Surface modification of polyethylene terephthalate (PET) and oxide coated PET for adhesion improvement

Juliane Fichtner, Tobias Beck, Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology FEP; Dresden, Germany

Frank Simon, Leibniz Institute of Polymer Research; Dresden, Germany

Abstract

The lifetime of diverse material multilayer-systems (oxide/organic) is mainly determined by the adhesion between its layers. In this work, different surface modification techniques and their impact on wetting behavior and adhesion were tested. For this purpose contact angle, X-Ray photoelectron spectroscopy (XPS) and pull-off measurements were performed. For further proof of the suitability for high barrier multilayer systems UV-VIS and permeation barrier measurements were accomplished.

Keywords

adhesion, plasma treatment, oxide films, surface energy, electron beam curing, surface energy, wetting behavior

Introduction

Multilayer-systems made out of diverse materials have many different applications, such as food packaging, decorative products and flexible electronics.

We analyzed a PET substrate based layer system made by stacking zinc tin oxide (ZTO) or silicon oxide (SiO_x) and acrylic based varnish layers on top of each other (figure 1) as they are a potential multilayer system for high permeation barrier systems.

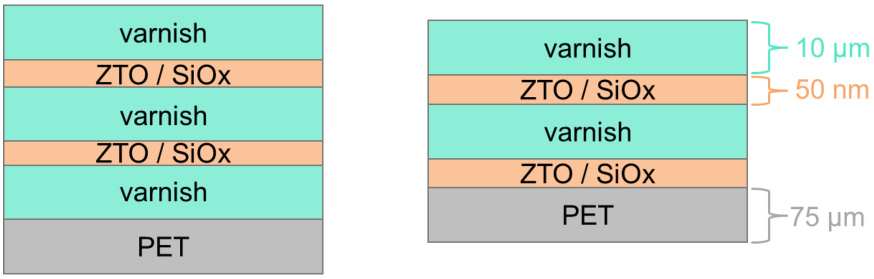

Figure1: scheme of potential high barrier multilayer-systems

The purpose of high permeation barrier systems is the prevention of oxygen and water vapor destroying organic electronics. The simpler solution of using a rigid glass barrier instead of a multilayer-system would reduce the flexibility of the structure

The challenges of multilayer-systems are the low surface energy and adsorbed impurities on the surface of the polymer web and the oxide layers that interfere with the adhesion to the following varnish layer [1]. Therefore a sufficient surface modification is necessary to improve the wetting behavior and the adhesion of the layers to each other.

Materials and Experimental Methods

The 50 nm oxide films of ZTO and SiO_x were produced in the roll-to-roll laboratory vacuum coater *labFlex®200* at Fraunhofer FEP, Dresden. The layers were deposited on a 75 µm thick and 220 mm wide poly (ethylene terephthalate) (PET) Melinex 401 CW web of DuPont Teijin Films.

The ZTO layers were sputtered by a single magnetron. Hence a metallic zinc tin target (52 wt% zinc, 48 wt% tin) was used. By introducing oxygen to the process, a zinc-tin-oxide film was generated.

For the deposition of the SiO_x layers a plasma enhanced chemical vapor deposition technique (PE-CVD) was used. The precursor was hexamethyldisiloxane (HMDSO), which was mixed with oxygen (HMDSO:oxygen, 1:2).

Low pressure plasma treatment

All experiments with the low pressure plasma treatment were done in the roll-to-roll laboratory vacuum coater *labFlex®200*. A schematic illustration of the process setup is shown in figure 2.

