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Maleic anhydride film deposition through an active screen plasma system

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Abstract. The active screen plasma system has been extensively studied over the past few years, mainly for plasma nitriding purposes. This technique also provides possibilities of treating non-electrical conducting materials, such as polymeric ones, which is unattainable with a conventional DC plasma system. In this work, an active screen plasma setup for maleic anhydride (MA) film deposition on a glass substrate was used. The plasma working gas was a mixture of argon and MA vapour. Films obtained through conventional plasma discharge were compared with the active screen deposition process, in both DC and pulsed-mode plasma. The samples were characterized through Fourier-transform infrared spectroscopy and static contact angle between the film's surface and droplets of distilled water. Film thickness measurements were performed through profilometry. Results showed that MA films obtained through the active screen system are thicker and more efficiently preserve the anhydride groups than those obtained from conventional plasma discharge.

Keywords. Film deposition; maleic anhydride; active screen.

1. Introduction

Active screen plasma has drawn some interest in the last few years, mainly for plasma nitriding purposes, the so-called 'active screen plasma nitriding'. In the 'active screen plasma system' (ASPS), the plasma cathode region is located in the cage, not directly on the samples. This prevents the direct bombardment of energetic ions onto the pieces, as it occurs in conventional plasma processes. The disadvantages caused by the direct influence of the discharge energy on the surfaces of the work load are possible damages caused by edge effects, the generation of hollow cathode discharges, inhomogeneous temperature distributions, sputtering of atoms, surface over-heating or the occurrence of the arcing phenomena [1]. The workpieces located inside the cage are maintained at floating potential, which has values between -10 and -20 V in most cases. This way, the energy delivered to the workpiece due to the positive ion bombardment is mild and does not produce excessive sputtering from surface or excessive heating of the part to be treated. The plasma heats the screen up, and radiation from it provides the heat that brings the components to the required temperature [2]. Through controlling the plasma's power and temperature, its chemical reactivity can also be controlled, which depends on the ratio of reactive molecules created from the precursor gas in the chamber. For example, Hamann *et al* [3] studied the formation of reactive products in a plasma generated in an active-screen low-pressure H_2–N_2 gas mixture containing small amounts of CH_4 and CO_2. They found that the concentration of reaction products

NH_3, HCN, CO and H_2O is easily controlled through the power and temperature of the plasma generated at the active screen. Besides those molecules, reactive species are also produced as atomic, molecular and ionic excited states (for example, N^{+2}-(0-0), N, N^+ and the N_2-(0-0) band). Active screen plasma has also been used for surface functionalization of polymers. For example, Kaklamani *et al* [4] were successful at using the ASPS, with N_2–H_2 plasma, to modify the surface chemistry of UHMWPE without altering its mechanical properties and topography.

In this work, an ASPS was used for the deposition of maleic anhydride (MA) polymer films. MA is an interesting material for the synthesis of thin films due to the double bond and the reactive anhydride group [5–7]. Many techniques can be used to polymerize MA through conventional methods [8,9], however, they require expensive equipment, the use of chemical solvents and reaction times may be too long. There exist previous studies on the chemical structure and properties of MA films deposited through conventional plasma processes [6,7,10–14]. Their chemical and physical properties are directly related to the extent of fragmentation that occurs during film deposition. As a result, the maintenance of reactive or functional species from the monomer can be a challenge, due to the complex nature of the plasma process, since the MA functional group can be lost during the growth of the film [7,10]. Even in low-power plasma, the ring of the MA monomer might be opened. Therefore, films grown on a substrate may contain different products (due to the dissociation of the monomer) instead of the desired anhydride

Table 1. Samples' nomenclature and experimental setup.

	Experimental parameters			
Experimental mode	Deposition time (min)	Voltage (V)	Duty cycle (%)	Working gas pressure (Torr)
Continuous mode – AS (CAS)	10 and 20	300	—	3.3×10^{-1}
Pulsed mode – AS (PAS)	10	170	60	3.3×10^{-1}
Continuous mode - no AS (CNAS)	10 and 20	350	—	3.3×10^{-1}
Pulsed mode – no AS (PNAS)	10	350	60	3.3×10^{-1}

groups. In most cases, the processes of fragmentation can be partially controlled through the deposition parameters, such as plasma current and voltage (plasma power), working gas pressure and substrate temperature [7,10]. Pulsed plasma is an alternative to change the plasma power relatively to the continuous powered plasma, since the plasma ionization rate depends on the frequency of voltage pulsing and the duty cycle. By pulsing the voltage with short pulses, the average energy of the electrons increases, as well as the population of species created because of the higher energy electrons [15]. On the other hand, the power of a pulsed plasma system can be lower than that of the continuous mode, thereby producing less damage to the functional group and improving the polymerization of MA [6,7,10,12–14].

