Synergy between Plasma-Assisted ALD and Roll-to-Roll Atmospheric Pressure PE-CVD Processing of Moisture Barrier Films on Polymers

Sergey A. Starostin,* Wytze Keuning, Jean-Paul Schalken, Mariadriana Creatore, W.M.M.(Erwin) Kessels, Jan B. Bouwstra, M.C.M.(Richard) van de Sanden, Hindrik W. de Vries.

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Dr. S.A. Starostin, Prof. M.C.M. van de Sanden, Dr. H.W. de Vries
Dutch Institute For Fundamental Energy Research (DIFFER)
P.O.Box 6336, 5600 HH Eindhoven
The Netherlands
Email: s.a.starostin@differ.nl

W. Keuning, J.-P. Schalken, Dr. M. Creatore, Prof. W.M.M. Kessels, Prof. M.C.M. van de Sanden
Department of Applied Physics
Eindhoven University of Technology
P.O. Box 513, 5600 MB Eindhoven
The Netherlands

Dr. M. Creatore, Prof. W.M.M. Kessels
Solliance Solar Research
High Tech Campus 5, 5656AE Eindhoven
The Netherlands

Dr. J.B. Bouwstra
FUJIFILM Manufacturing Europe B.V.
P.O. Box 90156, Tilburg
The Netherlands

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Abstract

The synergy between fast (1600 nm·min^{-1}), roll-to-roll plasma-enhanced chemical vapour deposited (PE-CVD) SiO_2 layers and plasma-assisted atomic layer deposited (PA-ALD) ultra-thin Al_2O_3 films has been investigated in terms of moisture permeation barrier properties. The effective and intrinsic water vapour transmission rates (WVTR) were studied as a function of the number of ALD cycles. It was demonstrated that a synergistic combination of a silica buffer layer deposited on polymer with an ultra-thin (≤ 2 nm) alumina barrier film can provide excellent intrinsic (10^{-5} - 10^{-6} g·m^{-2}·day^{-1}) and good effective ($\sim 10^{-3}$ g·m^{-2}·day^{-1}) WVTR values, while both single layers individually exhibit poor barrier performances with effective WVTR values of ≥ 1.0 g·m^{-2}·day^{-1}.
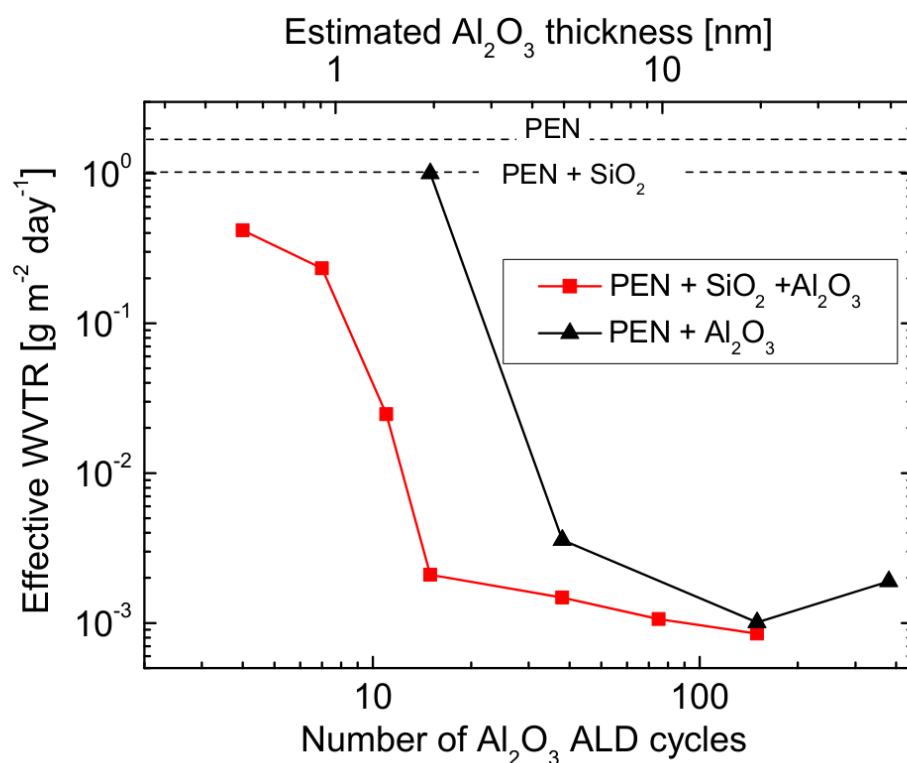
Introduction

