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Effect of O_2 Partial Pressure on AlO_x Thin Films Prepared by Reactive Ion Beam Sputtering Deposition

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ABSTRACT

The barrier and optical properties of AlO_x thin films on polycarbonate deposited by Reactive Ion Beam Sputtering (RIBS) were investigated at different oxygen partial pressure. We measured the deposition rate of AlO_x thin films. As the oxygen partial pressure increased, the deposition rate increased then decreased. The changes of deposition rate are associated with the properties of deposited films. The properties of deposited AlO_x thin films were studied using X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM). Optimum deposition parameters were found for fabricating aluminum oxide thin films with high optical transparency for visible light and low Oxygen Transmission Rate (OTR). The optical transmittance of AlO_x thin film deposited on polycarbonate (PC) showed the same value of bare PC.

Key words : ***AlO_x thin film, Reactive Ion Beam Sputtering (RIBS), Oxygen partial pressure, Deposition rate, Oxygen Transmission Rate (OTR)***

1. Introduction

Deposition of aluminum oxide thin films on plastic substrate has been extensively studied for the last few years.[1,2] At first, using thin transparent metal oxide films for flat panel displays, food and medical device packaging applications stimulated this interest in AlO_x thin films. The coatings of plastic films with thin aluminum oxide layers offer a wide range of applications at potentially low coating cost. For example, the wear protective layers were used for window films, solar mirrors, lamp reflectors, and decorative films. And also interfacial layers were for dew inhibition of greenhouse films and improved printing, laminating characteristics.[3] Compared with metal barrier films, the oxide barrier thin films have a number of advantages such as transparency, recyclability, retortability, and microwave compatibility.[4] To achieve an improvement of barrier properties, however, the control of the stoicheometric ratio, metal oxide formation mode, and surface morphology should be preceded.[5,6] The main purpose of this research is to investigate the effects of oxygen partial pressure on optical and barrier properties of AlO_x thin films.

2. Experimental

The AlO_x thin films were deposited on polycarbonate (PC) substrates at room temperature in a vacuum chamber equipped with a 5 cm cold hollow cathode ion source (PLATECH LTD). The thickness of all deposited films was fixed at about 300 Å. The Oxygen Transmission Rate (OTR) was measured at 30°C and 0% RH by using an Oxtran 2/60 instrument from Modern Controls Inc. Composition analysis of the fabricated films was conducted by XPS (ESCA LAB 220-XL, VG Scientific). The surface structure and roughness of the aluminum oxide barrier coating was examined by using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The optical transmittance of the films was characterized by UV-Visible spectrometer. The refractive index (n) of the AlO_x thin films was measured by using ellipsometry.

3. Results and Discussion

The changes in the deposition rate strongly imply that an oxide layer is formed on the target, and that is subsequently sputtered onto the substrate. Thus, we determined the deposition rate of AlO_x thin films according to oxygen partial pressure shown in Fig. 1. It was possible to observe from this figure that the deposition rate increases slightly while the oxygen partial pressure increases from 7×10^{-5} to 1×10^{-4} Torr. This increase in the deposition rate could be attributed to the formation of sub oxides loosely bonded on the target surface.[6,7] However, the deposition rate decreases above 2×10^{-4} Torr. This decrease could be explained by the fact that the ratio of sub oxides to oxide decreased.[8] Note also that such a tendency of the deposition rate versus the oxygen partial pressure is similar to the results reported

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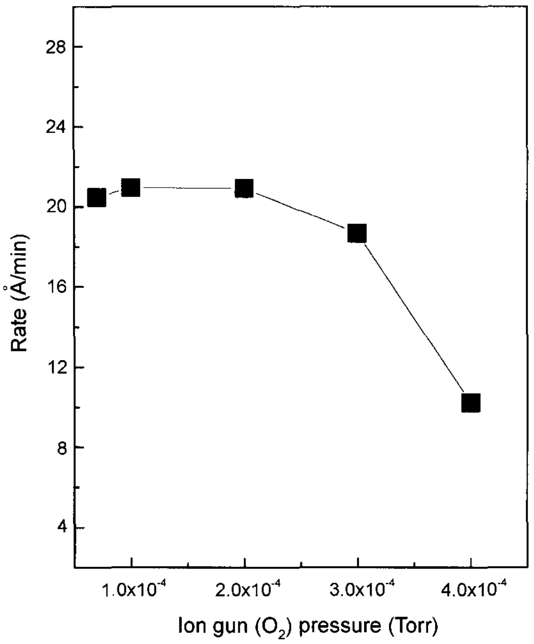


