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Titania Coatings on Polyethylene Terephthalate: Adhesion and XPS Studies

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Titania coatings have been deposited on polyethylene terephthalate (PET) by the r.f. magnetron sputtering method in an oxygen-argon plasma from a titanium target and in a pure argon plasma from a titania target.

The dependence of the structural properties and the composition of the deposited films on the sputtering pressure and the r.f. power have been studied. In order to improve the adhesion strength between the titanium oxide films and their substrate, various cold plasmas are used to treat the polymer surface. These treatments' influence on the adhesion is studied by using the fragmentation test. The best results are obtained with a carbon dioxide plasma. The adhesion of the titania coating on the PET film also depends strongly on the deposition conditions. The highest values are reached when the titanium oxide films are deposited by the reactive sputtering process and when the elaboration parameters combine a total pressure as low as 0.8 Pa and a power density of 2.54 W cm⁻². The titania/PET interface, investigated by XPS, suggests the formation of Ti-O-C bonds in the first stage of the deposition of the titania films obtained by the reactive magnetron sputtering process, while no chemical reaction seems to occur between the PET and the titanium oxide film sputtered under a pure argon plasma.

Keywords: RF magnetron sputtering; reactive and non-reactive sputtering; titanium and titania targets; cold plasma; argon plasma; oxygen-argon plasma; carbon dioxide plasma treatment of PET; titania thin films; structure and composition of sputtered films

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1. INTRODUCTION

Polymer films coated with ceramic materials have aroused a growing interest in a variety of domains such as food packaging, medicine, etc. The study of these assemblies meets industrial needs for limiting the oxidation of the stocked foodstuff by decreasing gas permeation, especially oxygen permeation.

This study investigates titania coatings on PET. Titanium oxide presents very remarkable characteristics [1–5] not only thanks to its stability but also due to its low chemical reactivity and its excellent properties (high refractive index, transparency in the visible range, absorption of ultraviolet radiation below 380 nm). It would, thus, constitute a good barrier to gas diffusion and protect the polymer against photodegradation.

Numerous techniques can be used to obtain titanium oxide in the form of a thin film [6–9]. Among them is magnetron sputtering which allows the elaboration of deposits with large area uniformity and high density. This method presents two main variants: reactive and non-reactive sputtering.

We have employed for the first time the sputtering of a metal titanium target by an argon-oxygen plasma [10]. By this means, we have obtained titania films with different compositions that vary slightly as a function of the operating conditions. These deposits are crystalline and fragile; they often do not present the degree of compactness required for a good gas-barrier. Contrary to the reactive process, the sputtering of a titania target by a high-purity argon plasma allows us to obtain amorphous deposits [11]. Consequently, a comparative study between the properties of titanium oxide films elaborated by these two methods is essential.

Moreover, a major requirement is that the coating adheres to its substrate in order to assure the durability of the assembly. This characteristic depends on the substrate properties, on the ceramic layer and on the interfacial zone.

In this article, the influence of the deposition parameters on the properties of titania films elaborated by reactive and non-reactive sputtering is presented. The improvement of adhesion between the coating and the substrate by the use of plasma treatments is also studied. In addition, XPS analyses are performed in order to obtain a

good understanding of physico-chemical interactions created in the interfacial region.

2. EXPERIMENTAL DETAILS

Plasma treatments of the bi-stretched PET film (Terphane from Rhône-Poulenc) and the elaboration of titania coatings are achieved in a cathodic sputtering unit (Alcatel SCM 601) which is equipped with a radiofrequency generator (13.56 MHz).

Depending on the sputtering process, the targets (100 mm diameter, 99.9 % purity) are titanium metal or titania and the sputtering gas is, respectively, a mixture of argon-oxygen or a high-purity argon plasma. These targets are fixed on equilibrated magnetron effect cathodes. The PET substrate is fixed on a cooled substrate holder. It is placed directly towards the magnetron axis and maintained during all of the studies at a distance of 70 mm from the target (maximal distance allowed by the apparatus giving a good coating uniformity). The sputtering processes are very stable. The deposition rate varies from 8 to 30 nm h⁻¹ when the titanium target is sputtered (depending on deposition parameters) and from 70 to 250 nm h⁻¹ when the titania target is used (as a starting material).

Before the deposition, the titanium target is presputtered in a pure argon atmosphere (pressure: 1Pa; r.f. power: 2.54 Wcm⁻²) for about 15 min with a shutter covering the substrates, in order to remove the target surface oxide layers. This removal is controlled by analysing the plasma with an uv-visible spectrometer. The oxygen partial pressure in the gas mixture is adjusted with an accuracy in the order of 0.1% by means of a Datametrics-Dresser flowmeter system; this allows one to maintain very low variations of oxygen partial pressures.

The X-ray diffraction measurements are carried out by using a Siemens D 500 diffractometer (Cu K α_1 radiation). The cross-sectional structure of the films is observed by means of scanning electron microscopy (SEM). In order to prevent charge build-up, a thin gold film is sputtered on the sample. The gas permeation measurements are performed on a Lyssy GPM 200 apparatus using a 25 cm² test area. The composition of the titania coatings is determined by Rutherford backscattering spectrometry (RBS) [12]. Fourier transform infra red

(FTIR) spectra of the deposited films are recorded by using a Perkin Elmer 16 PC spectrometer. The substrate temperature during deposition is measured using a nickel-chromium/allied nickel thermocouple.

The different gases used for the pre-deposition treatment of the PET films are: argon, argon-oxygen mixtures and carbon dioxide. The application time is 25 s, typically, for a sputtering power of 0.3 W cm^{-2} and a pressure of 1 Pa.

Fragmentation and peeling tests are carried out by using an Adamel Lhomargy DY 22 traction device with a 100 N sensor. The titania coatings (200 nm thickness) are deposited on the central part of the polymer substrates ($15 \times 100 \text{ mm}^2$). The traction speed is the slowest possible (1 mm/min) in order to obtain maximum elongation without rupture.

