Microelectronic Engineering 148 (2015) 17–20

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Effect of passivation layers by liquid phase deposition (LPD) on moisture and oxygen protection for flexible organic light-emitting diode (FOLED)

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ARTICLE INFO

Article history:
Received 17 June 2015
Received in revised form 22 July 2015
Accepted 25 July 2015
Available online 31 July 2015

Keywords:
Barrier layer
Silicon dioxide (SiO_2)
Liquid phase deposition (LPD)
Flexible organic light-emitting diode (FOLED)

ABSTRACT

In this study, the silicon dioxide (SiO_2) films coated on plastic substrate are used as the water barrier layer by liquid phase deposition method. The result revealed that the maximum refraction index is up to 1.43 after undergoing N_2 ambient annealing for 2 h. After permeation test, the OH group is slightly observed in the Fourier transform infrared (FTIR) spectra, indicating that the LPD-SiO_2 film could suffice for the requirement of a water barrier layer of flexible organic light-emitting diode (FOLED).

1. Introduction

In the past years, organic light-emitting diode (OLED) has attracted much attention due to the excellence advantages such as fast response time, self-emission and wide viewing angle. Generally, the OLED is produced on the rigid glass substrate in practical application. For satisfied the people's requirements that include thinner, lighter and smaller, the plastic substrate has to be used as the OLED substrate. In contrast with plastic, glass is very brittle, cannot be wound and is heavy, especially for large area display. These disadvantages can be overcome using flexible substrate that is robust, lightweight and cost effective. Thus, the flexible light-emitting diode (FOLED) is more suitable to fit in modern OLED.

Unfortunately, there is a critical thermal-stress problem at anode (usually use indium tin oxide (ITO) in OLED)/plastic due to the different thermal expansion coefficients (TECs). Besides, the plastic cannot tolerate the scrape on its surface, i.e., weak mechanical resistance and easily absorbs oxygen and humidity in contrast with common glass substrate [1,2]. Based on the above reason, the deposition of a buffer layer such as silicon dioxide (SiO_2) between ITO and plastic substrate is an essential technology for flexible OLED. However, the SiO_2 is considered as a gas barrier or a hard coat film. This buffer layer has been grown by various methods including thermal oxidation, plasma-enhanced CVD, liquid phase deposition (LPD), etc. [3–9]. Among these methods, the LPD process is the only method that works at room temperature so that there is a thermal-stress free interface. By this LPD method, the SiO_2 can be obtained not only on glass but also on plastic [5,10–12]. However, the permeation rate of a water vapor test of LPD-SiO_2 through the plastic substrate has not been studied in detail. Thus, this study extends prior study of LPD-SiO_2 growth on plastic with special focus on the permeation rate of a water vapor test.

2. Experimental procedures

LPD-SiO_2 films were deposited in a system equipped with a Teflon vessel, heater, controlled dripper for aqueous boric-acid (H_3BO_3) solution, magnetic stirrer and water bath. The starting solution is a commercial 34 wt.% hexafluorosilicic acid (H_2SiF_6) solution from which a saturated-growth solution with the H_2SiF_6 concentration of 3.09 M purchased from J. T. Baker in the USA was prepared. The silicic-acid powders ($SiO_2 \cdot xH_2O$) were added to saturate the solution and were thoroughly mixed by stirring for 6 h to ensure a saturated solution at room temperature. To ensure solution saturation, saturation solution can be examined by adding H_2O_2 to the solution and observing the color of the solution. After adding H_2O_2 to the solution, the unsaturated solution will appear clear, and the saturated solution will exhibit a yellow/gold color. The undissolved silicic acid powder was then filtered out through a 0.2 μm Teflon filter. H_2O is added into the solution to obtain a supersaturated solution of SiO_2. Then boric acid (H_3BO_3) is added to the

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http://dx.doi.org/10.1016/j.mee.2015.07.008
0167-9317/

solution to obtain a growth solution. The solution is stirred for 35 min after adding H_2O, and for 30 min after adding boric acid. At the end of this time, the supersaturated solution has become the growth solution. Description of the apparatus is shown in Fig. 1 and basic LPD equilibrium equations may be obtained from our previous studies [6,13].

