Evaporated aluminum on polypropylene: oxide layer thicknesses as a function of oxygen plasma treatment level

Donald J. McClure
3M Corporate Research and Acuity Consulting and Training
23002 Dunham Lake Road, Siren, WI 54872
715-689-2902 AcuityCT@hotmail.com

Carolin Struller
Technische Universität München and Fraunhofer IVV, Freising, Germany

Prof. Dr. Horst-Christian Langowski
Technische Universität München and Fraunhofer IVV, Freising, Germany

Abstract

Biaxially oriented polypropylene (BOPP) film samples were metalized in an industrial roll-to-roll vacuum web coater following various levels of oxygen plasma treatment. The aluminum adhesion, barrier properties, and the oxide layer thicknesses on both sides of the aluminum layer were measured. The plasma treatment increased the level of oxygen containing groups on the BOPP surface. Low treatment levels led to increases in the measured aluminum adhesion.

Introduction

This is a follow-up to a pair of papers[1, 2] presented at AIMCAL in 2010 that examined aluminum layers deposited at varied thicknesses onto polyester film. It was found that aluminum oxide layers formed on both sides of the aluminum metal film and the former were consistently 3.0-3.3 nm thick, that the optical properties of the films matched values calculated based on bulk optical constants when the aluminum thicknesses used were the aluminum metal thicknesses, that the electrical conductivities were consistently lower than might be predicted from bulk properties with the errors worse for thinner films, and that the crystalline domains in the aluminum films showed a preferred 111 orientation.

The films in the first study had no plasma treatment, and it seemed important to look at the effect of oxygen plasma treatment on the aluminum oxide layer thicknesses. BOPP is a good substrate choice because, unlike PET, BOPP has no oxygen in its polymer backbone. It seemed reasonable to expect significant differences in the aluminum oxide layer thicknesses when comparing aluminized untreated BOPP with that of aluminized oxygen-plasma-treated BOPP. The data do not support that expectation.

Sample preparation time was minimal because the second author had just completed an extensive study[3] on oxygen plasma treatment on BOPP as part of her thesis work. This work is not yet published, but she generously shared her data and samples of her films for analysis. Highlights of her results are presented below, but, so as not to compromise future publications of her work, this paper will hide the absolute plasma treatment levels.

The current paper uses TEM to characterize the oxide layers on either side of aluminum films deposited on plasma treated and untreated BOPP substrates and uses x-ray diffraction to characterize the effects of the plasma treatment on the deposited aluminum layers.

The study performed in the thesis work and its reporting are both very comprehensive. To whet the reader's appetite, the abstract for the thesis is shared below.

> To gain a better understanding of the adhesion mechanisms between untreated and pretreated biaxially oriented polypropylene (BOPP) film and evaporated aluminum, a special BOPP homopolymer film was modified by a low-pressure oxygen plasma inline prior to metallization in an industrial roll-to-roll vacuum web coater. By varying plasma power input and exposure time via web speed, different plasma treatment levels have been achieved. The non treated and treated surfaces were characterized by X-ray photoelectron spectroscopy (XPS), contact angle (surface energy) measurement and atomic force microscopy (AFM) while the treated and metallized film was investigated regarding its aluminum adhesion and barrier properties. The plasma was found to induce a considerable change on the BOPP film surface by incorporation of oxygen containing polar chemical moieties, revealed by XPS and surface energy results. Additionally, crosslinking upon the polymer surface was detected by surface energy measurement. The functional groups resulted in an increase of the measured aluminum adhesion. On higher plasma intensities overtreatment lead to the formation of a weak boundary layer consisting of low-molecular weight oxidized material, and thus a decline of aluminum adhesion resulted. AFM indicated a slight change in surface topography owing to plasma treatment and confirmed the existence of low-molecular-weight material on treated BOPP. Further investigations on aluminum adhesion suggested that covalent bonds are the dominating mechanism responsible for adhesion of aluminum to plasma treated BOPP. While a considerable improvement of oxygen barrier with increasing plasma intensity was observed, water vapor barrier was only slightly enhanced. This confirmed that moisture permeation through polymer films coated with a metal layer is controlled by different mechanisms than oxygen permeation.

