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Permeation barrier properties of thin oxide films on flexible polymer substrates

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ABSTRACT

Solar cells and organic electronic devices require an encapsulation to ensure sufficient lifetime. Key parameters of the encapsulation are permeation barrier, UV stability, temperature stability, optical transmission spectra and mechanical stability. The requirements depend very much on the specific application. Many work groups suggest multilayer stacks to meet the permeation requirements. In this paper the permeation barrier properties of the different constituents of such a multilayer stack are characterized. Different layer materials are compared regarding their water vapour and oxygen permeability as well as the influence of process parameters is examined. Finally temperature dependent permeation measurements are used to characterize the permeation mechanisms in the different constituents of the multilayer barrier.

1. Introduction

Compared to conventional panel devices, flexible displays and flexible solar cells not only have the potential to reduce the production costs by applying highly productive roll-to-roll coating processes, they also open new markets and applications. One major challenge on the road to new products is the encapsulation of such flexible devices. Therefore a lot of research has been done within the last 10 years to develop flexible encapsulation techniques. Many groups thereby focus on the barrier performance against the permeation of water vapour and oxygen. These gases lead to a degradation of the active absorber material and the transparent front electrode [1,2]. However, also the stability of the encapsulation against ultraviolet light (UV) and its thermal and mechanical stability play an important roll. This paper reviews the requirements for the encapsulation focusing on flexible terrestrial solar modules and introduces an all-in-vacuum roll-to-roll multilayer encapsulation concept that can be used for both direct encapsulation and producing a barrier foil. The concept is based on the combination of reactive dual magnetron sputtering and a magnetron based plasma enhanced chemical vapour deposition process (Magnetron-PECVD).

Permeation barrier and optical properties of sputtered barrier layers on polymer substrates are presented as the key part of the multilayer stack. The influence of the sputtering process parameters is investigated and temperature dependent permeation measurements are used to characterize permeation mechanisms in both the sputtered and the Magnetron-PECVD layers.

2. Requirements for encapsulation of flexible solar cells

2.1. Requirements and testing methods

Terrestrial photovoltaic modules are designed for a long-term use of at least 25 years. The international standard IEC-61646 [3] contains a comprehensive list of requirements that need to be fulfilled by photovoltaic modules. One of the most critical tests is the damp heat test, in which solar modules must be stored at 85 °C and 85% relative humidity for 1000 h. The efficiency of the modules must not fall below 95% of the original value after that test. Another strong test is the exposure to UV irradiation of the solar cells according to IEC-61345. The solar modules are exposed to UV light with the irradiance of 7.5 kWh/m^2 in the wavelength range between 280 nm and 320 nm and 15 kWh/m^2 between 320 nm and 400 nm.

Moisture causes a degradation of both the active absorber material and the transparent front electrode [1]. Organic solar cells also need to be protected against ultraviolet light. Therefore the key parameters for an encapsulation of flexible solar cells are:

- Barrier against permeation of water and oxygen.
- High optical transmission.
- UV stability and (depending on absorber material) UV absorption or reflection.
- Mechanical stability against bending and local mechanical impacts like scratches or hail.
- Thermal stability in a temperature range between −40 °C and +85 °C according to IEC-61646

The permeation barrier requirements are mainly determined by the solar cell absorber material that is used. The strongest requirements are set by organic solar cells. A water vapour transmission rate (WVTR) of 10^{-6} g/(m^{2}d) and an oxygen transmission rate (OTR) below

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10^{-3} $cm^3/(m^2d\ bar)$ are needed to avoid degradation of the organic semiconductor material [2].

3. Multilayer encapsulation concept

The common understanding of how permeation works is that the gas transport through inorganic layer takes place at layer defects (e. g. pinholes) [4–6]. The solid-state diffusion is several orders of magnitude lower and therefore negligible [7]. Because of that current research concentrates on minimizing the number and size of defects in a single layer or minimizing the effect of defects by making a multilayer stack. Single layer optimization has been done by various techniques, such as ion beam assisted sputter deposition or PECVD [7] or atomic layer deposition (ALD) [8]. WVTR values below 10^{-3} $g/(m^2d)$ have been reported in a batch process.

An advanced concept is based on a combination of at least two barrier layers and an interlayer to a multilayer stack (Fig. 1). The interlayer interrupts the growth of defects and increases the path of the permeating gas. This results in both lower steady state permeation and an increase of the lag-time of the permeation. Graff et al. demonstrated that with using a multilayer system the lag-time of the permeation can be extended to several years [9]. Also mechanical stress in the hard inorganic layers can be compensated by a much more flexible polymeric interlayer.

Often sputtering is used for the deposition of the barrier layers. The interlayer is commonly based on acrylate polymers that are deposited by a laquering [10] or flash evaporation process [11]. In such concepts completely different processes with different deposition conditions have to be combined. In [12] the multilayer barrier concept of the FEP was initially presented. The main difference to other approaches is that only magnetron processes are used to deposit the complete multilayer stack. The barrier layers are deposited using reactive dual magnetron sputtering, while the polymer-like interlayer is grown using the Magnetron-PECVD process presented in [12,13]. This allows an in-line deposition of the complete layer stack in one machine in adjacent deposition stations using the same process equipment.

