

Barrier property Enhancement of Plastic Substrates for Flexible Display by Inorganic-organic Hybrid Multilayer

Hyun Gi Kim, Hyunsun Ryu and Sung Soo Kim

College of Environmental and Applied Chemistry

Reigional Innovation Center for

Components and Materials for Information Display

Kyung Hee, Seocheon/Youngin, Suwon 449-701, Korea

phone:82-31-201-3257, e-mail: sungkim@khu.ac.kr.

Abstract

Inorganic-organic hybrid multilayers were formed on the plastic substrate to enhance the barrier properties of substrate to water vapor and oxygen transport. Plasma pretreatment of substrate with Ar/O₂ lead to adhesion improvement and the densification of inorganic layer on the substrates. Combination of SiO_xN_y layer and silane-nanoclay composite layer offered quite good barrier properties (WVTR and OTR) to PES substrate.

silane-nanoclay composite to enhance the water vapor and oxygen barrier properties, which overcame the shortcomings of inorganic layer. Formation of inorganic-organic multilayers on flexible PES substrates was investigated and performance of LC cells with layered PES substrate was fabricated to characterize the barrier properties.

1. Introduction

Development of plastic substrates have been great issues for flexible display fabrication which has advantages over the conventional one in terms of weight, thickness, flexibility, shock resistance, etc. However, the permeation of water vapor & oxygen through plastic substrates seriously deteriorates the performances, and it is the one of the major problems to overcome in flexible display development. Several attempts have been made to reduce the permeation rate by forming inorganic layers on the substrate such as silicon oxide, silicon nitride, silicon oxynitride, etc [1-3].

Plasma enhanced chemical vapor deposition (PECVD) is regarded as one of the good candidate processes that allow the deposition of inorganic layer at low temperature. Generally, inorganic layers are rough and have many micro- or macro-defects and pinholes, which caused more permeation through the substrates. Organic layers with silane-nanoclay composite are need to reduced defects of inorganic layers. Also, nanoclays create a "tortuous path" so that drastically increase the time for oxygen & water vapor to diffuse through the polymer [4]. In this work, inorganic-organic hybrid multilayers were formed to enhance the barrier performance. The inorganic layers were deposited by PECVD process, where HMDSN was introduced by bubbling with nitrogen as a liquid silicone source. Organic layers were coated using

2. Experimental

The schematic diagram of PECVD apparatus used in this work for the pretreatment and the deposition of SiO_xN_y are shown in the Figure 1. Hexamethyldisilazne (HMDSN, Sigma-Aldrich Co. 98%) used as liquid silicon source and it was introduced into the reactor by nitrogen bubbling at a fixed temperature of 60 °C. The HMDSN/N₂/Ar/O₂ gas mixtures were supplied to the reactor through the mass flow controller. The plasma pretreatment with O₂/Ar gas mixtures was performed prior to deposition of SiO_xN_y.

Montmorillonite-based clay with different organic modifiers namely Cloisite15A, were added into organosilane(γ -APS, Sigma-Aldrich Co. 99%) for preparing composite solution. The concentration of clay in solution was varied from 1 to 5wt%. The organosilane-nanoclay composite solution was stirred for 3h, and was subsequently ultrasonicated for 3hr. Spin coating was performed at 1500rpm for 30sec. The organosilane-nanoclay composite layer was subsequently cured at 100 °C for 24hr under air.

The chemical composition of the plasma pretreated surface of PES and the deposited SiO_xN_y layer were investigated using a X-ray photoelectron spectrometer (XPS, K-Alpha, Thermo electron, UK). Surface images of each layer were obtained by a Atomic force microscope (AFM, Nanoscope IIIa, Digital Instrument, USA) and Field Emission Scanning electron microscope (FE-SEM, JEM-2100F, JEOL, JAPAN).

The water vapor and oxygen transmission rate were measured using WVTR (PERMATRAN-W Model 3/33, MOCON Inc. USA) & OTR (OXTRAN Model 2/20, MOCON Inc. USA) measurement system, respectively.

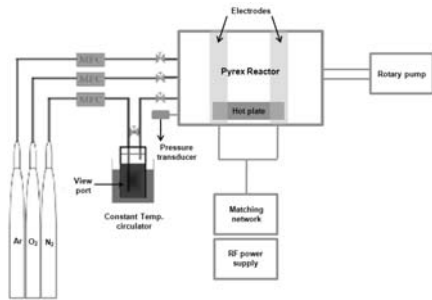


Fig. 1. Schematic diagram of PECVD.