Highlights of the thesis report results

The metallizer used was a 2007 General Vacuum Equipment K4000 vacuum roll-to-roll coater with a thermal resistive PVD source and a proprietary oxygen plasma treatment tool. The metalizer was described in detail in the thesis but also in a paper at last year's conference[1].

The BOPP film for the thesis effort was chosen to minimize the presence of additives. It was isotactic (isotactic share > 95%) BOPP homopolymer film, supplied by Kopafilm Elektrofolien GmbH (Nidda/Ober-Schmitten, Germany). Commonly, this type of film is used as a dielectric layer for capacitors. To minimize additives, the BOPP film was produced from a base resin that contains just the essential stabilizers (antioxidant and acid scavenger, see Table 1). No further additives were added during manufacturing process. Despite having no antiblocking or slip agents, good handling of the film was insured by structural features located on the side not to be metallized. These surface features prevent blocking of the film by acting as spacers between the individual film layers. No corona pre-treatment of the film was performed.

Kopafilm BOPP	
Composition*	
High-molecular-weight phenolic antioxidant (Irganox 1010)	4412 ppm
Acid scavenger (calcium stearate)	65 ppm
Film thickness*	18 µm
Density*	905 ± 5 kg/m³
Melting range*	160 - 165 ℃
Degree of crystallinity (determined via DSC)	50 - 55 %
WVTR (23 ℃, 85 % RH)	1.6 g/(m ^{2}·d)
OTR (23 ℃, 50 % RH)	1915 cm ^{3}/(m^2·d·bar)
Surface energy (total)	27.1 ± 1.2 mJ/m²

*Data supplied by manufacturer

Table 1. Properties for the film used.

A model of the plasma treated aluminized film is shown in Figure 1. The thesis work studied a wide range of observable functional changes as a function of the plasma treatment level seen by the BOPP film prior to metallization, as described in the abstract. This paper quantifies the aluminum oxide layer thicknesses and aluminum film crystallinity for selected samples. The aluminum hydroxide layer drawn in Figure 1 is not quantified in this work.

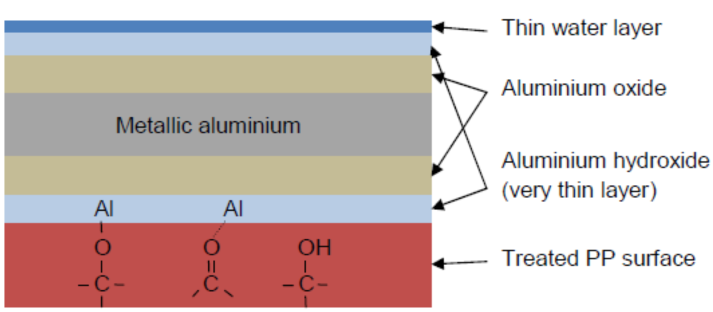


Figure 1. Schematic cross section of the interfaces for aluminum deposited on plasma treated BOPP.

Figure 2 plots the oxygen content of the plasma treated film determined by XPS before metallization as a function of plasma treatment level (from the thesis, with the plasma treatment energy density units removed). The general shape of the curve with a rise in oxygen concentration with treatment level is not unexpected. Detailed XPS deconvolution techniques were used to separate the O and C signals and assign the various peaks into several chemical groups and bond types (for details see the thesis).