The 180° peeling test pieces consist of an assembly: aluminium support (2 mm thick)/double sided tape/PET film/ TiO_x coating/ethylene acrylic acid (EAA) copolymer film thermally bonded to the coating (pressure: $3 \times 10^5 \text{ N m}^{-2}$; temperature: 100°C ; time: 90 s). The peel rate is 50 mm/min. The measurements are made at room temperature.

X-ray energy dispersion spectrometry (XEDS) investigations have been made for the purpose of studying the peeling nature (adhesive or cohesive). For these measurements the samples surface are bombarded by a 30 keV electron beam.

The XPS measurements are recorded on a Riber Nanoscan 50 spectrometer equipped with a MAC 2 analyser and $\text{MgK}\alpha$ excitation radiation. The study is performed under ultra high vacuum (pressure $3 \times 10^{-8} \text{ Pa}$). The spectrometer energy scale is calibrated using the Ag $3d_{5/2}$ core level (at 368.0 eV) and all the peak binding energies are referenced to the C1s binding energy of hydrocarbon components, set at 285.0 eV.

3. RESULTS AND DISCUSSION

3.1. Structural Analysis and Composition

X-ray diffraction study shows that all the titania coatings obtained from a TiO_2 target are amorphous, irrespective of deposition

conditions. As far as the coatings elaborated by the reactive sputtering of the titanium target are concerned, we observe the anatase structure with a preferential orientation along the (101) crystal planes (Fig. 1). We note that the crystallinity of the titanium oxide films increases with the r.f. power and decreases very clearly when the total pressure

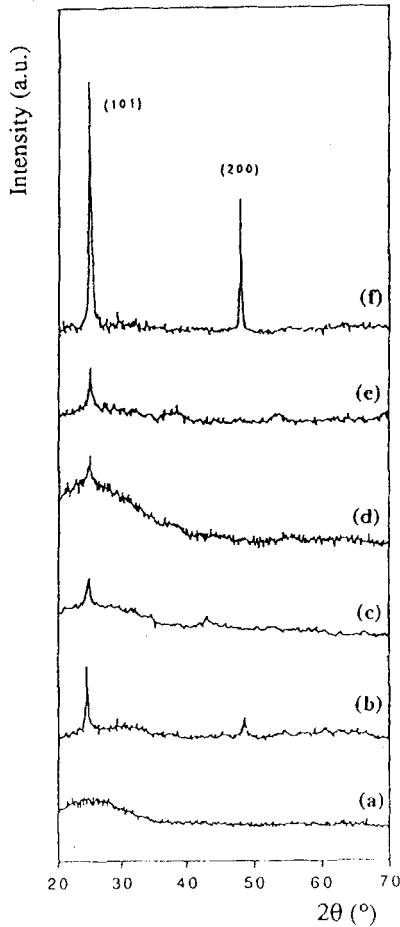


FIGURE 1 X-ray diffraction spectra for titanium oxide films at different conditions: (a) ceramic target; for the other spectra the target used is titanium (oxygen partial pressure: 0.15 Pa), the r.f. power and the total pressure are, respectively: (b) 2.54 W cm^{-2} , 1 Pa; (c) 2.54 W cm^{-2} , 2 Pa; (d) 2.54 W cm^{-2} , 5 Pa; (e) 1.9 W cm^{-2} , 1 Pa; (f) 3.81 W cm^{-2} , 1 Pa.

increases; the coating elaborated at a high pressure is almost amorphous. This variation may be explained according to the variation of the kinetic energy of the sputtered particles; the mobility of these particles on the surface of the growing film increases with their energy and, therefore, favours the crystallisation. Amorphous anatase, rutile and mixtures of anatase-rutile phases have been observed in former studies for titania films deposited by the sputtering method [13–15]. Okimura *et al.* found a rutile phase when the films are deposited at low pressure (0.27 Pa) while the anatase phase is formed for high pressures (2.7 Pa). Those differences can be explained not only according to the deposition method, but also to the conditions used (target to substrate distance, geometry of the enclosure, substrate temperature, etc.).

The scanning electron micrographs of the titania coatings (Fig. 2) show that the increase in the r.f. power leads to an increase in the compactness of the coatings. The columnar morphology observed at a low r.f. power (0.96 W cm^{-2}) is replaced by a dense structure with a smooth topography for high r.f. powers (more than 2.54 W cm^{-2}). This densification during growth is due to the bombardment of the deposited film by the energetic sputtered particles and the species neutralised and backscattered by the target.

For a fixed r.f. power of 1.9 W cm^{-2} , the decrease in the total pressure leads also to an increase in the density of the deposited films. This is likely due to the decrease in the number of collisions between the sputtered particles and the plasma species; most of the sputtered atoms reach the substrate surface with a normal incident angle and with sufficient energy to be moved. Consequently, very compact deposits are obtained under these conditions. The titanium oxide film microstructure fits the predictions of the Thornton structure zone model [16].

As can be seen, the optimisation of coating properties as a function of the sputtering parameters is delicate. We note, for example, that the crystallinity decreases when the oxygen partial pressure increases and when the r.f. power decreases. The coatings deposited at high total pressures (more than 5 Pa) are also almost amorphous. Nevertheless, these deposits exhibit a very pronounced columnar structure that allows diffusion and adsorption of gas molecules (notably oxygen) and do not thus constitute a good barrier to gas diffusion [17].

