ARTICLE IN PRESS

Surface & Coatings Technology xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Surface & Coatings Technology

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

Roll-to-roll deposition of silicon oxynitride layers on polymer films using a rotatable dual magnetron system

Anika Himmler[a,*], Matthias Fahland[a], Volker Linß[b]

[a] Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology FEP, Winterbergstr. 28, 01277 Dresden, Germany
[b] VON ARDENNE GmbH, Am Hahnweg 8, 01328 Dresden, Germany

ARTICLE INFO

Keywords:
Silicon oxynitride
Roll-to-roll
Magnetron sputtering
Rotatable magnetrons

ABSTRACT

High performance permeation barrier coatings are usually multilayer stacks consisting of inorganic and organic layers. Besides the water vapor transmission rate, the optical properties of such layers have a high importance. This contribution focuses on the deposition of silicon oxynitride as an inorganic layer. This material attracts a widespread interest due to its varying refractive index depending on its oxygen and nitrogen content. The experiments were carried out in a roll-to-roll coating machine using a rotatable magnetron system. The layers were deposited by reactive pulse magnetron sputtering using targets of 1 m length. It was established that the ratio of oxygen to nitrogen in the layer was not only determined by the reactive gas mixture but also by the chosen set point of the closed loop control. Both the Secondary Ion Mass Spectrometry and the Glow Discharge Optical Emission Spectroscopy measurements revealed a vertically different composition of the SiO_xN_y layers. This could be supported by the simulation of the optical properties of the layers.

1. Introduction

Organic electronic devices, like light emitting diodes (OLEDs) or organic photovoltaics (OPV) are sensitive to reactive gases like water vapor and oxygen. These gases lead to a degradation of either the metal anode or the organic materials [1–4]. Therefore it is inevitable to protect the devices from the ambient atmosphere. Flexible devices made on polymer films deserve special attention. They are very interesting for applications in mobile or wearable technologies. However, the polymer substrates themselves are permeable for the above-mentioned gases. Therefore transparent protective layers need to be deposited on the polymer film surface in order prevent the permeation [5]. Various materials have been tested for such kind of barrier layers. Common inorganic barrier layers are for example aluminum oxide [1,6–10], silicon oxide [1,3,11–14], silicon nitride [2,15,16] and zinc tin oxide [1,7,13,17]. However, it has turned out to be nearly impossible to achieve the necessary protection level by a single layer only. In case of OLED, the water vapor transmission rate (WVTR) needs to be in the range $< 10^{-6}$ g/m^2/day in order to ensure a lifetime of $>$ 10,000 h [5]. Single layers of the common inorganic oxides or nitrides materials achieve WVTR values in the range from 10^{-4} to 10^{-2} g/m^2/day. The major source of leakage are the defects in the layers which in turn often have their origins in imperfections of the polymer surface.

Various attempts have been made in order to overcome this difficulty. Special smoothing layers have been shown to decrease the defect level. Atomic layer deposition have been applied in order to cover the defects in a conformal way [18]. The most promising approaches have been the introduction of nanolaminate structures [10] or multilayer stacks consisting of inorganic and organic layers [5,6,19–21].

In a stack of polymer and Al_2O_3 layers, a WVTR in the 10^{-6} g/m^2/day range was demonstrated [22]. The WVTR of such stacks could be optimized by replacing Al_2O_3 by other layers like i.e. silicon nitride. However, the difference in the refractive indices between silicon nitride and the polymer layers can lead to disturbing optical interferences. Therefore, it is necessary to adjust the refractive index of the inorganic layer.

Silicon oxynitride (SiO_xN_y) is a material with an adjustable refractive index depending on its oxygen and nitrogen content [23–26]. Furthermore, this material shows good oxygen barrier properties [12,16,27–31]. Therefore it is an ideal candidate for the usage in multilayer permeation barrier laminates. This report focuses on the layer composition and the optical properties of the deposited layers.

There are different methods to deposit silicon oxynitride like chemical vapor deposition [24,28,32] and sputtering [23,25,30,33,34]. For the reactive sputtering with two reactive gases, there exists different ways to control the process. Sproul et al. [35] discussed several approaches of partial pressure control for a stable sputtering process. He

---

* Corresponding author.
E-mail address: anika.himmler@fep.fraunhofer.de (A. Himmler).

https://doi.org/10.1016/j.surfcoat.2017.11.032
Received 16 June 2017; Received in revised form 19 October 2017; Accepted 13 November 2017

Please cite this article as: Himmler, A., Surface & Coatings Technology (2017), https://doi.org/10.1016/j.surfcoat.2017.11.032

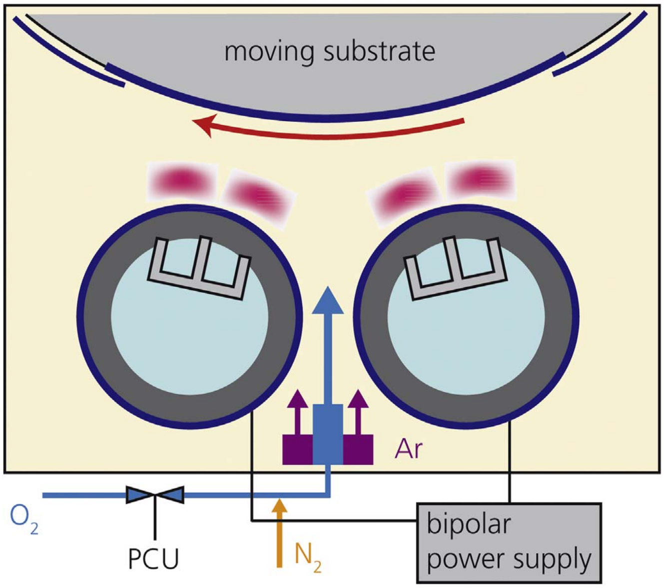

Fig. 1. Scheme of the deposition zone inside the roll-to-roll tool.

had shown that partial pressure control of both gases is required for successful stable and reproducible two-gas reactive sputtering.

