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The effect of argon plasma treatment on the permeation barrier properties of silicon nitride layers

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ABSTRACT

In this work we produce and study silicon nitride (SiN_x) thin films deposited by Hot Wire Chemical Vapor Deposition (HW-CVD) to be used as encapsulation barriers for flexible organic photovoltaic cells fabricated on polyethylene terephthalate (PET) substrates in order to increase their shelf lifetime. We report on the results of SiN_x double-layers and on the equivalent double-layer stack where an Ar-plasma surface treatment was performed on the first SiN_x layer. The Ar-plasma treatment may under certain conditions influences the structure of the interface between the two subsequent layers and thus the barrier properties of the whole system. We focus our attention on the effect of plasma treatment time on the final barrier properties. We assess the encapsulation barrier properties of these layers, using the calcium degradation test where changes in the electrical conductance of encapsulated Ca sensors are monitored with time. The water vapor transmission rate (WVTR) is found to be $\sim 3 \times 10^{-3}$ g/m^2·day for stacked SiN_x double-layer with 8 min Ar plasma surface treatment.

1. Introduction

Permeation of oxygen and water vapor into the active layers of organic electronic devices can lead to a serious deterioration of their performance. Permeation is therefore a serious problem for devices made on flexible plastic substrates which, unlike glass, have poor barrier properties. Thus for many devices such as organic light emitting diodes, organic solar cells and flexible displays that can be rolled up, the permeation barrier layers are absolutely necessary. The thin layers of transparent materials such as silica, silicon nitride or alumina which have high intrinsic impermeability are often used as barrier layers. Single layers of these materials often have pinholes through which water molecules (which are more reactive than oxygen molecules) can diffuse up to the organic device surface and thus deteriorate the device [1–3]. Due to that reason, more and more researches have been focused on minimizing the number and size of defects in a single layer or minimizing the propagation of defects by developing a multilayer stack [4]. Recently, almost defect-free layers were successfully deposited using the Atomic Layer Deposition (ALD) technique [5,6]. However, on the one hand this technique is extremely slow in terms of deposition rate; on the other hand the number of materials that can be deposited is limited [7]. An effective approach recently reported [7–11] is to deposit multilayers of organic/inorganic films because organic layers can absorb the stresses generated at the interface with hard layers when the devices are bent. This route seems particularly interesting if one is able to deposit both the organic and inorganic layers in the same reactor, which is not our case. We opted for the double-layer deposition of inorganic films (silicon nitride) using the Hot Wire Chemical Vapor Deposition (HW-CVD) method with a substrate temperature of 100 °C, to be compatible with the use of organic layers or flexible polymeric substrates (polyethylene terephthalate, PET) [12]. This deposition technique was chosen because, in comparison with the conventional plasma assisted CVD (PECVD) technique, the hydrogen concentration in the deposited layers is lower and conformal coverage is better [13]. Other advantages mainly result from the absence of ion bombardment during film growth, combined with a high efficiency of pyrocatalytic decomposition of the source gases, NH_3 and SiH_4, on the filament surface. Moreover instead of alternating hard layers (inorganic) and flexible layers (organic) we focused on the inorganic/inorganic interfaces and utilized an Ar plasma surface treatment after deposition of each SiN_x layer [14].

For the commercial use of organic devices fabricated on plastic substrates (PET), there is a wide range of permeation requirements depending on the used materials and final applications. Some recent studies demonstrate that the encapsulation of organic photovoltaic cells with barrier materials corresponding to a water vapor transmission rate (WVTR) in the range between 10^{-4} to 10^{-3} g/m^2·day (amount of water molecules diffusing through a unit area of the barrier film per unit time under conditions of the test) is sufficient to achieve lifetimes of several thousands of hours in operation [11,15,16]. The main characteristics required for the permeation barrier films are their high density, defect-freeness, good adhesion, thermal stability and uniform thickness.

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Moreover, high electrical resistivity, high transparency in the visible region, low residual stress and the ability to be deposited at low temperature are required for these thin-film materials [4].

The objective of this work is to study the barrier properties of thin SiN_x single-layer thin-films deposited by HW-CVD, either directly stacked on top of each other or piled up with an argon plasma surface treatment realized between two successive single-layers. In this work we have studied double-layers of SiN_x thin-films with and without Ar plasma surface treatment. The idea behind the use of the argon plasma surface treatment between two successive SiN_x single-layers is to make a break of the propagation of the pinholes from one single-layer to the other. In effect the plasma treatment makes an atomic rearrangement at the interface level [14], which increases the effective diffusion time ("lag-time" defined as the time required for the permeate to diffuse through the whole thickness of the barrier layer [16–18]) of the water molecules toward the organic device surface. We measure the WVTR values for SiN_x double-layers stacked on PET substrates, with and without argon plasma surface treatment and compare these values with WVTR values measured on uncoated PET substrates. The effect of high-frequency (13.56 MHz) Ar-plasma surface treatment on the WVTR of SiN_x double-layers is studied as a function of Ar plasma treatment times.

2. Experimental details

For HW-CVD a single coil shaped tantalum filament (*diameter* = 0.5 mm, *length* = 15 cm) is heated up to 2000 °C with a filament to substrate distance fixed at 7.5 cm. The filament is first heated up to the working temperature, in a hydrogen atmosphere, and then the source gases, NH_3 and SiH_4, are added. The working pressure is 25 mTorr for all SiN_x depositions. During the heating time, a shutter is moved to the closed position in order to protect the substrate from the spurious species emitted from the filament. The substrate temperature (T_{sub}) is fixed at 100 °C in order to be compatible with the plastic substrates. The substrate temperature is measured with a thermocouple embedded in a stainless steel substrate-holder, close to the substrate. This means that, especially for the depositions made nominally at 100 °C, the temperature of the film growing surface is certainly higher than the substrate-holder temperature due to the heating from the hot filament [12].