Fig. 1. Deposition rate vs oxygen partial pressure of AlO_x films on PC.

previously.[9] As this change in the deposition rate was expected to have an effect on the surface structure and the properties of AlO_x films, the oxide phase in the deposited AlO_x thin film increased, affecting the composition ratio of AlO_x thin films.

Fig. 2 shows Al 2p (a) and O 1s core level state of XPS. The binding energy of Al 2p and O 1s appeared at 75.4 and 530.26 eV.[10] This indicated the oxidized state formation of aluminium irrespective of oxygen partial pressure. This result was attributed to fast oxidation reaction of aluminium when compared with other metals.[10] Fig. 3 revealed oxygen to aluminium ratio according to oxygen partial pressure. As oxygen partial pressure increased, oxygen to aluminium ratio increased and saturated. Below 2×10^{-4} Torr, the oxygen to aluminium ratio was little higher than that of bulk Al_2O_3, assuming that Al_2O_3 powder was stoichiometric

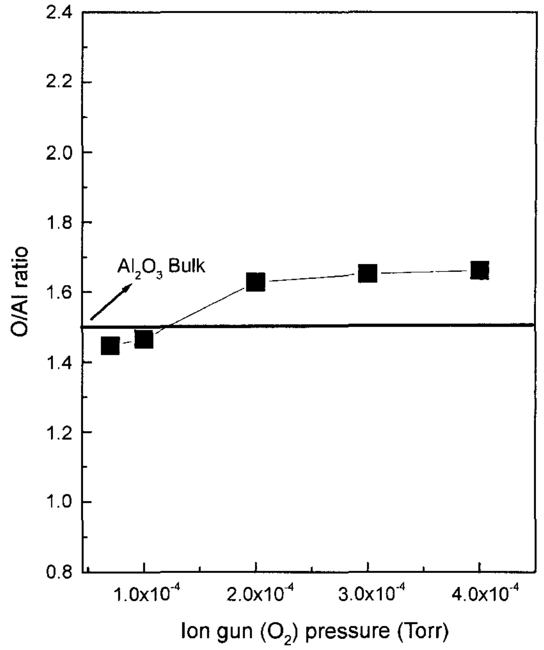


Fig. 3. Oxygen to aluminium ratio (O/Al) of AlO_x films according to oxygen partial pressure.

