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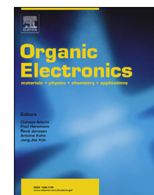

Surface modification of polymeric substrates to enhance the barrier properties of an Al_2O_3 layer formed by PEALD process

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Aluminum oxide (Al_2O_3) layers were deposited on various polymeric substrates by a low frequency plasma-enhanced atomic layer deposition (PEALD) process. Polyethylene naphthalate (PEN), polyethylene terephthalate (PET), and polyethersulfone (PES) were tested as substrates for barrier films. Each substrate has its own characteristics to have influences on the Al_2O_3 layer formation and penetration into the substrate, which greatly affected the barrier properties. Prior to the deposition process, polymeric substrates were pretreated in argon and oxygen plasmas, and surface energy was leveled up due to the formation of polar group. Characterizations of the Al_2O_3 layer by Time of Flight - Secondary Ion Mass Spectrometry (ToF-SIMS) revealed that plasma treatment lowered the level of OH^- in Al_2O_3 layer. X-ray photoelectron microscopy (XPS) confirmed that A12p peak of Al_2O_3 layer was shifted to a higher core level by plasma treatment. Density of the layer on the plasma treated surface was greater than that of untreated surface. It was found that plasma treatment of the surface had significant effects on the formation of the Al_2O_3 layer, which much improved the barrier performance. Optical transmittance was little affected by plasma treatment and PEALD process. After oxygen plasma pretreatment, the WVTR of the Al_2O_3 layer deposited on the plasma-treated PEN substrate was around 7.2×10^{-4} g/m^{2}day, which is significantly lower than that of the untreated substrate.

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1. Introduction

Replacing glass substrates with polymeric substrates has received much attention in flexible optoelectronics such as flexible organic light emitting diodes (OLED) and organic photovoltaics because of their light weight, robust profile, flexibility, portability, and the engineering design freedom afforded by their characteristics [1].

Semi-crystalline polymeric substrates such as polyethylene naphthalate (PEN) and polyethylene terephthalate (PET) are very promising substrate materials [2]. They possess good transparency and have been widely used for flexible substrates. Rahy et al. reported that carbon nanotube-coated PEN films are applicable for constructing flexible electronic devices such as solar cells, OLEDs, and touch panels [3]. Cho et al. also reported the fabrication of OLED devices on highly flexible PET coated with transparent conducting oxides [4]. The combination of polyethersulfone (PES) and polycarbonate is an amorphous polymer which is regarded as a promising alternative for flexible substrates. In particular, PES substrates have good clarity and a high thermal resistance for operation at high temperatures [5]. Therefore, many research groups demonstrated that PES substrates could be used as substrates for flexible devices such as liquid crystal displays [6], OLEDs [7], and organic thin film transistors [8]. However, polymeric substrates still have many technical problems that have to be resolved for their use as substrates in flexible displays.

In particular, the permeation of atmospheric gases such as water vapor and oxygen through polymeric substrates can degrade the organic materials and metallic cathode in OLED devices fabricated on flexible substrates [9]. Therefore, when polymeric substrates are used in a flexible display, a permeation barrier layer should be added to prevent the diffusion of both water vapor and oxygen.

Inorganic thin films grown by an atomic layer deposition (ALD) method can act as an effective permeation barrier layer. The advantage of the ALD technique is its ability to produce densely packed, defect-free, and highly uniform layers. Generally, inorganic thin layers grown by thermal ALD show better moisture

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permeation barrier characteristics than layers grown by plasma-enhanced ALD (PEALD). The reason for this result is that thin layers deposited by PEALD have lower densities due to many relative defects. However, during the PEALD process, the use of oxygen plasma enables the deposition process at a relatively low temperature with a shorter process time than thermal ALD [10]. Also, the inorganic layer grown by thermal ALD could be inferred to nucleate inside the polymer matrix, whereas the layer grown by plasma enhanced ALD could make a more discrete interface due to additional functional groups generated on the polymer surface during the early process steps. Wilson et al. investigated TMA adsorbed on a variety of polymer films using a quartz crystal microbalance sensor with the nucleation and growth of an Al_2O_3 layer grown by thermal ALD [11]. They reported that the total growth of Al_2O_3 after the same number of cycles was very similar on both uncoated Si(100) wafers and polymer-coated Si(100) wafers, regardless of the very different nucleation behaviors on various polymers.

However, despite the many applications of the PEALD technique, there is little understanding of the nucleation and growth of thin layers deposited on polymeric substrates by PEALD. The absence of chemical groups on the polymer surface initially suggests that the nucleation of ALD should be very difficult [12]. Therefore, surface modification such as plasma pretreatment is required to modify the nature of the polymer surface. Plasma pretreatment can remove the contaminants existing on the surface of most plastic substrates and functionalize the polymer surface by introducing polar groups such as hydroxyl (−OH), carbonyl (−C═O), and carboxyl groups (−COOH). It is has been demonstrated that this functionalization can lead to better wettability and improved adhesion or bonding ability between polymer surfaces and other materials deposited on these surfaces [13].

