A Study on Properties of PVA/SiO_2 Organic-inorganic Hybrid Materials Barrier Layer Coated on Flexible Substrate (PEN)

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Abstract

Barrier coating properties of PVA/SiO_2 on the flexible substrates (PEN) have been investigated. Thin layer of PVA/SiO_2 organic-inorganic hybrid materials were deposited on PEN substrate by the spin-coating. The optical properties and surface roughness of barrier layer on flexible substrate were characterized by AFM, UV-Vis and WVTR/ OTR.

1. Introduction

Flexible electronic devices are expected to lead the next generation devices for the displays (flexible LCD (liquid crystal display) [1], flexible OLED (organic light emitting diode) [2, 3] and solar electric generation systems (organic solar cell, bulk hetero-junction solar cell) [4]. Till date three kinds of major flexible substrates are in use; thin glass, metal foil and plastic substrate [5]. In our present work we have used plastic substrate, especially PEN (polyethylene naphthalate) as the substrate for flexible devices.

It is widely observed that the electronic devices are degraded by permeation of water vapor and oxygen; especially the plastic substrates are the weakest among all substrates. So for the increase of device life time, prevention of permeation of water vapor and oxygen is highly essential [2, 6]. In this work we applied wet coating of PVA/SiO_2 organic-inorganic hybrid materials layer by spin-coating method. We have optimized the coating conditions and measured the optical and surface properties of deposited barrier layer. The aim was to decrease the WVTR (water vapor transmittance rate) and OTR (oxygen transmittance rate) to increase the life time of electronic devices.

2. Experimental

2.1. PEN substrate preparation

The PEN (polyethylene naphthalate) was investigated as the potential substrate for flexible electronic devices. The PEN substrate was first cleaned by TCE (trichloroethylene), acetone and methanol with ultrasonification for 5 min, respectively, followed by a N_2 blow-drying. After wet chemical cleaning, the PEN substrate was treated with O_2-plasma at a power of 50 W and a pressure of 200 mTorr to make surface hydrophilic. After cleaning and surface treatment the contact angle was measured and compared.

2.2. Preparation of hybrid solution

The PVA/SiO_2 hybrid solution was prepared by using the slight modification of Dukjoon Kim's method [7].

PVA powders (2 g) (high- and low- molecular weight) were first dissolved in 20 ml D.I. water (deionizated water), and the solution was stirred for more than 12 hours at the room temperature. Separately TEOS (tetraethylorthosilicates), ethanol and D.I. water were mixed at 1:2:2 molar ratios (standard by TEOS) and partially hydrolyzed with acid HCl catalyst to obtain the TEOS sols.

The prepared TEOS sol of 0.01, 0.02, 0.04 and 0.07 mol, respectively, was mixed with PVA solution at room temperature and stirred for 2 hr to produce PVA/SiO_2 hybrid coating solution with different concentrations.

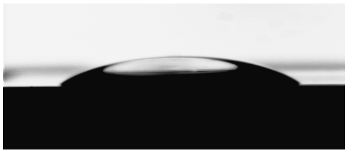
2.3. PVA/SiO_2 coated PEN substrate

PVA/SiO_2 hybrid gel-coating solution was coated on PEN substrate by spin-coating (6000 rpm, 30 sec) method, and then barrier-coated PEN substrate was dried in an oven (90 ℃) for 3 hr. To investigate the surface morphology (roughness) of barrier-coated flexible substrate, atomic force microscopy (AFM) technique was used. We also measured the substrates' optical properties by optical transmittance (UV-Vis) and the substrates' barrier properties by oxygen transmittance tester (OX-TRAN 2/21 MD) and water vapor transmittance rate tester (PERMATRAN-W 3/33 MA).

3. Results and discussion

Fig. 1 shows the O_2-plasma pre-treatment results of substrate surface (dropping solution is PVA/TEOS (0.01 mol/L) mixing solution), and it clearly indicates the decrease of contact-angle by the increase of the treatment time. It is believed that the hydrophilic property of the substrate is improved by the O_2-plasma pre-treatment

(a) base film

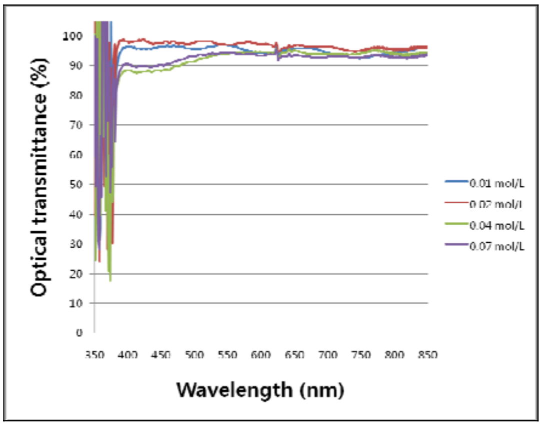


(b) 5 min

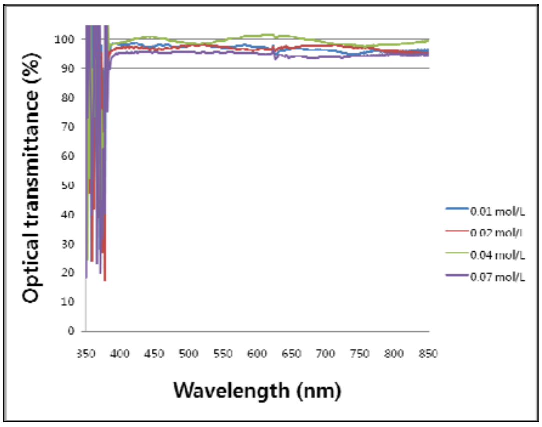
(c) 10 min

Fig. 1. Contact angle variation vs. O_2-plasma pre treatment time (dropping solution: PVA/TEOS (0.01 mol/L)).