The development of flexible electronics, including photovoltaics, displays and smart packaging, demands novel transparent encapsulating materials to quantitatively limit the ingress of moisture and oxygen. Prolonged life time stability can be achieved by encapsulating the device between flexible systems consisting of polymer substrates coated with a thin gas/moisture diffusion barrier layer. However, finding a cost-effective way to produce large-area, uniform and excellent barrier coatings with low local defect levels is a challenging and urgent task. A valid solution is to combine low costs and high throughput processing offered by the atmospheric pressure (AP) PE-CVD with the high density and conformality of thin layers delivered by the plasma assisted atomic layer deposition (PA-ALD).[1,2]

It should be emphasized that the higher throughput, required for industrial viable manufacturing, generally also implies the decrease of the barrier film thickness. In the case of ultra-thin gas/moisture diffusion barrier layers, the morphology and properties of the substrate play an important role. While the ALD technology is well known for the excellent conformality of the films in microelectronics applications, the direct deposition on flexible polymeric webs imposes additional challenges. The surface roughness of optical grade polymer foils is relatively high and in the order of few nanometers; the polymeric chains are not necessarily rigidly cross-linked, which can affect the quality of ultra-thin inorganic films. Even dense polymeric webs typically contain atmospheric gases and moisture which can outgas slowly in vacuum or at elevated temperature and affect the deposition process. Thus one can expect that upgrading the polymer with an inorganic buffer layer produced by a fast, cost-effective process such as roll-to-roll atmospheric pressure PE-CVD can be a valid approach. This consideration is supported also by the recently highlighted remarkable performance of hybrid inorganic layers comprised of an inorganic dyad or a nano-laminate

heterogeneous structures serving as diffusion barriers.[3-7] Nevertheless, despite the excellent barrier film properties obtained using this approach, the above-mentioned experiments were carried out at low pressure and using relatively low deposition rate solutions.

The focus of the present contribution is therefore to show how the silica-like buffer layer produced by the industrially compatible atmospheric pressure roll-to-roll PE-CVD process on the polymer substrate can influence the performance of the thin and ultrathin PA-ALD alumina moisture barrier films.

Experimental Part

 The studied bi-layers combine a 80 nm thick buffer SiO_2 film prepared by AP PE-CVD and Al_2O_3 capping layer fabricated by PA-ALD. A thermally stabilized polyethylene 2,6 naphthalate (PEN) foil (100 µm thick Dupont Tejin PQ65FA) was used as a substrate.

A detailed description of the roll-to-roll AP PE-CVD reactor as well as of the conditions for the plasma-enhanced silica-like film deposition has already been given elsewhere.[8] The schematic picture of the setup is shown in Figure 1a. In this system a high current diffuse dielectric barrier discharge (200 kHz, 20 W·cm^{-2}) between two rotary drum electrodes (R=120 mm) was employed to synthesize a silica-like layer from tetraethyl orthosilicate (TEOS) monomer in the $N_2/O_2/Ar/TEOS$ 15.0:1.8:1.0:(1.0×10^{-2}) slm gas mixture. The gaseous gap between the electrodes was 0.5 mm, effective deposition width 150 mm and web speed 400 mm/min.

