Enhancement of the barrier performance in organic/inorganic multilayer thin-film structures by annealing of the parylene layer

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ABSTRACT

A multilayered barrier structure was fabricated by chemical vapor deposition of parylene and subsequent plasma-enhanced chemical vapor deposition of SiO_x or SiN_x. The barrier performance against water vapor ingress was significantly improved by annealing the parylene layer before the deposition of either SiO_x or SiN_x. The mechanism of this enhancement was investigated using atomic force microscopy, Raman spectroscopy, and X-ray diffraction. The surface roughness of the parylene before the deposition of either SiO_x or SiN_x was found to correlate closely with the barrier performance of the multilayered structures. In addition, removing absorbed water vapor in the film by annealing results in a lower water vapor transmission rate in the transient region and a longer lag time. Annealing the parylene leads to a large decrease in the effective water vapor transmission rate, which reaches $7.2 \pm 3.0 \times 10^{-6}$ g/m^2/day.

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1. Introduction

The rapid development of organic electronics is leading to a number of promising devices in the area of energy sources and conservation, while also advancing display technology, sensors, and thin-film transistors [1–3]. One obstacle to this development is the susceptibility of these devices to water vapor and oxygen, which are well-known to cause rapid degradation in many organic electronic devices [4–7]. To guarantee the minimum lifetime needed for commercialization, high barrier performance encapsulation materials and structures must be developed and have been the object of much experimental research. However, there is a dearth of comprehensive studies linking the characterization, modeling, and diffusion mechanism of water vapor through encapsulation materials. Such studies are necessary to advance the understanding of thin-film encapsulation and to find methodologies that greatly improve the performance.

A number of approaches to encapsulation have been developed, including the use of thin-film coatings, metal lids, glass, and the sealing of devices between two glass or plastic substrates treated with barrier films. Of the various encapsulation approaches, thin films have attracted the most attention due to their light weight, transparency, and high mechanical flexibility. To achieve high barrier performance using thin films, understanding the permeation mechanism through thin film is critical. It should be noted that the permeation mechanisms of water vapor in organic and inorganic thin films are different. The barrier properties of organic polymers have been investigated and are well-known [8–10]. The internal lattice structure of polymers is dynamic, such that the entanglement of polymer chains creates interstitial spaces that change with time. Water vapor permeates through these interstitial spaces, which are often short-lived and of varying size and geometry [8–10]. However, the permeation mechanisms in inorganic thin films are still under investigation. The permeation through a deposited inorganic thin film is expected to occur through macro and nano-scale defects, including interstitial spaces [8,9,11]. Hence, by applying an organic layer between the inorganic layers, defects in the inorganic film are interrupted and do not form continuous channels through the film structure. While it is known that this type of structure provides better barrier performance, the mechanism by which it is improved is not yet clearly understood. In this study, multilayered structures consisting of alternating SiO_x or SiN_x as an inorganic layer and parylene as an organic layer were fabricated by vacuum deposition. The barrier performance was investigated by determining the effective water vapor transmission rates (WVTRs) based on the Ca corrosion test. We also investigate how the inorganic and organic layers affect the barrier performance. It was found that annealing the organic layer before depositing the inorganic layer resulted in an improved barrier performance. The mechanism of this improvement was investigated by atomic force microscopy (AFM), Raman

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spectroscopy, and X-ray diffraction (XRD). In addition, the finite element method (FEM) was carried out to investigate the permeation rate, assuming the presence of absorbed water vapor before annealing and no absorbed water after annealing.

2. Theoretical background for diffusion through a multilayered structure

We consider the diffusion of water vapor through a multilayer consisting of n-component films. Each constituent film is formed of a different material with a different thickness, as shown in Fig. 1. Here, we provide the basic idea of this approach for water vapor flux in the steady state and transient region. A detailed derivation can be found elsewhere [5,12,13]. In this study, we assume that the properties of all the materials are independent of their concentration, and that the diffusion follows Fick's law. The concentration at the interface, λ, and the flux, J, are time dependent in the transient region, but they become independent of the time after the lag time has elapsed. In the steady state,

$$\lim_{t \to \infty} J(t) = J_{ss} \tag{1}$$

and J_{ss} (flux in steady state) can be written in the form of Eq. (3), derived from Eq. (2), which is the diffusion equation for 1-dimensional and steady state conditions,

$$\frac{d}{dx}\left(D_i \frac{dC_i(x)}{dx}\right) = 0 \tag{2}$$

$$J_{ss} = \lambda_1 \sum_{i=0}^{n} \frac{\frac{D_i}{L_i}}{\prod_{j=0}^{i-1} k_j} \tag{3}$$

where $k_j = S_i/S_{i+1}$. The length of ith component is described as L_i. Also, $C_i(x)$, D_i, and S_i are the concentration at position x, the diffusion coefficient, and the solubility coefficient of ith component, respectively. Similarly, time-dependent flux, $J(t)$ is in the form of Eq. (5), derived from Eq. (4), which describes 1-dimensional and transient conditions.

