same increasing behaviour. Since Ar and He emissions can be related to the density of electrons with energy higher than ~13.5 and ~23.0 eV, respectively, it can be concluded that an oxygen content increase in the feed, whatever monomer is used, only results in an electron density increase, without important effects on the electron energy distribution function. It follows that, in the explored experimental conditions, actinometry can be safely utilised for all detected species, whatever are their excitation threshold energies.

In Fig. 2, the relative actinometric concentration trends of followed species have been plotted as a function of O_2-to-HMDSN ratio in the feed. It is important to stress that almost the same emission trends, as a function of O2-to -monomer ratio have been observed when HMDSO fed plasmas are utilised. In this analysis the actinometric trends, i.e. the ratios of emissions I_x/I_{act}, have been assumed to be representative of concentration trends. It is worthy to report here that even though H-atoms have been detected, their actinometric behaviour has not been considered representative of concentration trends since other studies confirmed that for H-atoms chemical excitation channels are also possible (ref. 11).The trends of Fig. 2 lead to a clear picture of the reactions occurring in the plasma phase. The rapid increase of CO relative concentration and the contemporaneous decrease of C and CH radicals denotes that CO (and eventually CO_2 molecules) must be formed by reaction of O-atoms (and/or O_2 molecules) with the HMDSO molecules and with C-containing fragments in the plasma phase. Similarly, the relative concentration of SiO and Si radicals are characterised by opposite profiles. The increase of SiO and the contemporaneous opposite decrease of Si radicals by adding O_2 to the feed can support the hypothesis that SiO fragments are mainly produced by the homogeneous gas phase reaction consuming silicon atoms. On the other hand, the production of SiO radicals through heterogeneous reactions can be decisively ruled out also on the basis of the absence of any SiO emissions when a "dirty" reactor (i.e. severely contaminated by residual organosilicon layers formed in many runs with the sole monomer as feed) was exposed to O_2-Ar discharges. This undoubtedly confirms the fact that also in glow discharges fed by HMDSO/O_2 mixtures, the contribution of heterogeneous reactions to the production of SiO radicals can be considered negligible. This point is

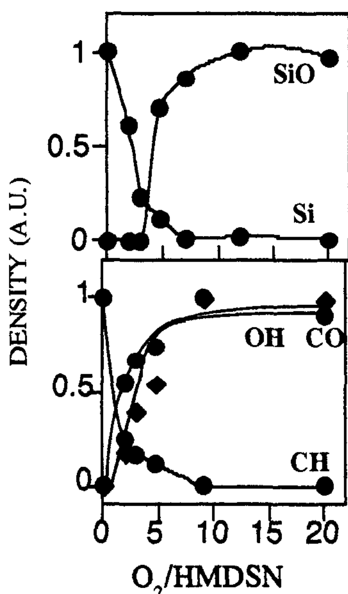

Fig. 2 Relative concentration trends of detected species in plasma phase as a function of feed composition.

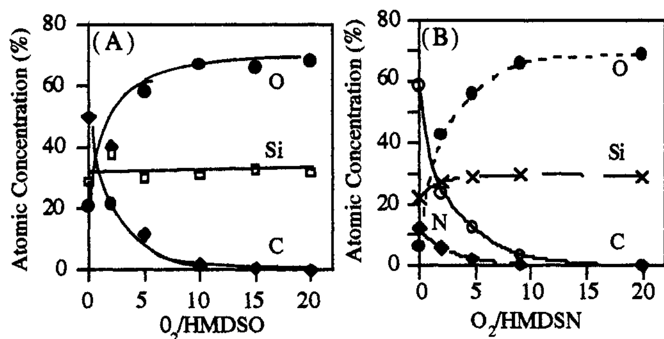

Fig. 3 Surface composition of deposited films as a function of (A) O_2-to-HMDSO and (B)O_2-to-HMDSN ratio in the feed.

particularly important since in organosilicon-oxygen plasmas operating in conditions suitable to deposit conformal SiO_2 for microelectronics applications much importance is generally given to an heterogeneous mechanism of oxidation.

Atomic surface compositions of the films deposited from HMDSO-O_2 and HMDSN-O_2 fed plasmas are plotted in Fig. 3A and B, respectively, as a function of O_2-to-monomer ratio in the feed. The trends are very similar to the profiles reported by other authors (ref. 19,20). In our case the most important piece of information is the qualitative agreement between the trends of some species followed in the plasma phase and the surface film composition. In particular, the increase of the oxygen content in the films well matches the rising profile of the relative concentration of SiO radicals in the plasma, on the other hand, the decreasing profile of the concentration of C-containing species in the plasma phase, such as C and CH radicals, is in agreement with the decreasing trend of carbon content in the material. Si content in the film is almost constant, even though Si-containing groups in the gas phase are reduced. This finding suggests the hypothesis that Si-polymer precursors in the gas phase are replaced by SiO-precursors upon O_2 addition to the feed.

