

Self-assembled monolayers as a defect sealant of Al₂O₃ barrier layers grown by atomic layer deposition



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ARTICLE INFO

Keywords:

Self-assembled monolayers
Barrier layer
Flexible display
WVTR
Al₂O₃
Polymeric substrate

ABSTRACT

Self-assembled monolayers (SAMs) were applied to seal defects present in Al₂O₃ barrier layers fabricated on PEN substrate by plasma enhanced atomic layer deposition (PE-ALD), and the effects of the SAM in enhancing the barrier properties were studied. Pinhole defects of Al₂O₃ single layers were covered by SAM based on a 1-dodecanethiol (DDT) precursor. To investigate the formation of SAMs on Al₂O₃ layers, contact angle measurements and field-emission-transmission electron microscopy (FE-TEM) were employed. We found that the barrier properties of Al₂O₃ with SAM were significantly improved compared to those of Al₂O₃ single layers. The SAM/Al₂O₃/Ag/PEN multilayer structure showed a superior water vapor transmission rate (WVTR) less than $5.0 \times 10^{-5} \text{ g m}^{-2} \text{ day}^{-1}$ at 38 °C and 100% relative humidity, demonstrating its applicability for flexible displays. Mechanical stability was investigated using U-folding bending test. The WVTR of the SAM/Al₂O₃/Ag/PEN multilayer remained less than $5.0 \times 10^{-5} \text{ g m}^{-2} \text{ day}^{-1}$ after 25,000-cycles bending test using a 5 mm bending radius.

1. Introduction

For flexible optoelectronic applications including bending or folding, glass substrates should be replaced with plastic substrates such as polyethylene naphthalate (PEN), polyethersulfone (PES), polyethylene terephthalate (PET), or polyimide (PI) [1]. However, the fabrication of devices such as organic light emitting diodes (OLEDs) or organic photovoltaics on such flexible plastic substrates entails many problems. Especially, the permeation of water vapor and oxygen through these substrates can allow oxidization of the organic material in the flexible devices, deteriorating their performance and lifetime [2]. Commercial plastic substrates have very high water vapor transmission rate (WVTR) of about $1 \text{ g m}^{-2} \text{ day}^{-1}$; the WVTR is defined as the amount of water permeant diffusing through a fixed area under constant conditions [3]. To reduce the WVTR of substrates for flexible device applications, additional layers with excellent barrier performance are required. Barrier requirements depend on the type of device, but the WVTR for flexible OLED devices should be less than $10^{-6} \text{ g m}^{-2} \text{ day}^{-1}$ [4].

To achieve excellent barrier performance, one promising method is to use inorganic gas barrier layers fabricated by various deposition techniques such as sputtering [5], chemical vapor deposition [6], and atomic layer deposition [7]. However, when an inorganic layer

comprising a single component is deposited, nano- or microscale pinholes could be created due to the rough surfaces of plastic substrates and particles generated by process imperfections [8]. Such pinholes can deteriorate the performance of the gas barrier and thus worsen the mechanical properties of the inorganic layers [9]. It is well known that WVTR tend to decrease with increasing thickness of the inorganic barrier layer. However, this tendency is limited to a critical thickness because some pinholes remain regardless of the thickness of the inorganic layer [10]. To enhance the barrier properties of single-component inorganic layers, many research groups have focused on fabricating multilayer structures comprising alternating layers of single-component inorganic layers [2]. Also, including an additional organic layer between inorganic layers is expected to improved barrier properties by suppressing the growth of defects in the inorganic layers [8]. Acrylate [11] and epoxy [12] are desirable materials for fabricating the organic layers in organic–inorganic hybrid structures. However, the synthesis and/or coating processes for such organic layers are rather complicated.

Thus, the use of self-assembled monolayer (SAM) can be a simple alternative method to add an organic layer. In general, a precursor for the formation of SAM consists of three different parts: a head group that reacts with the substrate, an alkyl group that promotes the formation of a consistent monolayer, and a terminal group that determines the

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functions of the monolayer. Because the formation of such monolayers is not influenced by the shape and/or size of the substrate, the SAM method can be applied to substrates with various morphologies. Owing to this advantage, SAM have been studied in various fields including nanopatterning, surface modification, and organic electronic device fabrication [13].

In the present study, Al_2O_3 single layers were formed on PEN substrates using plasma enhanced atomic layer deposition (PE-ALD) process. The pinhole defects present in Al_2O_3 layers of various thicknesses were monitored. To evaluate the effect of SAM in sealing the pinholes, monolayers were fabricated from a 1-dodecanethiol (DDT) precursor and were confirmed using energy dispersive spectroscopy (EDS) elemental mapping coupled with field-emission-transmission electron microscopy (FE-TEM). Also, the barrier and mechanical properties of passivation layers including SAM were characterized in terms of WVTR and optical properties.

2. Experimental details

To investigate the effects of SAM in improving the barrier properties of inorganic layers deposited on PEN, we tested six different structures, as shown in Fig. 1. These structures were given the sample names of S1 (PEN substrate), S2 (8 nm Ag/PEN), S3 (SAM/8 nm Ag/PEN), S4 (40 nm Al_2O_3 /PEN), S5 (40 nm Al_2O_3 /8 nm Ag/PEN), and S6 (SAM/40 nm Al_2O_3 /8 nm Ag/PEN). Prior to their use to form various types of barrier layers, the PEN substrates were ultrasonically cleaned in isopropyl alcohol for 20 min and dried at 80 °C for 60 min in a convection oven to remove residual water.

