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Broadband antireflective coating stack based on mesoporous silica by acid-catalyzed sol-gel method for concentrated photovoltaic application

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ABSTRACT

Silica multi-layer stacks have been designed with the aim to provide broadband antireflective (AR) properties for glass components in concentrated photovoltaic (CPV) application. Silica porous coatings were grown by combining acid-catalyzed sol-gel route and evaporation induced self-assembly (EISA) method with four types of organic/inorganic systems. Sols were prepared using tetraethylorthosilicate (TEOS) as inorganic precursor assembled with two di-block copolymers, one tri-block copolymer and one cationic surfactant as organic templates. Optical properties were characterized by ellipsometry and spectrophotometry while the material structure was analyzed by environmental ellipsometric porosimetry (EEP) and atomic force microscopy (AFM). The concentration of inorganic and organic phases was optimized and a broadband AR bi-layer stack was obtained providing a 7.2% (under the reference AM1.5 solar spectral irradiance) increase in transmittance over bare glass in the wavelength range 300–2000 nm when coated on both sides.

1. Introduction

Glass is extensively used in optical and optoelectronic applications such as lenses, screens, substrates for photodetectors, sensors and solar cells assemblies, due to its high optical transmission in a wide wavelength range of the solar spectrum, as well as its high thermal and mechanical stability and relatively low cost. These features justify its use in assembly systems whose application implies exposure to harsh environmental conditions (such as heat, ultraviolet radiation and corrosive media), and needs protection and insulation such as photovoltaic modules [1–3].

Particularly, concentrated photovoltaic (CPV) technology has the potential of becoming the large-scale generation of clean-renewable energy with competitive costs [4]. This technology is based on expensive high efficiency multi-junction III-V solar cells that can currently yield up to ~ 46% conversion efficiency [5] at cell level and 38.9% at module level [5,6], operating at light concentration levels up to 1000 × thanks to refractive or reflective cost-effective optical elements, which permit to reduce cell area. The III-V multijunction solar cells are active in a large part of the solar spectrum, and therefore, in order to harvest the full potential of the cells, the module design needs to optimize the optical transmission over the broad wavelength range of 300–2000 nm (broadband performance). An efficient and inexpensive optical design partly compensates the higher cost of multi-junction III–V solar cells [7].

Float glass with low iron content is commonly used for module protection to enhance radiation transmission towards solar cells [2]. However, although this glass exhibits high transparency, Fresnel reflection losses up to 8% [2] are produced at the interface, due to the difference between the refractive indexes of glass and the surrounding medium, generally air.

Antireflection effect between two media with different refractive indexes can be achieved by several approaches such as surface texturing [8,9], interference-type layer stacks by destructive interference of light reflected at different interfaces [10] and multi-layer stacks with graded refractive index structure (GRIN) [1]. Total reflection of the system can be minimized by adjusting the refractive index and thickness of each layer. For a GRIN structure system, depending on the application, antireflective (AR) multi-layer stack may consist of a single layer covering a narrow spectral bandwidth or multiple layers permitting to achieve a broadband optical performance [1].

The required value of refractive index of some the layers partaking in a AR multi-layer stack with GRIN structure needs to be very low and bulk materials cannot meet this criterion. An alternative way is based

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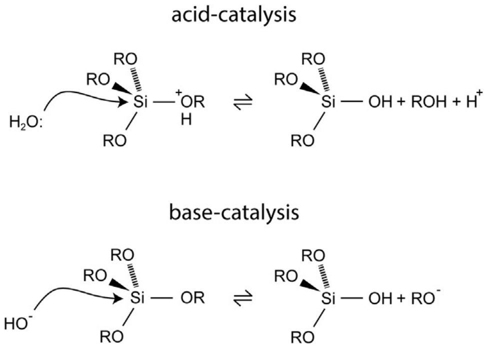

Fig. 1. Hydrolysis of monomeric alkoxysilane under acidic and basic conditions.

on the introduction of voids into the coating materials. Most studies regarding AR coatings following this strategy are based on porous SiO_2 material [11–35]. Moreover, sol-gel method is one of the most attractive processes, offering a precise control of microstructure of the fabricated material by governing features such as volume and size of pores, the surface area and the homogeneity of the coating materials [36,37]. The structure and porosity of the fabricated coating material depend on the relative rates of the hydrolysis and condensation reactions [38] of the sol-gel precursors, and the pH has a crucial influence as well [39,40]. When the hydrolysis reaction of monomeric alkoxysilanes is approached under acidic conditions (see Fig. 1), the alkoxide group is protonated in a first step and electron density is withdrawn from silicon making it more electrophilic and susceptible to water attack [41]. Under basic conditions (see Fig. 1), the water dissociation takes place producing nucleophilic hydroxyl anions, which react with silicon. Successive hydrolysis steps get progressively slower under acidic conditions and faster under basic conditions [42,43] provoking a remarkable difference in the obtained sol and therefore in the structure of the coating material. In basic conditions, small and highly branched agglomerates form a colloidal sol and the coating presents a particulate and porous structure [44] with weak bindings between particles and poor abrasion resistance. In acidic conditions, sol results in chain-like structure and the formed coating is a network-like dense material [38,44] with strong adherence to the substrate and high mechanical properties. In order to obtain porous materials by acid-catalyzed synthesis route, evaporation induced self-assembly method (EISA) was first reported by Asefa et al. [45] and Brinker et al. [46]. Since then the combination of various sol-gel precursors (such as Si, Ti, Zr alkoxides) and various surfactants (anionic, cationic, amphiphilic block copolymer surfactants) has permitted to obtain a large number of mesostructures with pore dimension range from 2 to 20 nm [47]. Trough the preparation of an acid-catalyzed sol containing an inorganic precursor and a surfactant in alcohol medium, the surfactant form micelles that act as structure directing agent (SDA). During the sol to gel transition, the self-assembly of surfactant micelles leads to the creation of an organized texture acting as a template for the inorganic network growth. After elimination of surfactant by calcination, a film with mesoporous structure is obtained.