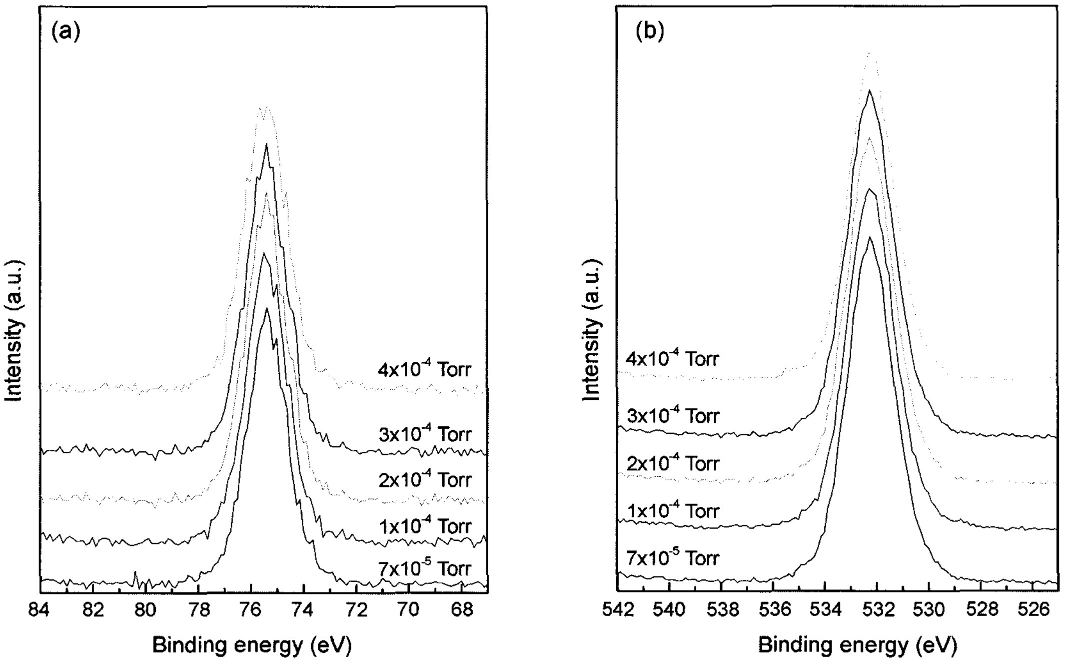


Fig. 2. Al 2p (a) and O 1s (b) core level state of AlO_x thin films as a function of oxygen partial pressure.

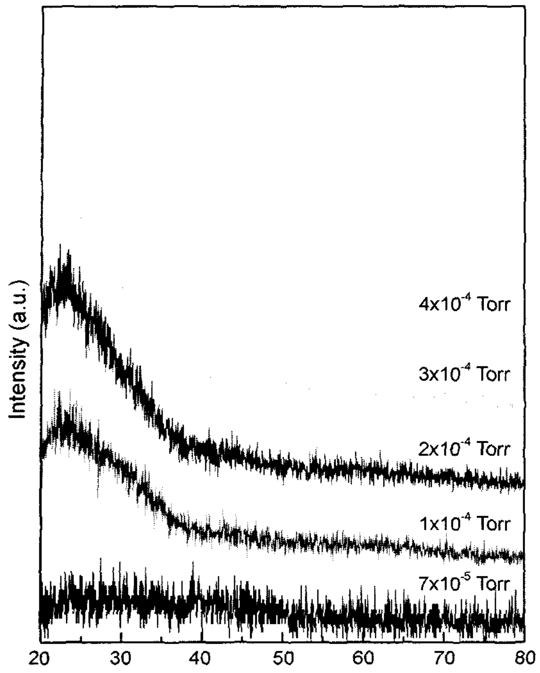
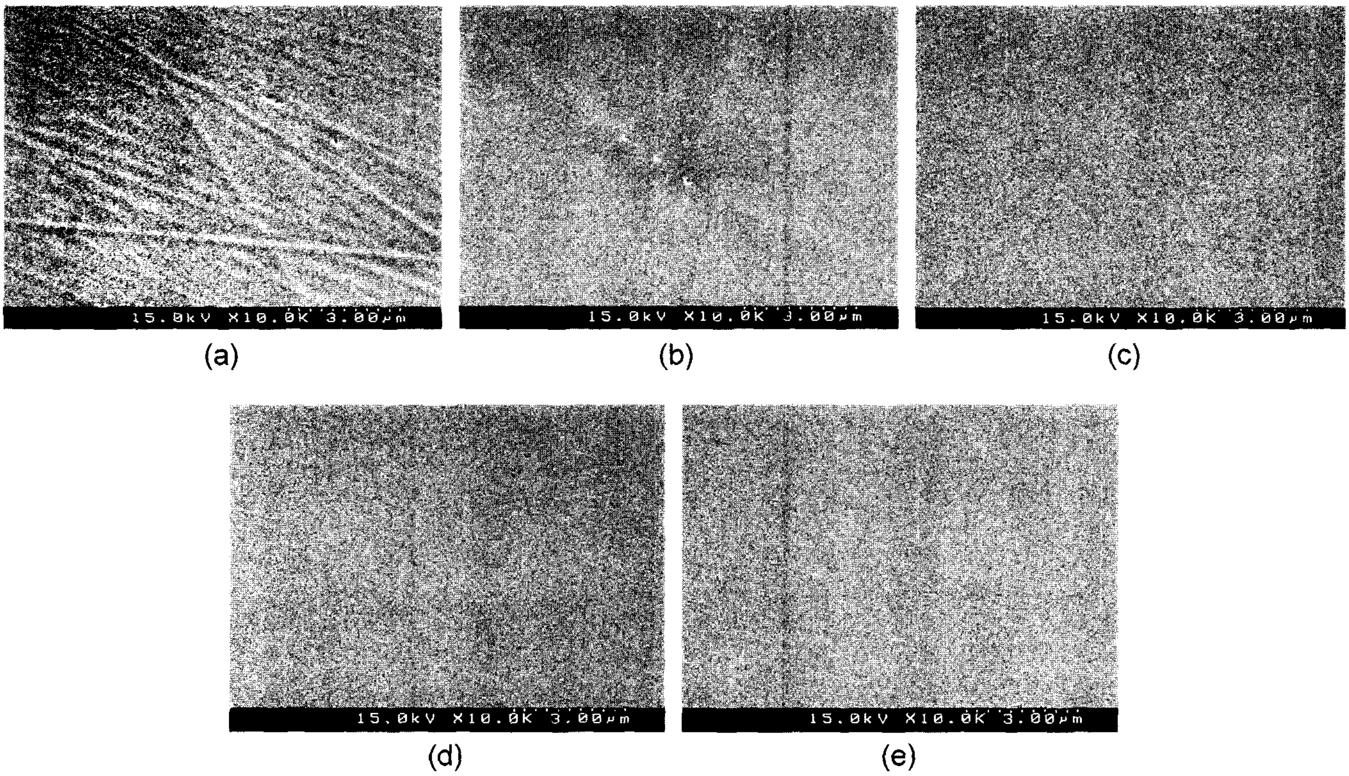


