A stacked organic/inorganic vapor barrier structure encapsulated flexible plastic substrates prepared using plasma-enhanced chemical vapor deposition

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1. Introduction

Gas barrier coatings on flexible substrates have received much attention in high-tech optoelectronic devices [1]. Due to the plastic substrates are poor in barrier against the vapor permeation, a hermetic encapsulation technique using a sheet attached by a bead of UV cured epoxy resin is currently applied to the plastic devices [2]. However, these types of seals are generally too large and heavy to strengthen the superiority of plastic substrates. Accordingly, research on the ultra-thin encapsulation structure based on vacuum deposition technology is essential. Transparent inorganic layers have been widely used as fundamental gas barrier films [3-4]. Unfortunately, the formation of microcracks and/or pinholes due to the considerable stress resided in the inorganic layer when deposited on plastic substrates always degraded the resulting barrier performance. Consequently, a multilayer structure consisted of stacked organic/inorganic layered-structure has been demonstrated in recent reports [5-7]. Such barrier structures are typically prepared by different deposition technologies, resulting in the deposition inconvenience and additional budget for apparatus. In this work, we devised pairs of organic/inorganic structure prepared exclusively through a plasma-enhanced chemical vapor deposition (PECVD) technology, using the same organosilicon monomer, as a vapor barrier coating on PET substrates. By adopting the main structure of a stacked organosilicon/silicon oxide (SiO_x) multilayer with a low residual internal stress, a water vapor transmission rate (WVTR) lower than 5×10^{-3} g/m²-day was achieved from the pairs of such structure encapsulated the polyethylene terephthalate (PET) substrate.

2. Experimental procedure

The vapor barrier structure was consecutively deposited on cleaned PET substrates (~ 210 μ m) through a conventional PECVD system, using tetramethylsilane (TMS, Si(CH₃)₄) organosilicon liquid monomer. The organosilicon film was achieved from the plasma-polymerization of TMS monomer, while the inorganic SiO_x film was synthesized from the TMS-oxygen gas mixture in the glow discharge. The deposition temperature was set at 120°C to acquire a porous-free a-SiO_x barrier structure. The deposition parameters were controlled to obtain a well-adherent layered-structure to the PET substrates [8]. Film thickness was measured using a surface profile system. Chemical bonding states were examined using a Fourier transform infrared (FTIR) spectrometer. Adhesion behavior was conducted by the standard tape-peeling test (ASTM D3359). Surface morphologies were observed via an atomic force microscopy (AFM). The residual stress was measured by the beam bending method using a thin film stress measurement instrument. WVTR of the encapsulated PET substrates was measured using a water vapor transmission rate measurement system (MOCON Inc.) at a temperature of 40°C with a relative humidity of 100 %.

3. Experimental results

Figure 1 depicts one pair of the stacked organic/inorganic vapor barrier structure prepared through PECVD technology, using TMS monomer. The chemical



→TMS plasma polymerization

Fig.1 Schematic structure of one pair stacked organic/inorganic vapor barrier structure.

bond nature of the room-temperature- and 120° C-deposited inorganic barrier layer as well as the organosilicon film conducted from FTIR measurements are shown in Figs. 2(a)-(c). The Si-O-Si chemical bond were predominated over the spectrum of the inorganic barrier layer and porous-related hydroxyl (-OH) chemical bond was almost absent (Fig. 2(b)), indicating that it was a porous-free and close-packed a-SiO_x film which benefited for the barrier application. The plasma-polymerized film prepared using TMS monomer consisted of Si-C chemical bonds with functional C-H bonds (Fig. 2(c)), showing the organic-like film exhibited hydrophobic surface. A 200 nm-thick SiO_x



Fig.2 FTIR spectra of the (a) room-temperature-deposited SiO_x film, (b)120°C-deposited SiO_x film and (c) organosilicon film.

film possessed the best effective permeability was designed as the main barrier layer. The inset organosilicon film plasma-polymerized from TMS monomer was controlled as 40 nm to improve the SiO_x film adhered to PET substrate. The adhesion behaviors of the SiO_x barrier layer with and without an organosilicon film assessed by standard tape-peeling test are shown in Figs. 3(a) and 3(b). The SiO_x film totally peeled off the PET substrate, whereas an excellent adhesion (rank 5B) was available for the organosilicon/SiO_x barrier structure. Meanwhile, the residual compressive stress accumulated in the SiO_x film (~ 875 MPa) also was effectively reduced by insetting the organosilicon film, resulting in the barrier structure with minimum compressive stress (~ 80 MPa). The WVTR of the



Fig.3 Tape-peeling test results of the (a) SiO_x barrier layer and (b) organosilicon/SiO_x barrier structure deposited on PET substrates.