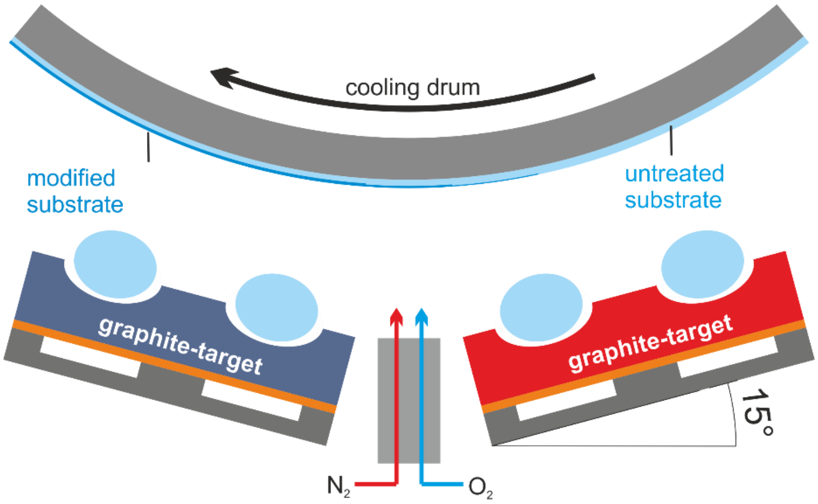

Figure 2: scheme of roll-to-roll low pressure plasma treatment

The required plasma was generated by a planar double magnetron in bipolar mode. A graphite target and two different gases in different compositions (oxygen, nitrogen) were analyzed. To examine different intensities of the treatment the electrical power, the web speed and the process pressure were varied as seen in table 1.

Table 1: varied process parameter of low pressure plasma treatment

process parameter	symbol	range
electrical power	P_E	1 kW – 5 kW
web speed	v_W	1 m/min – 5 m/min
process pressure	p	0,5 Pa – 2,5 Pa

For a better comparison of the different samples, a correlation between the individual parameters was combined in the activation intensity X_i.

$$X_i = (I_1 + I_2) \cdot t$$

Thus I_1 and I_2 are the electrical currents of the magnetrons, which are directly assessable at the current source. The current increases with power and pressure. Therefore both parameters can be combined by using the current.

t is the time of the samples in the plasma zone and can be calculated by the following formula:

$$t = \frac{w_t}{v_w}$$

Thereby w_t is the length from the left edge of the left target to the right edge of the right one.

Varnish layer manufacturing

The used acrylic based varnish was *ESH-Lack LM 4191* (*Lott-Lacke*). It was deposited by a wire-bar applicator with a layer thickness of 10 µm. Afterwards the wet varnish layers were cured by atmospheric pressure electron beam radiation in the stationary laboratory unit *REAMODE*, which is equipped with a linear electron beam system *EBE-150/270* (figure 3).

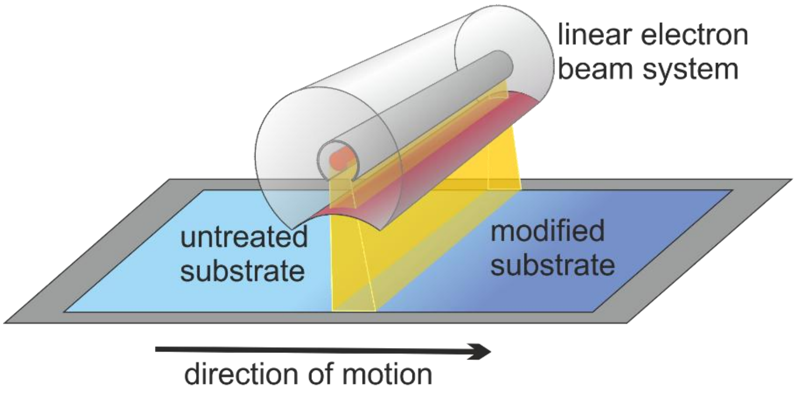

Figure 3: scheme of the atmospheric pressure cross-linking process by means of electron beam radiation

The used curing dose was 25 kGy. Consequently the acceleration voltage was set to 150 kV, the electron current was 2 mA and the motion speed was 150 mm/s.

Surface energy / Contact angle measurements

To reduce the amount of samples, they were screened by using the ethanol-water test inks *Reihe C* by *Plasmatreat GmbH*. Samples which did not show variations in surface energy of more than five percent, were removed from the trial.

All contact angle measurements were done with the *OCA 20* by *dataphysics*. The used software was *SCA 20*. All contact angles were measured after 8 to 10 days to ensure the stability of the surface. The measurement was dynamic and the denoted contact angles were the advancing angle. For this purpose 5 µl of deionized water was provided and further filled with 10 µl with a dispense rate of 0.25 µl/s. Afterwards the drop was soaked in using the same dispense rate. The whole sequence was filmed with 25 pictures per second and evaluated by tangent method.

