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Deposition of transparent and flexible nanolayer barrier on standard coating materials for photovoltaic devices

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ABSTRACT

Hydrophobic layers are generated and chemisorbed onto standard coating materials for photovoltaic (PV) devices in order to improve their barrier properties against the atmospheric degradation agents and achieve a higher lifetime for the coated devices. The hydrophobic layers are deposited on PET–SiOx substrates using two different molecules (alkylsilanes and fluoroalkylsilanes) as precursors. High liquid barrier properties are achieved for the fluoroalkylsilane coated PET–SiOx, best results being average water contact angle >130° and average oil contact angle >90°. A chemical mechanism hypothesis is provided in order to explain the different reactive behavior observed for the PET–SiOx samples with alkylsilanes and fluoroalkylsilanes, respectively. Moreover, the oxygen barrier properties are significantly improved by the fluoroalkylsilane layer deposited in ethanol, that leads to a 70% reduction of the Oxygen Transmission Rate (OTR) compared to that of the uncoated PET–SiOx substrate.

1. Introduction

The economic viability of photovoltaic (PV) devices is strongly dependent upon equipment cost and durability. During their usage, these devices can be exposed to extreme weather conditions and thus they need to be protected by coatings and encapsulants. However, even such coatings and encapsulants can degrade over time due to weather conditions, leading to potential efficiency loss and damage of the photovoltaic devices [1]. In general, the coating degradation can be of the following types: thermal, oxidative, photoinduced, mechano-chemical, chemical, metal-catalyzed, and combinations of these [1,2]. Furthermore, also soil (e.g. dust, limestone) deposition [3] on the frontsheet surface can reduce the coating transparency and, as a consequence, the efficiency of PV devices.

Nowadays, the following main properties are basically required for solar cell coating materials to ensure PV device durability: UV, oxygen and water barrier [4], thermal stability, transparency, anti-reflectance [5], anti-soiling, flexibility, affordable cost, and electrical isolation [6]. Some of these properties are competitive ones. For instance, high barrier properties may be achieved by increasing the number of coating layers [7]. However, a higher number of layers normally increases the cost and reduces the coating transparency and flexibility [8]. In order to maintain a high efficiency during their lifetime solar cells require coating materials with several functions that are usually achieved with multilayer

coatings [9,10], in which one or more layers have a specific functionality, such as gas and moisture barrier [11,12], liquid barrier and self-cleaning properties [13]. A reduction of the number of layers would lower costs and also help to maintain a high transparency and flexibility.

An effective solution for overcoming these drawbacks is represented by a single layer transparent nanocoating showing at the same time two barrier functionalities, such as both liquid and gas barrier properties. This solution would allow us to reduce the number of coating layers necessary for the solar cell protection and thus would lower costs. Another important need for this nanocoating is related to the coating process conditions that should be suitable for a simple and low cost industrial upscaling.

As far as the liquid barrier coating is concerned, several methods are reported for obtaining hydrophobic or superhydrophobic surfaces. In general, these methods try to imitate the hydrophobic mechanism which can be observed on natural objects such as the lotus leaf (the so called "lotus effect"). The very high water repellence (superhydrophobicity) that is exhibited by the leaves of the lotus flower allows the dirt particles to be picked up by water droplets due to a complex micro- and nanoscopic architecture of the surface on which hydrophobic waxes are imposed. One of these methods for obtaining hydrophobic surfaces is represented by the Self Assembly of Monolayers (SAM) using precursor molecules with high hydrophobic properties in order to create protective nano-coatings. In particular, this method was applied by means of alkylsilanes and (fluoro)alkylsilane deposition on glass substrates [14] and successfully allowed us to obtain hydrophobic surfaces. Other methods that are employed to achieve

superhydrophobicity are based on the introduction of a two-scale roughness (micrometric and nanometric scales), together with chemical functionalization. An example is provided by the super-hydrophobic and low light reflectivity silicon surfaces prepared by (Au)-assisted etching to form nanoscale roughness and thereby form hierarchical structures by metal-assisted etching of micron-size pyramid textured surfaces [15], followed by surface fluorination with perfluorooctyltrichlorosilane (PFOS), and by heat treatment at 150 °C to complete the hydrophobic surface modification. Moreover, it is worth mentioning the use of nanoparticles (NPs) that has been imposing as an effective way to control the surface nanoroughness. A simple approach was recently demonstrated by dip-coating a 60 nm single layer of SiO_2 NPs onto an amine-terminated self-assembled monolayer (SAM)-coated glass/silicon oxide substrate, followed by perfluorosilane deposition [16]. Another method [13], proposed for creating transparent and superhydrophobic surface suitable for solar cell applications, is based on the coassembly of amine-functionalized silica NPs [17] of two different sizes (100 and 20 nm) followed by perfluorosilane deposition. This method [13] allows us to obtain very high hydrophobic properties and is applied on different substrates (glass, silicon, polyester materials). However, it is a multi-step process involving plasma treatment steps of the substrate surfaces as well as high temperature steps (>150 °C). As for the gas barrier properties of the hydrophobic layers of alkylsilanes and fluoroalkylsilanes deposited on PET–SiOx substrates, oxygen barrier improvements are reported [18], with an oxygen transmission rate reduction of 40%, as compared to the substrates without the hydrophobic layers.

Although the related works [13,15–18] report very interesting results in terms of achieved hydrophobicity on substrates potentially applicable to the solar cell sector, they are likely to turn out to be expensive and difficult to be implemented at an industrial level because they are based on multi-step processes, including complex and high temperature steps. Most of them do not include an analysis of the gas barrier properties of the hydrophobic coatings.

