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Aluminum oxide barrier coating on polyethersulfone substrate by atomic layer deposition for barrier property enhancement

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ABSTRACT

Aluminum oxide layers were deposited on flexible polyethersulfone (PES) substrates via plasma enhanced atomic layer deposition (PEALD) process using trimethylaluminum (TMA) and oxygen as precursor and reactant materials. Several process parameters in PEALD process were investigated in terms of refractive index and layer thickness. Number of process cycle increased the thickness and refractive index of the layer to enhance the barrier properties. Non-physisorbed TMA and unreacted oxygen were purged before and after the plasma reaction, respectively. Identical purge time was applied to TMA and oxygen and it was optimized for 10 s. Thinner and denser layer was formed as substrate temperature increased. However, the PES substrate could be deformed above 120 °C. Aluminum oxide layer formed on PES at optimized conditions have 11.8 nm of thickness and reduced water vapor transmission rate and oxygen transmission rate to below 4×10^{-3} g/m² day and 4×10^{-3} cm³/m² day, respectively. Polycarbonate and polyethylene naphthalate films were also tested at optimized conditions, and they also showed quite appreciable barrier properties to be used as plastic substrates.

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1. Introduction

Physical vapor deposition (PVD) and chemical vapor deposition (CVD) processes have been proposed for the formation of thin oxide layer on substrates. Sputtering process has been employed for the deposition of aluminum oxide layers among several PVD processes [1,2]. However, PVD process has limitation in complete layer coverage and resulted in void formation during the filling process of high aspect ratio features. Whereas, CVD processes have been commonly used to overcome the poor coverage by PVD process by controlling the surface reaction [3].

Conformal deposition was attained by CVD process which was secured by the uniform precursor flux on the substrate surface. However, aluminum oxide layer deposited by CVD process still has surface roughness problem, and various research works have been proposed to improve the topography and the planarization. Atomic layer deposition (ALD) process has emerged as a promising candidate to extend the capabilities of CVD techniques [4], which is based on the principle of saturated mechanism by chemisorption [5]. ALD is known to be capable of producing densely packed, highly uniform, and conformal layers on the substrate. During the ALD process, each precursor was chemisorbed individually onto the substrate rather than reacted in the gas phase. Gas-phase reactions are inhibited by purging with inert gas

between each pulse cycle. Under ideal conditions, substrate-precursor reactions are self-limited and the surface is saturated with precursor fragments at the end of each pulse. Ligands in the fragments are eliminated by reaction with the other precursor during the next pulse. Since the growth reactions occur only at the surface, deposition rate is slow. However, ALD technique has the advantage of atomic-level control of film thickness, conformality, and uniformity. Therefore, ALD process has been widely used for the deposition of thin oxide layer with good barrier properties [6].

Generally, Al₂O₃ layers were grown using trimethylaluminum (TMA, Al(CH₃)₃) and H₂O as precursors. Recently, ozone and oxygen are used as oxidant materials in ALD process to replace the conventional source, H₂O. They are gaining much interest, because ozone and oxygen are more reactive than H₂O. When the oxygen is used, chemical activation of oxidant has already occurred in the gas phase, which can lower the deposition temperature [7]. Elliott et al. investigated the effect of growth temperature on the structural and morphological properties of Al₂O₃ films deposited via ALD, comparing the effects of H₂O and O₃ as oxygen sources [8]. Langereis et al. reported the observation that –CH₃ and –OH surface groups are predominantly formed after the TMA and oxygen plasma half-cycles, respectively, and they proposed surface reactions for plasma-assisted ALD of Al₂O₃ [9].

ALD process can deposit smooth, conformal, and pinhole-free films with a nearly featureless structure. Therefore, the thin oxide films deposited by ALD process are good candidates for barrier layer of plastic substrates. Groner et al. reported good barrier properties of Al₂O₃ layer with thickness of 10–25 nm, which are formed from sequential TMA and

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water vapor exposures [10]. Erlat et al. reported the N-doped Al_2O_3 layer can easily be deposited by plasma-assisted atomic layer deposition as admixing nitrogen to the oxygen plasma [11].