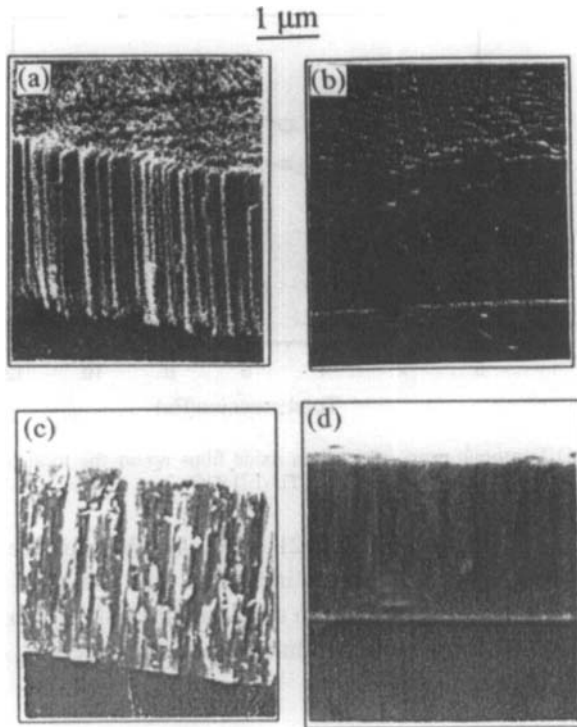


FIGURE 2 SEM micrographs of titania films deposited at different pressures (target: titania, r.f. power: 1.9 W cm^{-2}): (a) 5 Pa; (b) 0.2 Pa and at different r.f. powers (target: titanium; pressure: 1 Pa; oxygen partial pressure: 0.03 Pa): (c) 0.96 W cm^{-2} ; (d) 2.54 W cm^{-2} .

RBS analyses show that the composition of titanium oxide deposits directly depends on deposition conditions (Fig. 3). The atomic ratio of oxygen to titanium varies from 1.96 to 2.12. It increases with the total pressure independent of the gas used (argon or argon-oxygen mixture). We note that the excess of oxygen detected by RBS measurements corresponds to the growth of a porous structure.

For a thorough examination, FTIR analyses of titania films elaborated under various plasma pressures have been performed. The measurements reveal the presence of two absorbance bands, the first located at 500 cm^{-1} is attributed to Ti-O stretching mode [18, 19] and the second, a very broad one situated between 2600 and 3800

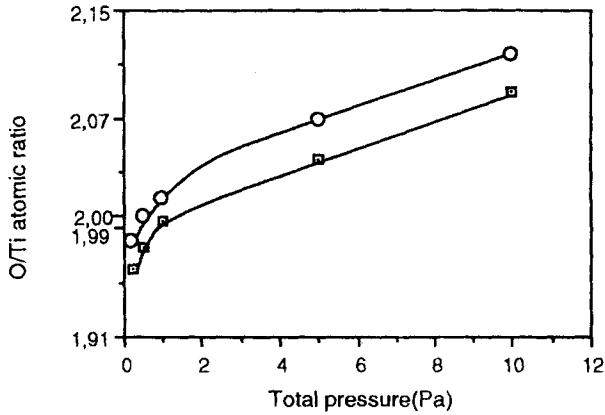


FIGURE 3 O/Ti atomic ratio in titanium oxide films *versus* the total pressure (r.f. power: 1.9 W cm^{-2}), the target used is: (○) Ti; (□) TiO_2 .

cm^{-1} , is due to OH groups [20, 21] (Fig. 4). We can see that the number of these hydroxyl groups increases with the total pressure. This suggests that the incorporation of the additional oxygen, which is more extensive when the coatings have a porous structure, occurs in the form of OH groups.

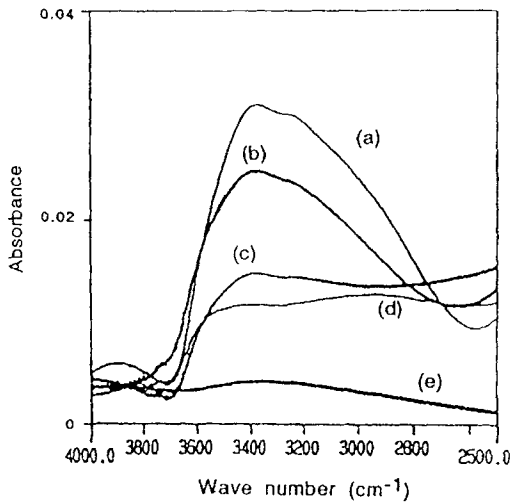


FIGURE 4 FTIR spectra of titania films deposited from titania target at different pressures (r.f. power: 1.9 W cm^{-2}): (a) 10 Pa; (b) 5 Pa; (c) 3 Pa; (d) 1 Pa; (e) 0.5 Pa.

3.2. Adhesion Study

3.2.1. Influence of PET Surface Treatment on Adhesion

Former studies performed in our laboratory [22] have shown that PET surface treatment by a cold plasma leads to a functionalisation of its surface. In principle, this must favour polymer-ceramic interactions and will allow an improvement in the adhesion between the coating and its substrate.

To study the influence of the surface PET treatments, we have characterized the adhesion by the fragmentation test [23]. In this test, the traction force applied to the substrate produces a shear stress, $\tau(x)$, at the PET-coating interface; this latter induces a tensile stress, $\sigma(x)$, in the coating. When the breaking resistance of the deposited coating, σ_0 , is attained, cracks transverse to the traction direction appear in the coating (Fig. 5). This ceramic fragmentation continues until the shear stress, τ_0 , is reached (Fig. 6). After that, there is a loss of adherence and the coating fragments beginning with the largest (width d) which pull away from the substrate. The interfacial shear resistance, τ_0 , that characterizes the adhesion is given by the relation:

$$\tau_0 = k \sigma_0 t/d$$

where k is a constant and t is the coating thickness.