Considering the fact that the maintenance of the anhydride group is essential to grow MA films and that, to the best of our knowledge, there are no studies in the literature involving anhydride film deposition using an active screen, this paper investigates the maintenance of the anhydride group, under continuous and pulsed plasma, with the sample under floating potential placed into the active screen.

2. Experimental

2.1 *Materials*

The MA monomer used in this work was obtained from Sigma-Aldrich, with a purity of 98.5%. The working gas was Ar 99.999% and the substrate was a glass sheet.

2.2 *Plasma polymerization of MA*

Plasma polymerization of MA was carried out in a glass chamber of approximately 20.0 cm in diameter and a height of 18.0 cm, with a grounded stainless-steel base and asymmetric electrodes. The glass substrates were cleaned with ethanol prior to the plasma treatment. The reactor's pressure was pumped down using a rotary pump from Adixen to the base pressure of 10^{-3} Torr and the films were grown at a work pressure of 3.0×10^{-1} Torr, monitored with a Pirani vacuum gauge. The working gas was a mixture of Ar (flow of 48 sccm) and MA vapour. The deposition times were 10 and 20 min.
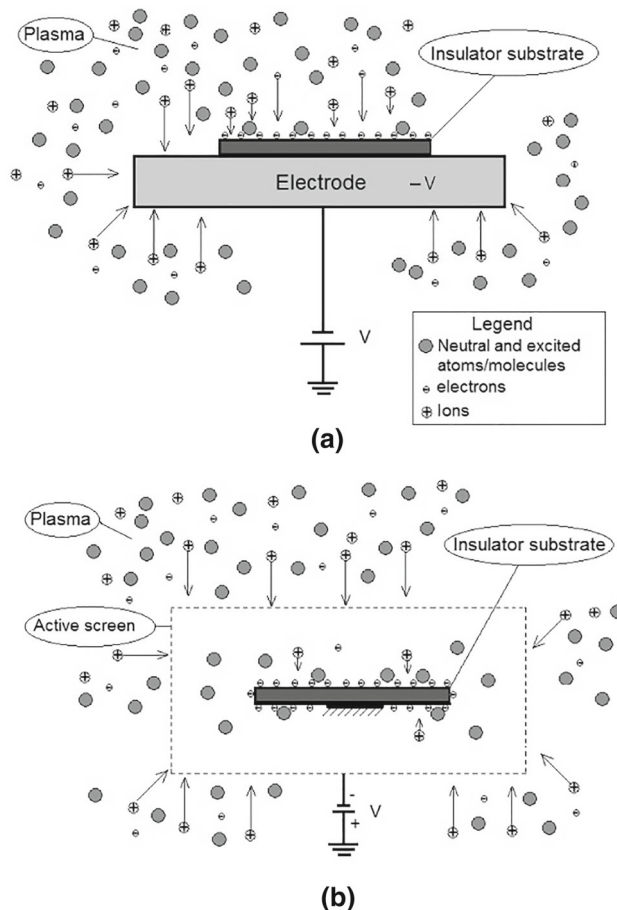

Figure 1. Representation of two electrode geometries used in this work for growing films of MA on a glass substrate: (**a**) the glass substrate is placed on the flat electrode and (**b**) the glass substrate is housed in an AS.

After completing the process, the monomer flow was allowed to continue for 2 more minutes, and finally the chamber was evacuated back to base pressure before being opened to atmospheric pressure. The floating potential was measured against ground, using a conductor probe. Table 1 presents the used nomenclature and experimental setup.

The polymerization experiments were carried out in two modes: DC discharge and pulsed discharge. Figure 1 shows

an overview of the experiment in two different setups: (a) with active screen (AS) and (b) without AS. The flow of MA from a heated reservoir to the chamber was controlled through a needle valve. The gas mixture was 90% Ar and 10% MA, which was adjusted through partial pressure of each gas: first, the Ar flow was set (until the pressure in the chamber reached 0.54 Torr); then, MA was allowed to flow, until the pressure reached 0.60 Torr.