XPS measurements

All XPS measurements were done at the Leibniz Institute of Polymer Research using the spectrometer *Axis Ultra* by *Kratos Analytical*. A monochromatic Al Kα1.2 X-Ray tube with a power of 300 W at 20 mA was used for excitation. To determine the kinetic energy a hemispheric analyzer with a pass energy of 160 eV for spectral overviews and 20 eV for high resolution spectrums were used. All binding energies were referred to the C1s peak for unsaturated hydrocarbons (E_b= 284.76 eV) and saturated hydrocarbons (E_b= 285.00 eV). To quantify the typical element peaks a baseline correction according to Shirley [2] was undertaken.

FTIR-ATR measurements

All FTIR-ATR measurements were done by the FT-IR spectrometer *Spectrum 2000* by *Perkin-Elmer*. The used ATR attachment was the *Golden Gate*^{TM} by *Specac*, which was equipped with a germanium crystal. The measurements were taken with a spectral resolution of 2 cm^{-1}, a mirror speed of 0.2 cm/s and scan number of 16.

Pull-Off measurements

To test the adhesion properties, pull-off tests were done using the *Positest AT-A* by *DeFelsko*. Therefore dollies with a diameter of 20 mm were glued to the samples with 2K-epoxy *Pattex Extrem Fest*. The dollies were pulled off after 24 hours with a rate of 0.2 MPa per second.

Results and Discussion

The correlation of the contact angle and the activation intensity for oxygen and nitrogen plasma gas is shown in figure 4.

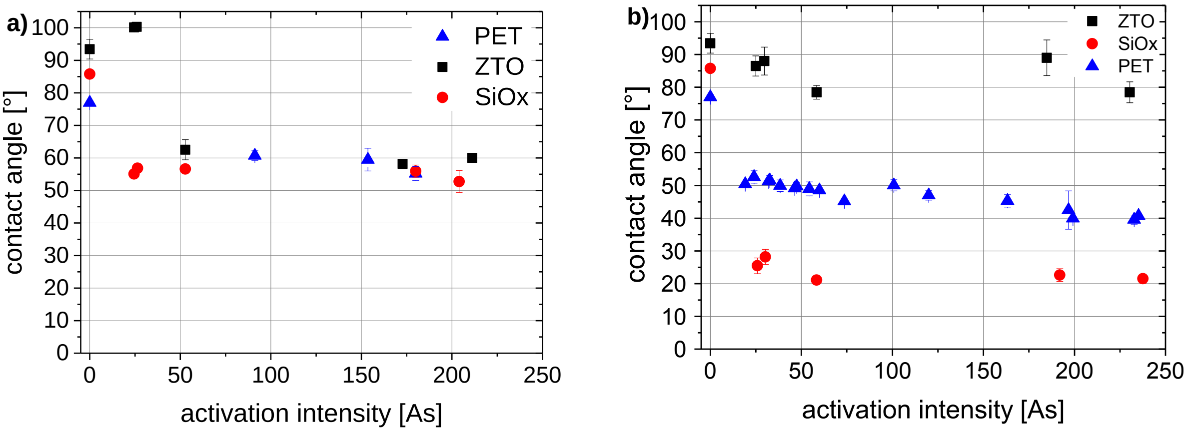

Figure 4: correlation between the contact angle and the activation intensities for low pressure plasma treatment by using a graphite target, a): nitrogen, b): oxygen

The results indicate a contact angle decrease for all substrates and both gases compared to the untreated substrates. The use of nitrogen results in similar contact angles for all substrates (figure 4 a). The oxygen plasma causes a specific surface modification, which varies with each substrate. The lowest contact angle was reached for PET and SiO_x.

For further investigations XPS measurements were performed, to determine the chemical modification on the surfaces. Figure 5 shows the C1s peaks of untreated PET and PET, which were treated with oxygen plasma.