Edy et al. investigated the effect of argon plasma treatment on the deposition of an Al_2O_3 layer on a plastic substrate by ALD. They concluded that the introduction of plasma pretreatment is crucial for the initial growth of ALD and plasma-assisted ALD and is also mostly responsible for the enhancement of surface wettability [14].

In this study, the effects of plasma pretreatment on the formation of thin inorganic layers were investigated. The plasma pretreatment of various polymeric substrates such as PEN, PES, and PET was conducted by using a microwave plasma system with oxygen and argon. As a permeation barrier layer, an Al_2O_3 layer was deposited on plasma-treated substrates using the PEALD process. The permeation properties of an inorganic layer fabricated on polymeric substrates with and without plasma pretreatment were characterized by means of the water vapor transmission rate (WVTR). The effect of the plasma pretreatment on the barrier performance of the inorganic layer will be discussed.

2. Experimental details

2.1. Surface modification by plasma treatment

Prior to plasma pretreatment, PEN (200 μm, Teonex Q51, Teijin DuPont Co.), PES (200 μm, Glastic PES, I-components Co.), and PET (100 μm, Tetoron G2, Teijin DuPont Co.) substrates were cut into 100 × 100 mm pieces and then cleaned in an ultrasonic chamber for 10 min with isopropyl alcohol. The substrates were dried in a convection oven at a temperature of 80 °C. As shown in Fig. 1, the plasma pretreatment was performed using a microwave plasma system (Plasma-Preen II System Model 973, Plasmatic Systems, USA). Polymeric substrates with a size of 100 × 100 mm^2 were mounted on a grounded electrode and treated with argon or oxygen plasma. The flow rate was 5 standard cubic feet per hour and the pressure was 700 Torr. The plasma power was set to 700 W. The treatment time was varied among 3, 5, 10, and 15 s in order to determine the optimum conditions. The contact angle was measured by a Phoenix 300 (SEO Ltd., Korea) instrument to confirm the change of the surface nature after plasma pretreatment. Deionized water was chosen as the test liquid and the contact angle was measured at a temperature of 26 °C and 40% RH.

2.2. PEALD process for Al_2O_3 layer formation

As shown in Fig. 2, the Al_2O_3 layers were deposited on plasma-treated substrates by low-frequency PEALD and compared to layers deposited on untreated substrates. Trimethylaluminum (TMA) was used as a precursor for the Al_2O_3 layer formation. Argon gas of 99.999% purity was flown into the reactor chamber at a flow rate of 500 sccm and a pressure of 1 Torr. Argon was also used as the carrier gas for each precursor as well as the purge gas after each cycle. TMA was kept at a temperature of 20 °C. The substrate was maintained at 120 °C in the chamber during the deposition process for all of the samples. For the Al_2O_3 deposition, one cycle consisted of the sequential injection of a TMA pulse (1.0 s), argon purge (5.0 s), oxygen pulse (4.0 s), and argon purge (5.0 s). A radio frequency (RF) plasma pulse that was capacitively coupled with a low frequency (500 kHz) plasma source was applied for 3.0 s only during the oxygen pulse to produce oxygen radicals. The RF plasma power was 500 W and the electrode-substrate distance was 50 mm, as optimized in previous work [15].

2.3. Characterizations

The contact angle values were determined using a contact angle measurement system (Phoenix 300, SEO Ltd., Korea). Deionized water was chosen as the test liquid and the contact angle was measured at a temperature of 26 °C and 40% RH. The chemical composition of the layer was analyzed using X-ray photoelectron spectroscopy (XPS) with a K-Alpha system (Thermo Scientific, UK) and an Al Kα X-ray source was used with a micro-focused monochromator. The refractive index of the layer was measured by using a spectroscopic ellipsometer (V-VASE, J. A. Woollam Inc., USA). ToF-SIMS was performed on a ToF-SIMS V instrument (ION-TOF GmbH, Munster, Germany) equipped with a C_{60}^{+} ion source for abrasion and a Bi_3^{+} liquid-metal ion source for analysis. The WVTR values for the Al_2O_3 layer deposited on various polymeric substrate (100 × 100 mm^2) were determined at 38 ± 1 °C and 100% RH using AQUATRAN Model 1 (MOCON Inc., USA). The detection limit level of the instrument is 5 × 10^{-4} g/m^2day. The optical transmittance of the samples was measured in the wavelength range from 350 to 780 nm by a UV/visible spectrometer (MCPD-3000, Otsuka Co., Japan).

3. Results and discussion

3.1. Plasma treatment

As shown in Fig. 3, the water contact angle measurements were used to examine the effect of plasma pretreatment on the changes of the surface nature of various polymeric substrates. The measured contact angles for untreated PEN, PES, and PET substrates were 50.9°, 65.8°, and 61.7°, respectively. Due to the hydrophobic surface nature of the polymeric substrates, when TMA precursor was introduced into the ALD chamber for the deposition of inorganic layers, they could not easily adsorb on the surface of the substrates uniformly. Also, they tend to diffuse into the near surface region of the polymeric substrate which has free volume. Therefore, it is hard to form a continuous layer from the earlier step during the ALD process [16]. When a polymeric substrate is exposed to plasma, it