4. Experimental setup

Single layer development was done in the laboratory scale roll-to-roll web coating machine labFlex® 200 (Fig. 2, see [12] for details). The machine can handle webs with a width of up to 220 mm. The web speed is adjustable between 0.1 and 20 m/min. Each of the three chambers in the machine, one winding (I) and two process chambers (II and III in Fig. 2), is pumped separately. The process chamber (II) contains a radio frequency plasma and ion source that can be used for substrate pre-treatment. Reactive pulsed magnetron sputtering and magnetron-PECVD are done using the dual magnetron sputter system (DMS) in the bottom chamber (III). The DMS consists of two equal rectangular magnetrons with a target area of 349.6×121 mm^2 each. Metal targets were used for the reactive sputtering. The magnetrons were switched alternately as cathode and anode using a mid-frequency pulsed power-supply (iPulse® by Fraunhofer FEP) with a

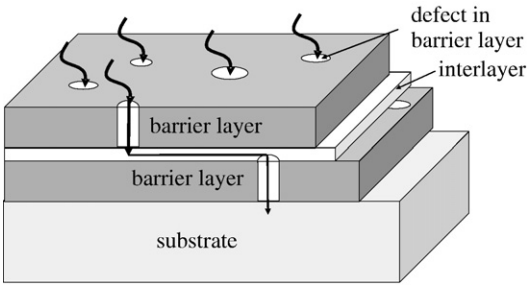

Fig. 1. Multilayer barrier structure consisting of at least two barrier layers and an interlayer.

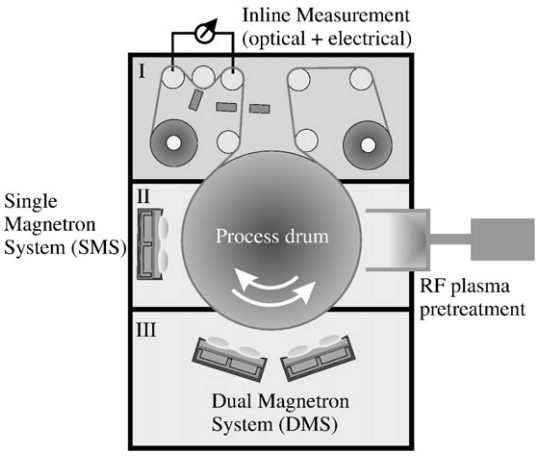

Fig. 2. Laboratory scale roll coater labFlex® 200 with the winding chamber (I), the middle deposition chamber (II) and the dual-magnetron chamber (III).

frequency of 50 kHz. The process gas was argon and the reactive gas oxygen. The oxygen flow during the sputtering process has been controlled by means of an optical emission detector (USB4000 spectrometer by Ocean Optics) in combination with a proportional-integral-differential-control unit (FEP PCU®) and piezo valves.

Fig. 3 shows the intensity of the metallic emission line of Al (396 nm) versus the reactive gas flow for the sputtering of aluminium oxide. In a metallic deposition mode ((1) in Fig. 3) this intensity is high and metallic layers are grown. At decreasing intensity setpoints the oxygen concentration in the layer increases. The preferred reactive working point ((2) in Fig. 3) is given by the highest intensity of the metallic line that allows absorption free transparent layers. In this transition mode the oxygen flow is decreasing slightly for lower intensity setpoints. In (3) the intensity of the metal line reaches a minimum and the oxygen flow is increasing again. The process is running in an oxide mode. The deposition rates are significantly lower compared to the transistion mode (2) and the metal mode (1). Further details about reactive sputtering have been published by Berg and Nyberg [14] in a comprehensive review article.

If not denoted differently all layers presented in this paper have been deposited at a reactive working point in transition mode (2). The layer thickness has been adjusted by changing the web speed. During all experiments the substrate temperature has been held near room temperature by cooling the process-drum with 20 °C cooling water.

Magnetron PECVD layers were deposited using the same dual magnetron system with titanium targets. The reactive gas flow was held at a fixed value. In addition to argon and oxygen the monomer hexamethyldisiloxane (HMDSO: $(CH_3)_3$–Si–O–Si–$(CH_3)_3$) was injected using a special MKS Mass Flow Controller.

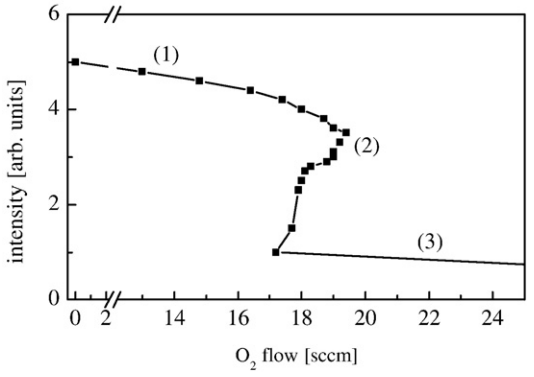

Fig. 3. Intensity of the aluminium metallic emission line at 396 nm versus reactive gas flow for the reactive sputtering of aluminium oxide. (1) metallic mode, (2) preferred reactive working point in transition mode, (3) oxide mode with poisoned target.