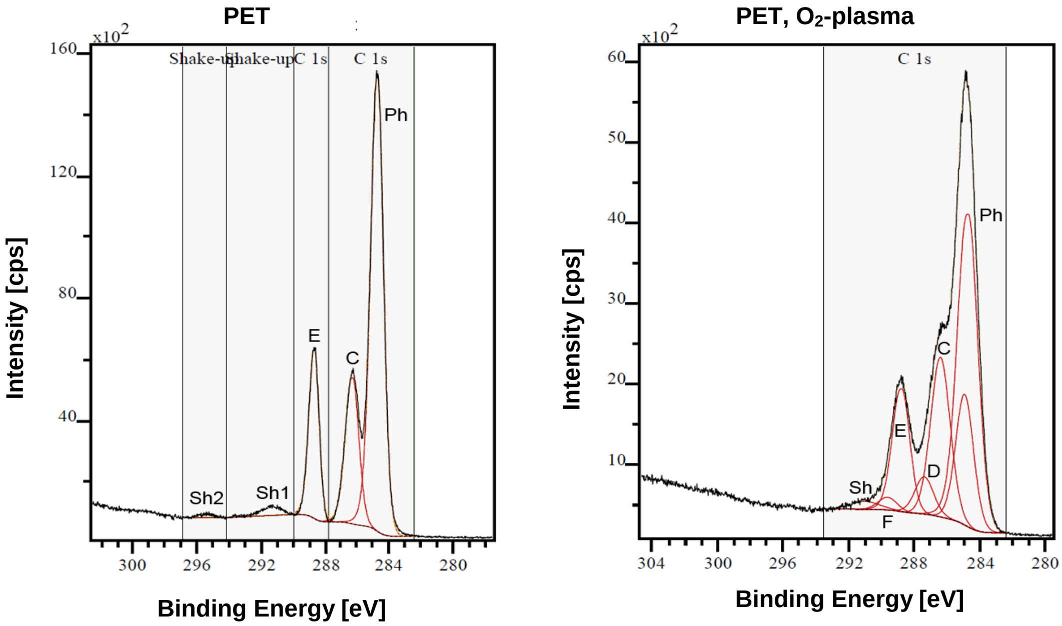

Figure 5: C1s-Peaks of untreated PET and O_2-plasma (graphite target) treated PET: Ph (C of phenyl ring), C (C-O), E (carboxylic acid ester), Sh (π-electrons), D (C-keto group), F (C-carboxyl group)

The results indicate a splitting of the C1s peak of the untreated PET into three different component peaks at 284.8 eV, 286.3 eV and 288.7 eV. Furthermore two weak shake up peaks are eminent at 291 eV and 295.5 eV. The peak at 284.8 eV represents the phenyl ring, the peak at 288.7 eV the carboxylic ester acid and the peak at 286.3 eV incorporates the carbon atoms, which are bound to one oxygen atom, one carbon atom and to hydrogen atoms respectively [3]. The measured relative fraction of Ph:C:E is 61.4:20.6:18.0. The small deviation from the ideal ratio of 60:20:20 can be explained by terminal groups (C-H, C-OH) on the polymer chain and by thin oil films on the PET surface [1]. The two shake up peaks are indicators for delocalized π-electron systems. The XPS analyses of the O_2-plasma treated PET shows new component peaks for keto groups (287.4) and carboxyl groups (289.7). Figure 6 illustrates the correlation between the different atom percentage and the C1s component peaks to the activation intensity, when PET is treated with-plasma.

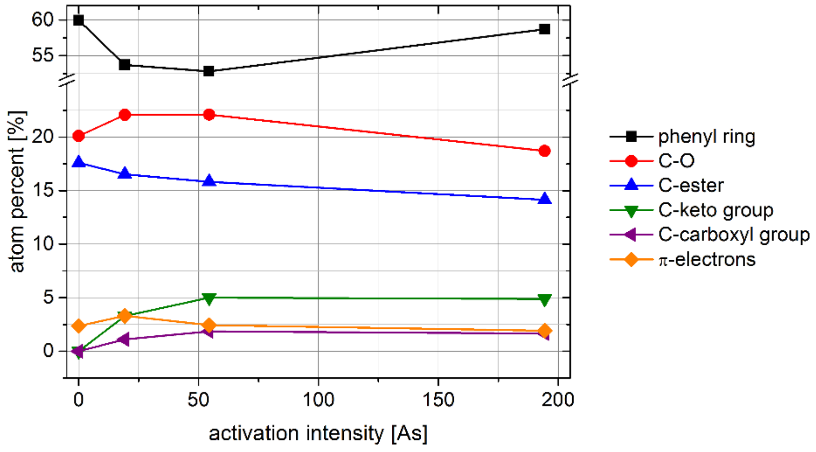

Figure 6: dependency of atom percentage of the C1s component peaks of activation intensity of the O_2-plasma treated PET-samples