Fig. 4. XRD pattern of AlO_x thin films according to oxygen partial pressure.

ratio of 1.5. From these results, above oxygen partial pressure of 2×10^{-4} Torr, we found that AlO_x thin film was formed on PC with Al_2O_3 bulk composition ratio and stoichiometric ratio of AlO_x thin film is achieved by the characteristics of Ion Beam Sputtering Deposition (IBSD) technique when compared with other techniques such as PECVD and evaporation.[11] The improvement of stoichiometric ratio could be directly related to the densification of the deposited AlO_x thin film. By means of formation of AlO_x thin film with stoichiometric ratio, we found that the state of deposited AlO_x thin film is homogeneous.

In order to confirm oxide phase, we conducted XRD measurement. The results were shown in Fig. 4. We can't find any characteristics peaks of aluminium and so we see that metal oxide thin films were formed at all oxygen partial pressure The hindrance of deposited film compactness resulted from pinhole due to dust particle that introduced during deposition process. SEM examination of the AlO_x thin film according to oxygen partial pressure demonstrated the presence of defects as shown in Fig. 5. At 7×10^{-5} Torr and 1×10^{-4} Torr of oxygen partial pressure, a few micro order pinholes were observed. But above 2×10^{-4} Torr, micro order pinhole was not detected. From these observations, we will expect the improvement of oxygen permeability due to defect reduction. And also the results of previous studies were somewhat different from the present results. In the previous studies, many microscopic order pinholes were observed. But in our experiments, we can only see a few pinholes. This difference is contributed to the decrease of dust particle due to low-pressure process of RIBS. The presence of microscopic defect in the coating may be resulted from



(a) (b) (c)

(d) (e)

Fig. 5. SEM micrographs of AlO_x films prepared on polycarbonate at different oxygen partial pressure : (a) 7×10^{-5} Torr, (b) 1×10^{-4} Torr, (c) 2×10^{-4} Torr, (d) 3×10^{-4} Torr, and (e) 4×10^{-4} Torr.