The PA-ALD depositions have been carried out in an Oxford Instruments FlexAL Mark II. The schematic image of the reactor is presented in Figure 1b. The PA-ALD cycle comprises the following steps: $Al(CH_3)_3$ (trimethylaluminum, TMA) dose (20 ms), precursor purge (1.5 s), O_2 plasma (200 W, inductively coupled plasma; 2 s or 10 s at 15 mTorr), and plasma purge (1 s). All PA-ALD layers presented in this article have been deposited at 80 ^{o}C and each deposition has been started with a 5 minute pre-heating of the sample. More details about the

reactor, process, and material properties can be found elsewhere.[2,9] The film growth rate of the described PA-ALD process is ~0.13 nm per cycle. This value was measured by means of spectroscopic ellipsometry for a film grown on a silicon wafer. It should be noted that due to the interfacial layer formation the exact determination of the thickness for ultra-thin layers ($\leq$5 nm) grown on polymeric or porous substrates is not a trivial task. Therefore the data are presented as a function of the number of ALD cycles.

The effective water vapour transmission rate (WVTR) was measured using a Technolox Deltaperm instrument (ASTM D 1434-82 (2003), sensitivity of 2 10^{-4} g·m^{-2}·day^{-1}) for the conditions of 40 $^{\circ}$C, 90% RH. The sample area for the test was 50 cm^2. To reach stable transmission rate a 50 – 100 hrs measurement time was required. During the measurement the WVTR value was recorded each minute. The average of the last 100 experimental points was presented as the characteristic effective WVTR with the standard deviation being below 1%. The WVTR value of the pristine PEN substrate is 1.7 g·m^{-2}·day^{-1}. Atomic force microscopy (AFM, Park Systems NX10) measurements were carried out in contactless mode using Si tips (8 – 10 nm). The captured AFM images were then processed using open source Gwyddion software for the surface profile analysis.[10] The Ca-test has been used to measure the intrinsic WVTR at 20 $^{\circ}$C, 50% RH (measured far away from pinholes/defects in the film) of the above mentioned barrier layers. The Ca-test has been performed according to the description given by Keuning et al.[11]

Results and Discussion

In order to create an inorganic buffer layer between the polymer and permeation barrier, the silica-like film was deposited on a polymeric surface by atmospheric pressure PE-CVD. As recently discussed,[8] the porosity and barrier properties of silica films have been found to be controlled by the specific energy delivered per precursor molecule (TEOS) in the discharge plasma. Higher specific energy values result in denser films but this typically goes at the

expense of the deposition rate. The SiO_2 films employed in the present work were deposited at a relatively high rate of 1600 nm·min^{-1} and a specific energy of about 1 keV per TEOS molecule. By means of XPS and ATR-FTIR analysis it was observed[8] that such rapidly deposited silica-like layers show significant amount of silanol groups (Si-OH), indicating porosity, while the carbon content remains low (< 1%). These conditions result in an effective WVTR of 1.0 g·m^{-2}·day^{-1} for 80 nm- thick silica layer, and a barrier improvement factor (BIF) of only 1.7 with respect to the pristine polymer.

The surface morphology of the pristine PEN foil and PEN with 80 nm thick silica-like layer is presented in Figure 2. Although the substrate foil is relatively smooth (root mean square roughness rms = 1.68±0.02 nm), it can be expected that the complex 3D grains morphology seen in the AFM micrograph (Figure 2a) affects the nucleation and growth of ultra-thin barrier films. The deposition of a silica-like buffer layer (Figure 2b) results in further surface smoothening (rms = 1.47±0.02 nm) and the fine grain polymer structure cannot be distinguished anymore. The height of the small features in Figure 2b is not exceeding 5-6 nm (see AFM line profile).