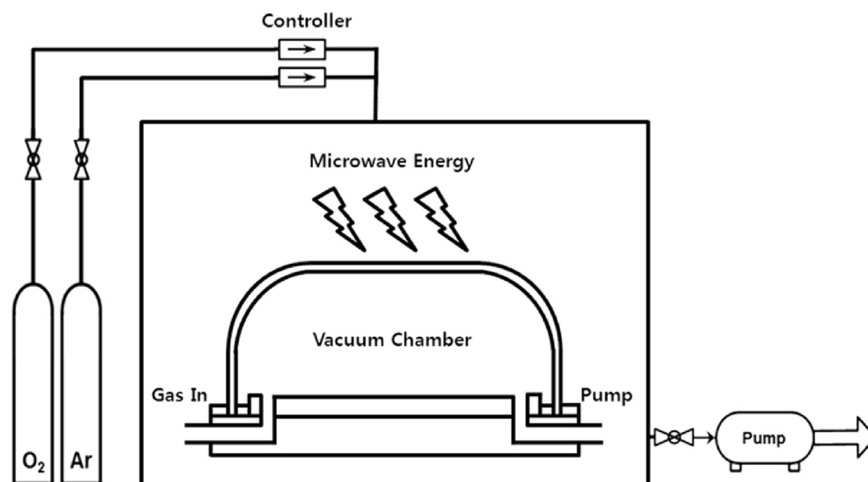


Fig. 1. Schematic of the plasma treatment system.

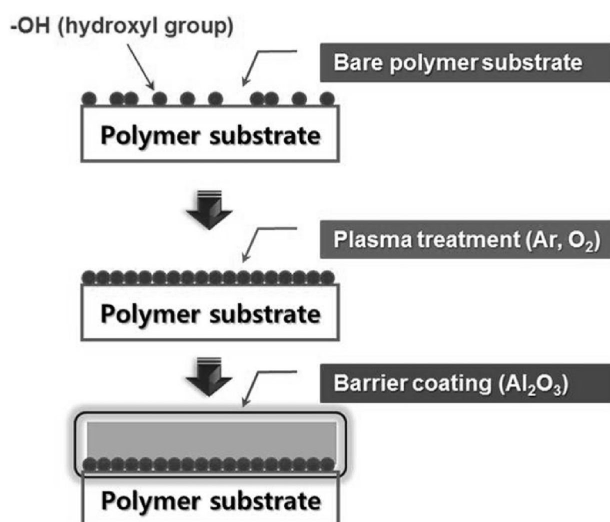
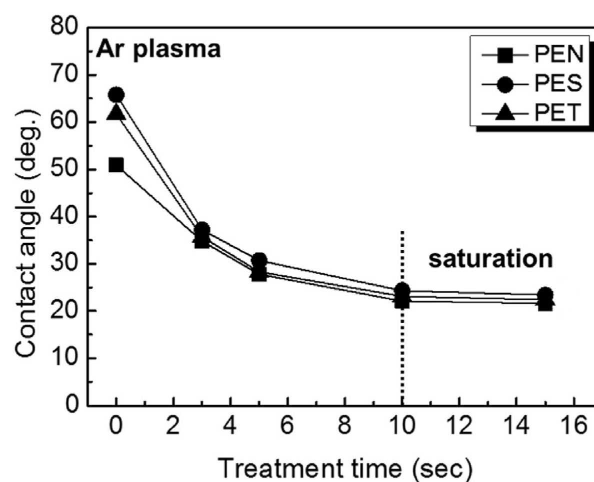


Fig. 2. Schematic of the plasma treatment process on a polymer substrate utilized prior to PEALD of the Al_2O_3 layer.



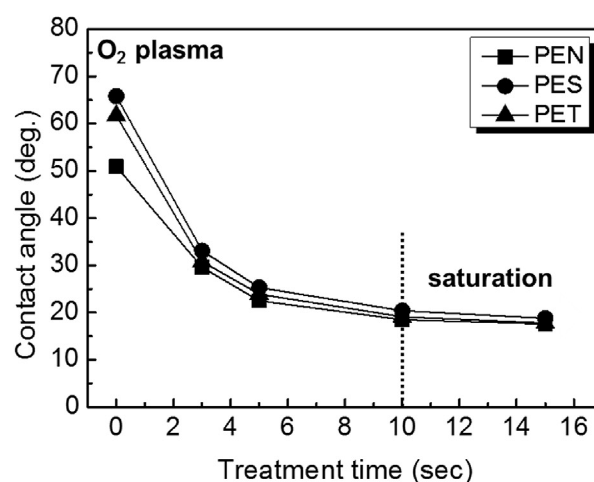


Fig. 3. Contact angles of the PEN, PET, and PES substrates as a function of the treatment time in argon and oxygen plasmas.

can cause physical sputtering and chemical reaction of reactive species, which results in a change of the intrinsic properties at the surface [17].