Figure 1a shows a schematic setup for growing films of MA in an ASPS. The glass substrate reaches floating potential due to the excess of electrons accumulated on its surface, relative to the ions, coming from the plasma [16,17]. Notice that, in this case, the plasma is generated outside the cage and the sample (inside the cage) is not in contact with the glow discharge. Figure 1b shows the other case, where the substrate is placed on the cathode's surface (the cathode is the holder for the substrate), which is interacting with the glow discharge. In such a case, the substrate's surface is also at floating potential, but it is very close to the glow discharge. In this configuration, the interaction between the plasma and the surface is more energetic and the bombardment by ions and electrons is more intense. In this work, experiments were carried out using both configurations described above, in order to evaluate the efficiency of the AS in growing films of MA.

The sample holder used in this experiment had the following dimensions: 3.3 cm width, 8.0 cm length and 0.7 cm thickness. The distance between the cathode and the anode was 10 cm. The deposition time was set to 10 and 20 min for continuous DC voltage and 10 min for pulsed voltage. The duty cycle for the pulsed mode was 60% ($t_{on} = 6\,\mu s$, $t_{off} = 4\,\mu s$ and $f = 100$ kHz). For the AS configuration, the cage had dimensions: $7 \times 11 \times 4.5$ cm, so that the substrate's surface (placed in the middle of the cage) was at least 3 cm away from the glow discharge produced outside the grid.

2.3 *Characterization techniques*

Fourier-transform infrared (FTIR) spectroscopy analysis of the samples was performed using a Perkin-Elmer Spectrum One with a resolution of 4 cm^{-1}, averaging over 32 scans. Potassium bromide (KBr) was used to analyse the MA monomer, while the samples with the deposited films were analysed directly on the substrate in a transmittance mode. FTIR spectroscopy is suitable for the analysis of MA films since it allows us to check for the possible presence of typical bands of MA at 1780 and 1860 cm^{-1}. The data were restricted to the region of 1500–2100 cm^{-1}.

The static contact angle was measured by the Sessile drop method using a 590 Ramé-hart instrument at 25°C. Distilled water droplets (of about 1 μl) were deposited on the sample's surface at two different sites. The average of 30 measured values for a sample was taken as its contact angle of water.

Film thickness measurement was carried out with a Bruker Dektak XT profiler. The tip radius was 12.5 μm, the force was equal to 3 mg and the repeatability was 4 Å. In order to

make the measurement of the film's thickness easier, a small glass mask was superposed on the substrate, prior to the film deposition. The thickness measurement was taken between the top of the film and the valley produced in the substrate due to the absence of the film in the regions where the mask had been placed.

3. Results and discussion

Table 2 shows input parameters, output parameters and results of plasma assisted deposition of MA films on a glass substrate, studied in this work. Experiments carried out in the AS and in the glow discharge had two plasma generation modes: (1) continuous voltage (DC) and (2) pulsed voltage (100 kHz) with a 60% duty cycle. The electrode voltage relative to ground was adjusted to enable maintaining the substrate's temperature lower than 50°C, therefore enabling the condensation and polymerization of plasma-activated MA monomers. For the CNAS condition (continuous, not AS), the necessary voltage to maintain the plasma was at least 350 V. However, for the PNAS condition (pulsed, not AS) with a 350 V cathode bias, the substrate reached temperatures above 100°C, hence a stable growth of MA films was not possible under such conditions, resulting in a film thickness lower than the resolution capacity of the profilometer, as shown in table 2. For all other conditions, the substrate's temperature was lower than 50°C. The temperature was also observed to increase slightly as the process time increases, as observed under CAS and CNAS conditions, from 10 to 20 min. The plasma current is higher for AS configurations due to two main reasons: (1) higher area around the grid that generates more plasma volume and (2) low electrical impedance in the plasma that may be attributed to geometric effects of the grid (small distance between the grid wires, around 1.0 mm), which produces an effect similar to the well-known hollow cathode effect [18]. The relationship between voltage and current provides an analysis of the discharge impedance, shown in table 2. The plasma impedance is lower for the 'AS' configuration and decreases in the pulsed mode, compared with the DC mode (continuous). Higher current values make the plasma more reactive (chemically activated), i.e., it is possible to create more reactive species such as ions, excited molecules (vibrational and/or rotational), dissociation of molecules and free radical formation. Thus, the AS setup is chemically more active than the parallel electrode configuration.

