Organic Electronics 53 (2018) 325–331

Contents lists available at ScienceDirect

Organic Electronics

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

Preparation and characterization of SiN water-vapor permeation barrier coated by aerosol-type liquid precursor delivery system equipped on a cyclic chemical vapor deposition system

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ARTICLE INFO

Keywords:
Liquid precursor
Delivery system
Water vapor permeation barrier
Organic light-emitting diode
Water vapor transmission rate

ABSTRACT

The preparation and characterization of SiN thin films using an aerosol-type liquid precursor delivery system (LDS) for application as a water-vapor permeation barrier layer in organic electronic devices is described. The proposed LDS consisted of three major parts: 1) an aerosol generator that transformed the liquid precursor to an aerosol molecule using a piezoelectric ultrasonic vibrator, 2) a vaporizer that transformed the injected aerosol molecules to a vapor state, and 3) a vapor storage canister. The instant evaporation fraction and maximum evaporation mass rate were measured to be 98.3% and 2.55 g/min, respectively. The temperature in the vaporizer was stable, showing a 1 °C variation from the set temperature. As the LDS temperature increased, the evaporation mass rate also increased from 0.035 to 2.55 g/min. A 30 nm thick SiN layer was prepared to evaluate the performance of the LDS, which was attached to a cyclic chemical vapor deposition system. The prepared SiN layer had a smooth surface with no defects or pinholes; the root mean square surface roughness of the prepared SiN film was measured to be 0.185 nm, which is adequate to be used as encapsulation layers in organic electronic devices. The water vapor transmission rate through the 30 nm thick SiN layer was calculated to be 1.31×10^{-6} g/m^2/day by Ca-degradation test. The results indicated that the produced films meets the requirement for application as an encapsulation layer to protect the organic layer in organic electronic devices from water vapor penetration, especially in organic light-emitting diodes.

1. Introduction

Organic electronic devices are considered to be next-generation electronic devices (following the Si era) for certain applications [1–9]. Organic electronic devices such as organic light-emitting diodes (OLEDs) [1–3], organic solar cells (OSCs) [4–6], and organic field effect transistors (OFETs) [7–9] employ organic materials as the active emission layers, absorption layers, and channel layers, respectively. However, organic materials are vulnerable to water vapor and oxygen and need to be passivated to protect them from these elements [10–12]. A significant issue in the passivation of organic electronic devices is obtaining a low water vapor transmission rate (WVTR) to enhance the lifetime (of the organic material) by protection against water vapor penetration.

Organic electronic devices can be fabricated on flexible plastic or foldable substrates with low glass transition temperature and high WVTR value [13]. To obtain long lifetime and stable operation of organic electronic devices fabricated on plastic flexible or foldable substrates, it is critical to prepare a water vapor permeation barrier at an extremely low temperature, especially below the glass transition temperature of the plastic substrates used [13,14]. The barrier must have no defects or pinholes since these are diffusion paths for water vapor to penetrate the organic layer. OLED displays, and lighting sources require more stringent water-vapor transmission rates (WVTRs) close to 10^{-6} g/m^2/day and an oxygen transmission rate (OTR) of 10^{-3} cm^3/m^2/day [15].

The water vapor permeation barrier layer (passivation layer) is prepared in the form of an organic/inorganic hybrid layer, or an inorganic multilayer based on rigid glass substrate at a high temperature (above 250 °C) [16–19]. However, the high temperature thin-film deposition process may cause thermal damage to the underlying flexible substrate. In a flexible organic electronic device application, a thin-film passivation layer should therefore be prepared below the glass transition temperature of the flexible plastic substrates that are used.

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https://doi.org/10.1016/j.orgel.2017.11.040
Received 15 September 2017; Received in revised form 18 November 2017; Accepted 26 November 2017

To prepare the passivation layer using inorganic materials, a gas phase precursor has been used. It is challenging to obtain high-quality thin passivation layers using this precursor at temperatures below 100 °C. To overcome this issue, liquid precursors that are stable at low temperatures have been adopted with a corresponding liquid precursor delivery system (LDS). Conventional bubbler-type LDS has employed a carrier gas to inject the precursor, mist phase, into the process chamber. The carrier gas requires a certain flow-rate range, reducing the identification of optimal process conditions. However, thermal energy must be supplied to vaporize the liquid precursor during evaporation, causing degradation or decomposition on account of the constant addition of thermal energy. Bubbler-type LDS is further limited because it is not easy to use an air-sensitive liquid precursor.

An alternative to bubbler-type LDS is direct injection of the liquid precursor into a heated process chamber. This method is limited in terms of maximum evaporation mass rate, which is an impediment to mass production applications. Development of an LDS that can address the drawbacks of bubbler- and direct-injection-type LDSs is thus needed.

In the present study, we have developed an LDS that employs an aerosol generator with a piezoelectric ultrasonic vibrator instead of a bubbler- or a direct-injection-type LDS to prepare a highly efficient water-vapor permeation barrier for application as an encapsulation layer in an organic electronic device. Typical characteristics, such as ability to maintain a stable temperature, maximum evaporation fraction, and instant evaporation efficiency have been evaluated. A 30 nm thick SiN water-vapor permeation barrier layer was prepared using this LDS with a cyclic-chemical vapor deposition (C-CVD) system at 100 °C. The surface roughness, morphology, and water-vapor permeation barrier properties of this film were analyzed.