There is a decrease of carboxylic acid ester and an increase of carboxyl groups, which can be related to a chain scission between the oxygen atom of the carboxyl group and the bounded carbon atom of the alcohol rest. The terminal carboxyl groups can be separated by decarboxylation, which leads to the occurrence of phenyl radicals. They oxidize to a stable keto group, which will then be bound to the phenyl ring [4, 5]. The increase of the atom percentage of the shake up peak at low activation intensity can be explained by a cleaning effect of the plasma.

The decrease of the contact angle at O_2-plasma treated ZTO samples in figure 4b can be explained by a cleaning effect of adsorbed fats [1].

The decrease of the contact angle at O_2-plasma treated SiO_x sample in figure 4b can be explained by an enrichment with oxygen. The SiO_x films exhibit a hybrid character. The oxygen of the plasma treatment leads to functional groups like hydroxy, keto and carbon acid groups, which enlarge the polar character of the SiO_x films. Accordingly the interactions with polar fluids like water increase.

At the same time the N_2-plasma treated samples were investigated by XPS measurements to clarify the chemical modification on the surface. Figure 7a shows the C1s and N1s peaks of the samples treated with N_2-plasma samples.

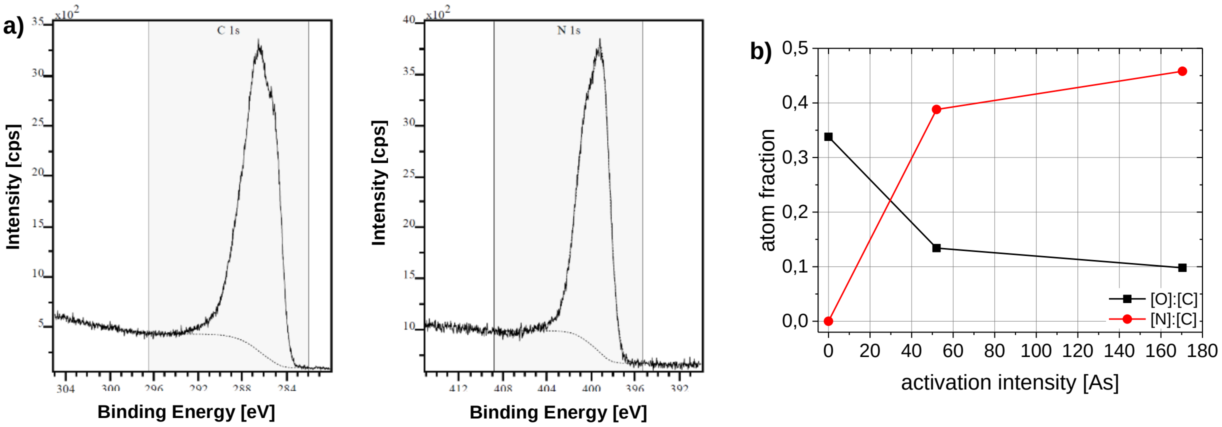

Figure 7: a) C1s und N1s Peak of PET after plasma treatment in nitrogen gas, b) atom fractions of oxygen and nitrogen to carbon after N_2-plasma in relation to the activation intensity

These peaks cannot be fragmented in clear component peaks. But it can be seen, that the atom fraction O:C is decreasing (0,34 to 0,1) and the atom fraction N:C is increasing (0 to 0,46) with increasing activation intensity (figure 7b). A possible explanation can be the deposition of carbon nitrides [6, 7]. The component peak in the N1s spectrum at the energy at less than 399 eV could be explained by non-stoichiometric carbon nitrides. Infrared spectroscopy measurements were done to further clarify the chemical character of the deposited CN_x layers. Figure 8a shows the FTIR-ATR spectra of a N_2-Ar-plasma treated sample. Argon was just used to sputter more material of the target and thereon create a thicker layer, which enables the FTIR-ATR measurement. It is assumed to have no effect on the layer composition. Furthermore an additional aluminum layer was deposited on the PET to increase the reflectance of the infrared signals and suppress the PET signal.