As our deposited films are elaborated under identical conditions (titanium target, total pressure: 1 Pa; oxygen partial pressure: 0.05 Pa; r.f. power: 1.9 W cm^{-2}) and have the same thickness (200 nm), σ_0 and t are constants, τ_0 is inversely proportional to the width of the largest

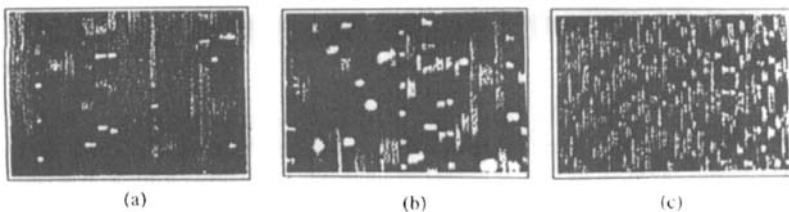


FIGURE 5 Fragment width of titania coatings ($\times 400$) deposited by the reactive sputtering process on: (a) the reference PET film and on the treated PET films by different cold plasmas: (b) Ar; (c) CO_2 .

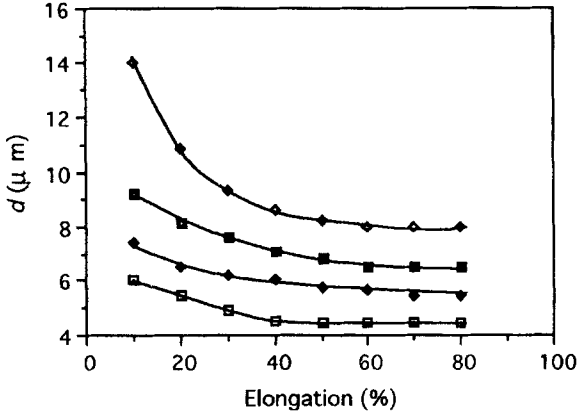


FIGURE 6 Fragment widths in titania coatings deposited by the reactive sputtering method *versus* elongation (in %) for a reference sample (◇) and for the samples in which the PET surface is treated by different cold plasmas: (■) Ar, (◆) Ar + 5%O₂, (□) CO₂.

fragment (d), hence proportional to the crack density ($1/d$). The width, d , of the fragments appearing in the titania coatings obtained by the reactive sputtering after different elongations of the PET substrate is presented in Figure 6. We note that, for a given elongation, the crack density increases when the polymer is subjected to a surface treatment. The highest value is obtained with a CO₂ plasma treatment.

It is interesting to determine the gain in adhesion when the PET films are treated by different plasmas. This gain is characterized by the ratio between the largest width of the debonded fragments from the reference PET (d_{ref}) and those of the samples preliminarily treated (d_{treated}). Table I shows that the adhesion strength, after the treatment, is increased by a factor that varies from 1.10 to 1.60 according to the nature of the plasma used. The best result is obtained with a CO₂ plasma.

TABLE I Gain in adhesion for titania coatings elaborated by the reactive process on the PET films subjected to various plasma treatments in comparison with the reference PET

Plasma treatment	Ar	Ar + 2%O ₂	Ar + 5%O ₂	Ar + 10%O ₂	Ar + 15%O ₂	CO ₂
Gain in adhesion	1.10	1.37	1.32	1.26	1.27	1.60

3.2.2. Influence of the Deposition Conditions on Adhesion

When the sputtering conditions are changed, the coating properties also vary. As it is hard to determine σ_0 , the fragmentation test is difficult to interpret. On the contrary, the 180° peeling test [24] allows the determination of the adhesion strength per unit of interfacial area, W , from the force, F , necessary for the rupture of the coating-substrate interface following the relationship:

$$W = 2F/\ell$$

where ℓ is the width of the coating-substrate separation front.

The PET and the EAA copolymer films are observed before and after the peeling tests in order to determine their surface composition (Fig. 7). We note the departure of the coating from the PET substrate to the copolymer film. The copolymer films are also observed after the peeling tests where titania films have been deposited on PET with increased thickness (Fig. 8). The RBS spectra show a more noticed presence of the thicker coatings. These results suggest that the disbonding of titanium oxide films occurs and spreads at the interface region.

Figures 9 and 10 show, respectively, the evolution of the peel energy *versus* the total pressure and the r.f. power for the coatings elaborated by the reactive sputtering process, the oxygen partial pressure being fixed at 0.05 Pa.

We note that the adhesion strength goes past a maximum value when the r.f. power is between 2.0 and 3.0 W cm⁻² and when the total pressure is in the region of 0.8 Pa. We have seen that the decrease of the total pressure and the increase of the r.f. power cause an increase of the kinetic energy of the incident particles towards the deposited film which increases compactness. This leads to the formation of an *interface region* with less voids; the contact area increases and so does the number of the atoms that participate in the bonding. Thus, we observe an increase in the adhesion strength.

Nevertheless, when the kinetic energy of the sputtered particles is very important, i.e. when the plasma pressure is lower than 0.5 Pa and when the r.f. power is higher than 3.5 W cm⁻², the substrate temperature increases from 20 to 90 °C and very significant intrinsic and thermal stresses are accumulated in the coating. They will