2. Material and methods

The aerosol-type LDS system consisted of three major parts: an aerosol generator, vaporizer, and a vapor storage canister, respectively presented in Fig. 1(a)–(d). Fig. 1 (a) shows a schematic diagram of the overall LDS with aerosol generator (Fig. 1 (b)), vaporizer (Fig. 1 (c)), and vapor storage canister (Fig. 1 (d)). Each part will be explained in detail subsequently.

The liquid phase precursor, which was stored in a canister, was transferred to the aerosol generator using a liquid mass-flow controller (LMFC). It was transformed to aerosol molecules using a piezo-type ultrasonic vibrator in the aerosol generator part, as shown in Fig. 1 (b). To effectively generate aerosol molecules, the liquid precursor was maintained at a constant level by interlocking the LMFC with a level sensor. When the volume of liquid precursor was reduced to a constant level, additional injection of liquid phase precursor was carried out by sending a signal from the level sensor. A piezo material (PZT) with frequency range 1.6–2.4 MHz was employed as the ultrasonic vibrator. The temperature in the aerosol generator could increase because of the continuous ultrasonic vibration, which could cause degradation of the liquid precursor. To avoid degradation due to thermal energy, the aerosol generator was cooled using a cooling jacket and maintained at room temperature.

The ultrasonic vibrator frequency should vary with the liquid precursor used because ultrasonic vibration might produce excess heat in the liquid precursor, which could affect its thermal stability owing to thermal damage. We have used an ultrasonic frequency of 1.6 MHz to generate hexamethyldisiloxane (HMDSN:$N[Si(CH_3)_3]_2$) aerosol molecules to prepare a SiN barrier layer. On the other hand, it was found that a frequency of 1.85 MHz was sufficient to generate an aerosol in the case of trimethylaluminum (TMA:$Al(CH_3)_3$) applied as an aluminum oxide barrier.

The transformed aerosol molecule was transferred from the aerosol generator to the vaporizer where the liquid-phase aerosol molecule could be changed to the gas phase. A gate valve between aerosol generator and vaporizer was installed for this purpose. Fig. 1 (c) shows a schematic of the vaporizer developed in our experiments. A rectangular-type heater block was diagonally positioned within the vaporizer with minimized spacing to maximize the volume of transformed gas phase precursor from the liquid-state aerosol molecule. Positioning and maximization of volume are depicted in Fig. 1 (c). A tungsten (W) heater block situated in a nickel (Ni) body was used in the vaporizer. The W heater block was electrically isolated by introducing MgO powder between them as electrical contact between them might occur in the form of electrical shorting. Feedthroughs were employed for electrode insulation.

It was critical to maximize the volume of the vaporized liquid precursor in the vaporizer because evaporation fraction efficiency determines the quality of the proposed LDS. Most of the aerosol molecules transferred from the aerosol generator could change to the gas phase by colliding with the W heater in the diagonally positioned Ni body.

The probability of transformed aerosol molecules colliding with the heater block was increased by positioning the heater block diagonally with minimum space. As the space between heater blocks was minimized, most of the transferred aerosol molecules were transformed to vapor phase. The temperature in the vaporizer was maintained to avoid reversion of the vaporized aerosol molecules to the liquid phase. The tungsten heater block was arranged diagonally to avoid this, The aerosol molecules transformed from the liquid precursor were effectively changed to the gas phase with instant evaporation fraction of 98.3%, which is explained below. The instant evaporation fraction was determined using the ratio of measured injection flow rate to the set injection rate.

As a final step, the vaporized gas phase liquid precursor was moved into vapor storage and injected into the process chamber when the injection signal was turned on, as illustrated in Fig. 1 (d). It was important to transfer the pure gas phase precursor into vapor storage. An isolation valve was thus installed between the vaporizer and vapor storage. To maintain constant pressure in the vapor storage, a feedback loop was installed with a pressure gauge. A mesh was also installed to vaporize a small fraction of the aerosol liquid precursor at the interface between the vaporizer and vapor storage canister. By introducing the mesh, the probability of transferred aerosol molecules being vaporized into the gas phase increased. The vaporized precursor was injected into the process chamber to prepare an SiN water vapor permeation barrier layer on the substrate with the carrier gas, by controlling the flow rate using a source mass flow controller. A bypass line was installed to exhaust un-injected vaporized precursor and carrier gas. The vapor storage canister was continuously heated above the critical temperature to prevent the gas phase precursor from reverting to liquid phase. The critical temperature was changed according to the transition temperature of the liquid precursor used, as with the frequency of the piezoelectric ultrasonic vibrator.

The proposed LDS was attached to a cyclic chemical vapor deposition (C-CVD) system to prepare a 30 nm thick SiN passivation layer at a temperature of 100 °C. Working pressure was maintained at 20 mTorr during SiN passivation layer deposition. To reduce defects and pinholes and get dense film of SiN, low working pressure (20 mTorr) was used. C-CVD system is a hybrid deposition system that has merits of the atomic layer deposition (ALD) and plasma enhanced chemical vapor deposition (PECVD) systems. In an ALD system, the precursor and reactant are fed into the process chamber separately with intermittent purge time. Ligand surrounding precursor is decomposed in the substrate by reactant that reaches the substrate and the plasma. In the C-CVD system, precursor and reactant were simultaneously injected into the chamber and mixed before reaching the showerhead system. Organic ligand decomposed twice in the C-CVD system. The first decomposition process occurred in the showerhead and the second one on the substrate with the aid of plasma. Details of the process parameters of C-CVD and the corresponding results are reported elsewhere [10,11].

Surface morphologies of the deposited layer were measured using