Regarding the floating potential, the highest absolute value $|-60\,V|$ was observed to occur for the AS configuration, in continuous mode discharge (CAS). This indicates an increase in electron flow compared with ion flow, from the glow discharge to the substrate (inside the cage), so that the floating potential is shifted to more negative values. The ion flow decreases towards the substrate, because the glow discharge occurs outside the cathodic cage. On the other hand, energetic electrons (high electronic temperature

Table 2. Input and output parameters for plasma polymerization of MA.

	Plasma mode	Input variables				Output variables				Results	
		Process time (min)	Cathode voltage (V)	Duty cycle (%)	Working gas pressure (10^{-1} Torr)	Plasma current I (mA)	Discharge impedance (V/I) (V mA^{-1})	Floating potential (V)	Substrate temp. (°C) (±2)	Films thickness (nm ±1)	Contact angle (°)
With AS	CAS	10	−300	—	0.6 ± 0.1	47 ± 6	6.3	−60	42	13	32 ± 1
		20							46	16	36 ± 4
	PAS (100 kHz)	10	−170	60	0.6 ± 0.1	135 ± 8	1.3	−19	45	30	26 ± 1
No AS	CNAS	10	−350	—	0.6 ± 0.1	23 ± 7	14.3	−15	34	6	9 ± 2
		20							36	9	19 ± 3
	PNAS (100 kHz)	10	−350	60	0.6 ± 0.1	143 ± 8	2.4	−10	120	<1	54 ± 1

energized by negative voltage in the grid) may reach the substrate. Despite the low flow of ions (for example, Ar^{+}), the energy at which the ions hit the substrate is higher, due to the larger floating potential at the substrate's surface. This may cause changes on the film, such as re-sputtering, monomer polymerization and/or degradation of molecules adsorbed on the substrate.

When the cathodic cage is powered in pulsed mode (PAS), a smaller floating potential is observed at the substrate (−19 V). The higher ionization rate in the grid's cathode provides a high plasma current (135 mA, see table 2) and higher ion flow to the substrate, with consequent decrease in the negative floating potential. The lower floating potential leads to lower energy of ion bombardment. The increase in ion bombardment intensity (with moderate energy) on the substrate's surface may provide important characteristics to the films; for example, (1) improved polymerization; (2) slightly changed molecular structure; (3) improved film adhesion on the substrate and (4) increased film density. However, if the ion bombardment is too energetic (for example, if the floating potential is too high), re-sputtering of the film may occur, which may produce overheating of the substrate. In our case, the film deposition under the PAS configuration was carried out with a floating potential of −19 V, which promoted the highest film growth rate (see table 2) with 30 nm thickness (for $t = 10$ min), while the CAS condition produced a film with 13 nm in thickness.

On the other hand, for the capacitive plasma configuration (without AC), the floating potentials are less intense, and the MA films are thinner. Using the same assumptions discussed above, that may be explained by the large increase in ions flowing to the substrate's surface, which decreases the floating potential. Table 2 shows that, for this configuration (no AS), the floating potential was −15 and −10 V for CNAS and PNAS, respectively. The films' thickness was lower, as shown in table 2 (6 nm for CNAS – 10 min; <2 nm for PNAS). The substrate enclosed by the plasma is undergoing intense bombardment by electrons, ions and radiation from the glow discharge. The temperature for the PNAS condition was about 120°C, which is excessive for the condensation and polymerization of the MA, probably evaporating the adsorbed molecules on the substrate.