In this work aluminum oxide layers were deposited on plastic substrates via plasma enhanced atomic layer deposition (PEALD) process using TMA and oxygen as precursor and reactant materials, respectively. Conditions for PEALD were investigated in terms of layer characteristics including thickness, refractive index, and chemical compositions. The barrier properties of aluminum oxide layer to water vapor and oxygen were characterized.

2. Experimental parts

2.1. Formation of aluminum oxide layer via PEALD process

TMA precursor has only six electrons in its valence shell to be electron deficient, which drives it toward dimer formation to achieve the configuration having eight electrons [12]. TMA is a liquid precursor of high vapor pressure (1117 Pa) at room temperature [5]. PEALD system was designed to use TMA and oxygen as precursor and reactant materials, in which cylindrical reactor with diameter of 300 mm was installed with a load-locked preparation chamber. TMA precursor was kept at 20 °C during the entire deposition process, and the background pressure was kept constant at 133 Pa. The substrate temperature was controlled within the range of 50–150 °C.

The electrodes are capacitively coupled with a low frequency (60 Hz) plasma source and the plasma power was fixed at 500 W. Aluminum oxide layer was deposited on the substrate by alternating supplies of TMA and oxygen. PEALD process cycle consisted of several steps as shown in Fig. 1. TMA was fed into the reactor by bubbling Argon carrier gas through its bottle at a flow rate of 100 sccm for 0.5 s. TMA was physisorbed on the PES (SBT200, i-component Co., Korea) substrate and non-physisorbed TMA was purged out by pure argon gas at 300 sccm for 3–15 s. Reactant oxygen was fed into the reactor at 300 sccm for 1.5 s, and then LF plasma pulse was applied for 3 s to produce oxygen radicals while oxygen feeding was maintained at 300 sccm. After plasma

reaction argon was then introduced into the reactor again to purge the unreacted oxygen between precursor pulses and to facilitate the generation of plasma during the deposition process. Purge time of oxygen was set identical to that of TMA. Background pressure was maintained throughout the process by another continuous argon stream supplied into the reactor at 500 sccm.

2.2. Characterizations of aluminum oxide layer

The thickness and refractive index of layer were measured by using a spectroscopic ellipsometer (V-VASE, J. A. Woollam, Inc., USA). The chemical composition of the layer was measured via X-ray photoelectron spectroscopy (XPS). The spectra were taken by using K-Alpha system (Thermo Scientific, UK.) and Al K α X-ray source was used with micro-focused monochromator. The base pressure of the ultrahigh vacuum chamber was lower than 3×10^{-7} Pa, and the resolution was 0.9 eV/104 counts per second.

Water vapor transmission rate (WVTR) and oxygen transmission rate (OTR) were measured using PERMATRAN 3/33 and OXTRAN 2/21 (Mocon Instruments, USA), respectively.

3. Results and discussion

3.1. Effect of number of process cycle

Number of process cycle was ranged from 50 to 200, and TMA and oxygen feeding time were set to 0.5 s and 4.5 s, respectively. Identical purge time was applied to both non-physisorbed TMA and unreacted oxygen as 3 s. As shown in Fig. 2, thickness of aluminum oxide layers grown at 120 °C, increased from 15.1 nm for 50 cycles to 48.5 nm for 200 cycles. Total thickness of aluminum oxide layer deposited on substrate was proportional to the number of process cycles. Also, the refractive indices increased from 1.6735 for 50 cycles to 1.6951 for 200 cycles. The refractive index tends to decrease by the incorporation of impurities at lower deposition temperature. Decrease of refractive index was also attributed to decrease the density of the layers. However, the refractive index of the thin layer obtained in this work was lightly increased with the number of process cycles, which assured the impurity proof of the devices.

