



Barrier property and mechanical flexibility of stress controlled organosilicon/silicon oxide coatings on plastic substrates



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ARTICLE INFO

Article history:

Received 12 April 2015

Revised 7 August 2015

Accepted in revised form 31 August 2015

Available online 5 September 2015

Keywords:

Organosilicon/silicon oxide

Water vapor permeation

Mechanical flexibility

Residual internal stress

Tensile strain

ABSTRACT

In this study, we demonstrated the effect of the organosilicon layer in the pairs of the organosilicon/silicon oxide (SiO_x) multi-layered structure on the barrier property to water vapor permeation and on the mechanical flexibility under tensile strain. The residual internal stress in the structure was controlled by introducing the organosilicon layer, thereby enhancing the structural barrier property. The experimental results showed that the thickness of the organosilicon layer required in each paired structure to minimize the structural stress was closely correlated to the surface and material properties of the underlying layer. Accordingly, the internal stress that existed in the 2- and 3-paired structures, as well as their barrier properties to the water vapor permeation, was optimized further by altering the thickness of the organosilicon layer that was deposited onto the surface of the SiO_x film. These pairs of multi-layered structures, in which the compressive stress had been minimized, cracked at a lower bending radius under static tensile strain than the SiO_x film with the same thickness deposited directly onto the polyethylene terephthalate (PET) substrate. In addition, the degradation in the water vapor transmission rate (WVTR) of the organosilicon/ SiO_x multi-layered structure deposited onto the PET substrate was less apparent than that of the PET coated only with a single SiO_x film. This was ascribed to the structure having fewer cracks than the single SiO_x film after being bent by the same tensile strain. Dynamic tensile strain also was conducted on these multi-layered structures to further confirm the structural reliability.

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1. Introduction

In recent years, significant research has been invested in the development of high-end, high-performance flexible electronics with foldable characteristics, such as solar cells, thin film transistors, light emitting diodes, and displays [1–5]. Generally, there are three choices for flexible substrates, i.e., polymer, thin glass, and metal foil substrates. Among these, polymer substrates are preferred, especially for applications with optoelectronic devices, because of their optical transparency, flexibility, lightness, ease of handling, and cost-effectiveness. However, many obstacles and challenges prevent flexible devices based on polymer substrates from being fully commercialized, because polymer substrates are poor in terms of surface hardness, sensitivity to solvents and other chemicals, and susceptibility to water vapor and oxygen permeation. Thus, transparent oxides or nitride barrier films, such as SiO_x , Si_3N_4 , AlO_x , TiO_x , and IZTO have been used extensively to encapsulate these substrates/devices [6–10]. Although depositing an inorganic film onto a polymer substrate leads to a significant reduction in the water vapor transmission rate (WVTR), this reduction falls short of the orders of magnitude required

for packaging flexible substrate/device. Therefore, a thick and quality inorganic film must be deposited onto the flexible substrate/device to provide an ultra-high barrier property. However, due to the significant discrepancies in the elasticity and other properties between the inorganic film and the polymer substrate, as well as the low deposition temperature, the resulting WVTR of the polymer substrate coated with a thick inorganic film is limited to the range of about of 0.1–0.01 $\text{g/m}^2/\text{day}$ at 25 °C with 100% relative humidity (RH) originating from the formation of the nanometer- to micrometer-sized defects and cracks in the barrier film [11–13]. Consequently, hybrid structures comprised of inorganic/inorganic or organic/inorganic multi-layered structures were designed to eliminate these defects in the inorganic layer and function to avoid the penetration of water vapor and oxygen molecules through the polymer substrate [14–17]. In our previous report, we described our development of an organosilicon layer to address adhesion to the polymer substrate [18]. Compressive stress in the SiO_x film deposited onto the substrate was demonstrated to be released effectively by introducing an adequate thickness of the organosilicon layer. The barrier property of the 1-paired organosilicon/ SiO_x multi-layered structure with a minimized internal stress apparently was more effective than a single SiO_x film [19]. Accordingly, the PET substrate provided an ultra-low WVTR (approximately 10^{-5} $\text{g/m}^2/\text{day}$) after it was coated with a 6-paired organosilicon/ SiO_x multi-layered structure.

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In addition to the urgent need to develop multi-layered structures with an ultra-high barrier property, these structures coated onto the polymer substrates also should be sufficiently robust to avoid cracking during bending. However, the inorganic material in the multi-layered structure usually is stiff and brittle, but the polymer substrate is flexible. The barrier property of the inorganic material is degraded due to the formation of cracks after bending. Accordingly, an investigation into the mechanical stress/strain distribution within the entire barrier structure during bending to a radius of curvature of a few centimeters also is critical to prevent the loss of its functionality. Although some papers have reported and discussed the flexibility of the single barrier layer, relatively few reports have examined the mechanical durability of the organic/inorganic multi-layered structures [20–23]. As a result, the aim of this study was to investigate the mechanical flexibility of the organosilicon/SiO_x multi-layered structure. To do so, we engineered the residual internal stress in the entire barrier structure by altering each thickness of the organosilicon layer in the multi-layered structures in detail for the first time. The critical radii associated with the initiation of the cracks were determined in these multi-layered structures as they were bent by tensile strain, and these radii were compared to that of the single SiO_x films directly deposited onto the PET substrates. The flexible stability of these barrier structures was studied through the evolution of the WVTR for the PET substrates that had been coated with these barrier structures and then bent by different tensile strains. In addition, dynamic bending tests were conducted on these samples to confirm their reliability.