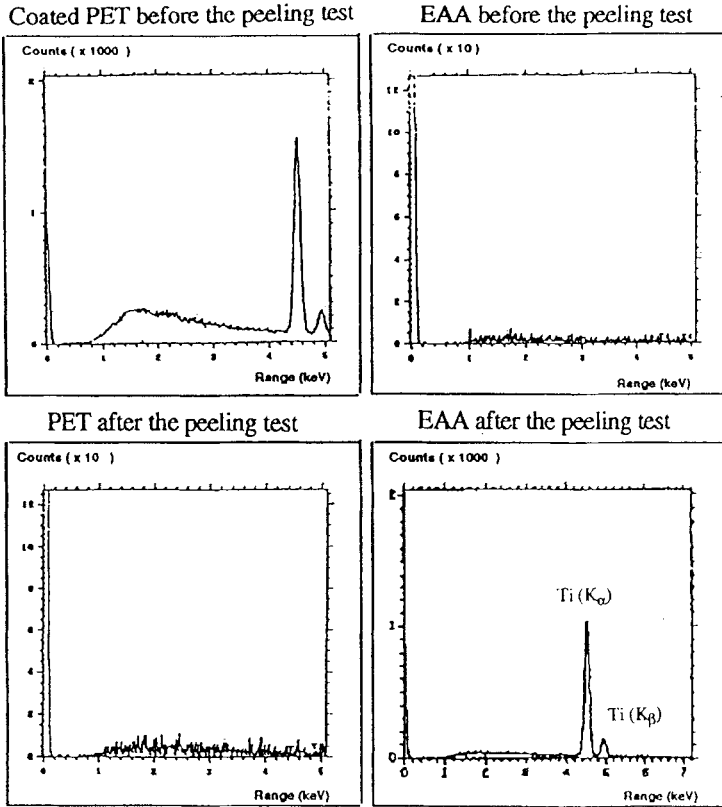


FIGURE 7 XEDS spectra of PET and EAA films before and after the 180° peeling tests.

contribute to the delamination of the coating and, consequently, will decrease the adhesion strength. Concerning the effect of the various cold plasma treatments of the PET surface, the peel test results confirm those obtained with the fragmentation test.

Adhesion variation of titanium oxide coating according to the elaboration process, may be appreciated in Figure 11, where the variable sputtering parameter is the r.f. power. Generally speaking, irrespective of operating conditions, the peel energy is more important for the coatings obtained by the reactive sputtering method.

In order to make a more significant comparison, we present in Table II two samples that have almost the same microstructure, the

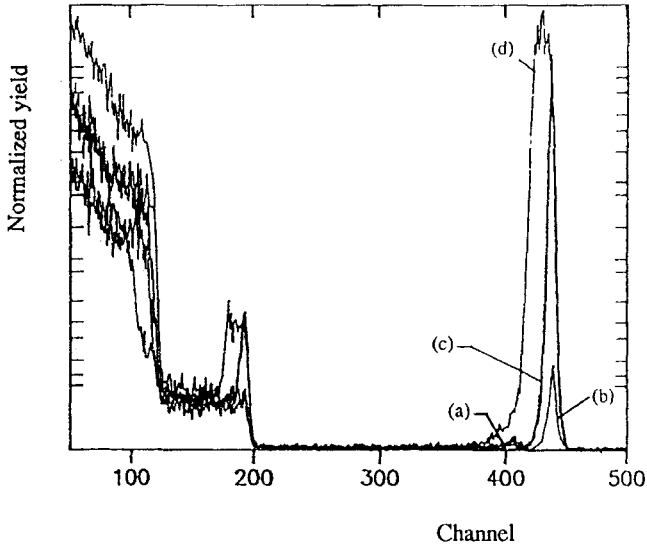


FIGURE 8 RBS spectra of EAA films after the peeling test; the thickness of the previously-deposited titania coating is: (a) 0 nm; (b) 30 nm; (c) 65 nm; (d) 100 nm.

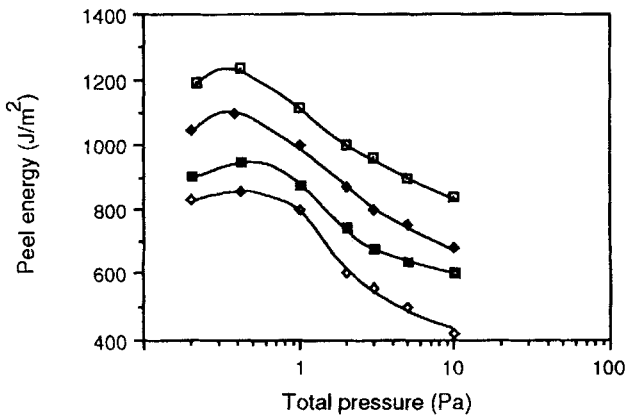


FIGURE 9 Variation of the peel energy *versus* the total pressure (Ti target, oxygen partial pressure: 0.05 Pa, r.f. power: 1.27 W cm⁻²) for a reference (◇) and for PET films treated with different plasmas: (■) Ar, (◆) Ar + 5% O₂, (□) CO₂ coated with titania films.

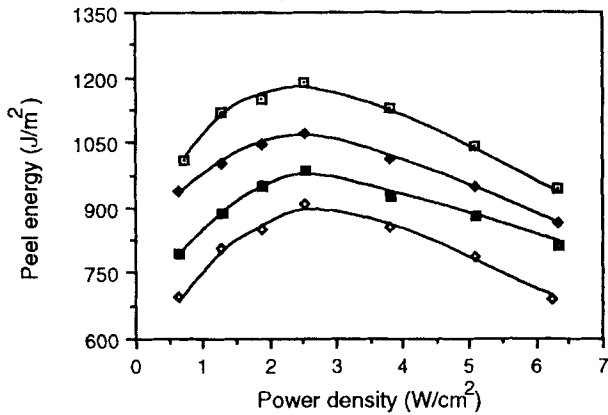


FIGURE 10 The dependence of the peel energy on the r.f. power (Ti target, oxygen partial pressure: 0.05 Pa, total pressure: 1 Pa) for reference (◇) and treated PET films: (■) Ar, (◆) Ar + 5% O₂, (□) CO₂ coated with titanium oxide films.