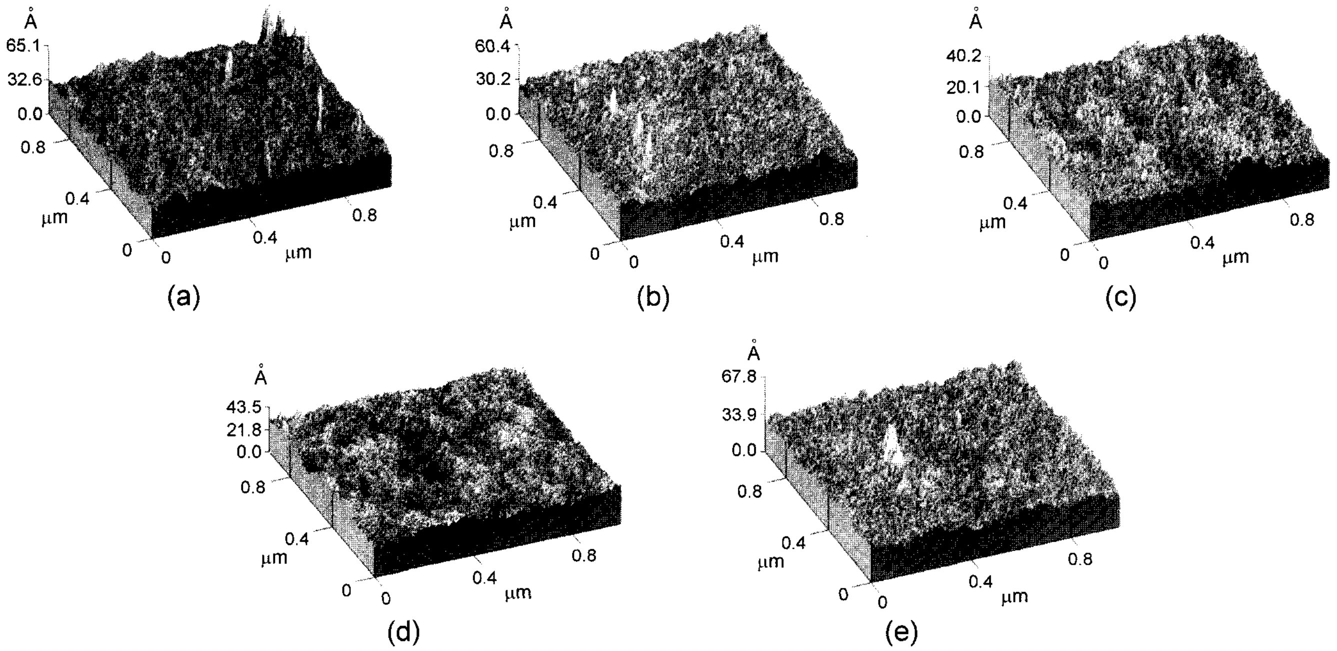


Fig. 6. AFM 3D images of AlO_x films deposited with oxygen partial pressure: (a) 7×10^{-5} Torr, (b) 1×10^{-4} Torr, (c) 2×10^{-4} Torr, (d) 3×10^{-4} Torr, and (e) 4×10^{-4} Torr.

stress during film growth at sites of high surface roughness.

To confirm alteration of surface roughness that have an influence on defect formation of deposited AlO_x thin film, we measured the AFM 3D images of AlO_x thin film deposited on PC as oxygen partial pressure increased as shown in Fig. 6. At 7×10^{-5} Torr, the surface morphology of AlO_x thin film showed agglomerated structure and then changed amorphous structure as oxygen partial pressure increased. We could directly relate surface morphology to the surface roughness. That is, as the agglomerated surface of AlO_x thin film was changed into amorphous, the surface roughness decreased. This result was due to the increase of oxide phase according to the alternation of sputtering mode. The previous reports showed that the agglomerated surface structure of Al_2O_3 thin film was converted to granular structure.[12] But in our results, agglomerated structure was transformed into amorphous structure. This result was attributed to the introduction of IBSD technique, which is suitable for low deposition temperature processing.