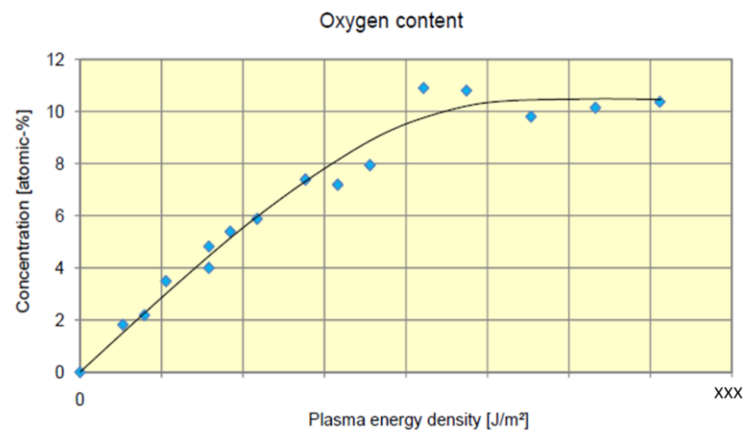


Figure 2. Oxygen concentration on the BOPP film surface
as a function of plasma treatment level.

The surface energy of the untreated and plasma treated BOPP films was also determined as a function of the plasma energy density. Detailed contact angle measurements using four test fluids and as well as test pens were made (Again more details are presented in the thesis). Aging effects on contact angle and surface energy were also described in the thesis. By way of summary of a much larger effort, the total surface energy as a function of plasma energy density is shown in Figure 3.

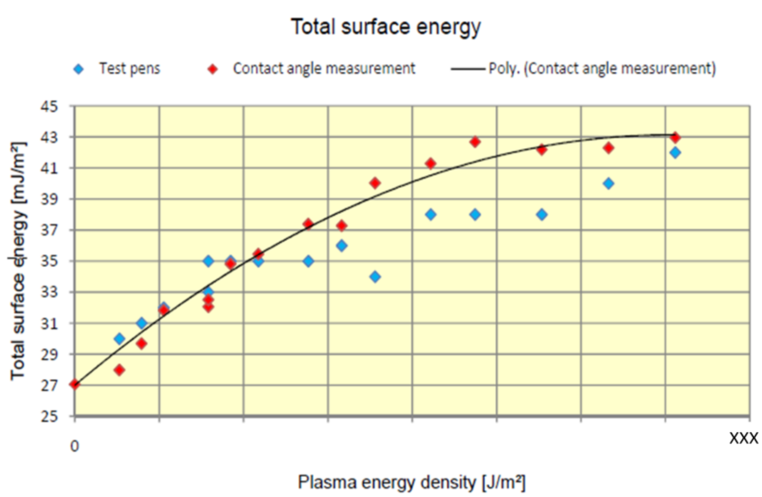


Figure 3. Total surface energy as a function of plasma energy density.

Surface roughness as a function of plasma treatment level demonstrated slight roughening due to plasma treatment. Peel strengths were evaluated with improved peel strengths observed for all plasma treatment levels and a maximum in the peel strength at intermediate treatment levels, see Figure 4. Maxima in the adhesion as a function of plasma treatment levels are often seen, as has been described[4] previously. Oxygen and water barrier properties were also extensively characterized. The oxygen barrier is improved with plasma treatment; the water barrier is less influenced by plasma treatment.

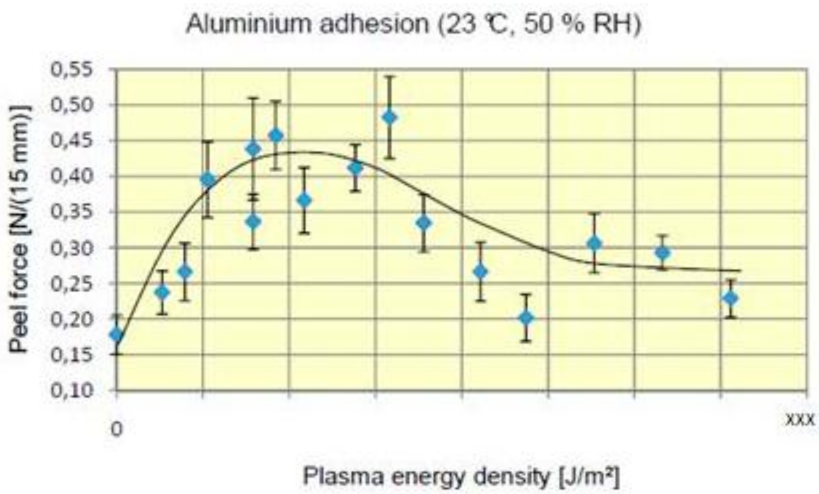


Figure 4. Peel strength (adhesion) as a function of plasma energy density.