The FTIR spectrum shown in figure 2 presents both typical bands to identify the anhydride group structure around 1780 and 1850 cm^{-1} [19], indicating the maintenance of that group after the plasma deposition. Typical functional groups of carboxylic bands around 1730 cm^{-1} can also be observed [18], which indicates the opening of the monomer's ring [7]. This is observed for all films grown in DC-plasma (under continuous discharge voltage) in both configurations, 'with AS' and 'not AS'. In addition, there are reports in the literature that poly(MA) may present a shift in the 1780 cm^{-1} band to a larger wavenumber at 1800 cm^{-1} [20]. Such a shift can be observed in the CAS configuration for deposition times of 10 (1809 cm^{-1}) and 20 min (1783 cm^{-1}) (figure 2a and b), indicating the presence of polymeric MA in the film.
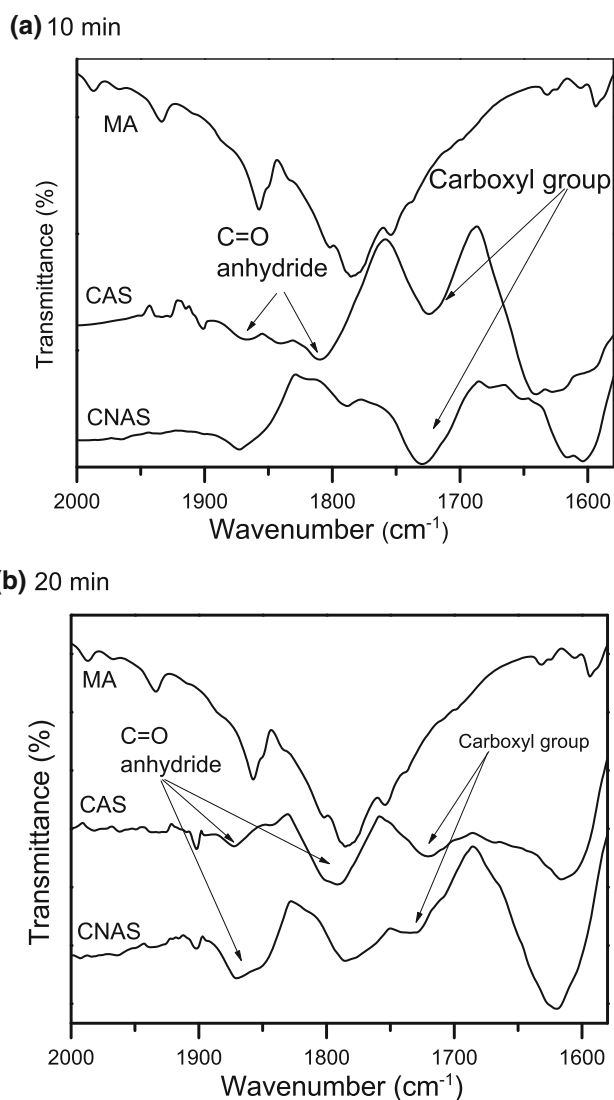
(a) 10 min

(b) 20 min

Figure 2. IR spectrum of MA monomer and film deposition in the continuous mode with and without AS (CAS), (CNAS): (**a**) 10 and (**b**) 20 min.

Moreover, no significant changes were observed in the shape of the FTIR spectrum for different deposition times (10 or 20 min).

Given that the absorbance of IR radiation depends on the film's thickness, then films with different thicknesses (deposited at different conditions, see table 2) may change the intensity of absorption peaks in the FTIR characterization. In order to mitigate such an effect, the ratio between the absorbance of the anhydride group (1780–1800) cm^{-1} and the carbonyl groups (1720–1750) cm^{-1} [21] was calculated as shown in table 3. The CAS configuration provides a higher ratio between those bands, indicating a better preservation of anhydride maleic rings. These results are in agreement with the contact angle measurements (table 2): the polymerization without the AS (CNAS) presented lower contact angle values. The enhancement in hydrophilicity can be attributed

Table 3. Values of absorbance ratio between C = O bonds of anhydride and carbonyl groups.

Deposition time (min)	Experimental setup	
10	CAS	1.6
	CNAS	0.6
20	CAS	1.2
	CNAS	1.2

to the increase in COOH groups [21] in the film on the substrate's surface. Besides, the contact angle for polymerization with AS (CAS) is near that of the neat MA (38°).