The substrates were the norbornene polymer (ARTON, JSR Corp., Saitama, Japan). First, the substrate is exposed to oxygen plasma (15 sccm, 1×10^{-3} Torr) for 2500 s. Second, the substrate is etched for 36 h in potassium manganese ($KMnO_4$, 0.26 M), chosen in part due to the low cost and low toxicogenic characteristics relative to other etching materials such as silane. Third, the substrate is immersed in 36% H_2O_2 for 40 h for OH radical formation on the plastic surface, which will favor the growth of SiO_2. Finally, the substrates are washed in de-ionized (DI) water and dried in nitrogen gas, at which point they are ready for the LPD.

After the SiO_2 deposited on the ARTON substrate, the post-annealing is respectively carried out in 150 °C N_2 ambient for 2 h. Subsequently, the permeation of a water vapor test is performed at 105 °C and 50% relative humidity (RH) for 24 h. For the characterization of the LPD-SiO_2 films on plastic, the film thickness and refractive index were measured by an ellipsometer (FiveLab-Mary-102, Kanagawa, Japan). The chemical composition is also analyzed by Fourier transform infrared (FTIR, Perkin Elmer, Wellesley, MA). Transmittance in the visible region is measured by a UV–visible Spectrophotometer (Hitachi U-3310, Tokyo, Japan). Film-surface roughness is evaluated by atomic force microscopy (AFM, Burleigh, Fishers Victor, NY). The x-ray photoelectron spectroscopy (XPS, Redwood, CA) is employed to measure the chemical bonding after the pretreatment process.

3. Results and discussion

Fig. 2 shows the relationship of deposition rate versus different temperatures at fixed H_2SiF_6 concentration (0.4 M) and different H_3BO_3 concentrations (0.008, 0.01 and 0.012 M), which indicates that the thickness of the oxide films increases nonlinearly at higher temperatures. Besides, the increase of the refractive index implies that the oxide film has a denser structure. Further confirmation comes from the AFM micrograph of Fig. 3 showing the root-mean-square roughness of the oxide film. And then the root-mean-square roughness of the oxide film described on Fig. 2 averages 2.5 nm for the average thickness of the film being 220 nm according to ellipsometric measurement. The smooth surfaces obtained for LPD films are probably due to the denser structure of the films.