Fig. 2 shows the results of the optical transmittance study of high molecular weight and low molecular weight PVA coated film on the PEN substrate. In general low molecular weight PVA coated film showed better transmittance, but the effect of TEOS content on the transmittance was minimal. Optical transmittance measured in this study was higher than 90% at all the samples when compared with that of the base PEN film.



(a) Optical transmittance of high molecular weight (146,000~186,000) PVA film.

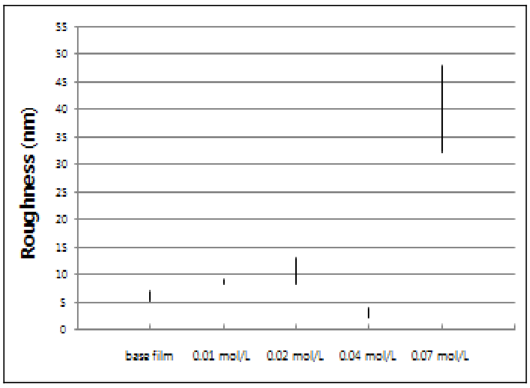


(b) Optical transmittance of low molecular weight (13,000~23,000) PVA film.

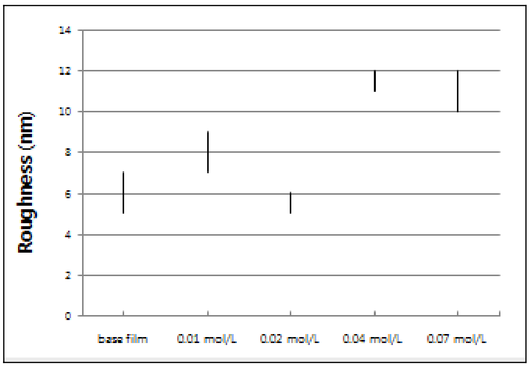
Fig. 2. Optical transmittance variation of PVA/SiO_2 coated PEN substrate at different molecular weight.

In the present work we have also optimized the roughness of PVA/SiO_2 coated film on PEN flexible substrate with high- and low- molecular weight PVA contents at different concentrations of TEOS.

Fig. 3 shows the AFM roughness variation of each sample with different conditions. By the AFM roughness measurement results we found that the roughness of barrier coated substrate at the low molecular weight PVA with TEOS concentration of 0.02 mol/L and high molecular weight PVA with TEOS concentration of 0.04 mol/L show the best result.



(a) High- molecular weight (146,000~186,000) PVA.



(b) Low- molecular weight (13,000~23,000) PVA.

Fig. 3. Roughness variation of each PVA/SiO_2 coated film surface with varying concentration of TEOS.

Table 1. shows the OTR of barrier layer coated PEN substrate. This result shows that after the substrate coating treatment, the OTR properties are decreased. It is clearly indicated that PVA/SiO_2 solution could be used for oxygen barrier layer.

TABLE 1. OTR values of high- and low- molecular weight PVA

	Bare	0.01 (mol/L)	0.02 (mol/L)	0.04 (mol/L)	0.07 (mol/L)
High M.W. (cc/ m^2-day)	3.12	2.92	1.86	1.87	2.372
Low M.W. (cc/ m^2-day)	3.12	1.84	1.578	1.77	2.15

Table 2. shows the WVTR of barrier layer coated PEN substrate. The result shows that high- molecular weight PVA film could not prevent the moisture.

TABLE 2. WVTR values of high- molecular weight PVA

	Bare	0.01 (mol/L)	0.02 (mol/L)	0.04 (mol/L)	0.07 (mol/L)
High M.W. (g/ m^2-day)	1.03	1.15	1.06	1.44	1.35

4. Summary

In this study we have optimized the thin film formation technology of barrier coating materials film (PVA/SiO_2) on the PEN substrate and developed thin film barrier with enhanced properties, which is expected to increase the device life time. Optical transmittance was over 90% after the barrier coating, and the surface roughness was under 10 nm for most cases allowing the process feasible for commercial applications. The hybrid barrier layer developed in this study could not however decrease the WVTR, although it could decrease the OTR.

5. Acknowledgement

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6. References

1. J. H. Lee, D-H. Kang, Y-D. Ko, J. Jang, D-S. Seo, I. Yun, *Expert Sys. Appl.,* **35**, 1311 (2008).
2. C. Charton, N. Schiller, M. Fahland, A. Holländer, A. Wedel, K. Noller, *Thin Solid Films,* **502**, 99 (2006).
3. K. H. Haas, S. Schwab, K. Rose, *Thin Solid Films*, **351**, 198 (1999).
4. P. Liu, T. H. Chen, W. Z. Pan, M. S. Huang, W. J. Deng, Y. L. Mai, A. B. Luan, *Chinese Chem. Lett.,* **19**, 207 (2008).
5. G. P. Crawford, Flexible Flat Panel Displays, John Wiley, England, (2005).
6. D. Kim, S. W. Kim, *Korean J. Chem. Eng.,* **20**, 776 (2003).
7. S. W. Kim, D. Kim, *Korean J. Chem. Eng.,* In Press (2008).