Interfacial Engineering in Solution Processing of Silicon-based Hybrid Multilayer for High Performance Thin Film Encapsulation

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A seamless organic/inorganic multilayer in a structure as poly-dimethylsiloxane (PDMS)/SiO_x/SiN_y/SiO_xN_y we named as "PONT" was solution-processed at room temperature, by combination of two Si-based polymers, UV-curable PDMS, perhydropolysilazane (PHPS) and their photochemical conversion under irradiation of vacuum ultraviolet (VUV) light (λ = 172 nm) in an N_2-filled glovebox, as thin film encapsulation (TFE) for organic light emitting diodes (OLEDs). PDMS precursors diluted with decamethylcyclopentasiloxane (D5) was directly coated to OLED to form a protective layer. The presence of soft, elastic PDMS, its surface conversion to SiO_x to improve wetting, and compositional gradient created by VUV irradiation resulted in strong adhesion at the interfaces and relaxed strain to avoid cracks in ultra-thin and high density SiO_xN_y to serve as a perfect barrier. Remarkably low water vapor transmission rate < 3.5×10^{-3} $g/m^2/day$ under 40°C, 90%RH was confirmed for a single PONT as thin as 280 nm. Standardized OLED devices with triple PONT coatings have 528 h stability under accelerated (60°C, 90%RH) degradation tests, without formation of non-emissive dark spots in OLEDs.

＜INTRODUCTION＞

Solution-processing of thin film encapsulation (TFE) has been a long anticipated technology to realize cost-efficient flexible organic light-emitting diodes (FOLEDs), since only sized-limited devices are currently achieved with expensive multilayered TFE by complex vacuum processing. However, establishing a solution-based process to achieve high performance TFE for FOLEDs is a real challenge. The entire process needs to be carried out under inert gas and at low temperature in order not to damage the highly sensitive OLED device and also to be compatible with plastic film substrates. The selection of solvents for coating solution, especially for the primary layer to be directly cast onto the OLED device, must be carefully made since most common solvents for inorganic and organic precursors can immediately destroy the underlying OLED. However, some kind of activation process, else than heating, must be applied to convert the precursors into solid films. Also, the reaction needs to be fast and scalable to large area, in order to guarantee the advantages of solution processing.

In spite of the tremendous past efforts to look for materials and methods for solution processing of TFEs, water vapor transmission rate (WVTR) of even the best examples still stay somewhere around 10^{-2} $g/m^2/day$[1]. More importantly than speaking about the choice of the materials for their intrinsic barrier properties, how to fabricate perfectly continuous thin layers without pinholes and cracks becomes the highest challenge, as they provide fast pathways for gases to pass through [2]. Good adhesion of hard and brittle inorganic layer to soft and elastic organic layer is needed to relax strain and avoid formation of cracks [3]. Since it is almost impossible to achieve a perfect barrier in a single coating even by employing gas phase processing, multiple coatings of alternating stacks were always needed [4].

In this work, we report the recent developed solution-processed TFE. By engineering the structure of the multilayered TFE, a single coating in a structure as Polymer/SiO_x/SiN_y/SiO_xN_y (PONT) as thin as 280 nm has achieved a barrier performance to equal the conventional glass encapsulation in the stability tests employing the standardized OLED devices.

＜EXPERIMENTAL SECTION＞

Structure of the OLED devices with TFE was shown in Fig. 1a. Decamethylcyclopentasiloxane (D5)-diluted UV curable polydimethylsiloxane (PDMS) precursor was directly coated onto the entire devices as the primary protective layer [5].

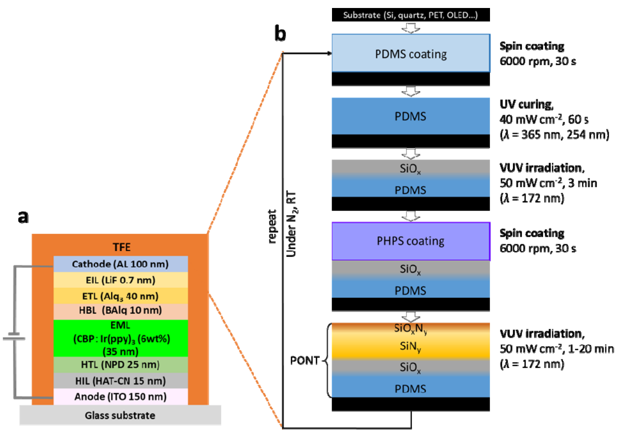

Fig. 1 (a) Structure of the OLED device with TFE; (b) Graphical flowchart to fabricate PDMS/SiO_x/SiN_y/SiO_xN_y (PONT) multilayer.

A multilayer in PDMS/SiO_x/SiN_y/ SiO_xN_y (PONT) structure could be fabricated through a sequence of PDMS coating, UV curing, vacuum ultraviolet

(VUV) reaction to convert the surface of PDMS into SiO_x, perhydropolysilazane (PHPS) solution coating, VUV reaction to convert PHPS into SiN_y and its surface into SiO_xN_y. The very surface to be coated with Si-based polymer solutions is always SiO_x to perfect the adhesion. Multiple coating of PONT is therefore easily achieved by simply repeating this sequence (Fig. 1b).