Plasma assisted-ALD Al_2O_3 layers of varying thickness were deposited on top of the silica-like buffer film. Figure 3 shows the effective WVTR values of the resulting bi-layers as a function of the number of ALD cycles. Already 15 cycles (≤2 nm in Al_2O_3 thickness) with a 2 s oxygen plasma step lead to an improvement of almost 3 orders of magnitude in moisture barrier performance, with respect to the PEN/SiO_2 system. Increasing the number of cycles above 15 did not significantly reduce the water vapour transmission, which suggests that Al_2O_3 film thickness of 2 nm is the upper limit of the critical thickness in the sealing process of the SiO_2 layer.

As a comparison, the performance of thin alumina layers deposited directly on PEN is shown in Figure 3. The relatively thick PA-ALD alumina film deposited on PEN has a similar barrier improvement as the silica-alumina bi-layers. However, a much larger number of ALD

cycles (> 38) was needed to reach the critical thickness (> 5 nm) which is in agreement with reports in the literature.[12] It is worth to mention that in our experiments we found that thin ALD layers ($\leq$ 38 cycles) produced directly on the PEN substrate often revealed a degradation behavior of the barrier already during the water vapour permeation measurements in the Deltaperm instrument. The WVTR barrier degradation may be related to the Al_2O_3 hydrolysis effect.[13] At an Al_2O_3 layer thickness of ~ 20 nm (150 ALD cycles), the barrier performance is independent of the substrate. This phenomenon was not observed for the barriers deposited on the silica-like buffer layer described above. The small increase in WVTR with increasing layer thickness may be attributed to the tensile stress that is commonly found in the ALD alumina films.[14]

The duration of oxygen plasma exposure step is known to be an important parameter for plasma-assisted ALD, as it can influence the initial nucleation of the Al_2O_3 film as well as the effectiveness of the methyl abstraction and oxidation process. According to a previous study,[9] the chemical analysis of the films revealed that the levels of C and H impurities were substantially reduced when increasing the O_2 plasma exposure. In addition to 2 s oxygen plasma pulse we therefore investigated the Al_2O_3 layer performance for an oxygen plasma exposure time of 10 s. These results are also presented in Figure 3. The difference between barrier layers produced on silica buffer at 2 s and 10 s of O_2 plasma is evident when a low number of ALD cycles (<15) is carried out. The ALD process with a longer plasma exposure time results in a faster decrease in WVTR with the number of cycles. At the same time the barrier performance of the thicker layers is approximately the same for the two ALD recipes. These observations may indicate that a longer plasma step promotes film nucleation, therefore affecting mainly the performance of ultra-thin layers (no. of cycles $\leq$10), while the permeation properties of the bulk layer remain approximately unaffected.

In order to discern between effective and intrinsic barrier performances, the bulk material permeation was characterised using the Ca-test. The Ca-test results of the PE-CVD silica/PA-

ALD alumina bilayer in Figure 4 provide the intrinsic WVTR data. The intrinsic WVTR shows a steep decrease with increasing number of ALD cycles for both cases of 2s and 10s oxygen plasma exposure time. Similar to the effective permeation value measurements, a longer oxygen plasma step results in very good intrinsic barrier values already after 11 ALD cycles. For a larger number of ALD cycles the barrier performance is approximately the same for both ALD recipes. Because the intrinsic WVTR values exclude the influence of large pinholes, the last observation confirms again that the duration of the oxygen plasma step in the PA-ALD process primarily affects the film nucleation mechanism. The ultimate intrinsic permeation level reached the 10^{-6} g·m^{-2}·day^{-1} range (comparable to the detection limit of the calcium test) which makes this barrier stack potentially suitable for OLED and thin film PV applications, provided an adequate control of the local defect density due to environmental contamination and handling.