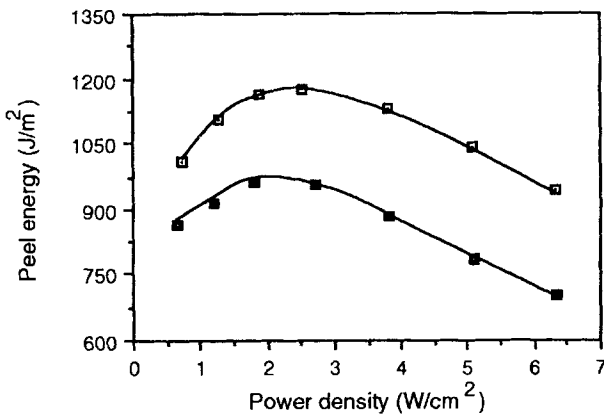


FIGURE 11 Variation of the peel energy of the titania coating (pressure: 1 Pa) on PET with the r.f. power: (□) reactive sputtering of Ti (oxygen partial pressure: 0.026 Pa); (■) sputtering of TiO₂.

TABLE II Variation of the peel energy with the nature of the target

PET	Peel energy (J/m ²)	
	titanium target	titania target
Untreated PET	815	780
CO ₂ plasma treated PET	1130	950

same refractive index ($n=2.35$ at $\lambda=500$ nm) and the same composition ($O/Ti = 2.0 \pm 0.01$). We note that only is the peel energy higher for the coatings deposited by reactive sputtering from the titanium target, but also the difference is accentuated when the PET surface is CO_2 treated.

It is worthy of note that the deposition rate of titanium oxide films and the kinetic energy of the sputtered particles from the titania target are more important than those obtained from the titanium target. In the first case, the sputtered particles reach the substrate surface with a sufficient energy to be embedded in the polymer and to contribute to a mechanical cramping of the coating. In the reactive process, the energy of the sputtered particles is less important; we expect, then, a lower

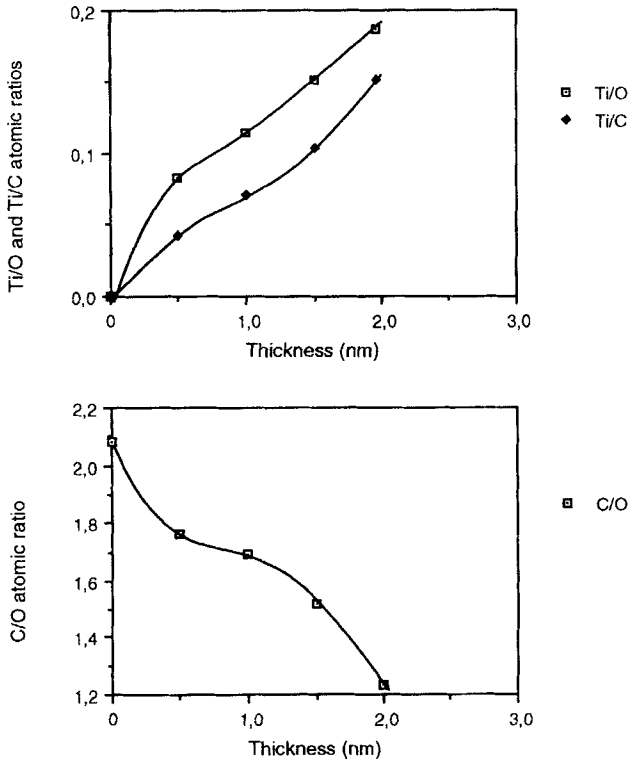


FIGURE 12 Variation of the Ti/O, Ti/C and C/O atomic ratios as a function of the thickness of the deposited layer by the reactive sputtering process (oxygen partial pressure: 0.026 Pa).

adhesion strength. The experimental results show an opposite evolution. This behaviour presumes the existence of two different mechanisms, depending on the sputtering process, that govern the adhesion of titania films on PET substrates.

For a clearer understanding of adhesion phenomena, a knowledge of the interfacial bonds formed between the titania coating and the PET film is required; this study is developed in the next section.

3.3. XPS Analysis

Chemical bonding at the PET surface and at the PET/titanium oxide interfaces has been characterized with X-ray photoelectron spectro-

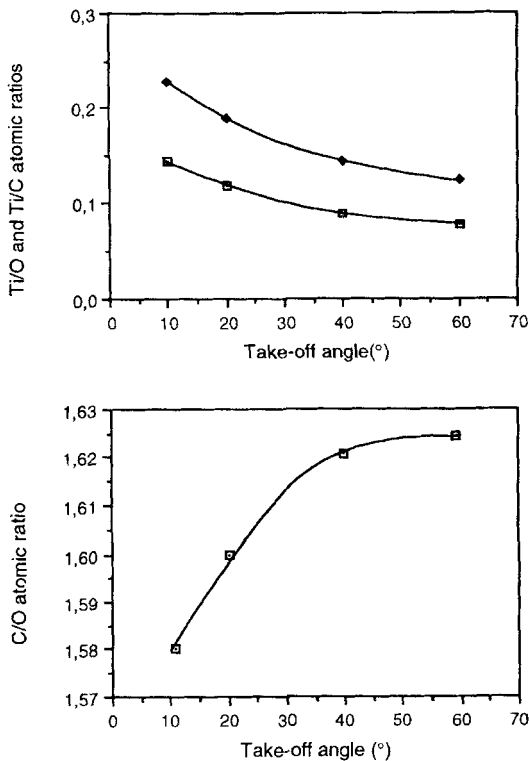


FIGURE 13 Variation of the Ti/O, Ti/C and C/O atomic ratios with the take-off angle in the 1 nm titanium oxide film thickness elaborated by the reactive sputtering process (oxygen partial pressure: 0.026 Pa).

scopy. This section considers in particular bonds created by the two methods of deposition of titanium oxides on CO_2 plasma treated PET films. XPS analyses are performed at 45° for coatings of various thicknesses and at different take-off angles for a thin titania coating 1 nm thick.