A high level summary of the varied effects of the plasma treatment from the thesis is shown in Table 2.

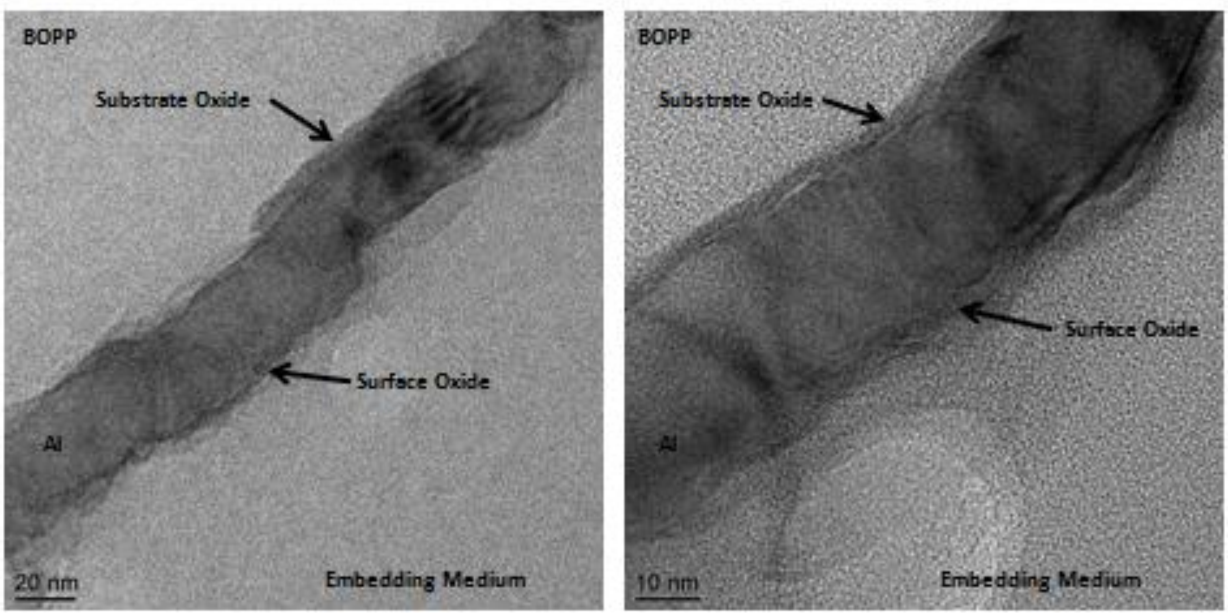
Measured characteristic	Change with plasma energy density (0 → xxx J/m^2)	
Oxygen concentration	↗→	Increase, constant level from xx x J/m^2 on
Amount of C-OH, C-O-C	↗↘	Maximum between xxx and xxx J/m^2
Amount of C=O, O-C-O	↗	Slight increase
Amount of COOH, COOC	↗→	Increase, constant level from xxx J/m^2 on
Contact angles	↘→	Decrease, constant level from xxx J/m^2 on (ethylene glycol shows steady decrease)
Surface energy	↗→	Increase, constant level from xxx J/m^2 on
Roughness	→	No clear tendency (possibly a slight increase compared to untreated film)
AFM adhesion	↗↘	Maximum between xxx and xxx J/m^2
Aluminium adhesion	↗↘	Maximum between xxx and xxx J/m^2
OTR	↘	Strong decrease, gradually levelling off
WVTR	↘	Slight decreases

Table 2. Summary of main results

TEM results

For this paper, samples prepared as part of the thesis work were analyzed using TEM and x-ray diffraction months after the aluminum films were deposited. For the TEM work, samples were sectioned using a cryo ultramicrotome. Measurement micrographs were done on a Hitachi H-9000 TEM at 300kV and 200,000x instrument magnification. X-ray fluorescence microanalysis was done on a JEOL 2100F at 200kV. The aluminum films in this work appeared to be quite polycrystalline compared to the set prepared on PET[2], making the measurements more challenging.

