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Moisture barrier and bending properties of silicon nitride films prepared by roll-to-roll plasma enhanced chemical vapor deposition

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ABSTRACT

In this study, we demonstrated a single-layer silicon nitride (SiNx) film deposited on polyethyleneterephthalate substrate as a moisture permeation barrier film that reduced the water vapor transmission rate (WVTR). The SiNx film was fabricated by roll-to-roll, plasma-enhanced chemical vapor deposition (R2R-PECVD) in widths as large as 500 mm. The effects of the NH_3/SiH_4 flow ratio on the SiNx properties were investigated according to their refractive index, optical characteristics, film density, WVTR, and chemical composition. The durability of the flexibility of the SiNx film was investigated via outer/inner bending test and cyclic bending fatigue test. The SiNx film showed excellent thickness uniformity and optical properties. At the NH_3/SiH_4 flow ratio of 3, the SiNx film exhibited the highest film density and the best moisture barrier performances of 1.67×10^{-3} g/m^2·day. The results of the inner bending test showed that the flexibility of the SiNx film was excellent. The test results showed that the failure bending radius was 2 mm. The durable flexibility of the SiNx film was influenced by the internal residual stress and microstructure. After 10,000 cyclic inner-bending fatigue tests, no crack was observed, and the WVTR values were maintained below 2.0×10^{-3} g/m^2·day. These results indicate that the single-layer SiNx film fabricated with a simple R2R PECVD has a high potential as a moisture barrier film for future flexible electronic applications.

1. Introduction

In recent years, the amount of research on manufacturing electronic devices using flexible substrates has increased significantly. Typical applications of flexible devices include organic solar cells, quantum dot displays, and organic light-emitting diode (OLED) displays [1–3]. In addition, there is an industrial need for devices fabricated on a polymer substrate because it enables efficient and inexpensive fabrication techniques, such as roll-to-roll (R2R) processing [4–6]. Because all polymer substrates can permeate small gas molecules, such as water vapor and oxygen, it is necessary to prevent the penetration these molecules into flexible devices that are manufactured using polymer web, which is generally referred to as the permeation barrier layer [7–10]. Permeation barrier layers have been used for several decades. In the early 1970s, thin opaque metallic films, such as aluminum, were commercially applied as permeation barrier layers on polymeric substrates for food packaging [11, 12]. In recent years, inorganic transparent oxide coating films, such as silicon oxide and aluminum oxide on polymer substrates, have been widely used as permeation barrier layer in the field of flexible electronic devices [13–15]. So far, research had been focused on the barrier films with multilayer of inorganic and organic films by combining inorganic coating technology such as sputter, atomic layer deposition (ALD), plasma enhanced chemical vapor deposition (PECVD) and organic coating technology based on wet coating. [16–20]. In particular, the PECVD is to be one of the promising technologies for the production of high-quality permeation barrier film on an industrial scale because of its low temperature and effective adhesion to the substrate [21–24]. In organic–inorganic multilayer films, inorganic thin films play a major role as a moisture barrier. And organic films provide good mechanical flexibility and act to separate defects by providing longer diffusion paths of moisture through defects in the inorganic layers [19]. Therefore, a multilayer moisture barrier not only provides better mechanical flexibility, but also lowers the water vapor transmission rate (WVTR) [25, 26]. However, the processes for preparing a multilayer barrier for OLED devices can be complicated and expensive because of low throughput and high investment. Therefore,

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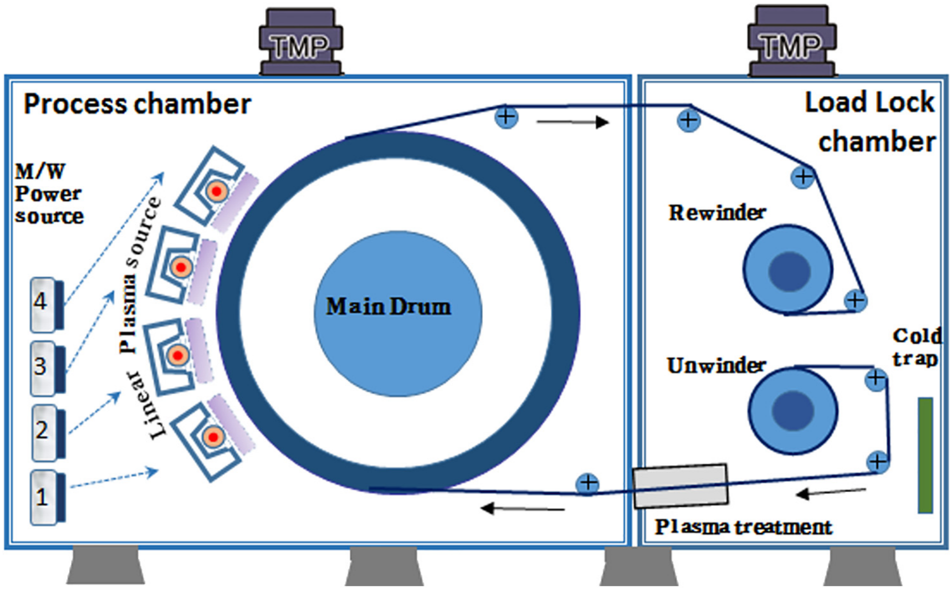

Fig. 1. Schematic illustration of the roll-to-roll PECVD system (roll coat 500 system).