The results above indicate a strong synergy between ultra-thin ALD capping layers and silica-like buffer films in the moisture barrier performance. This conclusion corresponds well with the behaviour previously observed for the similar hybrid PECVD/ALD layers (100 nm SiO_2 or SiN_x / 10-50 nm Al_2O_3),[3] which were grown, however, at low pressure on rigid substrate. The decrease in WVTR value of the bi-layer structures cannot be explained in the frame of the ideal laminate theory, considering that both layers individually provide only very minor improvement in barrier performance. A hypothesis is that water vapour permeation in fast deposited silica layers takes place via percolation through an interconnected network of nano-pores. In this case the dense ALD film will act as a sealing layer for the porous silica-like layer. The critical thickness of the sealing layer should thus be in the order of the characteristic pore size of the buffer film. This hypothesis is currently being investigated in a parallel research work by making use of ellipsometric porosimetry.[15] Other benefits of the SiO_2 buffer layer are a reduced susceptibility of the Al_2O_3 film to hydrolysis, and facilitated film nucleation of the ALD film by the presence of silanol groups.[8]

To summarize: In this work it was shown that enhancement of polymer substrate with an atmospheric pressure PE-CVD silica-like buffer layer enables ultra-thin (≤ 2 nm) barrier films developed by plasma assisted ALD. This synergistic bi-layer structure provides an effective WVTR barrier of $\sim 10^{-3}$ g·m^{-2}·day^{-1} (40 ^{o}C/90% RH) and an intrinsic WVTR of $10^{-5} - 10^{-6}$ g·m^{-2}·day^{-1} (20 ^{o}C/50% RH). With the current development of both processes, atmospheric pressure spatial ALD and AP PE-CVD,[8,16,17] the approach described in the present contribution can lead to a high throughput and a cost effective roll-to-roll method to produce excellent moisture barrier films.

References

[1]   F. Massines, C. Sarra-Bournet, F. Fanelli, N. Naude, N. Gherardi, *Plasma Process. Polym.* **2012**, *9*, 1041.

[2]   H.B. Profijt, S.E. Potts, M.C.M. van de Sanden and W.M.M. Kessels, *J. Vac. Sci. Technol. A* **2011**, 29, 050801.

[3]   N. Kim, W.J. Potscavage, Jr., B. Domercq, B. Kippelen, and S. Graham, *Appl. Phys. Lett.* **2009**, 94, 163308.□

[4]   A.A. Dameron, S.D. Davidson, B.B. Burton, P.F. Carcia, R.S. McLean and S.M. George, *J. Phys. Chem.* C **2008**, 112, 4573.

[5]   P.F. Carcia, R.S. McLean, M.D. Groner, A.A. Dameron, and S.M. George, *J. Appl. Phys.* **2009**, 106, 23533.

[6]   A. Bulusu, H. Kim, D. Samet and S. Graham Jr., *J. Phys. D: Appl. Phys.* **2013**, 46 084014.

[7]   L.H. Kim, K. Kim, S. Park, Y.J. Jeong, H. Kim, D.S. Chung, S.H. Kim, and C. E. Park, *ACS Appl. Mater. Interfaces* **2014**, 6, 6731.

[8]   S.A. Starostin, M. Creatore, J.B. Bouwstra, M.C.M. van de Sanden and H.W. de Vries, *Plasma Process. Polym.* **2015**, 12, 545.

[9]   J. L. van Hemmen, S.B.S. Heil, J.H. Klootwijk, F. Roozeboom, C.J. Hodson, M.C.M. van de Sanden, and W.M.M. Kessels, *J.Electrochem. Soc.* **2007**, 154, G165.

[10]   D. Necas, P. Klapetek, *Cent. Eur. J. Phys*. **2012**, *10*, 181 (www.gwyddion.net)

[11]   W. Keuning, P. van de Weijer, H. Lifka, W.M.M. Kessels and M. Creatore, *Vac. Sci. Technol. A* **2012**, 30, 01A131.

[12]   E. Langereis, M. Creatore, S.B.S. Heil, W.M.M. Kessels, and M.C.M. de Sanden, *Appl. Phys. Lett.* **2006**, 89, 81915.