C/O, Ti/O and Ti/C atomic ratios vary with the thickness of the coatings obtained by reactive sputtering of titanium (Fig. 12). As expected, the Ti/O and Ti/C atomic ratios increase with the coating thickness. The rapid decrease of the C/O ratio with the increase of the coating thickness reflects (a) the attenuation of the C_{1s} photoelectron intensity originating from the polymer substrate as it passes through the oxide coating; and (b) the increase of the O_{1s} intensity from the coating surface. In angle-resolved XPS, the analysis depth increases with photoelectron take-off angle and, inversely, the intensity of photoelectrons from the extreme surface increases at smaller angles. This explains the noted increase in Ti/O and Ti/C ratios and the decrease in the C/O ratio at smaller angles (Fig. 13).

The Ti 2p binding energies and the full width at half maximum (FWHM) are determined from a spectrum obtained from a titania

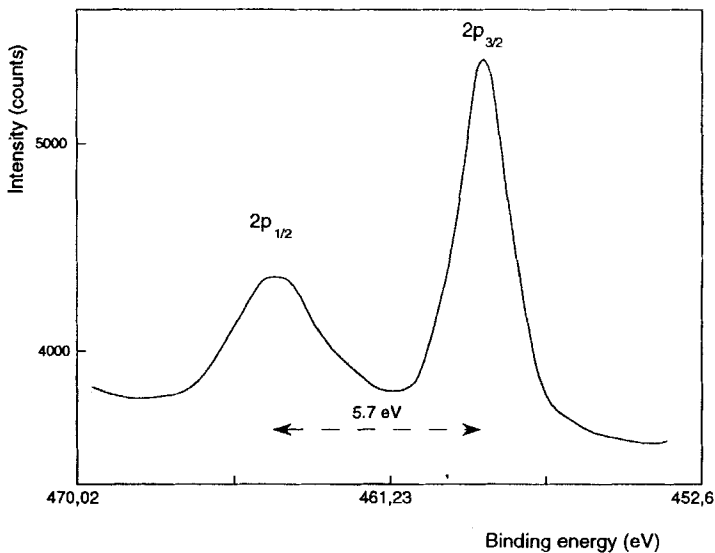


FIGURE 14 Typical Ti2p spectrum of titania films (the target used is titanium).

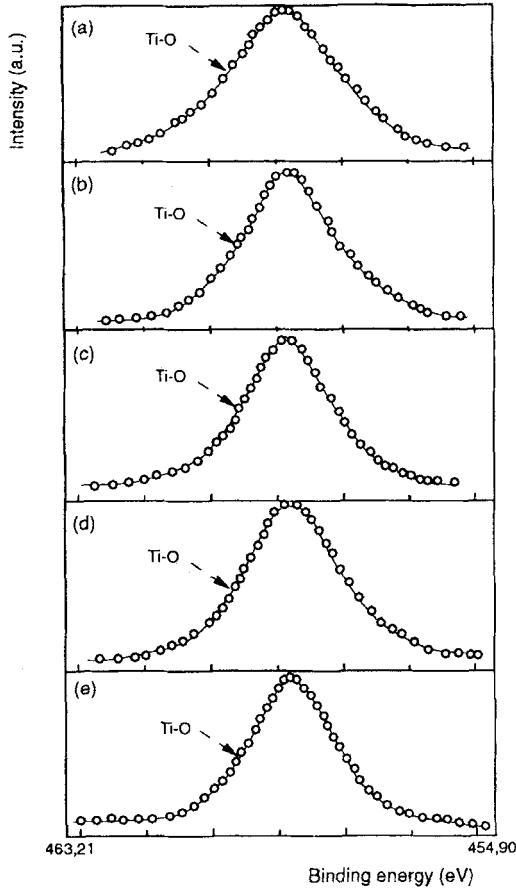


FIGURE 15 $Ti2p_{3/2}$ spectra of titanium oxide films elaborated from the titania target; their thickness is: (a) 1 nm; (b) 1.5 nm; (c) 2 nm; (d) 3 nm; (e) 20 nm. Open circles represent the experimental data.

coating 20 nm thick which is greater than the XPS analysis depth (Fig. 14) and can be assumed to be representative of the coating itself. The $Ti2p_{3/2}$ peak has a binding energy of 458.9 eV, an FWHM of 1.64 eV and the $Ti2p_{3/2}-Ti2p_{1/2}$ separation is 5.7 eV. These results are consistent with titanium in the coating having an oxidation state of +4, as in TiO_2 [25–30]. $Ti2p$ spectra of thin titania coatings of varying thicknesses on PET and obtained by sputtering a TiO_2 target

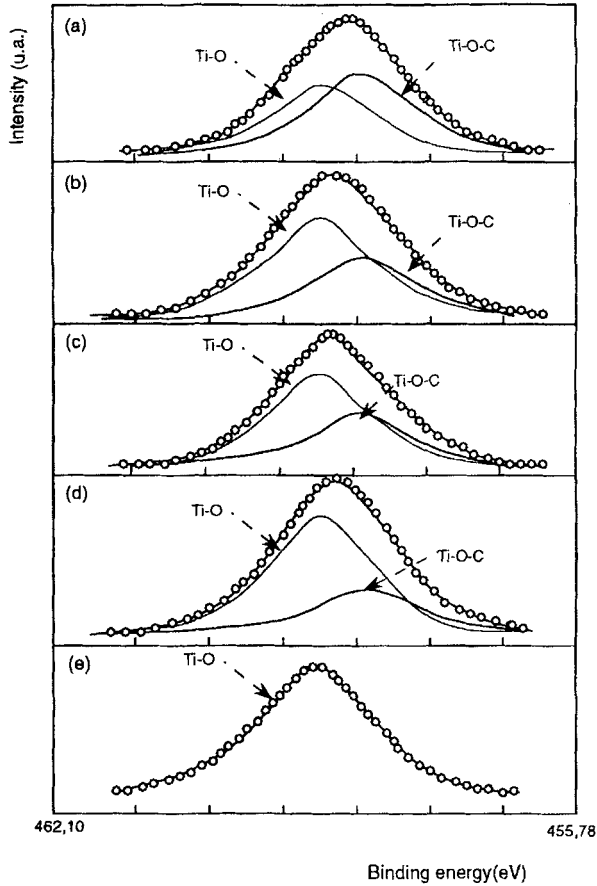


FIGURE 16 $Ti2p_{3/2}$ spectra of titanium oxide films deposited by the reactive sputtering process with different thickness: (a) 0.5 nm; (b) 1 nm; (c) 1.5 nm; (d) 2 nm; (e) 20 nm. Open circles represent the experimental data.

have similar binding energies and FWHM to those obtained from the 20 nm coating, irrespective of coating thickness (Fig. 15). Thus, it is concluded that this process generates titania deposits with a stoichiometry close to TiO_2 .