After pretreatment in both argon and oxygen plasmas, the contact angle started to decrease drastically with increasing treatment time and its reduction showed a tendency to saturate at pretreatment times above 10 s for all three polymeric substrates. In the case of pretreatment in oxygen plasma for 10 s, the contact angles of the treated PEN, PES, and PET substrates decreased to 16.6°, 18.2°, and 17.9°, respectively. These reductions of the contact angle demonstrate that polar groups such as hydroxyl (−OH), carbonyl (−C=O), and carboxyl groups (−COOH) could be generated on the surfaces of all three polymeric substrates after plasma pretreatment [13]. In particular, when the plasma-treated substrates were selected for the ALD of the Al_2O_3 layer, it was expected that the hydroxyl groups act as the reactive site for the precursors introduced into the ALD chamber. Therefore, the plasma pretreatment contributes to promote the formation of a continuous layer on the surface of polymeric substrates during the earlier ALD steps.

As summarized in Table 1, the plasma pretreatment had significant effects on the surface chemical composition, which was confirmed by the XPS measurements. After plasma treatment with argon and oxygen, it could be confirmed that the ratio of carbon

Table 1
The ratios of elemental C and O on PEN, PES, and PET substrates without and with pretreatment in argon and oxygen plasmas.

Substrates		Elemental ratio (at. %)		
		Untreated	Argon plasma (10 s)	Oxygen plasma (10 s)
PEN	C	81.08	70.30	71.08
	O	18.92	29.69	28.92
PES	C	84.04	72.83	64.42
	O	15.96	27.17	35.58
PET	C	75.42	73.72	74.42
	O	24.58	26.27	25.58

containing groups on the surface of the substrates decreased, which resulted in increases of the oxygen containing groups. These results infer that more reactive sites could be generated on the plasma-treated surface [18]. However, it would be considered that the degree of changes of the surface nature was quite different due to the intrinsic properties and whether they are amorphous or crystalline polymers. Also, although changes of the trends of the ratio of carbon and oxygen after plasma pretreatment did not depend on the plasma gases, an improvement of the surface energy could be confirmed with the three kinds of substrates in terms of increasing oxygen containing groups. These results are in good agreement with the contact angle results.

3.2. PEALD of the Al_2O_3 layer on polymeric substrates

In order to investigate the effect of the plasma-treated surface on the formation of an inorganic layer by PE-ALD, 40 nm thick Al_2O_3 layers were deposited on untreated and treated polymeric substrates (PEN, PET, PES). In our previous work, we have investigated the thickness effects of Al_2O_3 and ZrO_2 single layers on barrier properties [15]. WVTR values deceased with increasing layer thickness in both cases. However, decreasing rate got reduced to reach a saturation thickness and no more decreases of WVTR values were observed beyond 40 nm of thickness. Based on these results thickness of Al_2O_3 layers was kept as 40 nm in this work. As shown in Fig. 4, the amount of OH^- impurities in the Al_2O_3 layers was calculated utilizing the results of ToF-SIMS measurements. Also, the amount of AlO^- groups could be obtained from these results. Generally, as the Al_2O_3 layer is used as the barrier layer for a polymeric substrate, it is known that defects such as pinholes and impurity can create more pathways for the permeation of water vapor and oxygen. In particular, the OH^- impurities existing in the Al_2O_3 layer deposited by the ALD process can reduce the density of the deposition layer, which results in deterioration of the barrier properties [19,20]. Therefore, it is important that an inorganic layer with fewer impurities can be obtained as a promising barrier layer.

As shown in Fig. 4(a), the amount of OH^- impurities in the 40 nm thick Al_2O_3 layer on the PEN substrate pretreated in argon and oxygen plasmas is less than the amounts in the same layer on the untreated substrates. These results indicate that an Al_2O_3 layer with a higher density could be deposited after plasma pretreatment of the substrates. In the early steps of the ALD process, the reactive sites generated from plasma pretreatment play an important role to adsorb the reactants on the surface, which affect the improvement of the density of the Al_2O_3 layer. The nucleation of Al_2O_3 hardly occurred on the polymer surface due to the small amount of reactive sites. When TMA used as the precursor was introduced into the ALD chamber, some of it attached onto the polymer surface physically and the residue was purged out. At this step, if there were few reactive sites on the surface, most of the attached TMA was purged out. These phenomena are attributed to the difficulties of nucleation in the earlier step of ALD.

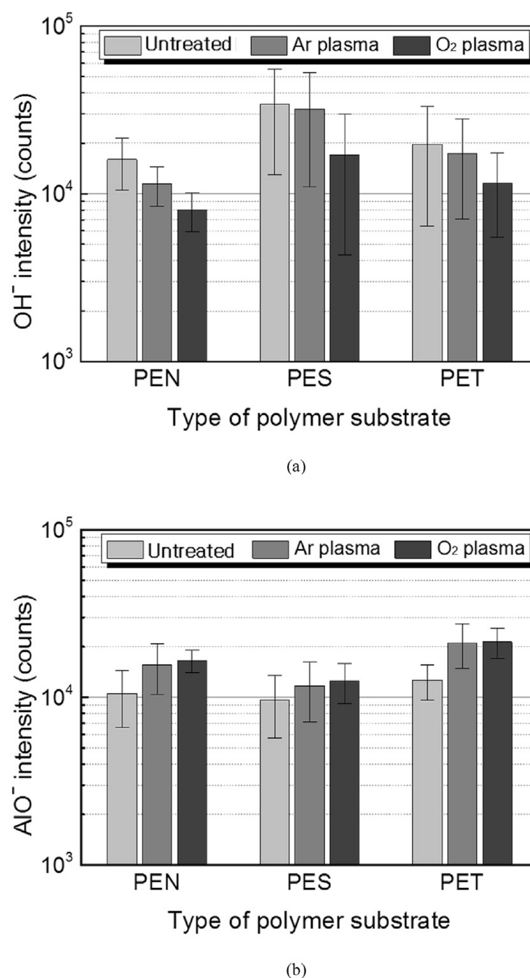


Fig. 4. Intensities of the peak areas of (a) OH^- and (b) AlO^- in the Al_2O_3 layers deposited on various polymer substrates without and with plasma treatment obtained from ToF-SIMS negative ion spectra.