Fig. 7 appeared the RMS value of AlO_x thin film according to oxygen partial pressure. The RMS value of AlO_x thin film decreased and showed constant value as oxygen partial pressure increased. The decrease in the RMS value attributed to increase in the oxide component in metal oxide thin film and the surface atom mobility of AlO_x thin film deposited by IBSD. At 1×10^{-4} Torr, the RMS value showed very low RMS value of 1.5 Å. This value was very lower than the existing value of AlO_x thin film deposited by other techniques.[13] Thus, we expected that AlO_x thin film with very flat surface resulted in the development of optical and barrier properties.

The study of relationship between morphological characteristics of barrier thin film and barrier properties was focused on gas permeability according to the increase in the deposited film thickness. More recent reports represented the correlation of barrier property and surface morphology that gas permeability decreased with a reduction in film roughness. We confirmed this relationship between Figs. 7 and 8. Fig. 6 shows oxygen transmission rate of AlO_x thin film according to oxygen partial pressure. The tendency of

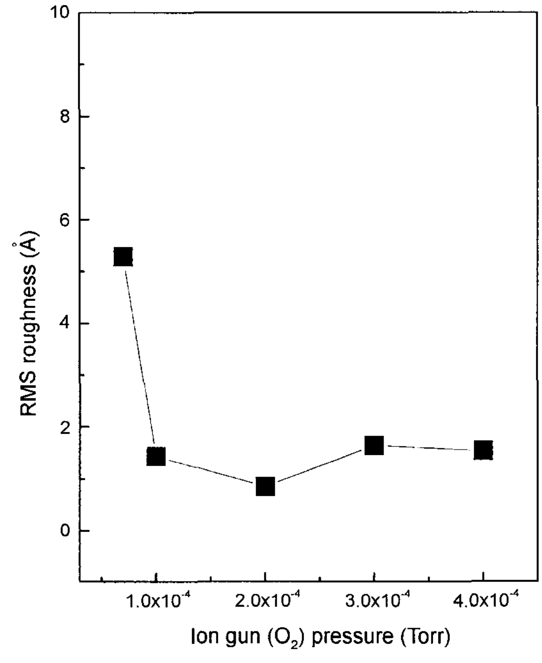


Fig. 7. RMS roughness of AlO_x thin films according to oxygen partial pressure.

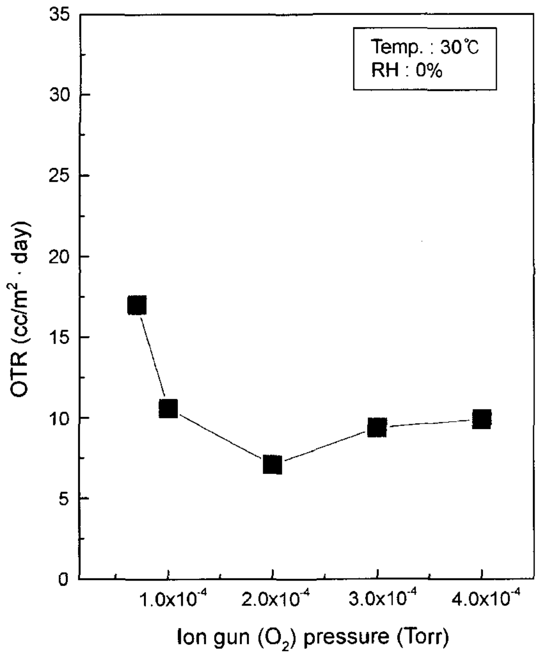


Fig. 8. Oxygen Transmission Rate (OTR) of AlO_x films according to oxygen partial pressure.