[13]   J.A. Bertrand, S.M. George, *J. Vac. Sci. Technol. A*. **2013**, 31, 01A122.

[14]   H.B. Profijt, M.C.M. van de Sanden, and W.M.M. Kessels, *J. Vac. Sci. Technol. A.* **2013**, 31, 01A106.

[15]   A. Perrotta, E.R.J. van Beekum, G. Aresta, A. Jagia, W. Keuning, M.C.M. van de Sanden, W.M.M. Kessels, M. Creatore, *Microporous and Mesoporous Materials* **2014**, 188, 163.

[16]   P. Poodt , A. Lankhorst, F. Roozeboom, K. Spee, D. Maas, and A. Vermeer, *Adv. Mater.* **2010**, 22, 3564.

[17]   A.S. Yersak, Y.C. Lee, J. A. Spencer and M. D. Groner, *J. Vac. Sci. Technol. A* **2014**, 32, 01A130.
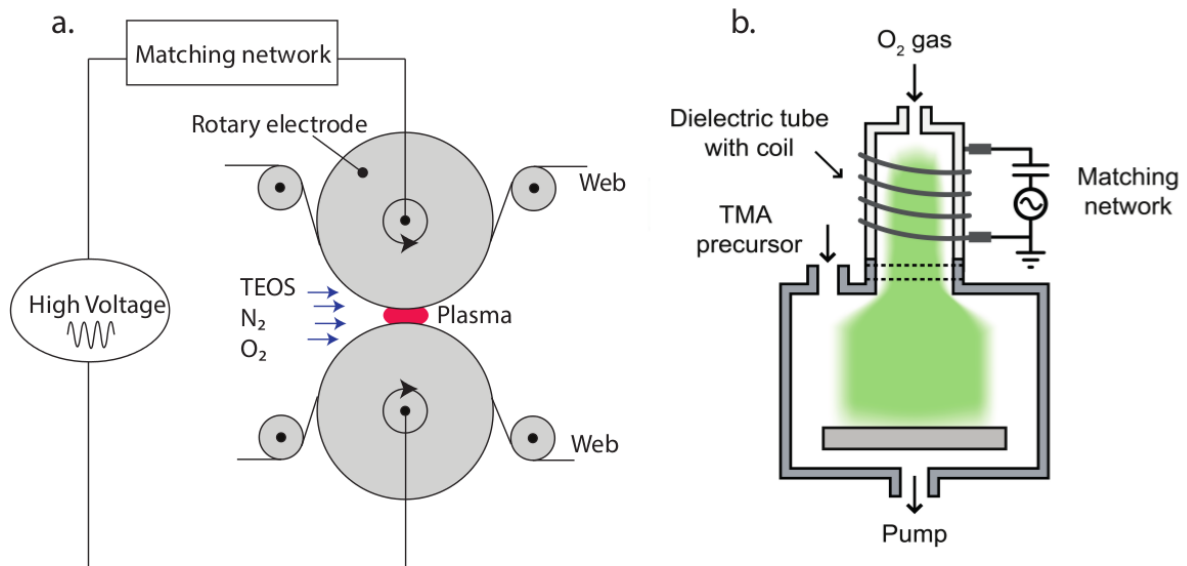
List of Figures

Figure 1. Schematic representation of a) atmospheric pressure plasma enhanced chemical vapour deposition reactor b) plasma assisted atomic layer deposition reactor.

Figure 2. AFM images of the a) pristine PEN substrate (1x1 $\mu m2$) rms = 1.68±0.02 nm and b) PEN substrate coated with 80 nm thick silica-like buffer layer (2x2 $\mu m2$)   rms = 1.47±0.02 nm.