However, reaction sites generated from the plasma pretreatment lead to larger TMA absorption on the surface in the initial step. These conditions are expected to contribute to the growth of a dense and continuous layer with few impurities. In such a sense, as shown in Fig. 4(b), the amount of AlO^- of the Al_2O_3 layer on the pretreated substrate was greater than that on the untreated substrate. These results indicate that plasma pretreatment contributed to form a promising Al_2O_3 layer with fewer OH^--impurities on PEN substrates. The same tendency was also obtained in the cases of the PET and PES substrates.

As shown in Fig. 5, the Al_2O_3 layers deposited on untreated and treated PEN, PES, and PET substrates were subjected to XPS depth profile analysis. Al, C, and O were selected to represent the composition of the Al_2O_3 layer deposited on the various polymeric substrates. Al concentration remains constant, while Al_2O_3 layer was etched. Then Al concentration decreased down to a negligible level when the polymeric substrate was etched. Some of Al_2O_3 was penetrated into the polymeric substrate, and the interphase region is defined as the region from the point with 99 at% Al to that with 1 at% Al. In order to obtain quantitative depth information of the Al_2O_3 layer and interphase region, the intensities of Al, C, and O along the etching time were measured.

During the feeding step TMA was adsorbed on the polymeric substrate, and excess or loosely adsorbed TMA was purged out during the purging step. Amount of TMA adsorbed depends on the