In ALD process, the growth rate of layer depended more on the number of process cycles rather than the cycle time or the intensity of the material pulse. The growth rate was determined as the total layer thickness divided by the number of process cycles. The growth rate was slightly decreased from 3.02 to 2.43 Å/cycle and refractive index was slightly increased from 1.6735 to 1.6951 by increasing the number of process cycles from 50 to 200. The growth rate and refractive index for amorphous Al_2O_3 using TMA and H_2O at 177 °C are

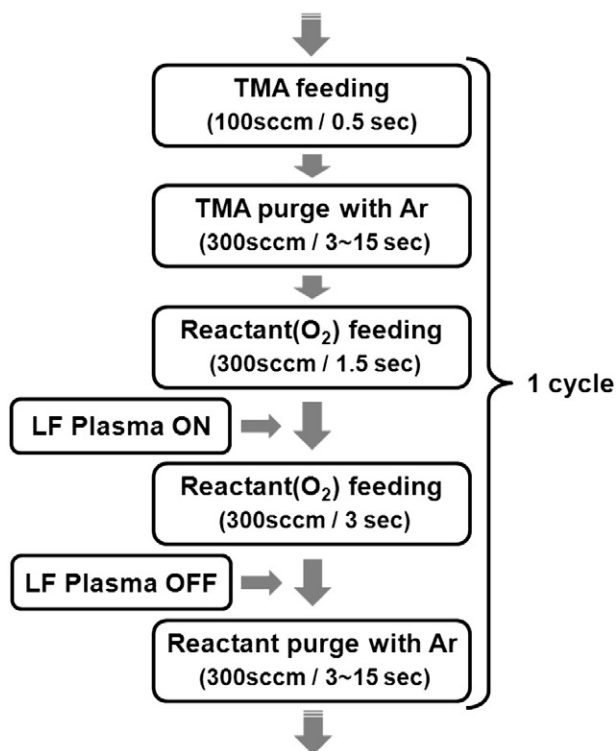


Fig. 1. Schematic of PEALD process cycle for deposition of the aluminum oxide layer.

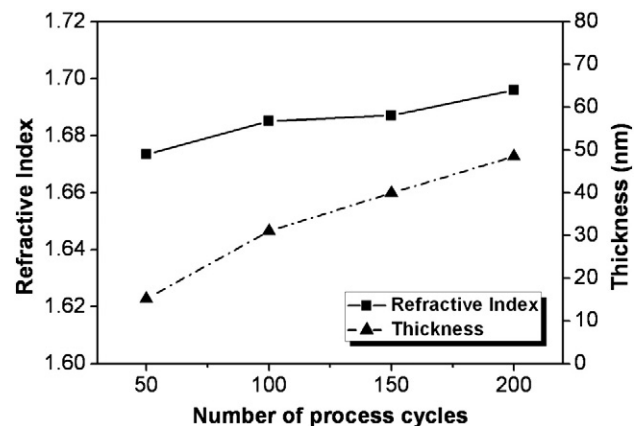


Fig. 2. Refractive index and thickness of aluminum oxide layer deposited on PES as function of the number of process cycle.

reported as 1.33 Å/cycle and 1.6, respectively [10]. This work was more effective for the formation of densely packed aluminum oxide layer using TMA and oxygen than the case using TMA and H₂O.

As shown in Fig. 3, atomic composition change of thin aluminum oxide layers was examined in terms of number of process cycles. Binding energy of each atoms, such as Al(2p), C(1s) and O(1s) and their atomic composition were changed a little with the number of process cycles. These results indicated that each layer deposited represented the similar stoichiometric characteristics irrespective of the number of process cycles [13].

Fig. 4 shows the variations of WVTR and OTR values of PES substrate as function of the number of process cycles. PES substrate with aluminum oxide layers deposited by 200 cycles reached the WVTR value of 4×10^{-2} g/m² day and OTR value of 8×10^{-2} cm³/m² day, which represented the great reductions of WVTR and OTR by three orders of magnitude when compared with those of bare PES substrate. Barrier property enhancement achieved in this work was superior to those reported for single layer barrier coating [9], and the improvement of barrier properties of layers could be attributed to the dense and conformal characteristics of aluminum oxide layers by ALD growth [14].