Figure 3.   Effective water vapour transmission rate as a function of Al_2O_3 plasma assisted-ALD cycles number. Triangles: Al_2O_3 deposition on pristine PEN with 2 s ALD plasma step. Squares: Al_2O_3 deposition on SiO_2 buffer layer with 2 s ALD plasma step. Circles: Al_2O_3 deposition on buffer layer with 10 s ALD plasma step. WVTR values of pristine PEN and PEN with SiO_2 buffer layer are also shown.

Figure 4. Intrinsic water vapour transmission rate of the bi-layers as a function of Al_2O_3 plasma assisted- ALD cycles number for plasma step duration of 2 s and 10 s.

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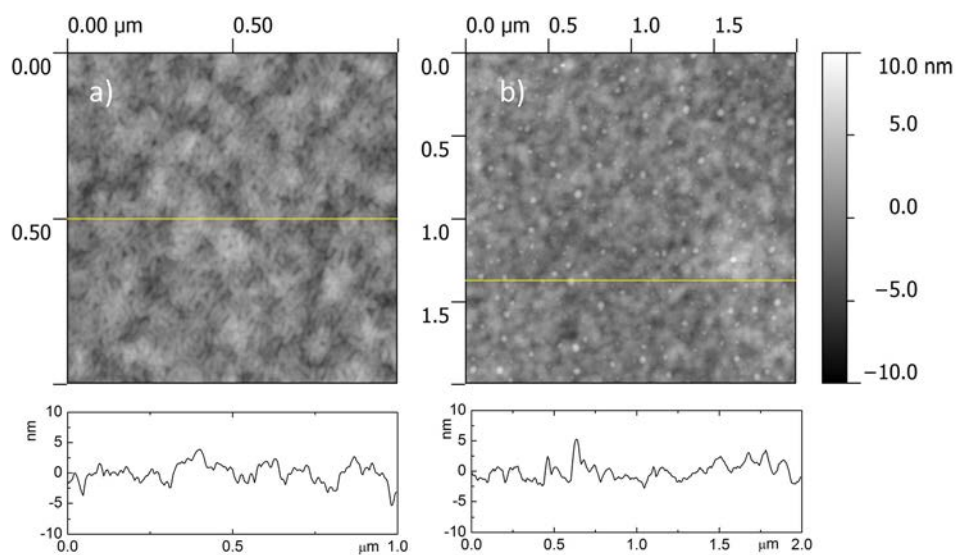
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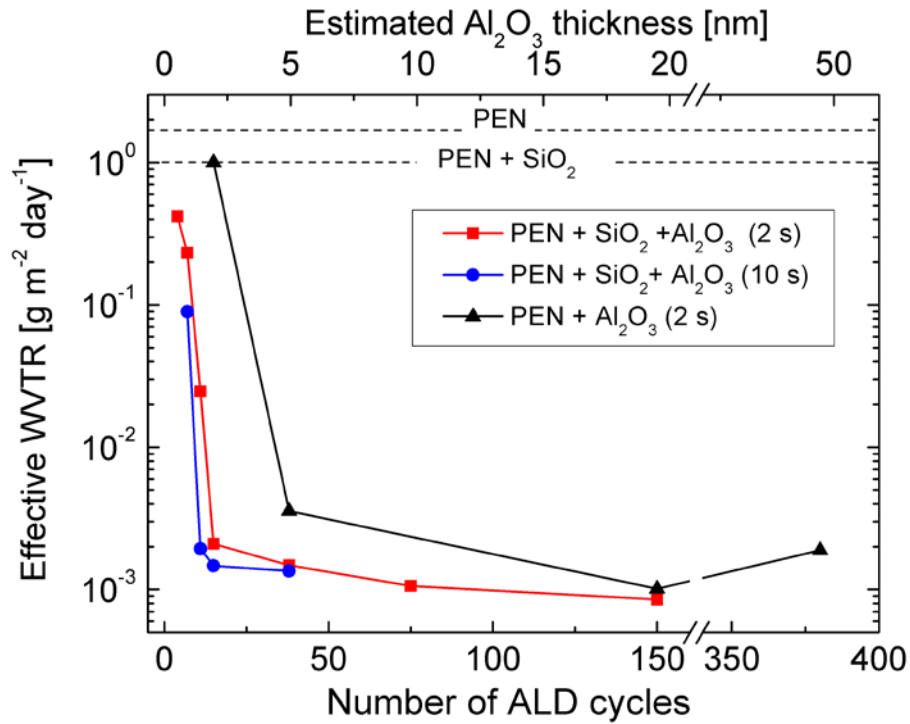
