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Enhanced moisture-barrier property of a hybrid nanolaminate composed of aluminum oxide and plasma polymer

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ABSTRACT

Ultra-thin aluminum-oxide layers were grown by atomic layer deposition, and plasma-polymer layers derived from an n-hexane precursor were prepared by plasma polymerization. Hybrid nanolaminates were fabricated using one-cycle-grown aluminum-oxide layers and 50 nm-thick plasma polymer layers, and their moisture-barrier property was measured by an electrical calcium test. The moisture-barrier property of the hybrid nanolaminates was exponentially enhanced as the number of dyads increased, indicating that an ultra-thin single-cycle-grown aluminum oxide worked as a good moisture barrier. A 20-dyad hybrid nanolaminate composed of two-cycle-grown aluminum-oxide layers and 50 nm-thick plasma-polymer layers shows a water vapor transmission rate of 1×10^{-3} g/m^2 · day.

1. Introduction

A moisture barrier is required to protect organic devices such as organic light-emitting diodes or organic photovoltaic cells from the lifetime drop via oxidation of the devices with moisture. An aluminum oxide (AlO_x) thin film grown by atomic layer deposition (ALD) has been extensively studied for thin-film encapsulation, which utilizes a moisture-barrier layer directly on the surface of the organic devices, as it shows superior moisture-barrier property, and ALD deposits the thin film efficiently over a large area of the device surface [1–3]. One method to enhance the moisture-barrier property of a thin AlO_x layer is to form a multilayered structure composed of inorganic AlO_x and an organic material. The inorganic–organic multilayer structure can be obtained by dividing the inorganic layer into a number of thinner layers and inserting an organic layer between the inorganic layers. This multilayer structure enhances the moisture-barrier property due to the inserted organic layers by creating a more tortuous moisture permeation path through defects in the inorganic layers [4].

In this study, hybrid nanolaminates composed of ultra-thin inorganic AlO_x layers and organic layers were fabricated and studied to elucidate how much the moisture-barrier property could be enhanced from that of each constituent layer. We used a polymer that was polymerized with an n-hexane precursor in Argon (Ar) plasma as the organic-layer material. The plasma polymerization is advantageous since the vacuum plasma deposition is compatible with vacuum ALD of an AlO_x layer to simplify the sequential growth process [5].

One- or two-cycle ALD-grown ultra-thin AlO_x layer has never been utilized in any hybrid nanolaminate structure before since a common understanding is that there is an incubation period to obtain a linear ALD growth rate on polymer surfaces and so the layer does not form a closed layer. In this study, we showed that the ultra-thin AlO_x layer forms a closed layer and so works as a good moisture barrier by measuring cross-sectional transmission electron microscopy (TEM) and an electrical calcium (Ca) test, respectively.

2. Experimental

The substrate utilized in this study was polyethylene naphthalate (PEN) film (Dupont Teonex, Q65FA). The substrate surface with 0.7 nm root-mean-square roughness was ultrasonically cleaned with acetone, followed by isopropyl alcohol, methanol, and finally deionized water for 20 min each. In-house designed and built deposition equipment was utilized to deposit the AlO_x by the ALD process, with two precursors of trimethyl aluminum (TMA) and water, which were vaporized at 5 °C and room temperature, respectively. The deposition was carried out at a substrate temperature of 80 °C. The AlO_x growth cycle was composed of a TMA injection for 2 s, purging with Ar for

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10 s, water injection for 2 s, and purging for 10 s. One cycle produced 1.1 Å-thick AlO_x on average at that temperature.

Plasma polymerization was carried out with an inductively-coupled plasma reactor, which was a coiled Pyrex chamber. The tube was 60 cm long and 8 cm in diameter. The chamber was evacuated to 1.0×10^{-3} Torr prior to supplying the monomers. n-Hexane was used as the monomer with Ar as the carrier gas. The flow rates of the monomer and carrier gas were 10 and 30 sccm, respectively, and the radio-frequency input power was 50 W. The plasma polymers and AlO_x were grown sequentially and alternately to prepare the organic–inorganic multilayer structures.

Barrier performance was determined by an electrical Ca test using a 200 nm-thick Ca layer with an area of 1 cm × 1 cm. The Ca layer was deposited on a glass substrate such that the Ca layer was connected to two aluminum electrical leads. The Ca layer was then covered with barrier-deposited PEN film, the edges of which were sealed with a UV-curable epoxy resin (UV resin ZNR 5570; Nagase & Co., Ltd. Tokyo, Japan). Electrical conductance through the Ca layer decreased during the Ca test measurement as the Ca was oxidized and moisture was transmitted through the barrier film. All Ca tests were conducted at 85 °C and 85% relative humidity to accelerate the measurements. For TEM analysis (JEOL JEM ARM 200F), a 20-dyad hybrid nanolaminate structure composed of two-cycle-grown AlO_x layer and 50 nm-thick plasma-polymer layer was fabricated on a silicon wafer. Here, a dyad refers to a pair of AlO_x and plasma-polymer layers.

3. Results and discussion

Nucleation and the growth mechanism during AlO_x ALD on polymer substrates have been reported with the following conclusions [6]. An initial nucleation period exists prior to linear ALD growth on the substrates. At the initial stage of AlO_x ALD, the injected TMA reactant diffuses into the near-surface region of the polymer and is retained by being adsorbed. Reactions between TMA and water form small AlO_x clusters in the near-surface region. During 10–15 cycles of successive TMA and water exposure, these AlO_x clusters grew and eventually grew together to form a continuous AlO_x layer. The nucleation and growth model was proposed, based on quartz crystal microbalance measurements of AlO_x ALD on low-density polyethylene [6].