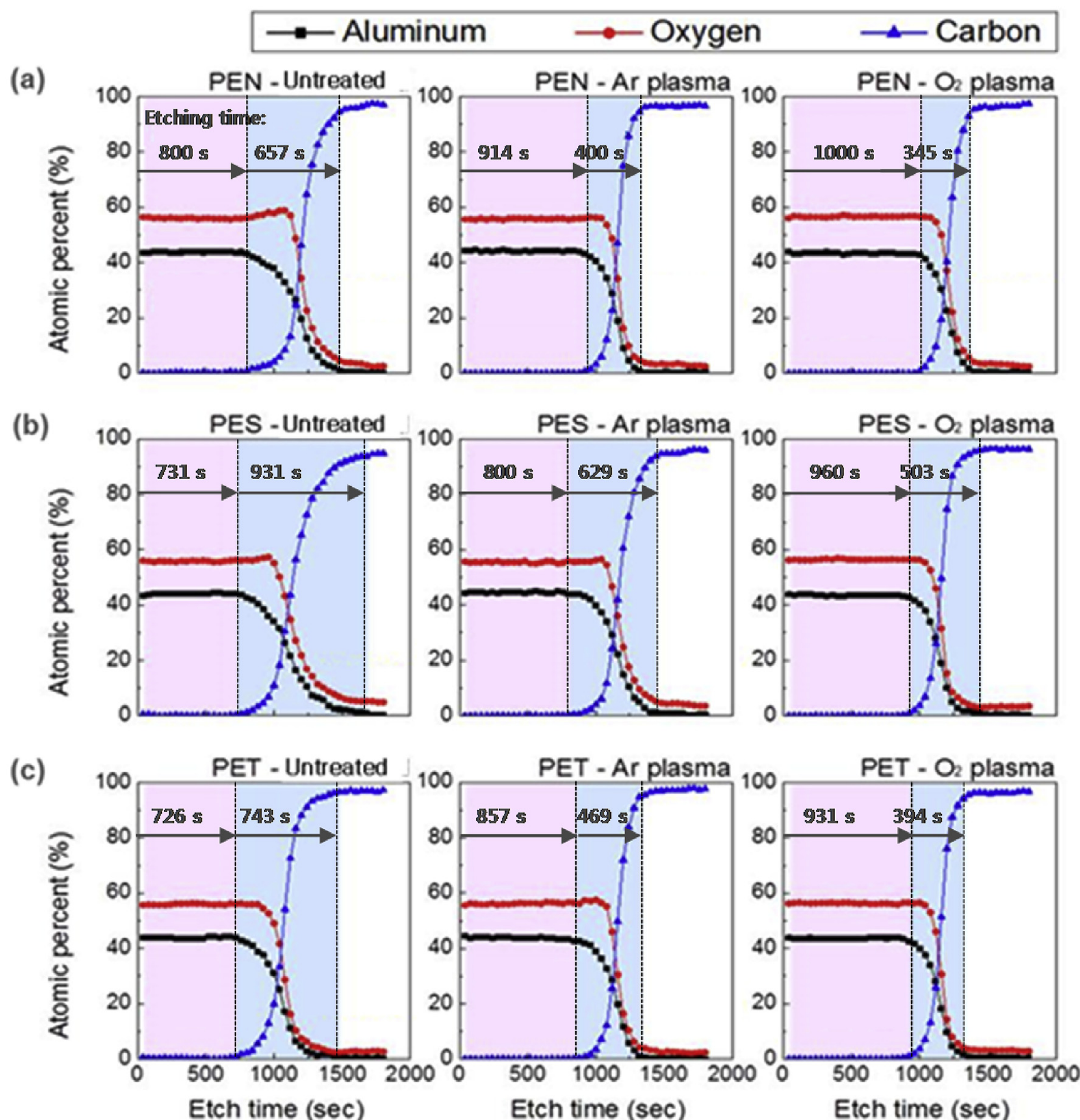


Fig. 5. XPS depth profiles of Al_2O_3 layers deposited on polymer substrates: (a) PEN, (b) PES, and (c) PET.

affinity between TMA and polymeric substrate [11]. As shown in Fig. 5 etching time for the Al_2O_3 layer on each layer was compared one another, and PEN had the longest etching time, which represents the Al_2O_3 layer on PEN substrate has greater thickness or greater density than the other substrates. Etching time for PEN interphase was smaller than those of PES, PET interphases, which means PEN had the least penetration of Al_2O_3. It is well known that PEN has relatively higher crystalline nature than PES, PET. Therefore, it was confirmed that characteristics of Al_2O_3 layer depend on the substrate surface properties.

When the polymeric substrates were plasma treated with oxygen or argon, the surface properties should be changed to affect the Al_2O_3 layer formation. For every substrate used in this work, etching time for Al_2O_3 was increased and that of interphase was decreased after the plasma treatment. Oxygen plasma treatment was slightly more effective than argon plasma treatment. Etching time for Al_2O_3 layer on PEN increased up to 1000 s and interphase etching time was reduced nearly by half to form a narrow interphase region. It could be deduced that the reactive sites generated from the plasma pretreatment bound the TMAs on the surface and the reaction could occur in the earlier steps. Similar trends were observed for PET and PES substrates, but PEN substrate was most effective in this case. Oxygen plasma treatment affected the formation of the continuous Al_2O_3 layer with high density on the PEN substrate, which is expected to show the better barrier properties.

The XPS spectra of the Al2p core levels are shown in Fig. 6. The Al2p peak at 74.3 eV is assigned to the Al(III) ions of the oxide matrix [21,22]. The Al2p peaks of the Al_2O_3 layer deposited on untreated PEN, PES, and PET substrates were observed at 73.78 eV, 73.82 eV, and 73.76 eV, respectively. It could be confirmed that the Al2p peak of the Al_2O_3 layer deposited on pretreated substrates shifted to a higher core level close to the identical position of the Al2p peak. In the case of argon plasma, the Al2p peaks of the Al_2O_3 layer deposited on pretreated PEN, PES, and PET substrates were observed at 73.98 eV, 74.08 eV, and 74.02 eV, respectively. In the

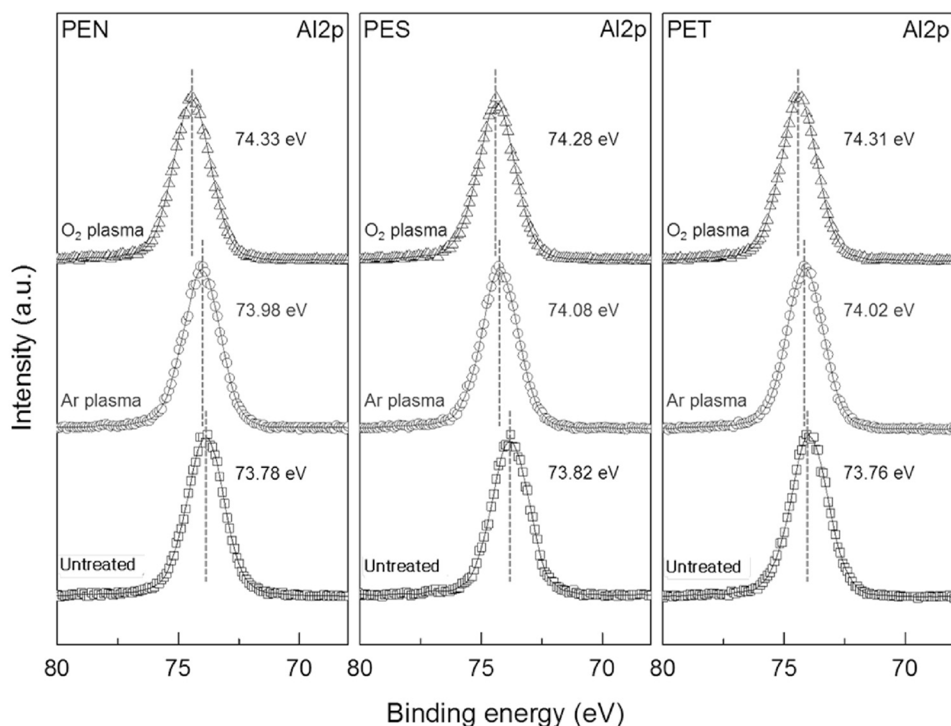


Fig. 6. Al2p XPS spectra of Al_2O_3 layers deposited on untreated and treated PEN, PES, and PET substrates.

case of oxygen plasma, the Al2p peaks of the Al_2O_3 layer deposited on PEN, PES, and PET were observed at 74.33 eV, 74.28 eV, and 74.31 eV, respectively. It was also confirmed that an Al_2O_3 layer with a chemical composition close to the theoretical stoichiometry was deposited on the plasma-treated substrates.