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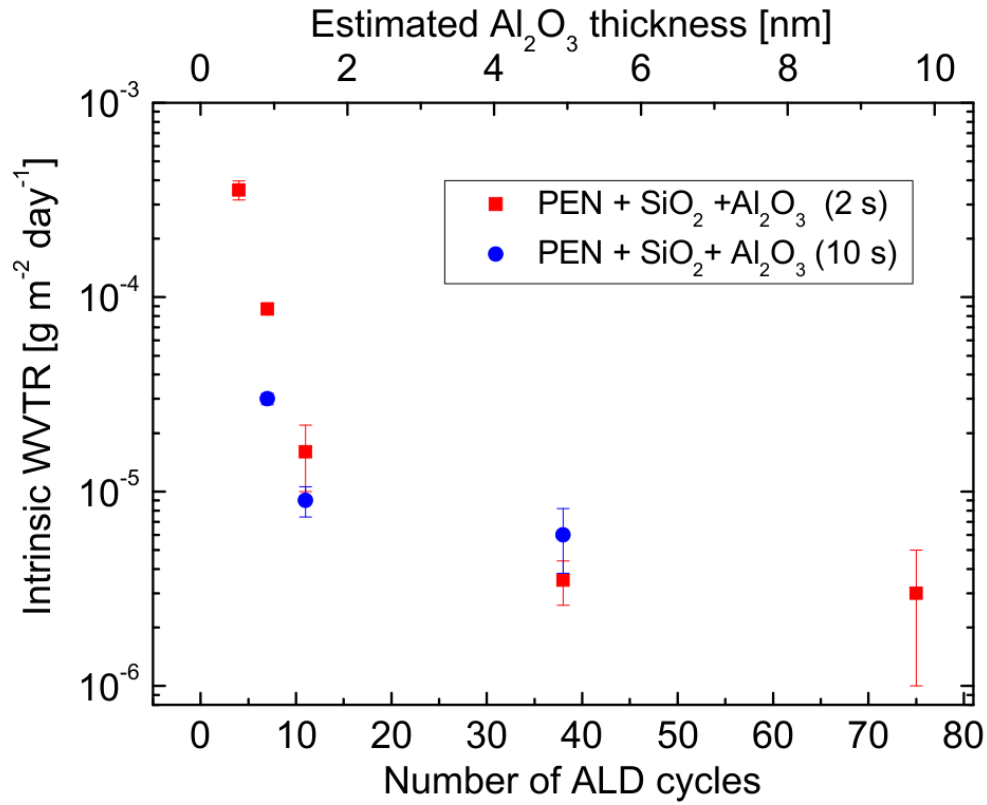layer are also shown.*

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Text and Figure for the Table of Contents

The article studies synergistic effect in combining industrially compatible roll-to-roll atmospheric pressure PE-CVD and plasma-assisted ALD technologies for moisture barrier fabrication on polyethylene 2,6 naphthalate (PEN) polymer. It is demonstrated that enhancement of polymer substrate with silica-like PE-CVD buffer layer enables ultra-thin Al_2O_3 barrier films prepared with less than15 plasma assisted ALD cycles.

Sergey A. Starostin,* Wytze Keuning, Jean-Paul Schalken, Mariadriana Creatore, W.M.M.(Erwin) Kessels, Jan B. Bouwstra, M.C.M.(Richard) van de Sanden, Hindrik W. de Vries

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