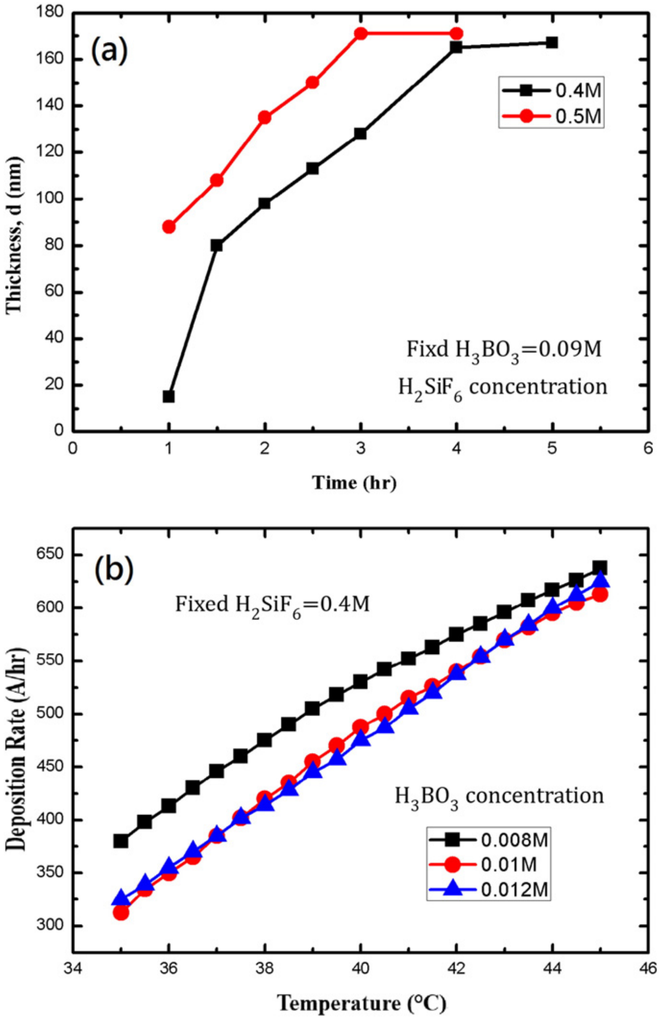

Fig. 2. The relationship of deposition rate and refraction index versus different temperatures at fixed H_2SiF_6 concentration (0.4 M) and different H_3BO_3 concentrations (0.008, 0.01 and 0.012 M).

Fig. 4 shows typical C (1S) XPS spectra for the ARTON surface without pretreatment, and for oxygen-plasma-plus-etching pretreatment. These spectra show a major peak at the CH_2 binding energy (284.4 eV) and a minor peak near the binding energy for C–O (286.4 eV). The most sharply defined minor peak is seen for the non-pretreated substrate. After oxygen-plasma treatment plus $KMnO_4$ etching, the binding energy of the 286.4 eV peak is shifted 0.1 eV to the right, 286.3 eV, and a new peak is observed at the COO binding energy of 288.4 eV. This behavior is presumed to be due to the presence of

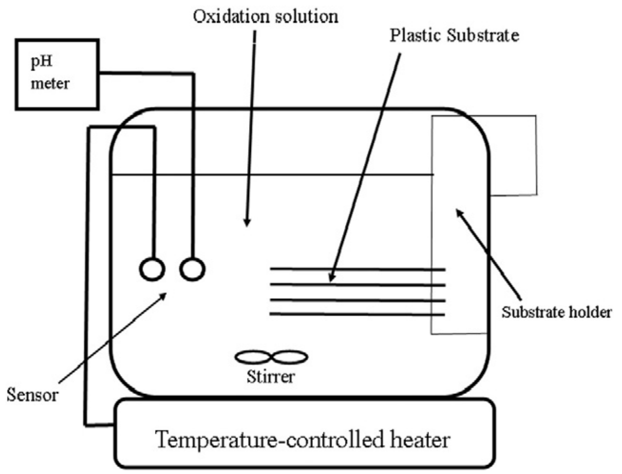

Fig. 1. The schematic diagram of the apparatus for LPD-oxide.

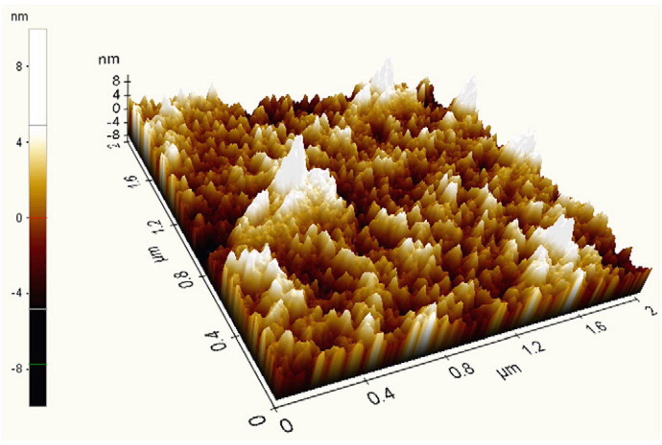

Fig. 3. The atomic force microscopy (AFM) images of LPD oxide.