Number of ALD process cycle should be optimized in terms of performance as well as energy consumption. When the number of process cycle exceeded 100, there were no more reductions of WVTR and OTR. However, the total process time and the energy consumption were proportional to the number of cycles. Therefore, number of process cycle was optimized as 100 for the conditions given as above in this work to obtain thin and dense layer with appreciable barrier properties.

3.2. The effect of purge time

The precursor and reactant purge time should last long enough to avoid the reactant mixing, which might cause subsequent CVD instead of ALD. The CVD growth is indicated by the rise in mass gain per cycle at short purge time [10]. Increase of purge time reduced impurity contents in the layer. The purge after precursor and reactant pulses could help effectively remove the gas products. In this work purge time was varied from 3 to 15 s, and identical purge time was applied to TMA and oxygen. As shown in Fig. 5, for aluminum oxide layer grown using 50 cycles at 120 °C, the thickness of layer decreased from 15.1 nm at purge time of 3 s to 11.8 nm at purge time of 10 s, and then increased slightly to 17.78 nm at purge time of 15 s. The refractive indices of 1.6735 (3 s), 1.7014 (10 s), and 1.6534 (15 s) were measured, respectively. Also, the growth rates of 3.02 (3 s), 2.36 (10 s) and 3.54 Å/cycle (15 s) were obtained, respectively. In case of using purge time of 10 s, the thinnest

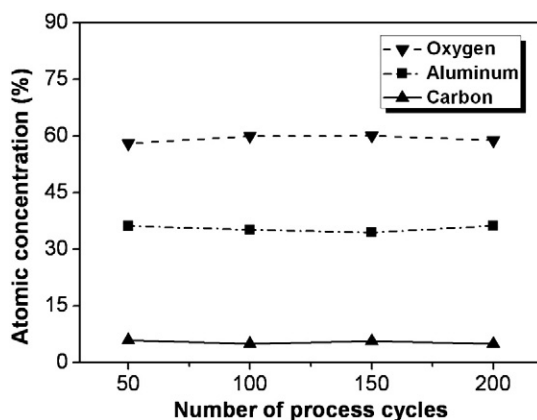


Fig. 3. XPS analysis of aluminum oxide layer deposited on PES as function of the number of process cycle.

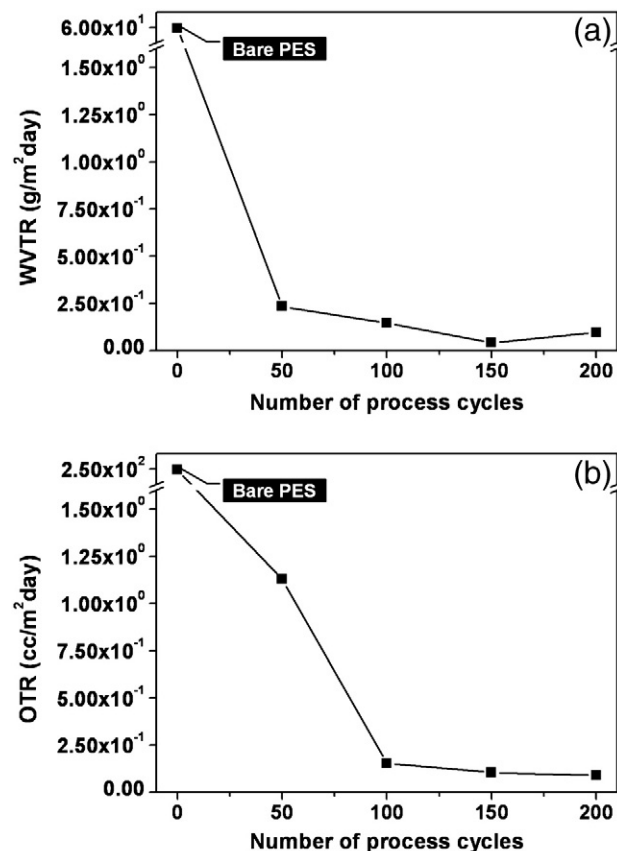


Fig. 4. (a) WVTR and (b) OTR of aluminum oxide layer deposited on PES as function of the number of process cycle.