＜RESULTS AND DISCUSSION＞

A cross-section of three times PONT coating on Si wafer was observed by transmission electron microscope (TEM) (Fig. 2). The four layers are clearly recognized in each PONT structure from the differences in contrast, they are seamlessly attached as the composition gradually changes. The soft PDMS appears the brightest for its low density, whereas the outermost SiO_xN_y thin layer derived from PHPS appears as the darkest. Also, complimentary line profiles of energy dispersive X-ray spectroscopy (EDS) elemental analysis for Si, N, O and C clearly show the gradually changing composition within the PONT structure and their seamless stacks. Perfect adhesion of the layers without voids and cracks makes it very promising as a TFE.

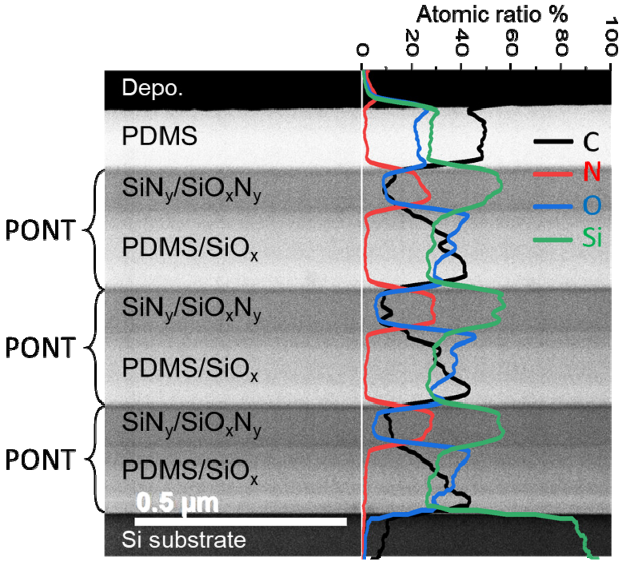

Fig. 2 Cross section TEM image and complimentary EDS elemental line profiles for Si, O, N and C of triple PONT coatings on Si and overcoated with PDMS.

Single and triple PONT TFE coatings were applied to OLED devices for stability tests, in comparison to those with $PDMS/SiO_x$ and the glass lid encapsulation. during constant current operation the device with a single PONT TFE shows gradually reduce its luminance to 80% of the initial value after 700 h, while the glass encapsulated device goes down to 76%. Microscope pictures of the entire emissive area of the OLED devices without and with respective encapsulations during accelerated degradation tests under 60˚C, 90%RH. The device with triple PONT coatings show almost no dark spots even after 528 h, while all others could not survive.

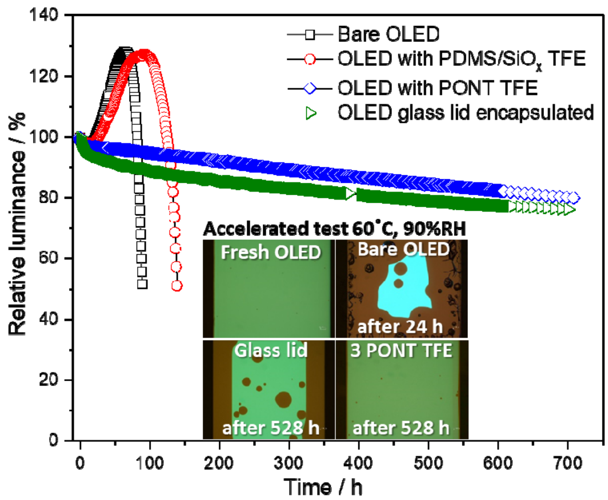

Fig. 3 Lifetime test under constant current operation of OLEDs with an initial luminance of 1,000 Cd/m^2 under ambient air (25˚C, 50%RH). Insert is microscope pictures of the entire emissive area (2.0 × 1.5 mm^2) of the OLED devices without and with respective encapsulations during accelerated degradation tests under 60˚C, 90%RH.

＜CONCLUSIONS＞

Combination of silicon based polymers of PDMS and PHPS as coating materials, and their photochemical conversion to $PDMS/SiO_x$ and SiN_x/SiO_xN_y by VUV irradiation made it possible to fabricate a totally seamless $PDMS/SiO_x/SiN_x/SiO_xN_y$ PONT structure. Interfacial engineering to convert the surface of PDMS to SiO_x was essential to improve the adhesion of the PHPS layer. The presence of soft and elastic PDMS as well as the gradient of composition by partial photochemical conversion by VUV were very important to relax the strain to avoid formation of cracks in the inorganic layer, especially for the outermost ultra-thin SiO_xN_y with the highest density. The defect free SiO_xN_y layer significantly contributed to blocking O_2 and water vapor to exhibit its high performance as TFE in spite of its limited thickness, as it already reached the level of glass lid encapsulation in the stability tests of standard OLED devices.

The outcome of the present study should be applicable for a variety of flexible organic devices because the PONT TFE can be fabricated directly onto sensitive organic materials. The entire process is carried out at room temperature and is solution-based, so that it might open the gate to roll-to-roll fabrication of large-area organic film devices at low cost.

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