Figure 5 provides a typical pair of images of the same sample at two magnifications. The substrate (BOPP), substrate oxide, aluminum layer, surface oxide, and embedding medium are labeled. The actual plasma treatment levels are not disclosed in this paper, rather the treatment levels are given as a percentage of that of the sample of the highest treatment level studied here. The latter treatment level was not the maximum treatment level studied in the thesis work but was well past the maximum in the measured adhesion level. The 39% treatment level in this paper was selected to be near (or just past) the treatment that corresponded to the maximum adhesion level.



100,000x instrument magnification 200,000x instrument magnification

Figure 5. A typical pair of TEM images of the same sample at two magnifications. The sample was treated at the 64% level.

Figure 6 displays the STEM images with x-ray fluorescence maps for aluminum, oxygen, and carbon for the non-plasma treated sample. Note the aluminum oxide layer at the substrate-aluminum interface, as well as the oxygen observed internally to the aluminum film, presumably along aluminum grain boundaries. It may be that these oxides form well after the deposition is complete by transport of oxygen through the BOPP substrate or through the aluminum film. Similar images of plasma treated samples also exhibited oxygen within the aluminum film.

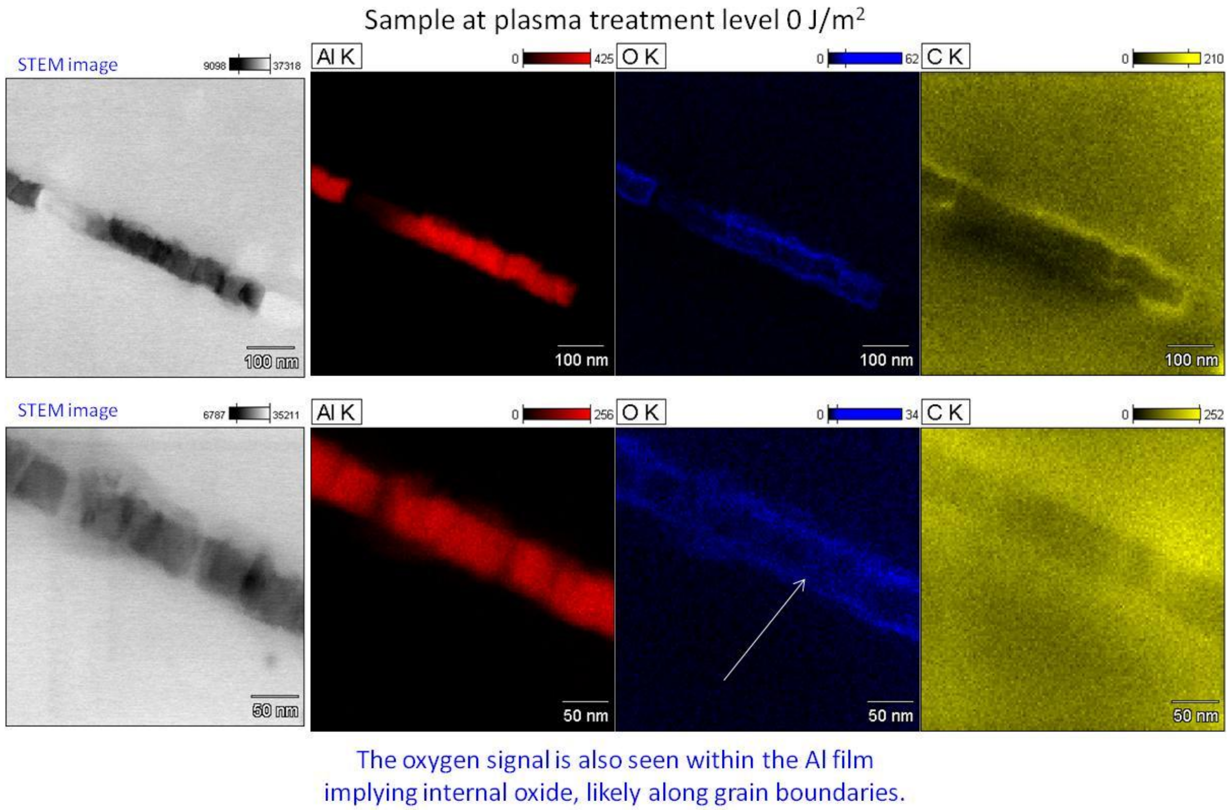


Figure 6. STEM images with x-ray fluorescence maps for zero plasma treatment level.

Examining TEM micrographs from samples at five treatment levels, the thickness of the oxide layers at the substrate-aluminum interface and the aluminum-air interface were determined. A previous paper[2] demonstrated that the embedding medium did not affect the oxide layer thickness measured at the aluminum-air interface for PET samples. The thickness results are shown in Table 3 and in Figures 7 and 8. The data show that all the layers are nominally comparable except the aluminum thickness for the zero plasma treatment level. Note that the lines in the figures are included to guide the eye and should not be taken to imply a dependence of thickness on plasma treatment level.

Plasma treatment level	Substrate oxide thickness (nm)	Aluminum thickness (nm)	Surface oxide thickness (nm)
0	2.7	40.0	2.9
14%	2.7	27.8	2.7
39%	2.9	27.1	3.0
64%	2.9	26.2	3.1
100%	2.8	26.1	2.7

Table 3. Thicknesses of the various layers as a function of plasma treatment level.

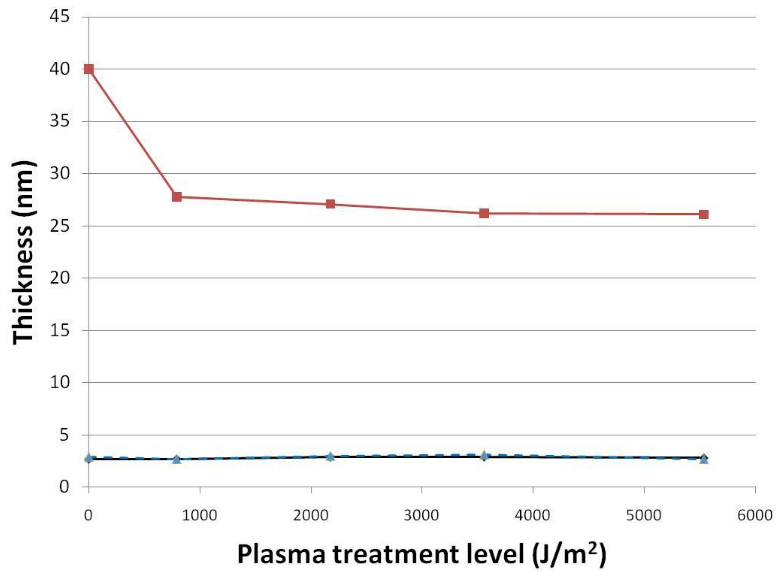


Figure 7. TEM thickness results for all layers.