3. Results and discussion

In order to improve the adhesion stability between the SiO_xN_y and PES substrates and to promote the formation of SiO_xN_y layer on the surface, plasma pretreatment using Ar/O₂ gas mixtures for various treatment time. Figure 2 shows the variations of surface energy and roughness of PES substrates by pretreatment with gas mixture(Ar/O₂). After plasma pretreatment, surface energy of the PES substrates increased due to increasing oxygen functionalities by plasma. Results show that PES substrates treated by plasma were improved wettability. When the PES substrates were treated for 60 sec, the smallest surface roughness was obtained. Decrease of surface roughness was caused by argon etching effect.[2]

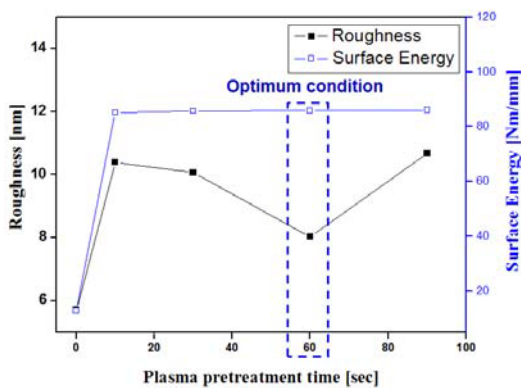


Fig. 2. Roughness and surface energy variations with time for pretreatment with Ar/O₂ gas mixture.

Figure 3 shows variation of atomic composition of the PES surface after pretreatment. Oxygen

percentage on PES surfaces increased with increasing treatment time until 60sec. These indicated that activated oxygen ions penetrated into the PES surfaces. Generally, the major effect of oxygen plasma was its chemical etching on most organic polymers while argon plasma formed a more compliant surface than the original one. Reason for no change in oxygen percentage and increasing in roughness after 60sec was caused by an interaction effect of gas mixtures.

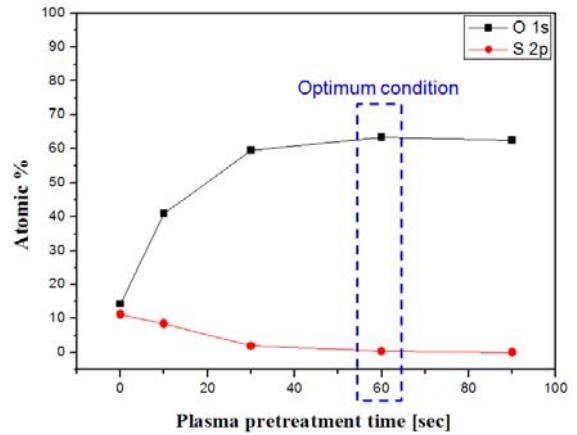


Fig. 3. Atomic contents variation with time for pretreatment with Ar/O₂ gas mixture.

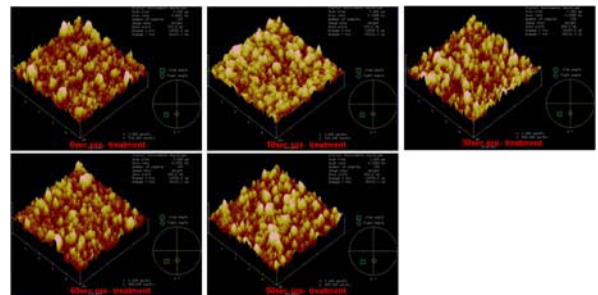


Fig. 4. AFM images variation with time for pretreatment with Ar/O₂ gas mixture.

Figure 4 shows the AFM images of SiO_xN_y deposited on PES with various plasma pretreatment times. Before pretreatment (0sec), the inorganic layer was partially deposited on PES substrates. However, when PES was plasma pretreated, inorganic layer was deposited uniformly due to oxygen functionalities generated by plasma treatment. These results indicated that plasma pretreatment was an effective method for promoting to form the inorganic layer on organic substrates. The corresponding results for roughness of deposited SiO_xN_y layer were shown in Figure 5. With increasing the plasma treatment time, the roughness was decreased due to the homogeneous

deposition on substrates.