$$\frac{\partial C_i(x,t)}{\partial t} = \frac{\partial}{\partial x}\left(D_i \frac{\partial C_i(x,t)}{\partial x}\right) \tag{4}$$

$$J(X_n, t) = \left[\sum_{i=1}^{n} \{H_i\}^{-1}\left[\lambda_1 \right.\right.$$
$$-\sum_{i=1}^{n}\left\{\frac{1}{D_i}\left(\prod_{j=0}^{i-1}K_j\right)\int_{X_{i-1}}^{X_i}\int_{x}^{X_i}\frac{\partial C_i(x,t)}{\partial t}dxdx\right\}$$
$$\left.\left.-\sum_{i=1}^{n}\{H_i\sum_{b=i+1}^{b}\int_{X_{b-1}}^{X_b}C_b(x,t)dx\}\right]\right] \tag{5}$$

Where,

$$H_i = \frac{K_i}{D_i}\prod_{j=0}^{i-1}K_j \tag{6}$$

Hence, the total quantity of permeant, $Q(t)$, up to time t through a unit area can be calculated by integrating the transient flux, $J(X_n, t)$ from 0 to time t.

3. Experimental details

As previously reported, a multilayer consisting of alternating SiO_x or SiN_x, fabricated by plasma enhanced chemical vapor deposition (PECVD), and parylene, fabricated by chemical vapor deposition (CVD), were deposited alternately. PECVD-deposited SiO_x and SiN_x were used to investigate how the different properties of the inorganic layer affect the overall barrier performance in the multilayered structure. The process temperature for both PECVD and CVD was kept under 110 °C and room temperature, respectively, to remain compatible with organic electronic devices [14–16]. Detailed process parameters such as reactant flow rate, pressure, and radio frequency power can be found in other reports [5,6,17]. To investigate the impact of annealing parylene on the barrier performance, parylene was annealed in a PECVD chamber at 110 °C for 15 min before each inorganic layer deposition.

To investigate the barrier performance of multilayered encapsulation structures, Ca samples were prepared, including an interlayer as shown in Fig. 2. Here, we define these measurements as the "effective" WVTR because the Ca corrosion test cannot readily distinguish between oxidation by O_2 and H_2O. The basic concept of this method and detailed experimental set-up have been described previously [5,18,19]. The effective WVTR of the encapsulation structure can be determined by monitoring the conductance (G) of the Ca sensor as a function of time based on the equation below:

$$WVTR[g^{-1}m^{-2}day^{-1}] = -n\,\delta_{Ca}\,\rho_{Ca}\frac{d(G)}{dt}\frac{l}{w}\frac{M(H_2O)}{M(Ca)}\frac{Area(Ca)}{Area(Window)} \tag{7}$$

where n is the molar equivalent of the degradation reaction, which is assumed to be 2. All values in Eq. (7) can be found in a previous report [5]. Additional characterization of the films was performed to investigate any physical changes. The surface morphology and roughness of the films were characterized using AFM. A Dimension 3100 scanning probe microscope (Veeco) with tapping mode was used. Raman spectroscopy was employed to investigate the change in crystallinity due to the annealing of parylene. Raman spectroscopy was performed with a Renishaw InVia system using a 488 nm laser with a 3000 l/mm grating.

4. Results

The effective WVTRs for the SiO_x/parylene and SiN_x/parylene structures as a function of the number of dyads are shown in Fig. 3. The data show a clear trend of improving barrier performance with an increasing the number of dyads. For SiO_x/parylene, the effective
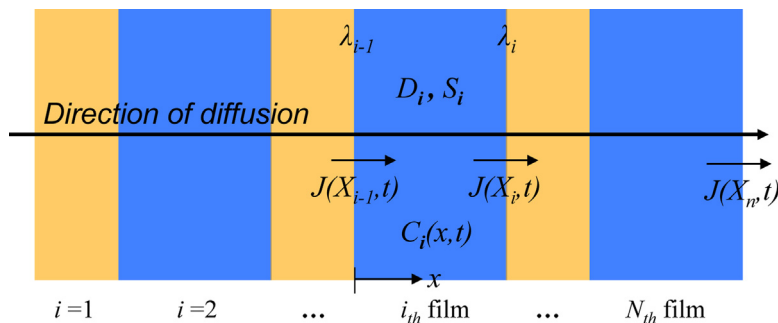

Fig. 1. Diffusion through a multilayer consisting of n layers showing the concentration, flux, and location notations.