For the S4, S5, and S6 samples, Al_2O_3 of 40 nm thickness was deposited by low-frequency PE-ALD using TMA and oxygen as precursor and reactant materials, respectively. The PE-ALD equipment used in this work has been described in our previous work [14]. Argon gas of 99.999% purity was flown into the reactor chamber at a flow rate of 500 sccm and produced a pressure of 0.4 Torr. Argon was also used as the carrier gas for the trimethylaluminum (TMA) precursor and as the purge gas after each cycle. The TMA precursor was kept at 20 °C throughout the deposition process, and all Al_2O_3 layers were deposited at a substrate temperature of 120 °C. Each cycle of the Al_2O_3 PE-ALD process consisted of a TMA injection pulse (1.0 s), an Ar purge (5.0 s), an oxygen pulse (4.0 s), and an Ar purge (5.0 s). A radio frequency (RF) plasma pulse that was capacitatively coupled with a low frequency plasma source was applied for 3.0 s only during the oxygen pulse in order to produce oxygen radicals. The RF plasma power and electrode-substrate distance were respectively fixed at 300 W and 50 mm [15].

For the S2, S3, S5, and S6 samples, an Ag layer of 8 nm thickness was deposited onto each sample by thermal evaporation at a constant deposition rate of 0.5 Å/s. For the S3 and S6 samples, the SAMs were formed using a DDT precursor ($\geq 98\%$, Aldrich Co., USA); these solutions were prepared according to a previously reported procedure [16]. DDT consists of an organosulfur head group that interacts with the metal substrate, a methyl end group that is exposed to the air, and a 9-carbon alkyl chain between the head group and the end group. To prepare the SAM solution, DDT precursor was added to anhydrous ethanol to a concentration of 5 mM, and the mixture was sonicated at room temperature for 10 min. The S2 and S5 samples were immersed in SAM solution at room temperature for 24 h. All processes were carried out in a nitrogen gas environment to avoid degradation of the SAM by exposure to water vapor in the air. The multilayer substrates were then removed from solution, rinsed with ethanol, and dried at 80 °C for 60 min in a convection oven to remove residual solvent.

The WVTRs for all samples were determined at 38 ± 1 °C and 100% relative humidity (RH) over a 48 h measurement period, using a AQUATRAN Model II (MOCON Inc., USA), which had a sensitivity limit of $5 \times 10^{-5} \text{ g m}^{-2} \text{ day}^{-1}$. Contact angles were measured using a contact angle measurement system (Phoenix 300, SEO Ltd., Korea). Deionized water was used as the test liquid, and contact angles were measured under the conditions of 26 °C atmospheric temperature and 40% RH. Barrier layer surface morphologies were imaged using an FE-TEM system (JEM-2100F, JEOL Ltd., USA), and their elemental compositions were determined by EDS (INCA X-Sight, Oxford Instruments, USA). Mechanical bending testing was carried out using a U-Folding test system (TCDM-111, YUASA, Japan). Sample optical transmittance was measured in the wavelength region of 350–780 nm by a UV/visible spectrometer (MCPD-3000, Otsuka Co., Japan).

3. Results and discussion

It is well known that single inorganic layers cannot satisfy the stringent barrier requirements of polymeric substrates for application in flexible electronics [17]. Due to the contamination that inevitably occurs during vacuum deposition, many defects are generated in single inorganic layers, which can allow the permeation of water vapor and oxygen [10]. In our previous work regarding single Al_2O_3 layers deposited on PEN substrates by PE-ALD, we found that WVTR decreased remarkably with increasing layer thickness [18]. However, no additional WVTR decrease was observed with increasing layer thickness beyond 20 nm, which was thus considered to be a critical thickness. These phenomena could be interpreted as arising from a defect-dominated permeation mechanism caused by pinholes. That is to say,

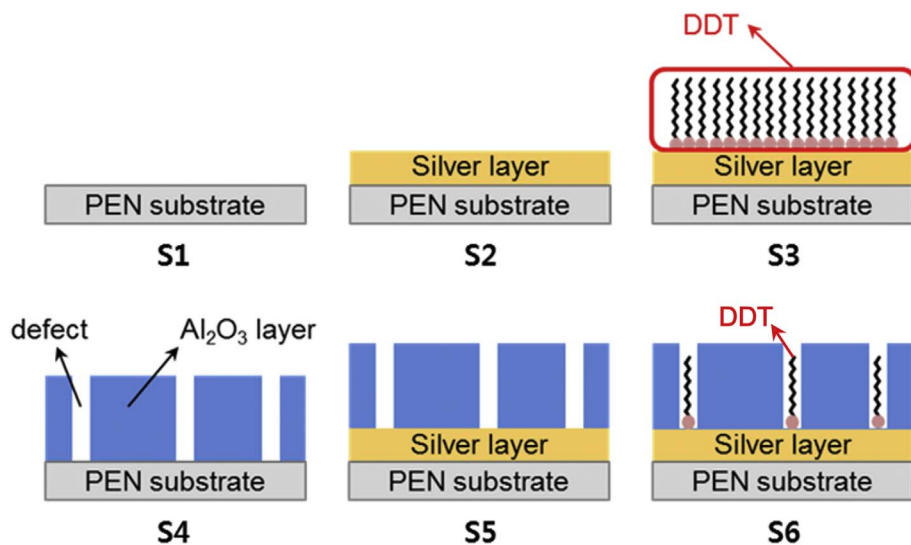


Fig. 1. Schematic diagrams of sample structures: (S1) bare PEN substrate; (S2) 8 nm Ag layer; (S3) SAM-treated 8 nm Ag layer; (S4) 40 nm Al_2O_3 layer; (S5) 40 nm Al_2O_3 layer deposited on an 8 nm Ag layer; and (S6) SAM-treated 40 nm Al_2O_3 layer deposited on an 8 nm Ag layer.

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