$Ti2p$ spectra of coatings obtained by the reactive sputtering process of a titanium target are broader, where the $Ti2p_{3/2}$ FWHM increases to 2.44 eV and the peak shape changes with coatings thickness

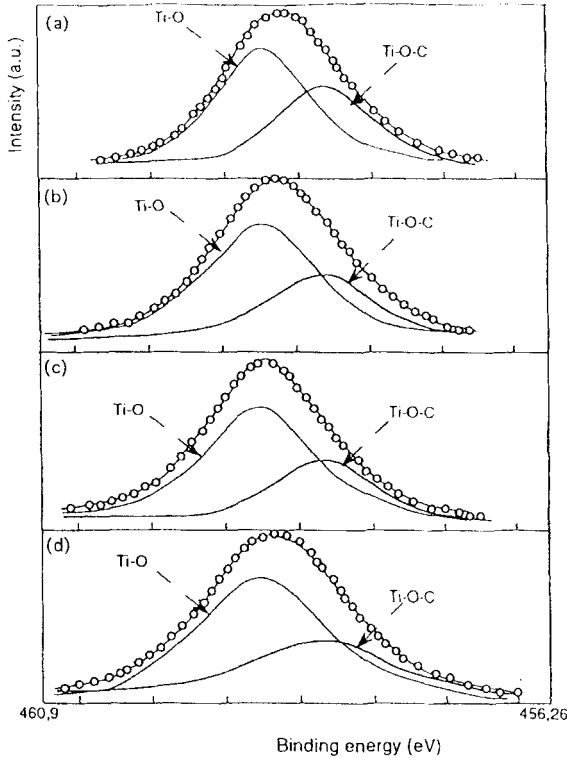


FIGURE 17 $Ti_{2p_{3/2}}$ spectra of titanium oxide films (thickness: 1 nm) elaborated by the reactive sputtering process for different take-off angles: (a) 60° ; (b) 45° ; (c) 30° ; (d) 20° . Open circles represent the experimental data.

(Fig. 16). The spectra can be fitted using two peaks: the Ti^{IV} species fixed at 458.3 eV with an FWHM of 1.64 eV and a second species with a binding energy of 456.3 eV. The second species could represent either a slightly substoichiometric oxide or, more probably, the formation of Ti—O—C bonds with the PET substrate. Indeed, this peak energy position is close to the one obtained by Wagner *et al.* for titanium atoms involved in Ti—O—C bonds present in titanium acetylacetonate [31]. Angle-resolved XPS of these coatings seems to confirm such an interpretation (Fig. 17) since this component increases in intensity with increasing take-off angle.

The relative contribution of this component also decreases as the coating thickness increases (Tab. III). Thus, this species appears to be

TABLE III Experimental values of the $Ti2p_{3/2}$ spectra components

Titania thickness (nm)	Electron take-off angle ($^{\circ}$)	$Ti2p_{3/2}$ components	
		Ti—O	Ti—O—C
0.5	45	47.8	52.2
1.0	45	61.4	38.6
1.5	45	65.6	34.4
2.0	45	72.6	27.4
1.0	20	70.1	29.9
1.0	40	63.7	36.3
1.0	60	58.4	41.6

formed at the coating/PET interface. The formation of such chemical bonds could explain the improved adhesion observed with coatings obtained by the reactive sputtering process.

When the ceramic target is used as a starting material, the high flood of the energetic sputtered particles impinging on the surface of the PET substrate does not seem to allow the establishment of Ti—O—C bonding. In this case, the adhesion is assured principally by a mechanical cramping of the coating on its substrate.

4. CONCLUSION

Titanium oxide films are deposited on PET substrates by reactive and non-reactive sputtering of titanium and titania targets, respectively. The results of X-ray diffraction show that the deposits are either amorphous or crystallized in the anatase form depending mainly on the sputtering method. The decrease of the sputtering power or the increase of the pressure are found to reduce crystallinity. A densification of the structure is also observed when the r.f. power increases and the pressure decreases. The excess of oxygen detected by RBS measurements is correlated with the growth of a columnar structure that favours the incorporation of OH groups.

Cold plasma surface treatments of PET are found to improve adhesion of the titania coatings. The gain in adhesion depends on the nature of the plasma and the best results are obtained for carbon dioxide. The influence of the deposition conditions on the adhesion strength is determined with the peel test. We find that the adhesion is

maximum for a sputtering power of 2.54 W cm^{-2} , for a total pressure of 0.8 Pa and when the reactive sputtering process is used.

XPS studies of the titania/PET interface suggest the formation of Ti—O—C bonds at the interface when the titania coatings are deposited in a reactive plasma on the activated PET substrate. The formation of such bonds could explain the better adhesion observed in the reactive process in comparison with the non-reactive one.

From these studies, it appears that the properties of the titania films and their adhesion strength on the PET substrates depend not only on the deposition parameters, but also on the sputtering process. Sputtering conditions can be optimised in order to confer the desired properties to the titania/PET assembly, suitable for industrial applications.

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