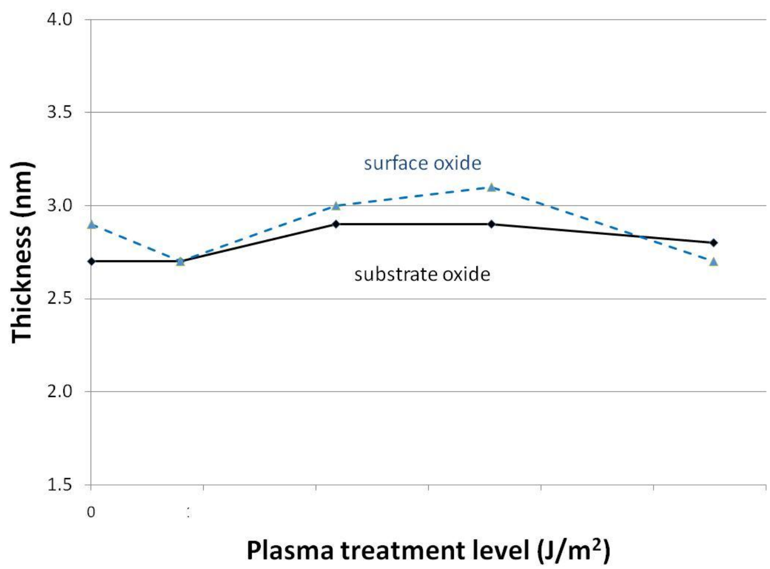


Figure 8. TEM thickness results for the oxide layers.

X-ray diffraction results

The results of x-ray diffraction studies of the samples are shown in Figures 9 and 10. Note the strong 111 peak intensities compared to the 200 peak intensities. For a randomly oriented specimen, the relative intensity of the aluminum (200) maximum should approach a value of 0.47 relative to the (111) peak intensity. Clearly the 111 orientation is strongly preferred, similar to what was observed[2] in the aluminum layers on PET. Note also the large apparent crystal size in the untreated sample. Unfortunately we cannot assign the large crystal size to the absence of plasma treatment because as noted above that sample was ~50% thicker than the plasma treated samples and greater thicknesses often enable larger crystallite sizes.