aluminum oxide layer having the higher refractive index value could be formed on PES substrates. These results indicated that purge time of 10 s was sufficient to purge both non-physisorbed precursor and unreacted reactants [10]. There were no significant changes in atomic composition and binding energy with increasing the purge times.

As shown in Fig. 6, increases of purge times of TMA and oxygen for deposition of aluminum oxide layer on PES substrate made contribution in reduction of both WVTR and OTR by three orders of magnitude, when compared to those of bare PES substrate. Especially, at longer purge time, the OTR can be reached to the level below 4×10^{-3} cm³/m² day (too low to be detected by MOCON systems). Although the carbon

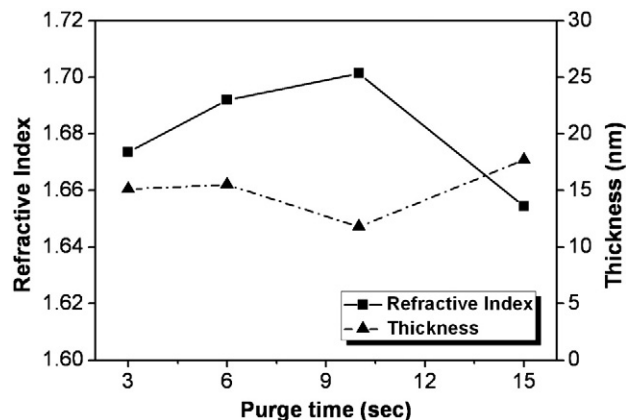


Fig. 5. Refractive index and thickness of aluminum oxide layer deposited on PES as function of the purge times.

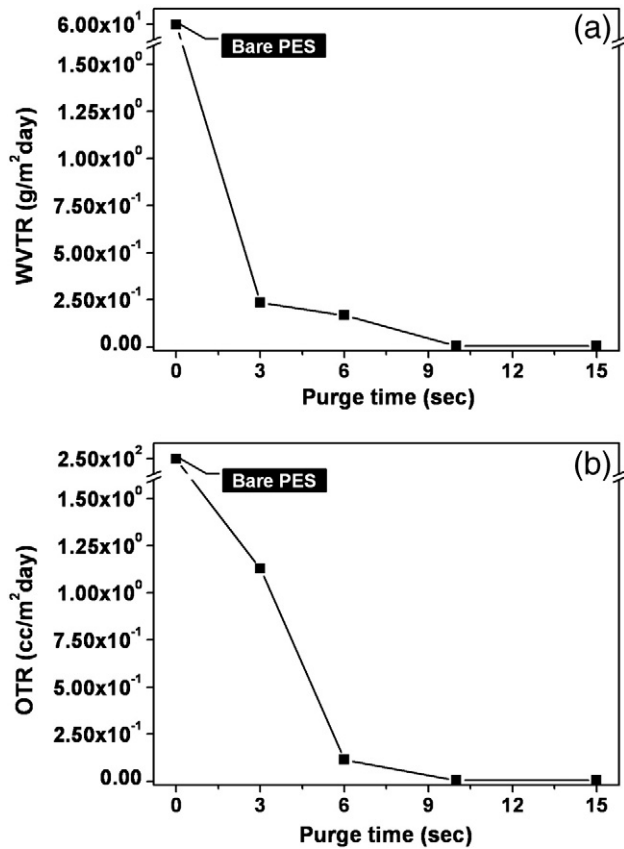


Fig. 6. (a) WVTR and (b) OTR of aluminum oxide layer deposited on PES as function of purge times.

concentrations are still detected, the aluminum oxide layers showed superior barrier properties.

