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Influence of the polymeric substrate on the water permeation of alumina barrier films deposited by atomic layer deposition

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A B S T R A C T

Atomic layer deposited (ALD) barrier films have been deposited onto a wide variety of flexible polymeric substrates to determine their effectiveness as moisture barriers for organic electronics. Little research has however been conducted on the contribution of the substrate to the barrier properties. In this study, alumina (Al_2O_3) barrier films have been deposited onto different polymeric substrates by ALD to investigate the effect of the substrate type and thickness on the water vapour transmission rate (WVTR). 24 nm Al_2O_3 films were deposited via plasma enhanced ALD onto 75 and 125 μm thick polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) substrates. Half of the substrates were also O_2 plasma pre-treated prior to Al_2O_3 film deposition to determine its effect on the WVTR. The WVTR of the substrates prior to barrier film deposition was measured using tritiated water (HTO) permeation. Prior to barrier film deposition, it was shown that the WVTR decreased as the substrate thickness increased while PEN had a lower WVTR than PET. After Al_2O_3 barrier film deposition, the WVTR followed the previously observed trend with lower WVTR for thicker substrates and for PEN over PET. The substrates O_2 plasma pre-treated prior to barrier film deposition also showed lower WVTRs, which were attributed to surface cleaning and improved film adhesion. The lowest WVTR measured was 3.1×10^{-3} g·m^{-2}/day for a 24 nm Al_2O_3 film deposited onto O_2 plasma pre-treated 125 μm PEN. These results demonstrate that the properties of the polymer substrate influence the WVTR even after barrier film deposition and can therefore be used to improve the barrier properties.

1. Introduction

Significant research into the development of organic photovoltaic cells (OPVs) and organic light emitting diodes (OLEDs) has been carried out over recent years. Polymers are typically used as the substrates for organic electronics such as OPVs and OLEDs as they are lightweight, cheap, transparent, printable and flexible. Polymer substrates however have high gas/vapour permeability. Barrier films are therefore required for both OPVs and OLEDs to achieve sufficient lifetimes for commercial application by preventing degradation from exposure to water vapour and oxygen [1]. It is generally believed that OLEDs require water vapour transmission rates (WVTR) in the range of of 10^{-6} g·m^{-2}/day to result in sufficient lifetimes [2]. Atomic layer deposition (ALD) is an ideal technique for the deposition of barrier films as it is a self-limiting technique where gas-phase deposition is used to produce conformal pinhole-free inorganic coatings. Atomic layer growth is achieved by alternate pulsing of precursor gases and inert gases. Inert gas pulses are used to clear the reactor chamber of excess precursor and by-products [3]. Inorganic layers produced by ALD have achieved lower water permeation with thinner layers than other techniques due to film integrity [4].

A number of metal oxide barrier films can be deposited using ALD, but alumina (Al_2O_3) is the most frequently used as a barrier film [5]. ALD frequently requires temperatures > 200 °C to produce dense, pinhole free films or requires plasma enhancement. Many polymers are however fragile with glass transition temperatures < 100 °C, therefore high temperature ALD is not suitable to protect organic electronic devices [6]. An advantage of Al_2O_3 barrier layers is the relatively high deposition rate (> 1 Å/cycle) at temperatures below 150 °C [7,8], which is make it suitable for temperature sensitive polymers. A number of studies have investigated the effect of single Al_2O_3 barrier films on the WVTR by varying a number of parameters such as film thickness and deposition temperature. It has been shown that increasing either the film thickness [9,10], deposition temperature [11,12] or both [13–19] decreases the WVTR. A wide range of WVTR values have been reported for single Al_2O_3 barrier films, which demonstrate that a number factors influence the WVTR. In particular, the WVTR is dependent on the temperature and relative humidity during measurement

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such that increases in either will increase moisture permeation. For single Al_2O_3 barrier films, the WVTR measurement conditions have been varied from ambient temperature and humidity [13] to 100% RH [9] and 85 °C [20]. Thus the WVTRs for a single Al_2O_3 barrier film have ranged from 10 g·m^{-2}/day for a 25 nm thick film deposited onto a 40 μm polylactic acid (PLA) substrate with thermal roll to roll ALD at 100 °C [21] down to 1.7×10^{-5} g·m^{-2}/day for a 25 nm thick Al_2O_3 film deposited onto a 125 μm polyethylene naphthalate (PEN) substrate with thermal ALD at 120 °C [20].