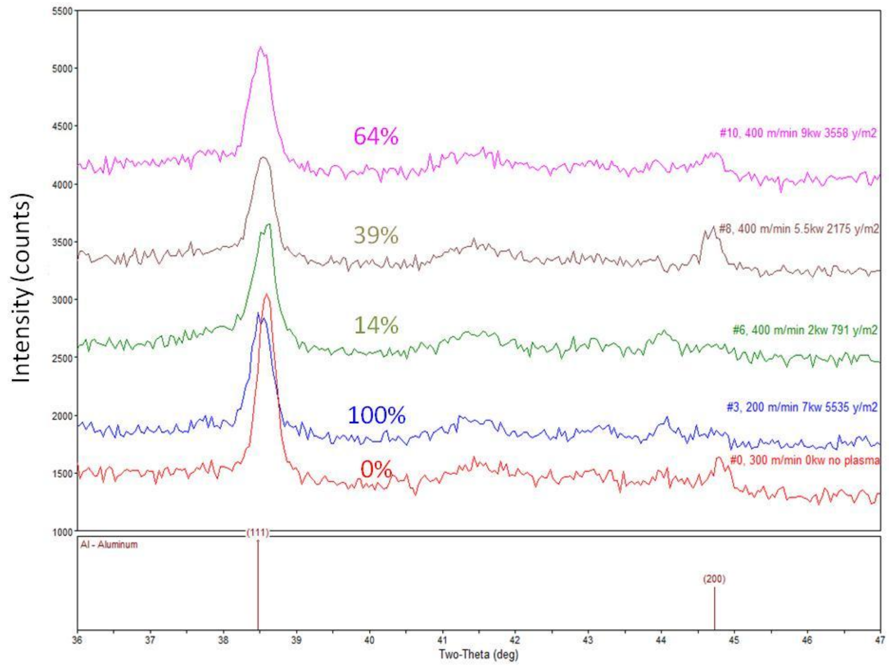


Figure 9. X-ray diffraction scans of the five samples

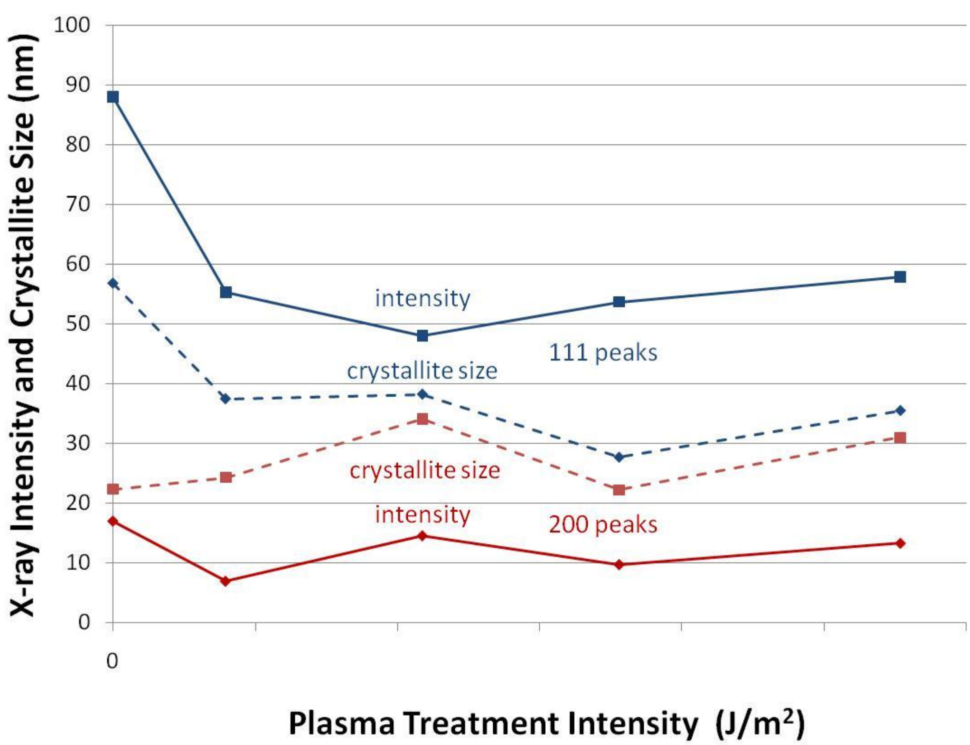


Figure 10. X-ray diffraction intensity and crystallite sizes derived from the scans in Figure 9.

Discussion

Aluminum oxide layers were found at both interfaces of samples of aluminum deposited onto untreated and plasma treated BOPP films. The observed oxide layers thicknesses did not vary with plasma treatment level. This observation suggests that at least part of the oxide layers observed likely grow after deposition is complete. A next step is to look at oxide layer film growth as a function of time after the deposition. The logistics of sample preparation for TEM make success unlikely if the oxide growth occurs in minutes but may be possible if the oxide growth occurs in hours.

The cause of an increase in the crystallite size for the aluminum sample deposited onto an untreated BOPP film could not be assigned to the lack of plasma treatment due to the extra thickness of the aluminum layer in that sample.

References

1. Nick J. Copeland and Robert Astbury, 2010 AIMCAL Conference*: Evaporated aluminum on polyester: optical, electrical, and barrier properties as a function of thickness and time (Part I).*

2. Donald J McClure and Nick J. Copeland, 2010 AIMCAL Conference*: Evaporated aluminum on polyester: optical, electrical, and barrier properties as a function of thickness and time (Part II).*

3. Carolin Struller, Thesis in partial fulfillment of the requirement for the degree of 'Diplom-Ingenieur' in 'Technology and Biotechnology of Food' at the Technische Universität München, performed at the Fraunhofer Institute for Process Engineering and Packaging (08 June 2010).

4. John Madocks, *Practical aspects of plasma treatment for thin film adhesion on polymer substrates*, in the Fall, 2010, issue of The Bulletin of the Society of Vacuum Coaters, page 34.