O1s XPS results for PEN substrates are given in Fig. 7. The Al—O bonding curve is attributed to the oxide ions of the alumina matrix, and the O—H bonding curve is attributed to the hydroxyl groups or contaminants [15,23]. Relative intensities of Al—O bonding curve and O—H bonding curve were 60.6% and 39.4% in Al_2O_3 layer on the untreated PEN substrate. After plasma treatment they were changed to 36.8% and 63.2% for argon plasma and to 34.1% and 65.9% for oxygen plasma, respectively. These results indicated that the residual OH-related ligands in the Al_2O_3 layer on plasma treated PEN substrates were decreased in the Al_2O_3 layer on the PEN substrates pretreated in argon and oxygen plasmas, which are consistent with the ToF-SIMS results for PEN substrates in Fig. 4(a). Same trends are expected for PES and PET substrates.

Fig. 8 shows the refractive index of the Al_2O_3 layer on untreated and treated polymeric substrates. The refractive index values of the Al_2O_3 layer on untreated PEN, PES, and PET were 1.684, 1.682, and 1.673, respectively. In the case of Al_2O_3 layer deposited on PEN, PES, and PET treated in argon plasma, the refractive index increased to 1.695, 1.687, and 1.692, respectively. In the oxygen case, the refractive index increased to 1.7, 1.695, and 1.696, respectively. The plasma pretreatment affected the increases of the refractive index of the Al_2O_3 layer on the three polymeric substrates, which explains the results of the XPS and ToF-SIMS analyses. In general, the refractive index depends on the molecular weight and molecular polarizability as well as the density.

Among these, density is a primary determinant of the refractive index because the refractive index results from the collective response of electric dipoles excited by an external applied field and the number of dipoles in a given volume is closely related to the

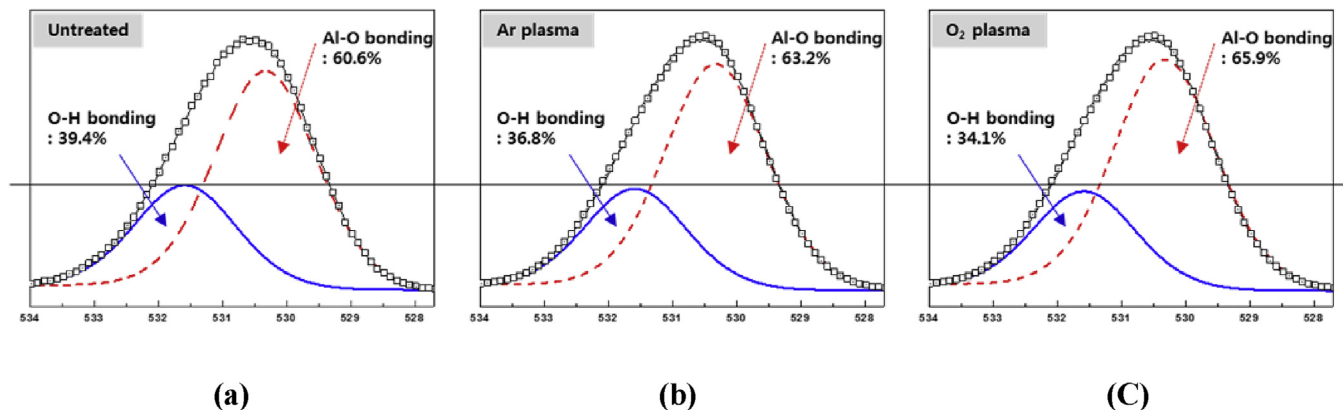


Fig. 7. O1s XPS spectra of Al_2O_3 layers deposited on untreated (a) and pretreated PEN substrates by argon (b) and oxygen (c) plasma.

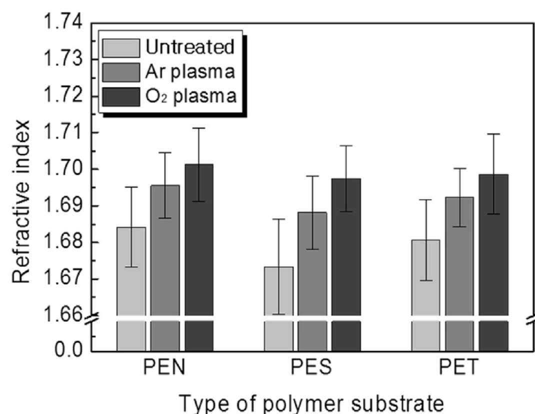


Fig. 8. Refractive index values of the Al_2O_3 layers deposited on untreated and treated polymer substrates.