This study aims to develop a novel, flexible and transparent nanocoating, obtained by integrating into a single layer both liquid and gas barrier functionalities by means of a simple and effective single step process carried out at room temperature, specifically applied to standard coating bilayers for PV cells. The improved barrier properties against oxygen and liquid atmospheric agents are expected to guarantee higher lifetime for PV modules with higher flexibility and transparency and at lower costs.

The novelty of the proposed approach consists in the study of a single step room temperature process. To our knowledge, both gas and liquid barrier properties of the modified surfaces were not investigated in the literature except for reference [18]. However, the optical transparency properties were not analyzed in [18] and the obtained performances in terms of gas (O_2) and liquid barrier improvement were too moderate to be considered of interest for PV applications.

2. Materials and methods

2.1. Materials

The following reagents were used: 1) octadecyltrimethoxysilane (OTS) provided by Aldrich and 2) 1H,1H,2H,2H-per-fluoro-decyltrichlorosilane (FAS), provided by Alfa Aesar. The (fluoro)alkylsilane deposition experiments were carried out on flexible and transparent bilayer substrates of 12 μm thickness provided by AMCOR[1], composed of a polymer substrate (PET) with an inorganic coating (SiOx) layer of ~50 nm deposited with Electron Beam Evaporation. Anhydrous toluene (distilled) and anhydrous ethanol ($H_2O \leq 0.01\%$), provided by Sigma Aldrich were used as solvent, alternatively.

2.2. Deposition experiments for the preparation of nanocoated samples

The film samples of PET–SiOx were accurately cleaned before the deposition chemical reaction, in order to remove all the impurities from the SiOx surface. The cleaning procedure consisted of subsequent dipping cycles with toluene and distilled water with intermediate drying in N_2 flow. The deposition experiments were performed in a glass batch reactor where the substrate was placed. The glassware was preliminary flame dried in order to remove any trace of water vapor and subsequently a N_2 atmosphere was maintained in the reactor. For the reaction experiments two solvents were used, toluene and ethanol. In a first experimental phase, silane deposition was performed by immersion of the substrate samples (surface area from 10 cm^2 to 80 cm^2) in 80 ml of a 1% (v:v) solution of silane (for both OTS and FAS experiments) in distilled toluene and under anhydrous conditions. Subsequently, different reagent v:v concentrations (1%, 3%, 5%), as well as a different solvent (ethanol), were used for the FAS deposition experiments. The reaction was stopped after 12 h and the obtained samples were then cleaned by subsequent dipping cycles with toluene and distilled water with intermediate drying in N_2 flow. PET–SiOx substrates were also dipped for 12 h in the solvents without reagents, in order to investigate eventual solvent induced modifications. *Codes of the produced samples*: the produced samples will be indicated from now on in the text according to the following nomenclature: RZ–S, where: R is the reagent that can be OTS or FAS, Z is the v:v percent concentration of R in the solvent and S is the used solvent, that can be T (toluene) or E (ethanol). All the obtained samples are listed below according to the above defined nomenclature: OTS1-T, OTS1-E, FAS1-T, FAS3-T, FAS1-E, FAS3-E, FAS5-T, and FAS5-E. The samples obtained by dipping the substrates in the solvents – toluene and ethanol – without reagents are indicated with PET–SiOx-E and PET–SiOx-T, respectively.

2.3. Characterization of the nanocoated samples

FTIR (Fourier Transform Infrared Spectroscopy) measurements were carried out on the uncoated and coated samples in the range of 4000–650 cm using a Nexus ThermoNicolet spectrometer equipped with a SmartPerformer accessory for ATR analysis. The hydrophobic properties of the obtained samples were assessed by means of static water contact angle measurements, performed by depositing 5 drops of distilled water of 2 μl on each side of the sample and then calculating the average values for each side. Experimental measurements were performed with a First Ten Angstrom Analyzer System 32.0 (mod. FTA 1000) according to the standard test method [19]. The oleophobic properties were also preliminarily investigated by means of static oil contact angle measurements performed by depositing 3 drops of 2 μl of polyalphaolefinic synthetic oil PAO6 on each side of the sample and then calculating the average value for each side. The OTR measurements were carried out with the Permeabilimeter GDP-C 165 provided by Brugger at 23 °C and under oxygen flow of 80 ml/min [20]; measurements at higher temperature (35 and 45 °C) were also performed for studying a temperature range closer to the actual operating conditions of the PV devices. The transparency was evaluated by measuring the UV–visible transmittance of the nanocoated surfaces from 200 nm to 800 nm with the UV–Visible Spectrophotomer λ 800 Perkin Elmer. The surface morphology was characterized using a Nanoscope V multi-mode Atomic Force Microscope (Digital Instruments) and the root-mean-square roughness (Rq) values were calculated on scan areas of 5 μm × 5 μm with the Software Nanoscope Analysis of Bruker (version 1.40). The thermal characterization was carried out with a Mettler Differential Scanning Calorimeter (DSC30), performing a dynamic 10 °C/min rate heating scansion of the uncoated and nanocoated PET–SiOx samples from −100 °C to 300 °C, followed by an isothermal scansion of 5 min at 300 °C, by a subsequent cooling up to −100 °C and then by a second heating up to 300 °C (both at 10 °C/min). The heat of melting, ΔHm, and cold crystallization, ΔHc, were determined by integrating