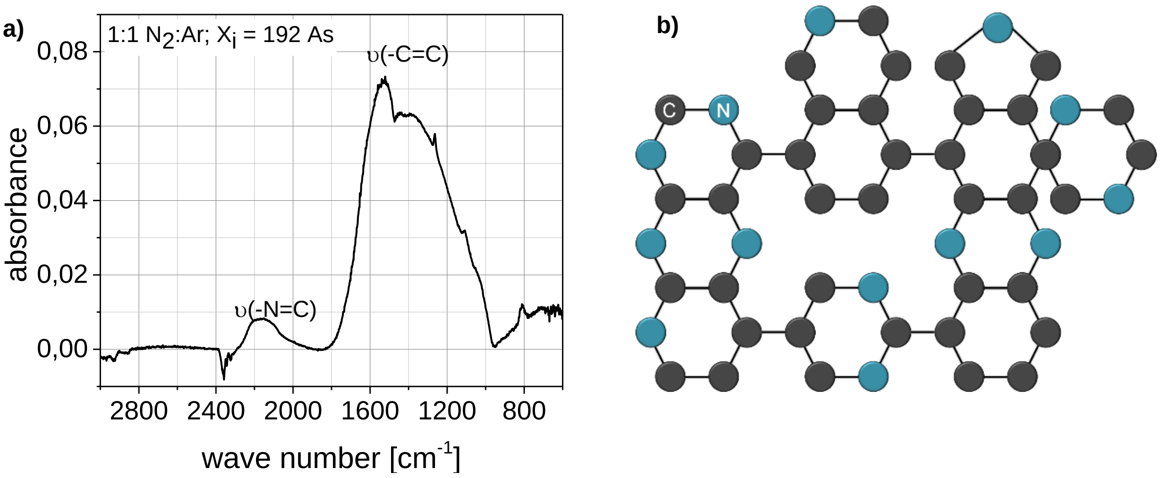

Figure 8: a) FTIR-ATR spectra of N_2/Ar-plasma and N_2/O_2/Ar-plasma treated aluminum samples, b) schematic representation of nitrogen-rich heterocyclic polymer network

The spectra of the N_2/Ar-plasma shows aromatic C=C ring vibration (1400 – 1600 cm^{-1}) and accumulated –N= vibration (2200 cm^{-1}). Therefore a polymer network of nitrogen-rich heterocycles like 1,3-Diazabenzene or 1,4-Diazabenzene could be deposited as a thin layer (figure 8b).
The relation of the varnish adhesion to activation intensity is shown in figure 9.

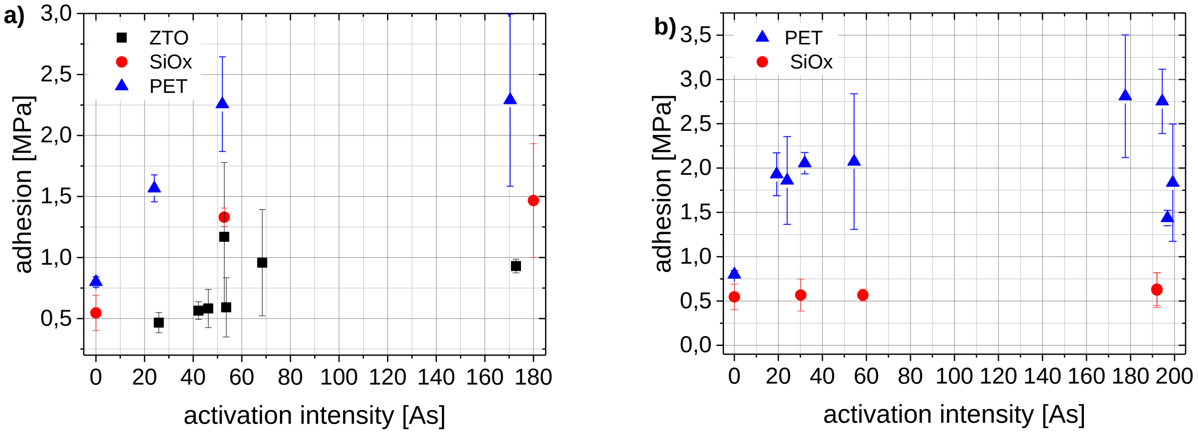

Figure 9: adhesion of an acrylic based varnish in dependency of activation intensity for a) N_2-plasma and b) O_2-plasma