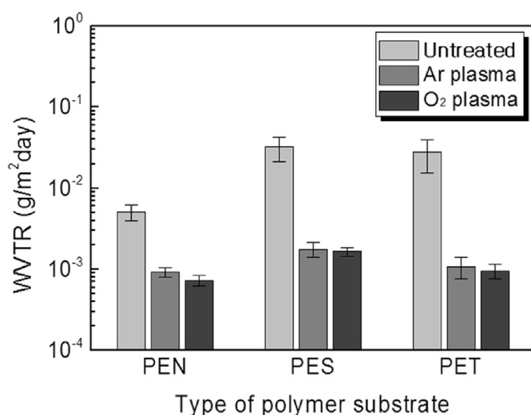


Fig. 9. WVTR values of the Al_2O_3 layers deposited on PEN, PES, and PET substrates, which were measured using MOCON AQUATRAN Model 1 at 38 °C and 100% RH.

density [24]. Also, it was reported that the refractive index of impurity-free Al_2O_3 was 1.767 [25] and the decrease of the refractive index was mainly caused by the incorporation of OH^- impurities. Therefore, an Al_2O_3 layer with a higher refractive index could be obtained on substrates pretreated in argon and oxygen, which resulted in increased densities.

The WVTR values for a 40 nm Al_2O_3 single layer deposited on the three different types of substrates with and without plasma treatment are shown in Fig. 9. The WVTR of the Al_2O_3 layer deposited on the untreated PEN substrate was 1.1×10^{-3} g/m^{2}day. After plasma treatment with argon and oxygen, the WVTR decreased to 9.2×10^{-4} g/m^{2}day and 7.2×10^{-4} g/m^{2}day, respectively. As mentioned earlier, the Al_2O_3 layer on untreated PEN has more OH^- impurities and a lower refractive index, whereas the layer on treated PEN has less impurities and a high refractive index. It was confirmed that a promising Al_2O_3 layer with a low WVTR value was formed on the plasma-treated PEN substrate.

In terms of chemical composition, the amount of oxygen containing groups increased after plasma pretreatment in oxygen and argon and they act as reactive sites with precursors on the surface of the PEN substrate. From these points of view, the Al_2O_3 layer becomes continuous in an earlier ALD step, which leads to further blocking the reactant diffusion into the near surface region of polymeric substrates. It was also confirmed that promising Al_2O_3 layers with high barrier properties could be formed on the various polymeric substrates. The optical transmittance results are summarized in Table 2, where the transmittance through air was used as a reference. It is generally expected that the differences of the refractive index would tend to affect the transmittance. However, it was confirmed that there was no decrease of the optical transmittance, irrespective of the increases of the refractive index of the Al_2O_3 layer on the plasma-treated substrates. In General, it is well known that the Al_2O_3 layer with amorphous structure has higher optical transmittance because they have large optical band gap (~8.8eV) [19]. Therefore, the Al_2O_3 layer deposited on polymeric substrates have no significant decrease of optical transmittance. Also, due to amorphous phase, all samples were expected to have no optical scattering caused by increasing the roughness or crystalline phase, resulting in less optical loss for the amorphous Al_2O_3 single layer deposited on the plasma-treated substrates. Even though the Al_2O_3 layer on the plasma-treated substrates have higher refractive index, there was no significant loss of optical transmittance. Because the relatively high refractive index could be obtained from the fewer OH^- -impurities Al_2O_3 single layer deposited on the plasma-treated substrates.

Table 2
Optical transmittances of the Al_2O_3 layers deposited on various polymer substrates.

Substrates	Inorganic layer	Transmittance (%, @550 nm)		
		Untreated	Argon plasma (10 s)	Oxygen plasma (10 s)
PEN	Al_2O_3	86.5	86.5	86.5
PES	Al_2O_3	88.7	88.9	89.3
PET	Al_2O_3	90.5	90.0	91.1

4. Conclusions

It was confirmed from etching test that thickness and density of Al_2O_3 layer depended on the surface property of each substrate. Penetration of Al_2O_3 into the substrate depended on the crystalline nature of substrate, and PEN had the smaller interphase thickness than PES and PET. The plasma pretreatment affected the increases of surface energy and oxygen containing groups on the PEN, PES, and PET surfaces. Plasma treatment also increased the etching time for Al_2O_3 layer and decreased the interphase thickness.

Characterizations of the Al_2O_3 layer deposited on untreated and treated polymeric substrates were performed in terms of chemical composition and physical properties. It could be deduced that the plasma-treated surface of the polymeric substrates affected the formation of the Al_2O_3 layer on the substrates. It was confirmed that the Al_2O_3 layer formed on plasma-treated polymeric substrates have a low level of OH^- impurities and a higher refractive index compared to untreated samples. It also shifted A12p peak of Al_2O_3 layer to a higher core level to attain the chemical composition of theoretical stoichiometry. The Al_2O_3 layer deposited on treated PEN substrates attained the lowest WVTR value of about 7.2×10^{-4} g/m^{2}day at 38 °C and 100% RH. The improvement of the barrier property was attributed to the formation of a dense and conformal Al_2O_3 layer by surface modification of the various polymeric substrates.

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