ALD barrier films have been deposited onto a number of different polymer substrates, including polyethylene terephthalate (PET) [22], polyetheretherketone (PEEK) [9], polyethersulfone (PES) [12,14,23], polycarbonate (PC) [14], PEN [13,20,24], PLA [21] and polyimide (PI) [21,25]. Prior to film deposition, these polymer substrates were found to have a wide variety of WVTRs: 1.4–3 g·m^{-2}/day for PET [26,27], 3.1 g·m^{-2}/day for PEEK [9], 34.1–92.8 g·m^{-2}/day for PES [12,16], 50 g·m^{-2}/day for PC [14], 0.5–1.3 g·m^{-2}/day for PEN [28,29], 39–53 g·m^{-2}/day for PLA [3,21] and 0.2–3 g·m^{-2}/day for PI [21,25]. WVTR is however not the only factor when choosing a substrate for OPVs and OLEDs. PEN has one of the lowest WVTRs but is more expensive than other substrates with a previously reported price of 22 euros per kg while PET is significantly cheaper at 8 euros per kg [30]. Substrate price is therefore an important consideration in the development of large scale OPVs and OLEDs as it can add significant costs to the device.

Although a number of different polymers have been used as substrates for ALD barrier film, only a few studies have deposited the same Al_2O_3 films onto different substrates. 25 nm Al_2O_3 films were deposited on cellulose, PLA and PI by roll to roll ALD. The WVTRs for the uncoated substrates at 23 °C and 50% RH, were 144, 39 and 3 g·m^{-2}/day respectively. After Al_2O_3 film deposition, the corresponding WVTRs decreased to 15, 10 and 2 g·m^{-2}/day [21]. The effect of the substrate on the WVTRs of different coated papers has also been investigated. The papers were extrusion coated with low density polyethylene (LDPE), polypropylene (PP), PET and PLA which had WVTRs of 2.8, 1.1, 22 and 72 g·m^{-2}/day respectively at 23 °C and 50% relative humidity. The deposition of 100 nm thick Al_2O_3 films via spatial ALD decreased the WVTRs to 0.5, 0.3, 0.5 and 4.3 g·m^{-2}/day respectively [31]. Another study investigated the barrier performance of single Al_2O_3 layers, approximately 12 nm thick, deposited on PES, PC and PEN substrates which had uncoated WVTRs of 60, 50 and 2 g·m^{-2}/day respectively. These WVTRs were reduced to 4.1×10^{-3}, 4×10^{-3} and $< 4 \times 10^{-3}$ g·m^{-2}/day respectively after Al_2O_3 deposition [14]. In all studies, the highest WVTR after the deposition of an Al_2O_3 barrier film was reported for the substrate with the highest uncoated WVTR, thus suggesting that the substrate does play a role in the WVTR of barrier film deposited onto a polymeric substrate.