The O_2-plasma could not improve the wetting behavior for ZTO layers, therefore no graph for ZTO in figure 9b is provided. The adhesion of the varnish on SiO_x layers could not be improved by O_2- plasma treatment, even though the contact angle measurements predicted it (figure 4b). That could be caused by oxygen plasma leading to a further oxidation of the SiO_x films. This leads to Si-OH groups, which interact well with water by hydrogen bonds, but do not have any effect on the varnish adhesion.

The O_2-plasma leads to keto and carboxyl groups at the PET surface, which further can be cracked by the electron beam at the varnish curing procedure and create a chemical bonding to the varnish. This leads to an increase of the adhesion from 0.7 MPa to 2.7 MPa,
The deposited nitrogen-rich heterocycles increased the adhesion of the varnish on all three substrates. It enabled the wetting of the ZTO substrate with the acrylic varnish, which was not possible before the treatment. Generally, a slight increase of the adhesion with increasing activation intensity can be seen. As seen in figure 7b, an increasing activation

intensity leads to an increase in nitrogen content. That means that an increase of nitrogen in the nitrogen-rich heterocycles improves the adhesion.

The variations between the adhesions from the N_2-plasma treated samples could be explained by the altered adhesion of the nitrogen-rich heterocycles layer onto the surface. So the maximum adhesion of the varnish on PET was 2.3 MPa, on SiO_x 1.5 MPa and on ZTO 1.2 MPa.

To evaluate the suitability of the technique for surface modification within high barrier multilayer systems, the visual transmittance, water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) were examined. Because of the decreasing visual transmittance of PET and ZTO by pure N_2-plasma (PET: 87.5 % to 75.5 %, ZTO: 78.4 to 67.5 %), different nitrogen-oxygen gas mixtures were tested (figure 10).

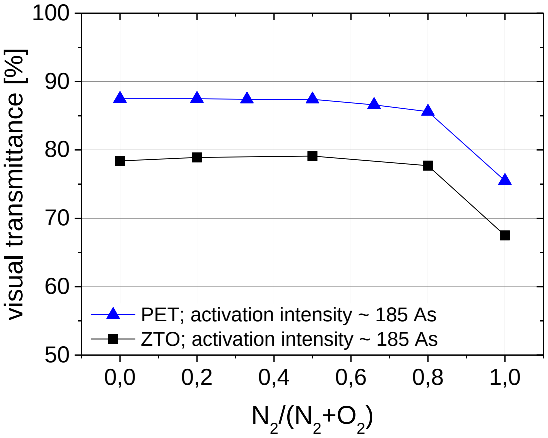

Figure 10: visual transmittance in relation to the volume fraction of nitrogen, graphite target low pressure plasma treatment, PET, ZTO

The figures illustrate that the visual transmission is nearly constant up to 80 v/v% nitrogen. Only further increase of the nitrogen content leads to a decrease of the visual transmittance. The contact angle measurements show that there is a decrease of contact angle with increasing nitrogen content at the ZTO samples and an increase of the contact angle at the PET sample (figure 11).

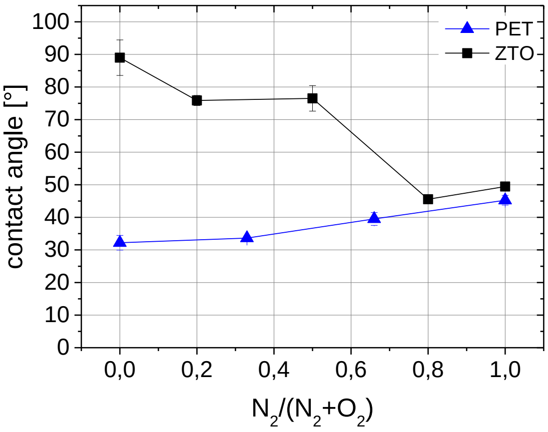

Figure 11: contact angle of PET and ZTO in relation to different N_2/O_2 gas mixtures at an activation intensity of 185 As to 200 As

At high oxygen contents, the carbon may burn to carbon monoxide, leaving little or no carbon to build up a nitrogen-rich heterocycle layer. The optimal gas composition for ZTO therefore is 80 v/v% nitrogen and 20 v/v% oxygen, while PET shows the lowest contact angles for pure oxygen plasma. The correlation of the different gas mixtures on the varnish adhesion on ZTO is shown in figure 12.