 SiO_x film and pairs of the stacked barrier structure coated on the PET substrates is shown in Fig. 4. The WVTR showed a little decreased as the thickness of the SiO_x film reached 600 nm, whereas the WVTR was markedly improved by coating with the stacked organosilicon/SiO_x barrier structure and reached to a value below the detection limit (< 10^{-3}



Fig.4 WVTR of the SiO_x barrier layer, and one, two and three pairs of organosilicon/SiO_x barrier structures.

 g/m^2 -day), as coated with a 6-pairs stacked barrier structure. The barrier performances of the samples shown in Fig. 4 are summarized in Table 1. The effective permeability of the coated barrier layer is expressed as [9]:

$$\frac{1}{\Pi_T} = \frac{d_T}{P_T} = \frac{d_s}{P_s} + \frac{d_c}{P_c} \tag{1}$$

where Π is the transmission rate, *P* is permeability and *d* is thickness. In addition, the subscript *s*, *c* and *T* denote as the substrate, coating, and composite (*s*+*c*) properties, respectively. Although the thicker SiO_x film (600 nm) deposited on the PET substrate resulted in a low WVTR, the derived effective permeability was lower than that of the 200 nm-SiO_x film coated on PET substrate. This revealed that the improvement of the incremental SiO_x film thickness on the vapor permeation was limited and saturated. By

contrast, the stress-released barrier structure constructed from the organosilicon/SiO_x layered-structure resulted in a positive contribution on the effective permeability, as increased with the pairs of the stacked structure. An excellent effective permeability (< 0.001 μ m-g/m²-day) was available for the PET substrate coated with a 6-pairs organosilicon/SiO_x layered-structure

Table 1 Barrier performance of the SiO_x film and pairs of organosilicon/SiO_x barrier structure.

Sample	dc (nm)	Composite	⁺ BIF	Effective
		WVTR		permeability
		(g/m ² -day)		$(\mu m - g/m^2 - day)$
bare PET	-	3	1	-
SiO _x	200	0.51	5.88	0.12
SiO _x	600	0.41	7.32	0.28
1- [*] pair	240	0.24	12.5	0.063
3-pairs	720	0.048	62.5	0.035
6-pairs	1440	< 0.001	> 3000	< 0.001
pair structure: organosilicon (40 nm)/SiO (200 nm)				

⁺BIF = (WVTR of bare PET/WVTR of coated PET)

4. Conclusions

A stacked organic/inorganic structure prepared by PECVD using the same TMS monomer was demonstrated to improve the vapor permeation of the plastic substrates. The residual stress in the 120°C-deposited SiO_x film synthesized from TMS-oxygen gas mixture effectively reduced by insetting a plasma-polymerized organosilicon film by TMS monomer, also resulting in an apparent reduction in the WVTR. The effective permeability of the stacked barrier structure decreased with increasing the pairs of the organosilicon/SiO_x layered-structure. An ultra-low WVTR (< 10⁻³ g/m²-day) was achieved from the PET substrate coated with a 6-pairs organosilicon/SiO_x barrier structure. Such quality vapor barrier structure is sufficient for the application on the package of plastic optoelectronic devices.

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References

- [1] S. A. Dayeh, D. P. Butler, and Z. C. Bulter, Sensors and Actuators A **118** (2005) 49.
- [2] S. J. Bae, J. W. Lee, J. S. Park, D. Y. Kim, and S. W. Hwang, Jpn. J. Appl. Phys. 45 (2006) 5970.
- [3] J. W. Han, H. J. Kang, J. H. Kim, and D. S. Seo, Jpn. J. Appl. Phys. 45 (2006) L827.
- [4] T. T. Pham, J. H. Lee, Y. S. Kim, and G. Y. Yeom, Surf. Coat. Technol. 202 (2008) 5617.
- [5] C. C. Chiang, D. S. Wuu, H. B. Lin, Y. P. Chen, T. N. Chen, Y. C. Lin, C. C. Wu, W. C. Chen, T. H. Jaw, and R. H. Horng, Surf. Coat. Technol. 200 (2006) 5843.
- [6] J. H. Lee, C. H. Jeong, H. B. Kim, J. T. Lim, S. J. Kyung, and G. Y. Yeom, Thin Solid Films 515 (2006) 917.
- [7] J. H. Choi, Y. M. Kim, Y. W. Park, J. W. Huh, and B. K. Ju, Rev. Sci. Instrum. 78 (2007) 064701.
- [8] D. S. Liu and C. Y. Wu, J. Phys. D: Appl. Phys. 43 (2010) 175301.
- [9] D. G. Howells, B. M. Henry, J. Madocks, and H. E. Assender, Thin Solid Films 516 (2008) 3081.