Treatment of the polymer surface by corona or plasma treatment has been shown to influence the surface chemistry, roughness and contact angle. Varying these substrate properties can influence ALD film deposition and therefore also the WVTR. During corona treatment, the surface is bombarded with oxygen, free radicals of oxygen and ozone generated by electrical discharge, all of which oxidize the surface. A similar effect occurs with plasma pre-treatments where the surface is exposed to an oxygen or air plasma generated by a radio frequency discharge. Polymer films are typically chemically inert with low surface energy which results in poor wetting and adhesion of deposited films. The surface oxidation induced by corona and plasma treatment typically increases the surface energy thus improving film adhesion. The surface chemistry, roughness and contact angle of the film may affect ALD deposition, especially during the initial stages of film formation. One of the reasons behind such behaviour may be the different amount of hydrogen bonded water on the surface. Corona treatment has shown to increase both the oxygen content and C—O functionalities of polyethylene (PE) and can also remove low molecular weight contaminants [32]. Both corona and plasma pre-treatment increase the number of polar surface groups and thus the higher surface energy leads to more homogeneous films and therefore enhanced barrier properties for thinner Al_2O_3 films [33]. A number of studies have shown that corona, air and oxygen plasma typically increase the oxygen concentration, increase surface energy, decrease contact angle and increase surface roughness [34–39].

A few studies have investigated the effect of corona or plasma pretreatment on moisture permeation. PP substrates have been corona and/or O_2 plasma treated prior to the deposition of AlO_x films by vacuum web coating. O_2 plasma treatment decreased surface roughness and increased the oxygen content on the surface which increased the adhesion of AlO_x. For smoother surfaces, there were less shadowing effects during deposition and therefore the films were more homogeneous with fewer defects [40]. In addition, Al_2O_3 and silica (SiO_2) films have also been deposited via ALD onto PE and PLA coated paperboard. Corona treatment decreased the contact angle and decreased some of the WVTR values, most noticeably for 25 nm Al_2O_3 and SiO_2 films on PE coated paperboard [32].

The present research investigates the effect of substrate thickness, type and O_2 plasma pre-treatment on the WVTRs of PET and PEN substrates before and after the deposition of Al_2O_3 barrier films by plasma enhanced ALD (PE-ALD). The effect of O_2 plasma pre-treatment on the surface of PET and PEN substrates was analysed by X-ray photoelectron spectroscopy, contact angle measurements and atomic force microscopy. The WVTRs before and after the deposition of Al_2O_3 barrier films were determined by tritiated water permeation. The substrate thickness, substrate type and O_2 plasma pre-treatment of PET and PEN substrates have all been shown to influence the WVTRs and can therefore be used to increase the effectiveness of Al_2O_3 barrier films.

2. Experimental

2.1. Materials

The biaxially oriented PET substrates were cut from a 75 μm thick, 300 mm wide roll (Multapex Pty. Ltd.) and from 125 μm thick, 600 mm wide roll (Goodfellow, UK). The biaxially oriented PEN pieces were cut from a 75 μm thick, 600 mm wide roll and from 125 μm thick 300 × 300 mm^2 sheets (both from Goodfellow, UK). The structures of the PET and PEN repeating units are shown in Fig. 1. Trimethylaluminium (TMA) (99.999%) was purchased from Strem Chemicals. Liquid scintillation cocktail (Ultima Gold™ uLLT) and tritiated water (37 MBq/

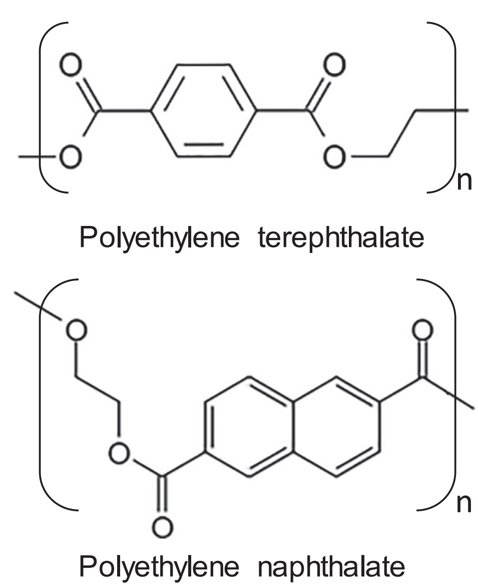

Fig. 1. Structure of PET and PEN repeating units.