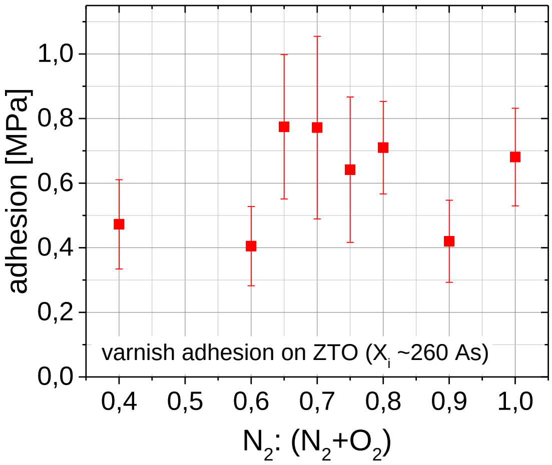

Figure 12: adhesion of the varnish layer on ZTO in relation to the nitrogen-oxygen gas mixture

The figure displays a maximum adhesion of 0.8 MPa at a nitrogen content of 65 v/v% to 70 v/v%.

To evaluate the impact of the treatments on the permeation barrier properties of the ZTO films, table 3 summarizes the water vapor transmission rates (WVTR) and oxygen transmission rates (OTR). The WVTR measurements were done at 38 °C and a relative humidity of 90 % and the OTR measurements at 23 °C and 0 % humidity.

Table 2: permeation barrier values in relation to the plasma treatment (graphite target) and electron beam radiation for 50 nm ZTO films

plasma gas	X_i [As]	WVTR [$g/(m^2*d)$]	OTR [$cm^3/(m^2*d*bar)$]
x	x	0,067	0,25
N_2	172,8	0,069	0,2
O_2	184,8	0,076	0,3

The numbers show that there is no influence on WVTR and OTR for low pressure plasma treatment (graphite target).

Conclusions

The work presented in this paper has demonstrated that a low pressure plasma treatment with graphite target and a nitrogen-oxygen gas mixture, with 65 v/v% to 70 v/v% nitrogen, can increase the adhesion of an acrylic based varnish on ZTO to 0.8 MPa. There is no impact to the permeation barrier (WVTR, OTR) and visual transmittance of the ZTO layer. The optimum treatment for PET is a low pressure plasma treatment with graphite target and pure oxygen gas. The adhesion of an acrylic based varnish could be increased to 2.7 MPa. The varnish adhesion onto SiO_x could be increased from 0.5 MPa up to 1.5 MPa by using a low pressure plasma treatment with graphite target and nitrogen process gas.

Acknowledgments

Essential results presented in this paper were obtained in a public project, funded by the Free State of Saxony.

Contact Details

Juliane Fichtner

juliane.fichtner@fep.fraunhofer.de

Winterbergstraße 28, 01277 Dresden

Phone: +49 351 2586 145

Literature

[1] W. A. Zisman, *Contact Angle, Wettability, and Adhesion* **1964**, Chapter 1, pp 1–51

[2] D. A. Shirley, *Physical Review B* **1972**, *5 (12)*, 4709.

[3] A. Vesel, M. Mozetic, *J. Phys.: Conf. Ser.* **2008**, *100 (1)*, 012027.

[4] L. Yang, J. Chen, Y. Guo, Z. Zhang, *Applied Surface Science* **2009**, *255 (8)*, 4446.

[5] Tarek S. Salem, *PET Surface Properties affected by low temperature plasma modification*, Mühlleiten **2009**.

[6] H. Sjöström, *J. Vac. Sci. Technol. A* **1996**, *14 (1)*, 56.

[7] W. T. Zheng, *J. Vac. Sci. Technol. A* **1996**, *14 (5)*, 2696.