2. Experimental

The organosilicon/silicon oxide (SiO_x) multi-layered structures were deposited consecutively onto the 200 μm-thick PET and silicon substrates by a plasma-enhanced chemical vapor deposition (PECVD) system, using the tetramethylsilane (TMS) monomer and TMS–oxygen (TMS–O₂) gas mixture. The deposition pressure, rf power, and temperature were fixed at 13 Pa, 70 W, and 120 °C, respectively. The gas flow rate of the TMS monomer for synthesizing the organosilicon and SiO_x layers was fixed at 60 sccm and the gas flow rate ratio (TMS/O₂) of the TMS–O₂ gas mixture was controlled at 0.5. The thickness of the SiO_x film in the multi-layered structure was controlled at 300 nm to study the barrier property and flexibility affected by the thickness of each organosilicon layer in the pairs of the multi-layered structures. Fig. 1 shows a schematic cross-section of the 3-paired organosilicon/SiO_x multi-layered structure. The thickness of the organosilicon layer in each of the pairs of multi-layered structure ranged from 15 to 90 nm.

Film thickness was measured using a surface profile instrument (Dektak 6M). The residual internal stress, σ_f , in the multi-layered

structure as a function of the thickness of the organosilicon layer deposited onto the silicon substrate was derived from the Stoney formula expressed as [20]:

$$\sigma_f = \frac{E_s d_s^2}{6(1-\nu_s) d_f} \left(\frac{1}{R_f} - \frac{1}{R_0} \right) \quad (1)$$

where E_s , ν_s , and d_s are Young's modulus, Poisson ratio, and thickness of the substrate, respectively. d_f is the total thickness of the multi-layered structure. R_0 and R_f are the radii of the sample curvature before and after depositing the multi-layered structure measured by the beam-bending method using a thin film stress measurement instrument (FLX-2320, Tencor). Because the surface of the substrate must be reflective for the incident beam, we used the silicon substrate as a substitute for transparent PET substrate to evaluate the internal stress in the barrier structure. Even though the values of the residual internal stress for these structures deposited onto the silicon substrate undoubtedly were different from the values derived from the structures deposited onto the PET substrate, they exhibited the same evolution of the curvature as confirmed by the surface profile observation. This implied that the discussion of the evolutions of residual internal stress derived from the barrier structures deposited onto the silicon substrate was reasonable. The adhesion behavior between the barrier coating and the PET substrate was evaluated by the American Society for Testing and Materials (ASTM) D3359 Scotch® standard tape-peeling test [21]. The fracture behavior associated with the onset and development of the cracks in these barrier structures under static tensile strain, which was examined using a simple-support bending facility of collapsing radius test, was monitored in-situ using an optical microscope. Also, dynamic bending tests were conducted using the universal testing machine (JIA-802PC) controlled at an external force of 0.5 kg and a bending speed of 100 mm/min at a curvature of 20 mm. The water vapor permeation of the coated samples was measured using a WVTR measurement system (MOCON Inc., PERMATRAN-W 3/61) at a temperature of 40 °C with 95% RH. For the barrier structures with permeation below the MOCON test limitation (i.e., WVTR < 10⁻³ g/m²/day), a calcium (Ca) degradation test under the same environment was conducted to evaluate the WVTR by observing the percentage of the area in which the color was changed within the dimensions of 15 × 15 mm using an optical microscope.

3. Results and discussion

The evolution of the residual internal stress and the WVTR of the 1-paired organosilicon/SiO_x multi-layered structure (i.e., 300 nm-thick SiO_x barrier film deposited onto various thicknesses of organosilicon layers) is shown in Fig. 2(a) (the values of the single SiO_x film deposited onto the substrate are also given for comparison). The internal compressive stress in the SiO_x film (approximately 498 MPa) could be balanced effectively by inserting the organosilicon layer (hereafter referred to as the first organosilicon layer). The residual internal stress of the organosilicon/SiO_x multi-layered structure was optimized at -90 MPa for the SiO_x barrier film deposited onto a 30 nm-thick organosilicon layer. This 1-paired multi-layered structure coated onto the PET substrate exhibited the lowest WVTR value of 0.28 g/m²/day whereas the 300 nm-thick SiO_x film directly deposited onto the PET substrate produced a WVTR of 0.38 g/m²/day. However, the internal compressive stress of the 1-paired multi-layered structure was increased when the thickness of the organosilicon layer was greater than 30 nm, which also resulted in the degradation of the barrier performance. The mechanism responsible for the enhancement of the barrier performance of the SiO_x film by inserting the organosilicon layer has been ascribed to the increased density of the packing and the improvement of the structural quality of the SiO_x film that was deposited onto the organosilicon layer with its abundance of C–H groups [19]. In addition, since single organosilicon layers with thicknesses of 15, 30, and 60 nm that were

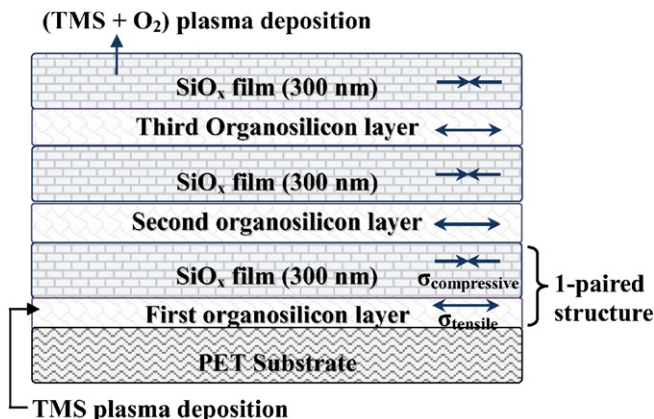


Fig. 1. Schematic cross-section of the 3-paired organosilicon/SiO_x multi-layered structure.

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