SiN_x single-layer films are optimized for their optical transmittance (T), refractive index (n) and deposition rate (r_d), in this order. We targeted highly transparent films in the visible and near infra-red region (transmittance > 80%) which are simultaneously dense ($n \sim 2$) and obtainable at a deposition rate, r_d, as high as possible. Highly transparent films are required for window layers in photovoltaic cells. A refractive index (n) of 2 means that the SiN_x films are dense and close to stoichiometry (as opposed to porous films which have lower n, and Si-rich films which have higher n but are not fully transparent). A high r_d is important for economic reasons in general and in this case in also avoiding long exposure of the plastic substrate facing the heated filament. Single-layers and double-layers of SiN_x thin films are obtained using optimized deposition conditions of 90% hydrogen dilution of silane and ammonia gaseous mixtures (here hydrogen dilution is defined as the ratio of hydrogen flow to the total gas flow) where the flow rates of hydrogen, ammonia and silane have been fixed at 54 sccm, 4 sccm and 2 sccm respectively; Ta filament current of 16 A, corresponding to a filament temperature of 2000 °C, which give films with transmittance, in the visible range, higher than 80%, $n \sim 2$ ($n = 2.01$ at 632.8 nm) and $r_d = 1.4$ Å/s. Due to the increase of the substrate temperature with time caused by the heated filament, the single-layer thickness was limited to 50 nm, which corresponds to 360 s of growth time, under the above described conditions. We note here that, compared to our previous work [12], the substrate-to-filament distance is now increased to 7.5 cm, in order to avoid excessive heating of the PET substrates which have a maximum working temperature of ~110 °C. Under these conditions we find that lowering the working pressure from 40 mTorr to 25 mTorr and using H_2 dilution of the reactant gases yields more dense and transparent films than could be obtained by using the optimized deposition parameters for the previous conditions where H_2 was not added [12].

In this study, we focused our attention on the surface compaction of the SiN_x single-layers by using Ar plasma surface treatment. The Ar-plasma treatment between successive SiN_x single-layers is carried out in a glow discharge chamber, where the sample is clamped to the top electrode and heated up to 100 °C and the bottom electrode is the rf-powered electrode. The sequence of SiN_x deposition and Ar treatment is performed without breaking the vacuum. This is achieved by moving the sample between two twin chambers connected by a gate valve.

The Ar treatment is performed at a working pressure of 50 mTorr and a power density of 350 mW/cm^2 using a 13.56 MHz rf-generator. The plasma treatment time is also varied (2, 5, 8, 10 and 15 min) in order to study its effect on the WVTR of the corresponding barrier structures. In this work we study the properties of SiN_x based-encapsulation systems consisting of two SiN_x single-layers (total thickness: 2 × 50 nm) either directly deposited one after the other or separated by an Ar plasma treatment performed during 2, 5, 8, 10 and 15 min.

The optical characterization of the layers is performed using the films grown on crystalline silicon wafers at the same substrate temperature (100 °C). The thickness of the single-layer film and the refractive index (n), are assessed by fitting the measured data of the UVISEL HORIBA Jobin Yvon spectroscopic ellipsometer measurements using the DeltaPsi2 fitting software tool. The dispersion relation for the dielectric constant used in the parameterization from which the film's optical constants are obtained, is based on the classical Lorentz dielectric function $\varepsilon(E)$:

$$\varepsilon(E) = \varepsilon_\infty + \frac{fE_0^2}{E_0^2 - E^2 + i\gamma_b E}$$

where ε_∞ is the high frequency dielectric constant, E_0, γ_b and f are, respectively, the resonance energy frequency, the line-width and the strength of the Lorentzian oscillator, related to the bound electrons.

The reflectance (R) and the transmittance (T) curves are measured using PerkinElmer Integrating Sphere on samples grown on PET substrate. The film characterizations are undertaken using the X-ray diffraction (XRD) and analysed with the system software. The surface roughness of the SiN_x single-layers as well as single-layers separated by Ar plasma surface treatments is measured using atomic force microscopy (AFM) technique.

To measure the water vapor transmission rate (WVTR) value, we use the electrical calcium degradation test [18–20] method implemented inside a glove box flushed with permanent nitrogen with less than 0.1 ppm of oxygen and water vapor. For the Ca degradation test, 100 nm Ca layer with an area of 1.13 cm^2 and aluminium contacts are deposited by thermal evaporation through shadow masks on the back side of the barrier coated PET substrates. The barrier coated substrates are degassed at 90 °C for about 6 h inside the glove-box prior to the Ca deposition. A low deposition rate of 0.2 nm/s (measured by using a calibrated quartz crystal microbalance near the substrate) and at a pressure of $<10^{-6}$ mbar is chosen to get a really smooth layer for both calcium and aluminium deposition. The Ca layer plus part of the Al contacts are then covered with a glass plate and the edges of which are sealed with epoxy resin (Nagase Chemtex Corp. XNR 5570). The resin is cured under a UV-lamp (365 nm wavelength) inside the glove-box. In order to check our sealing performance, the calcium test is also performed on a glass substrate (glass-glass sample). Therefore, the Ca layer is on one side of the barrier film and the other side is exposed to the environment (see Fig. 1). The calcium degradation test is performed under an ambient environmental condition. Water molecules in the environmental moisture after diffusing through the pinholes and defects inside the barrier, reach the calcium sensor and react with the sensor to form $Ca(OH)_2$ and thus reduce its conductivity.