Sputtering by rotatable magnetrons was used in the work reported in this paper. This is a method paving the way to potentially low production costs. The report focuses on the sputtering process and its influence on the layer composition and the optical properties of the silicon oxynitride layers. The permeation barrier properties will be presented in a future report.

2. Experimental

2.1. Roll-to-roll sputtering tool

The experiments were carried out in a roll-to-roll coating tool *coFlex® 600*. The details of the equipment were described elsewhere [36]. The SiO$_x$, SiN$_y$ and SiO$_x$N$_y$ single layers have been deposited by pulsed DC reactive magnetron sputtering using rotatable dual magnetrons (Soleras Ltd.). The arrangement can be seen in Fig. 1 showing the scheme of one deposition zone inside the roll-to-roll coating tool. Two undoped, plasma sprayed silicon targets (supplier: GfE FREMAT) were used, each having a length of 1000 mm. The substrate was a polyethylene terephthalate (PET, Dupont Teijin Films, Melinex 401, width: 600 mm, thickness: 75 µm).

The power supply was an *i*Puls®40 (Fraunhofer FEP). In this set of experiments, a fixed average plasma power of 10 kW was applied to each target. The system was operated in bipolar mode with a duty cycle of 9 µs on-time and 1 µs off-time for each half-cycle, resulting into a frequency of 50 kHz. Argon was introduced into the chamber by a mass flow controller (MKS instruments). The volumetric flow was kept constant at 200 sccm, corresponding to a partial pressure of 0.5 Pa.

2.2. Closed loop control system

In this paper, the discharge voltage was used as a reference value of the closed loop control for the reactive gas inlet. Thus the process could be stabilized in the transition mode. The flows of both oxygen and nitrogen were controlled by mass flow controllers. The channels for both gases were related to each other in a master/slave configuration. Thus it was ensured that the composition of the introduced reactive gas mixture was well defined. The variation of the ratio between the two reactive gases was achieved by changing the linking factor between the gas channels. The master mass flow controller was integrated in the closed loop feedback system.

2.3. Analytical methods

After the deposition, both the optical properties and the layer composition of the thin film coatings were analyzed. The transmittance and reflectance measurements were performed using a spectrophotometer (Lambda900, Perkin Elmer). The complex refractive index was simulated by the CODE software package (Theiss) using the optical data in the spectral range between 400 nm and 1500 nm.

The layer composition was measured by glow discharge optical emission spectroscopy (GDOES) [37] and secondary ion mass spectroscopy (SIMS). For the GDOES measurements, an argon plasma is ignited in front of the surface of the sample. In case of insulating samples, the process resembles a RF sputtering process. Sample atoms are removed by sputtering and subsequently pass the plasma zone. They are excited and contribute to the plasma emission spectrum. With a suitable calibration, the concentration of the elements in the sample can be determined by measuring the intensity of the element –specific emission lines. The GDOES measurements were performed using GD-Profiler 2 (HORIBA Jobin Yvon).

3. Results and discussion

3.1. Hysteresis and deposition characteristics

Oxygen and nitrogen were varied in the ratios 1:3, 1:1 and 3:1 of volumetric flow. The dependence of the target voltage on the reactive gas flow was measured for these mixtures. The experiments were complemented by the corresponding dependencies for pure oxygen as well as for pure nitrogen, resulting into a SiO$_x$ layer and a SiN$_x$ layer, respectively. The results are shown in Fig. 2.

The discharge voltage served as the reference point for the closed loop control, as described in the preceding section. It was possible to stabilize the process any set point along the displayed curves. For technical reasons only a part of the controlled oxygen hysteresis is pictured. The shape of the curves in Fig. 2 depend on the reactive gas composition during the sputtering process. The characteristic for pure oxygen was the only one showing the beginning of a clear S-shaped curve, as it is general typical for controlled reactive sputtering. With increasing nitrogen content the S-shaped effect disappears continuously.

For discharge voltage values of 330 V and below, all layers are absorption free with a absorption coefficient $k < 10^{-3}$ (open symbols

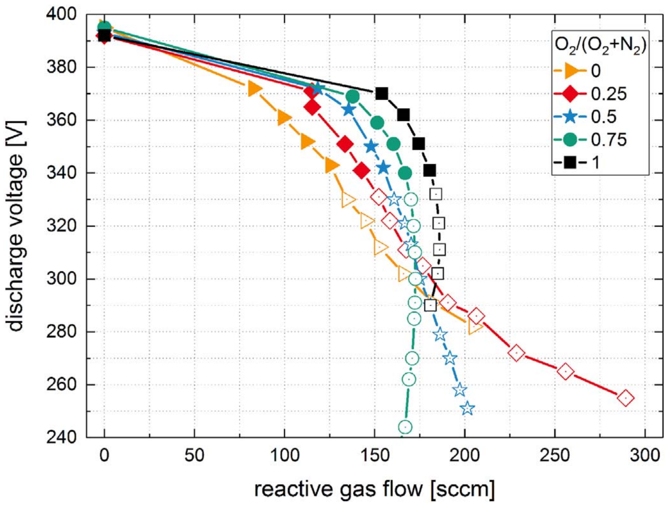

Fig. 2. Hysteresis with different reactive gas compositions. Open symbols indicates absorption free samples ($k < 10^{-3}$).