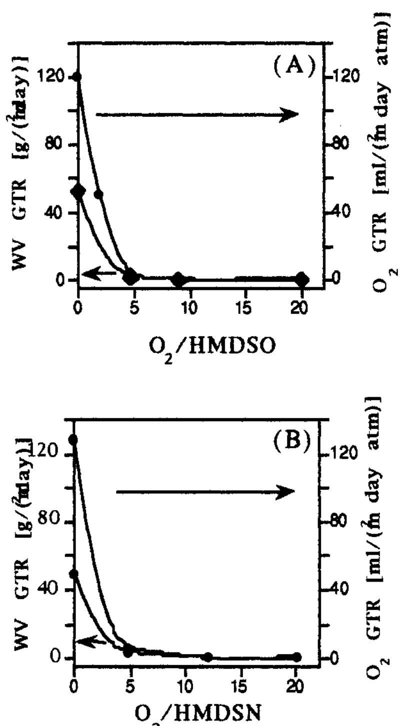

Fig. 4 O_2 and WV GTR of films deposited from (A) O_2/HMDSO and (B) O_2/HMDSN fed glow discharges.

H_2O vapour and O_2 GTR of 12 µm, HMDSO-O_2 and HMDSN-O_2, plasma coated PET substrates are reported in Fig.4A and B, respectively. It is evident that the permeability properties are independent from the monomer used, in fact, in both cases GTRs sharply decrease by increasing the O_2-to-monomer ratio in the feed. When O_2-to-monomer ratios ranging from 10 to 20 are utilised, excellent O_2 and H_2O vapour diffusion barrier layers have been obtained (O_2 GTR <0.5 cc/(m^{2}datm)) on conventional polymers used for food packaging. The lowest permeability values have been obtained for 500 Å thick films with SiO_2-like stoichiometry. It is important to stress that FT-IR investigations revealed the absence of OH and of Si-OH groups in high barrier films, both immediately after the deposition and after about 2 months. This finding can support the hypothesis that when oxygen-rich feeds and high power density, i.e. high monomer fragmentation conditions are utilised, materials with highly cross linked structure and with low ageing effects have been deposited.

DEPOSITION MECHANISM

The comparison between compositions of film surfaces and of plasma phase has allowed to propose a semi-quantitative model of deposition. Even though AOES is not able to give a fully quantitative insight on the absolute concentration of the emitting species, at least when O_2-rich feeds are utilised (O_2/HMDSO ranging from 10 to 20) plasma phase is mainly composed by SiO, OH, CO and other products from oxidation reactions, as eventually CO_2, H_2O, and SiO_2. It means that, at least in O_2-rich feeds, the high content of oxygen atoms and molecules promotes the consumption of C, CH, Si radicals and of the organic moieties of fragments produced in plasma phase. In other words, at high O_2-to-

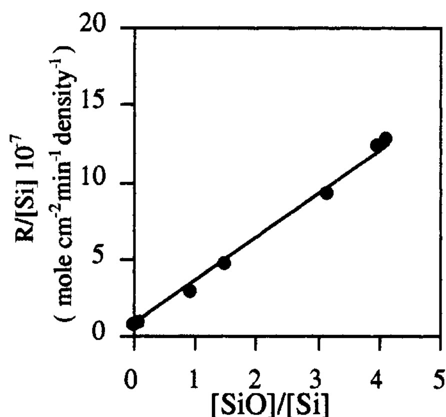

Fig. 5 Linear correlation between R/[Si] and Si-to-SiO relative concentration in the plasma.

HMDSO ratio, the concentration of complex fragments as $SiO_xC_yH_z$ and SiC_xH_y can be considered negligible. From this observation, when O_2-rich feeds and high power density conditions are utilised the following conclusions can be drawn:

(a) the contribution to deposition from $SiO_xC_yH_z$ and SiC_xH_y can be ruled out;
(b) the main film precursors are SiO radicals;
(c) the contribution to the deposition mechanism from CH, C, and Si radicals can be considered very low;
(d) SiO_2-like films are obtained.

The deposition rate expression can be written as:

$$Rd=K_1[Si]+K_2[SiO] \qquad (1)$$

In deposition rate expression Si-radicals concentration has been put as representative of C- and CH- fragments on the basis of similar concentration trends obtained from AOES investigations. In order to check the validity of this equation, in the O_2-to-monomer ratio ranging from 0 to 20, the variation of film structure and density occurring by changing film stoichiometry should be taken into account. From this point of view the deposition rate has to be referred to the *moles of polymer formed per unit time*. The apparent expression of deposition rate (2) can be rearranged as it follows:

$$R/[Si]=K_1+K_2[SiO]/[Si] \qquad (2)$$

R, can be expressed as:

$$R=Rd/M \qquad (3)$$

where M is the weight of molecular formula, calculated from XPS at each condition of feed composition. In Fig. 5 R/[Si] is plotted as a function of [SiO]/[Si]; the linear correlation obtained is a clear indication that the deposition rate equation (2) is correct, SiO (and eventually SiO_2) radicals mainly contribute to the deposition kinetics through gas phase direct deposition mechanism.