In our study, ultra-thin AlO_x ALD layers were prepared on a PEN substrate to understand the initial stage of the ALD. We measured the moisture-barrier property using the electrical Ca test with the ultra-thin AlO_x layers on the substrate obtained after one to nine ALD growth cycles. In the Ca test result shown in Fig. 1, the *y*-axis represents a reduction in electrical conductance through Ca until complete loss of the conductance when all Ca was oxidized with the moisture permeated through the AlO_x barrier on the PEN substrate. Therefore, the *x*-axis (time) represents the moisture-barrier property of the AlO_x barrier. A detailed description of the electrical Ca test can be found in the literature [7]. Unlike the aforementioned nucleation and growth model during AlO_x ALD on a polymer substrate [6], the barrier with one-cycle-grown AlO_x showed a better barrier property from that of a bare PEN substrate. Although the AlO_x layers grown with one to three cycles had a similar moisture-barrier property, the thicker AlO_x layers had a more enhanced barrier property whenever an AlO_x growth cycle was added. Thus, the ultra-thin ALD-grown AlO_x layer worked as a moisture barrier even with a thickness as low as that produced by one ALD growth cycle. As the typical AlO_x ALD growth rate was 1.1 Å/cycle, nine ALD cycles produced about 1 nm-thick AlO_x. However, we are unsure whether the actual thickness of the ultra-thin AlO_x in Fig. 1 was proportional to the number of cycles.

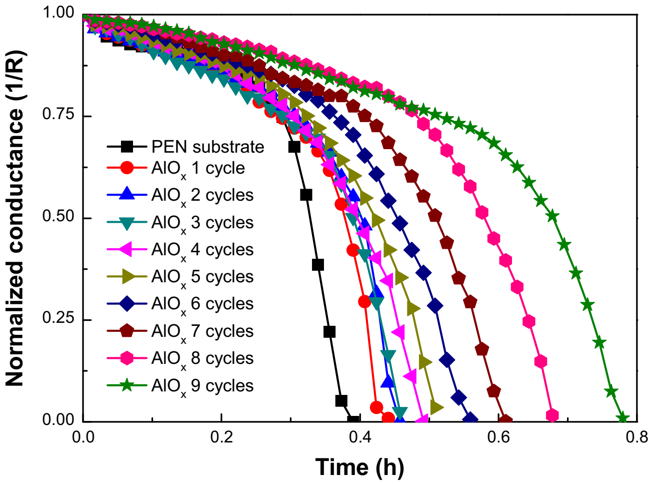

Fig. 1. Calcium test result of ultra-thin AlO_x layers grown by atomic layer deposition.

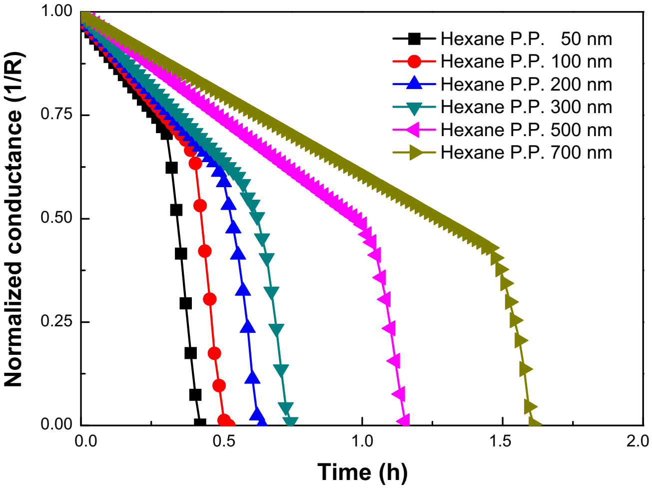

Fig. 2. Calcium test result of the plasma polymer derived from the n-hexane precursor by plasma polymerization.

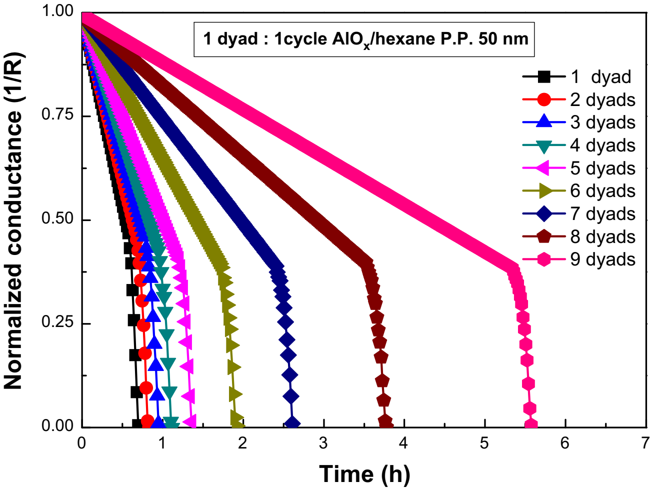

Fig. 3. Calcium test result of the hybrid nanolaminates composed of single-cycle-grown AlO_x and 50 nm-thick plasma polymer.

Fig. 2 shows the Ca test results for plasma polymer of various thicknesses derived from the n-hexane precursor. The hexane plasma polymer was grown on a PEN substrate. As the thickness of the plasma polymer increased, the moisture-barrier property accelerated. The Ca test result of the 50 nm-thick plasma polymer