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

Ming-Shiun Jeng 1, Chuan-Sheng Chuang 2, Li-Wen Lai 2, Bo-Yu Lin 1, and Day-Shan Liu 1

1 Institute of Electro-Optical and Material Science, National Formosa University, Huwei, Yunlin 63201, Taiwan
2 ITRI South, Industrial Technology Research Institute, Liujia Shiang, Tainan, 734, Taiwan, Republic of China

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 (SiOx) 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 μm) 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 SiOx 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-SiOx 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 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 organosilicon film as well as the organosilicon film. A 200 nm-thick SiOx film exhibited hydrophobic surface. A 200 nm-thick SiOx film, (b)120°C-deposited SiOx film and (c) organosilicon film.

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

Fig.2 FTIR spectra of the (a) room-temperature-deposited SiOx film, (b)120°C-deposited SiOx 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 SiOx film adhered to PET substrate. The adhesion behaviors of the SiOx barrier layer with and without an organosilicon film assessed by standard tape-peeling test are shown in Figs. 3(a) and 3(b). The SiOx film totally peeled off the PET substrate, whereas an excellent adhesion (rank 5B) was available for the organosilicon/SiOx barrier structure. Meanwhile, the residual compressive stress accumulated in the SiOx 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 organosilicon film, ~40 nm to improve the SiOx film adhered to PET substrate. This revealed that the improvement of the incremental SiOx film thickness on the vapor permeation was limited and saturated. By coating with the stacked organosilicon/SiOx barrier structure deposited on PET substrates. The WVTR showed a little decreased as the thickness of the SiOx film reached 600 nm, whereas the WVTR was markedly improved by coating with the stacked organosilicon/SiOx barrier structure and reached to a value below the detection limit (<10⁻³ g/m²-day) was achieved from the PET substrate coated with a 6-pairs organosilicon/SiOx layered-structure. Meanwhile, the stress-released barrier structure constructed from the organosilicon/SiOx 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 μm-g/m²-day) was available for the PET substrate coated with a 6-pairs organosilicon/SiOx layered-structure.

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>dc (nm)</th>
<th>Composite</th>
<th>¹BIF</th>
<th>Effective permeability (μm-g/m²-day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>bare PET</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SiOx 200</td>
<td>0.51</td>
<td>5.88</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>SiOx 600</td>
<td>0.41</td>
<td>7.32</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>1-pair</td>
<td>0.24</td>
<td>12.5</td>
<td>0.063</td>
<td></td>
</tr>
<tr>
<td>3-pairs</td>
<td>0.048</td>
<td>62.5</td>
<td>0.035</td>
<td></td>
</tr>
<tr>
<td>6-pairs</td>
<td>&lt;0.001</td>
<td>&gt;3000</td>
<td>&lt;0.001</td>
<td></td>
</tr>
<tr>
<td>6-pairs SiOx (200 nm)</td>
<td>0.24</td>
<td>12.5</td>
<td>0.063</td>
<td></td>
</tr>
<tr>
<td>3-pairs SiOx (200 nm)</td>
<td>0.048</td>
<td>62.5</td>
<td>0.035</td>
<td></td>
</tr>
<tr>
<td>1-pair SiOx (200 nm)</td>
<td>0.24</td>
<td>12.5</td>
<td>0.063</td>
<td></td>
</tr>
<tr>
<td>bare PET - 3</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

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 SiOx 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/SiOx layered-structure. An ultra-low WVTR (<10⁻³ g/m²-day) was achieved from the PET substrate coated with a 6-pairs organosilicon/SiOx barrier structure. Such quality vapor barrier structure is sufficient for the application on the package of plastic optoelectronic devices.

Acknowledgments
This work was supported by the National Science Council and Industrial Technology Research Institute (ITRI South) under no. NSC96-2221-E-150-072-MY3 and no. B200-99FE4.

References