PROCESS CONTROL

In Fig. 6A and B the carbon content in the films has been plotted as a function of the intensity ratio I_{CH}/I_{Ar} in the plasma phase, at different plasma power and pressure conditions, by changing feed composition when HMDSO and HMDSN monomers have been utilised, respectively.Whatever monomer has been employed, a linear correlation exists between the carbon concentration in the deposited material and the C-and CH- radicals concentration in the plasma phase, for all power and pressure conditions explored.

It is here important to stress that the carbon content in the material, as well as the CH- (and C-) radicals concentration in the plasma phase (C and CH actinometric concentration trends are similar) are not dependent on plasma pressure and power explored condition, only feed composition appreciably affects both deposited material and plasma phase composition. This means that, at least in our experimental conditions characterised by high monomer fragmentation, the carbon content of the growing films can be predicted during the deposition by means of simple

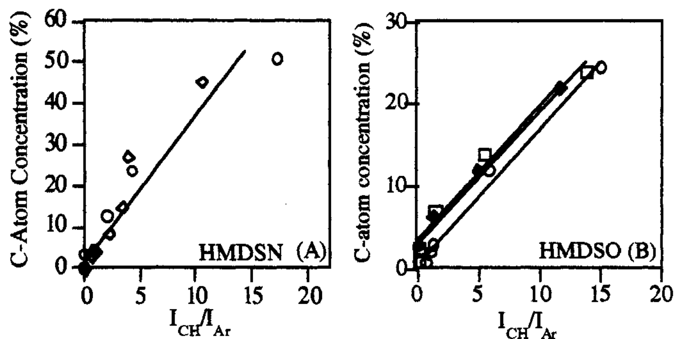

Fig. 6 Linear correlation between the carbon content in the films and the intensity ratio I_{CH}-to-I_{Ar} in (A) HMDSN and (B) HMDSO containing feeds at different plasma power and pressure.

spectroscopic measurements of gas phase concentration of detected C-containing radicals. From this point of view, Actinometry can be employed as a useful tool to *in situ* control the film stoichiometry, simply adjusting the feed composition in order to keep the C-containing radicals density content, i.e. to keep the selected CH-to-Ar emission ratio constant.A direct example of the importance of these correlations for industrial applications is given in Fig. 7, where the oxygen and the water vapour transmission rates of a 12 μm (HMDSN-O_2) plasma coated PET substrates are shown to be linearly correlated to the *in situ* optical parameter CH-to-Ar emission ratio. In other words:

$$GTR=K(I_{CH}/I_{Ar}).$$

The practical importance of this finding is that it defines the correlation between gas phase composition, film composition and barrier properties, and then solves the problem of a reliable and accurate control of process performances. On these authors opinion this is the first example in the literature of *in situ* monitoring, by means of actinometry, of the most important practical parameter for barrier films. From the practical point of view of process control for applications, the actinometric trend of CH radicals can be utilised as a chemical test parameter, independently of plasma power and pressure conditions, to *in situ* check the barrier properties of the films. From these experiments it can be drawn that at least when high monomer fragmentation conditions are utilised, the organic character is a key parameter and the only parameter determining the gas barrier properties of deposited films. At this moment, the reason why the carbon content affects the films permeability is not yet clear. In fact, the organic character could affect the material structure, promoting the growth of films characterised by low degree of cross linking, as well as by high gas solubility into the material.

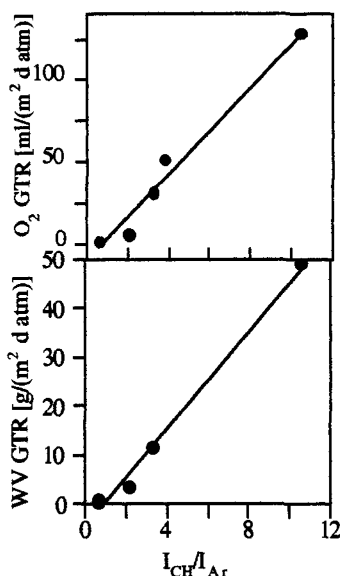

Fig. 7 O_2 and WV GTR for 12 μm PET films coated with HMDSO-O_2 fed glow discharges vs the I_{CH}-to-I_{Ar} emission intensity.

CONCLUSION

Despite the fact that actinometry can not be considered a 100%-quantitative technique for monitoring the trends of ground state concentrations of major fragments formed in the discharge, it has been successfully utilised from the point of view of process control for applications. The actinometric trend of CH-radicals can be utilised as a chemical test parameter, independently of plasma power and pressure conditions, (at least in high monomer fragmentation condition) to *in situ* check the barrier properties of the films. This is a striking result which should drive research efforts on the use of *in situ* actinometry for improving plasma processes applications in many industrial fields and, in particular, for food and pharmaceutical packaging. Both the deposition rate and the chemical composition of the films are fully consistent with a simplified kinetics in which, at least in high O_2-to-monomer ratio conditions, a major role is played by SiO fragments as well as by Si and C-containing ones.

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