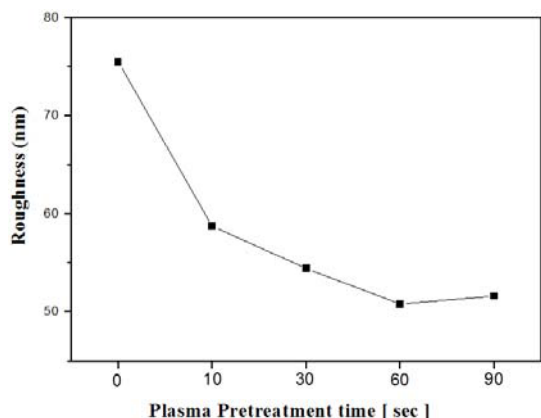


Fig. 5. Roughness change of deposited SiO_xN_y layer with plasma pretreatment time.

However, it was considered that many defects, such as pin hole, micro- and macro-defects were still existed on the our SiO_xN_y layer. In order to cover defects and to enhance barrier performances, composite layer with silane-nanoclay was overcoated on the SiO_xN_y deposited PES substrate. Multilayer with SiO_xN_y and organosilane-nanoclay composite layer offered quite good barrier properties as shown Figure 6.

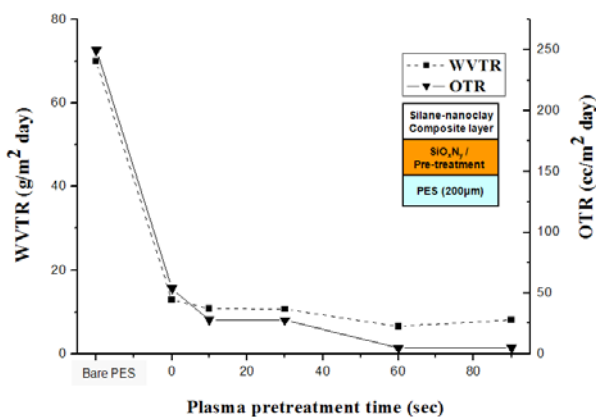


Fig. 6. Variations of WVTR and OTR of multilayer deposited PES with various plasma pretreatment time.

Figure 7 shows the WVTR and OTR of multilayer with SiO_xN_y and organosilane-nanoclay composite deposited PES with various nanoclay contents in composite layer. Barrier properties were little affected by nanoclay content, and it was optimized at 1 wt% of

nanoclay content in this work.

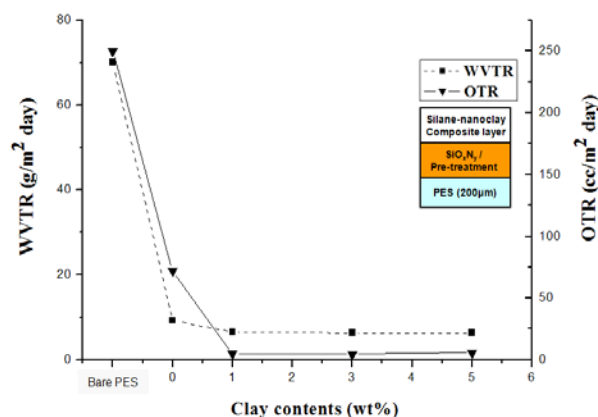


Fig. 7. WVTR and OTR of multilayer deposited PES with various clay contents.

4. Summary

The surface modification using plasma pretreatment with Ar/O_2 modified the substrate surface for better deposition of inorganic layer on PES substrates to secure the better barrier properties. The best pretreatment condition was found in this work. The silane-nanoclay composite layer was successfully obtained and led to enhance the barrier properties of the flexible substrates.

5. Acknowledgement

Authors would like to thank Regional Innovation Center - Components And Materials for Information Display (RIC-CAMID) of Kyung Hee University for supports

6. References

1. A. Bieder, *Surf. Coat. Technol.*, **200**, 928 (2005).
2. T.N. Chen, *Thin solid films*, **514**, 188 (2006).
3. J.H. Lee, *Thin solid films*, **515**, 917(2006)
4. Jaime C. Grunlan, *J. Appl. Poly. Sci.* **93**, 1102 (2004).