The spectra in figure 3 show a comparison between depositions in continuous and pulsed modes for 10 min of deposition with and without the AS. Figure 3a shows that, for depositions without the AS (PNAS), the bands corresponding to both compounds (carbonyl groups and MA) are very weak. This may be attributed to the lack of any film growth or a very thin film ($e < 2$ nm, see table 2). It was observed two characteristic bands in 1850–1800 and 1780–1740 cm^{-1} attributed to the anhydride group. No others carbonyl characteristic band was observed. Furthermore, the mean contact angle result is 54° (table 2), which is near to that of the substrate (47°), corroborating the hypothesis of no continuous film growth, in this case, as shown in table 2. In the CNAS sample, two carbonyl characteristic bands were observed (1729 and 1789 cm^{-1}). One of them was related to the aldehyde group (1740–1720 cm^{-1}), which indicates the opening of the monomer ring, and the other one is related to the anhydride group (two peaks were observed around 1780 and 1850 cm^{-1}). The lowest value of contact angle (9°) could be related to the presence of different carbonyl groups [21]. Furthermore, it has been related to in the literature a strong influence of film thickness on contact angle on the top of polymer thin films [22]. As the films become ultrathin ($h < 10$ nm), the long-range van der Waals forces with the substrate/film interface are strongly dependent on the film thickness and as a result, the surface energy may be a strong function of film thickness. It can decrease significantly the observed contact angle on ultrathin films, as in the CNAS sample (with 6.0 nm thickness) for which it was observed the lowest contact angle as 9°. Regarding FTIR results concerning PAS, figure 3b, it is possible to locate small peaks corresponding to MA and carbonyl groups. A wide band around 1850–1740 cm^{-1} is observed, which is a typical band region for functional groups of ester, carboxylic and anhydride groups, making it difficult to draw any conclusion about the MA rings' maintenance. The contact angle measurement for the PAS condition presents an intermediary value (26°). Such results suggest that some anhydride rings could be present, but, for the pulsed plasma condition used in this work, it is not possible to draw conclusions about the influence of the AS in the maintenance of the anhydride group.
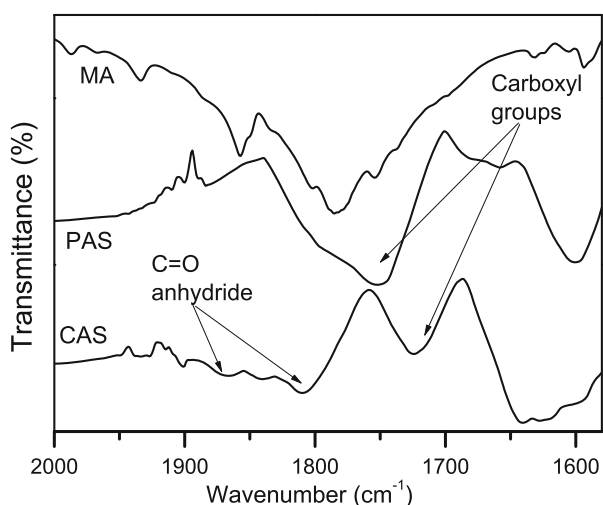
(a) 10 min
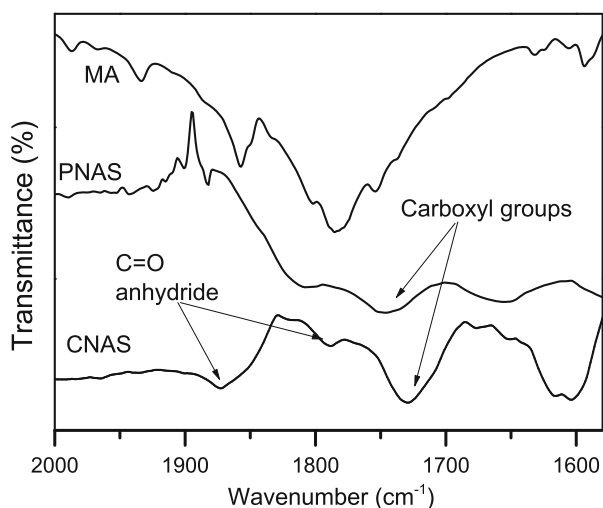
(b) 10 min

Figure 3. IR spectrum comparison between depositions in continuous and pulsed modes: (**a**) CNAS and PNAS and (**b**) CAS and PAS.

4. Conclusion

The AS plays a key role in producing a greater volume of the glow space in plasma, thus producing films with greater thicknesses. As the glow discharge is far from the substrate, its temperature can be maintained as low as 50°C, thus enabling the growth of films sensitive to high temperatures, such as MA. The pulsed mode with AS was the condition under which increased film thickness was achieved in the shorter deposition time. It is also the condition that allows the greatest flexibility for the process' parameters, such as plasma current/voltage, process temperature and, mainly, the floating potential. Moreover, these parameters can be adjusted to find the optimum working condition regarding the maintenance of the anhydride group.

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