3.3. The effect of substrate temperature

Fig. 7 shows the thickness and refractive index of aluminum oxide layer deposited at different substrate temperatures ranging from 50 to 150 °C at 50 cycles and 10 s of purge time. As the substrate temperature increased, the thickness was decreased and the refractive index increased. The increase of substrate temperature from 50 to 150 °C induced the decrease of growth rate from 8.487 to 1.465 Å/cycle. Therefore, desorption of TMA and oxygen at the surface could be enhanced at higher substrate temperature. Furthermore, the

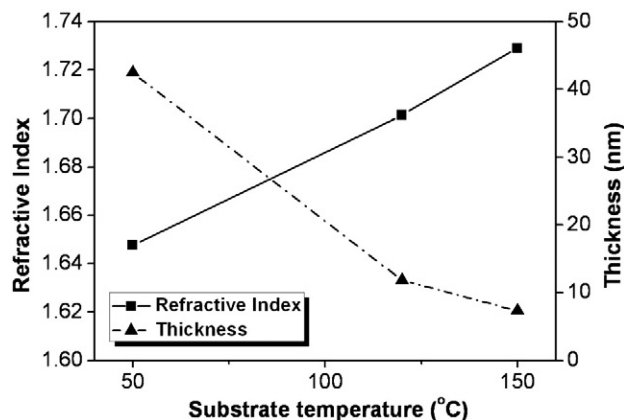


Fig. 7. Refractive index and thickness of aluminum oxide layer deposited on PES as function of substrate temperature.

decrease of layer thickness could be caused by densification of the amorphous film due to the increase of substrate temperature and the more efficient desorption of residual side products [15,16]. For the water-based process, the decrease in growth per cycle with increasing temperature has been related to thermal stability of the –OH surface groups which are involved in the chemisorption of TMA. The oxygen based ALD process shows a similar decrease, which indicates similarity between the surface groups involved in plasma assisted and thermal ALD process [9]. As shown in Fig. 8, the PES substrate having aluminum oxide deposited with 50 cycles at higher temperature shows four orders of magnitude reduction in both WVTR and OTR compared to the uncoated PES. These results were obtained at constant purge time of 10 s. The WVTR and OTR of the aluminum oxide layer deposited at 120 and 150 °C can be obtained below 4×10^{-3} g/m² day and 4×10^{-3} cc/m² day (too low to be detected by MOCON systems), respectively.

3.4. Application to other substrate materials

Quite appreciable barrier properties were obtained for PES substrate by PEALD process at optimized process conditions. Several polymeric materials have been tested as plastic substrates. We have applied PEALD process to other substrate materials such as polycarbonate (PC) (Glastic, i-component Co., Korea) and polyethylene naphthalate (PEN) (Q65, Teijin DuPont Films Co., Japan) films. Aluminum oxide layer was deposited on PC and PEN substrates at optimized conditions obtained in PES case; 10 s of purge time, at 120 °C of substrate temperature and 50 process cycles. Barrier property measurement results were summarized in Table 1.

Each bare substrate film was tested and showed different barrier properties depending on its chemical structure and film processing