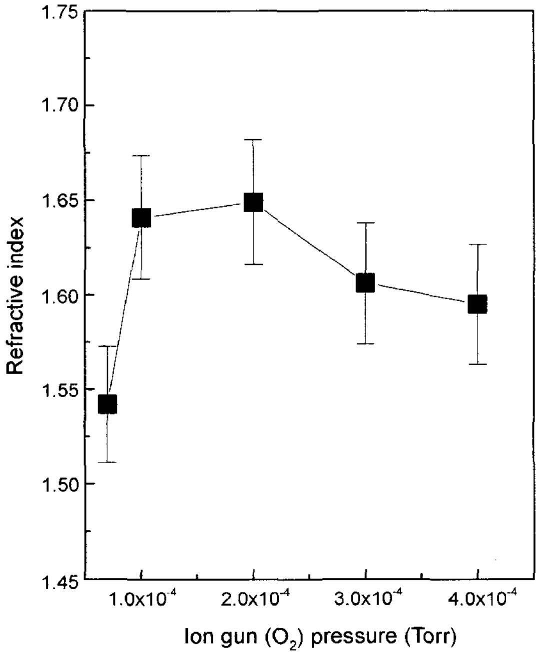


Fig. 9. Refractive index of AlO_x films deposited according to oxygen partial pressure.

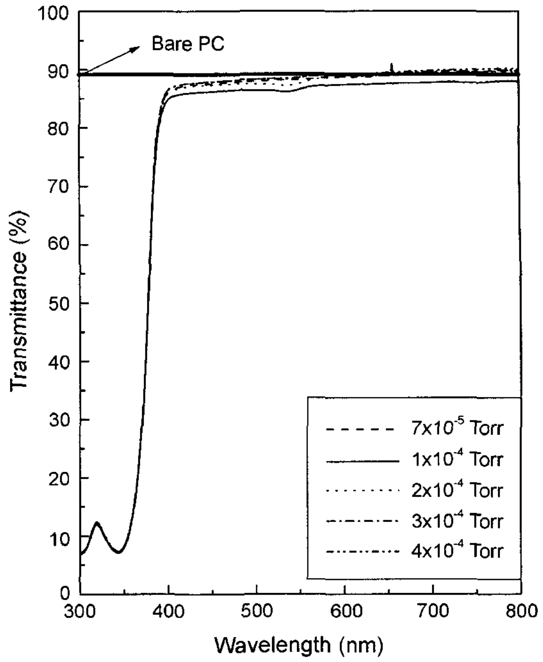


Fig. 10. Optical transmittance of AlO_x films deposited with oxygen partial pressure.

oxygen transmission rate according to the increase in the oxygen partial pressure was the same as that of surface roughness. Below 7×10^{-5} Torr, the OTR decreased abruptly and at 2×10^{-4} Torr, showed minimum OTR value and then constant value of OTR. Decrease in the OTR value could be attributed to the decrease in oxygen diffusion path because of low RMS value and the densification of deposited AlO_x thin film that resulted from the increase of oxide phase caused by the change of surface morphology and the defect reduction during the deposition of metal oxide thin film.

By virtue of measurement of optical properties such as refractive index, we will confirm the compactness of AlO_x thin film resulted from density increase. Fig. 9 shows the refractive index of AlO_x thin films according to oxygen partial pressure. According to increase in the oxygen partial pressure, the refractive index of AlO_x thin film increased and slightly decreased. But the decrease in the value of refractive index includes range (±2%) of error bar. The density of a thin film is related to refractive index by the Lorenz-Lorenz expression,[14] $d = k\ (n^2 - 1)/(n^2 + 2)$, where d is the density and k is a constant. Therefore, we expected that the results of refractive index be correlated to the formation of more densely packed structure by analysis of composition ratio and surface structure. Among the advantages of metal oxide thin films, when compared with metal film, the visibility of content is useful for especially medical barrier coating application. Fig. 10 showed the optical transmittance of the AlO_x thin film from 300 nm to 800 nm. In visible light region, the transmittance of AlO_x thin film according to oxygen partial pressure didnt alter largely. But the transmittance value of AlO_x thin film was the same as that of bare PC. We obtained colorless transparent film irrespective of oxygen partial pressure because of RIBS process induction, which is acceptable for optical coating and AlO_x thin film formation of stoichiometric ratio.

4. Conclusions

The effect of oxygen partial pressure on AlO_x thin films that is deposited on polycarbonate substrates was investigated. Our investigation found the optimum deposition parameters for fabrication of aluminum oxide thin films with the composition very near the bulk composition of Al_2O_3, and with a very flat surface and a dense structure. It was also demonstrated that ion beam deposition could be successfully used to fabricate thin films showing nice barrier and optical properties.

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