Table 1
Process parameters used in the SiNx thin film deposition in this experiment.

Substrate	Polyethyleneterephthalate (PET) web with 100 µm thickness, 520 mm width and 500 M length
Gas chemistry	Ar + NH_3 + SiH_4
Deposition temperature	Maintained lower than 45 °C
Microwave power	0.5–3 kW, 2.46 GHz
Base pressure	Lower than 9 × 10^{-4} Pa
Process pressure	Lower than 9 Pa
NH_3/SiH_4 flow ratio (R)	R = 2–9

there is a growing demand for development of a single barrier layer [27]. However, research regarding the mechanical flexibility and WVTR of the single barrier film is still lacking.

In this study, we focused on the development of a barrier film with an inorganic single-layer structure, which would advantageous in mass production in the future. A silicon nitride (SiNx) thin film was developed as a barrier layer material by forming a high-quality single-layer thin film using pilot-scaled, R2R-PECVD equipment. The performance of the moisture barrier and the optical performance of the SiNx film were investigated as a function of NH_3/SiH_4 flow ratio. The flexible durability was measured using the outer/inner bending and cyclic bending fatigue test.

2. Experimental procedure

The single-layer SiNx for the moisture permeation barrier was deposited on polyethyleneterephthalate (PET, SKC) substrate that was 100 µm thick, 520 mm wide, and 500 m long. A pilot-scale R2R-PECVD system (Roth & Rau AG, Roll Coat 500 system) was used to fabricate SiNx film on PET web for large-scale production. As shown in Fig. 1, the R2R-PECVD system consists of two main chambers: ① a process chamber including a main drum with adjustable temperature and four linear microwave plasma sources each with a gas shower head for injecting source and process gases such as NH_3, SiH_4, argon (Ar), NF_3; ② load lock chamber, including unwinding and rewinding systems, a cold trap for moisture removal, and plasma pretreatment equipment with an RF generator.

In order to form high-quality microwave plasma, a high voltage (over 3 kW) supplier with a 2.46 GHz microwave generator was used as a power source. One advantage of the microwave PECVD process is its ability to control precisely the coating composition by simply changing the feedstock gas mixture. Hence, we could easily control the chemical and mechanical properties of the deposited film. SiH_4 and NH_3 were used as reaction gases, and Ar was used as the diluent gas. The total flow rate of SiH_4 + NH_3 was maintained at 930 sccm, and the Ar flow rate was kept at 900 sccm. In order to achieve a stable plasma condition with a dimension of 500 mm in width, the microwave power that was applied to the copper (Cu) antenna in the quartz tube was controlled. The effects of the NH_3/SiH_4 gas on the physical and mechanical properties and moisture barrier performance of the SiNx film then were investigated by varying the ratios of the gas mixture. The detailed conditions for the fabrication of the SiNx barrier films are described in Table 1.

The cross-sectional film structure was measured using a field emission scanning electron microscope (FE-SEM; Tescan Mira 3 LMU FEG). The optical properties, such as transmittance and haze, were measured in the wavelength range of 300–900 nm by spectrophotometer (U-4100, Hitachi). The refractive index of each layer was determined by spectroscopic ellipsometry (M-2000, J. A. Woollam) using the Cauchy model. X-ray reflectivity (XRR, Rigaku, Globalfit) with Cu 2 kW was used to investigate the film density. The chemical compositions and bonding configuration were investigated using a Fourier transform infrared spectrometer (FT-IR, Bruker IFS-66/S, Bruker) in the mid infrared region (400–4000 cm^{-1}). To eliminate complicated and overlapped peaks originating from the PET, intrinsic silicon wafers (polished both sides) were used as substrates for film deposition in the infrared measurements. To determine the [N]/[Si] ratio for film stoichiometry, an equation with a refractive index of 3.3 for a-Si:H and 1.9 for a-Si_3N_4 was adapted assuming that the hydrogen bonding was ignored [28].

$$x = \frac{[N]}{[Si]} = \frac{4}{3}\frac{n_{a-Si:H} - n}{n + n_{a-Si:H} - 2\cdot n_{a-Si3N4}} = \frac{4}{3}\frac{3.3 - n}{n - 0.5} \tag{1}$$

The mechanical flexibility and durability of the SiNx barrier film were evaluated by outer/inner bending and cyclic bending fatigue tests using a lab-made tester. In the outer bending, the SiNx barrier layer was placed with the SiNx barrier layer side outwards (⌒) and subjected to tensile stress under bending. In contrast, the inner bending test, in which the sample is bent into a concave shape (‿), induces compressive stress on the SiNx barrier film. The bending test was performed from a flat position to a decreasing bending radius. The cyclic bending