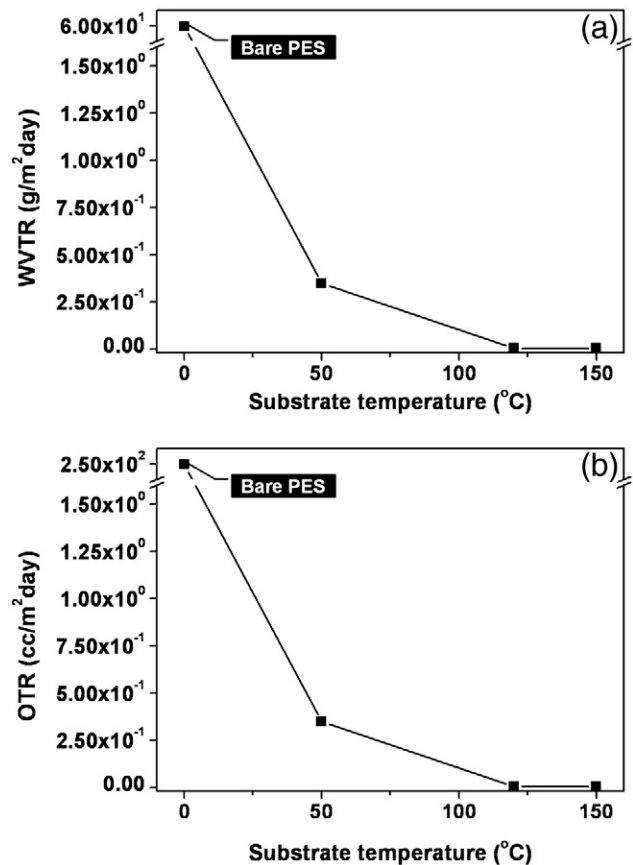


Fig. 8. (a) WVTR and (b) OTR of aluminum oxide layer deposited on PES as function of substrate temperature (TMA and oxygen purge time: 10 s).

Table 1

Comparison of barrier properties of aluminum oxide layer deposited on the several substrates.

Substrate	WVTR (g/m ² day)		OTR (cm ³ /m ² day)	
	Untreated	50 cycles	Untreated	50 cycles
PES	60	4.1×10^{-3}	250	$<4 \times 10^{-3}$
PC	50	4.0×10^{-3}	60	$<4 \times 10^{-3}$
PEN	2	$<4 \times 10^{-3}$	45	$<4 \times 10^{-3}$

Detection limit of MOCON apparatus: 4×10^{-3} g/m² day for WVTR and 4×10^{-3} cm³/m² day for OTR.

conditions. PEN showed the best barrier properties than the others, and PC had excellent OTR than PES. Each substrate film has its own advantages as well as disadvantages in terms of mechanical, thermal and optical properties. PES has superior thermal resistance than other polymer materials and it is regarded as one of promising plastic substrate materials. However, it has dimensional stability problems due to its high coefficient of thermal expansion (CTE) value. PEN has optical anisotropy problems in application to display.

After barrier coating by PEALD WVTR values of each substrate were much reduced to 4×10^{-3} g/m² day or below and OTR values were much reduced to below 4×10^{-3} cm³/m² day. In most cases WVTR and OTR values reached the value below the detection limit of MOCON apparatus. Therefore, barrier properties enhancement were attained by PEALD process for different substrates, and the process optimized in this work can be applied to other substrate than PES.

4. Conclusions

Aluminum oxide layers were well deposited on flexible PES substrates via PEALD system. Total thickness of aluminum oxide layer was proportional to the number of process cycles, refractive index was also increased. Number of process cycles was optimized as 100 in terms of barrier properties, energy consumption and process time. Improvement of barrier properties of thin aluminum oxide layers can be related to the uniform and conformal growth of the aluminum oxide layers.

Purge time was also a critical parameter to enhance the efficiency of ALD process by preventing the reactant mixing. 10 s was optimized

purge time for both non-physisorbed TMA and unreacted oxygen, which prevented subsequent CVD instead of ALD. Thinner and denser layer was formed as substrate temperature increased. However, the PES substrate should be processed below 120 °C to avoid the substrate deformation. Aluminum oxide layer formed on PES at optimized conditions has 11.8 nm of thickness and reduced WVTR and OTR values to below 4×10^{-3} g/m² day and 4×10^{-3} cm³/m² day, respectively.

Al₂O₃ barrier layer formation by PEALD was applied to other substrate materials such as PC and PEN. Each substrate material has its own barrier properties at its bare film state. But barrier properties after PEALD process sufficiently reduced below the apparatus detection limits to confirm the applicability of the optimized PEALD process developed in this work.

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