Although porous silica by sol-gel process has been widely used as AR coatings only in a few occasions has been reported for CPV technology, in which antireflection is required in a broadband range of the solar spectrum in order to cover the range of the multijunction cells operation. Most of the reported research work is focused on the design of mono-layer materials and studies their optical properties only in narrow wavelength band reporting transmission value at a single wavelength. The majority of these studies are based on glass dipping in sols prepared with tetraethyl orthosilicate (TEOS) [13–15,23,25,29,32–35,48–51] and mixture of TEOS and methyl triethoxysilane (MTES) [18–22,24,26,27,31], or even in commercial colloidal silica solution [11,12]. In this research field, Liu et al. [23] have worked with base-catalyzed sol-gel synthesis, which allowed to reach low refractive index equal to 1.22 (estimated from Fresnel equation) similar to the one obtained by Li et al. (experimental at 550 nm) [29], who used the silica coating as part of a multi-layer stack with ZnO_2 reaching high transmittance values (96.1% in the range 300–1200 nm). Some research [30–33,50] have combined base and acid-catalyzed conditions of sol-gel synthesis in order to reach a tradeoff between optical and mechanical properties. Another strategy to improve mechanical properties can be related to depositing an inner coating using acid-catalyzed sol and an external coating from a base-catalyzed sol [34,35]. In the field of acid-catalyzed sols, TEOS as a SiO_2 precursor has been successfully combined with organic molecules such as poly(diallyldimethylammonium chloride) [13], polyvinyl acetate [14] or assisted by the presence of surfactants as structuring direct agents (SDA), such as cetyltrimethylammonium chloride [15,16], cetyltrimethylammonium bromide (CTAB)/polypropylene glycol (PPG) mixture [28]. The mixture of TEOS and MTES as SiO_2 precursors has been studied assisted by polyethylene glycol (10) octadecyl ether (Brij76) [18], t-octylphenoxypolyethoxyethanol (Triton X-100) [19–22] and Triton X-100/polyethylene glycol mixture [24]. Other research works reported materials composed by several layers either as composite or layer stack with enhanced features such as self-cleaning or photocatalysis. For example, Li et al. [28] have modelled and synthesized bi-layer SiO_2 stack based on sol-gel with several molar ratio of CTAB/ PPG mixture as surfactant to obtain coating stacks combining materials with refractive index of 1.15 and 1.32 (at 550 nm) and thickness of 154 nm and 134 nm with the aim of obtaining excellent transmittance values at 532 nm and 1064 nm. Poly(ethylene oxide)-b-poly(propylene oxide)-*b*-poly(ethylene oxide) tri-block copolymer (Pluronic F127) is also a very commonly used SDA, and it has been reported for deposition of porous SiO_2 as part of multilayer stack with TiO_2 coatings [25–27]. In those studies, TiO_2 is intended to provide self-cleaning and photocatalytic properties, even though its incorporation has a detrimental effect in optical properties. To avoid this drawback Faustini et al. [26] have prepared porous SiO_2 with refractive index 1.23 (at 700 nm) and an external very thin coating of TiO_2.

Despite tailored refractive index coating deposition is a well-known subject in the state of the art, no much work has been found that experimentally obtains AR layer stack showing the theoretically optimized transmittance values in the range of multijunction cells operation.

This work is focused on the design and deposition of AR multi-layer stack for CPV application providing high transmittance values, spectrally tailored to the spectral response of multijunction solar cell. Since CPV technology is based on low cost optical elements, AR coating feasibility depends on the ratio between the coating processing cost and the enhanced efficiency of the photovoltaic system. Therefore, it is important to optimize the chemical process in order to find conditions that lead to very stable sols with extended pot life that permits to deposit repetitive coatings over time. A suitable AR coating stack should also ensure mechanical properties to withstand long-term durability with minimum transmission losses. An easy and efficient approach is presented herein, based on TEOS, acid catalysis and the use of four types of surfactants as SDA to generate robust processes and products useful to constitute an optimized AR multi-layer stack for glass substrates. AR bi-layer stack was successfully developed by deposition of sols with optimized organic/inorganic phases in order to obtain each single coating with the refractive index, porosity and thickness values that lead to obtain broadband AR performance required in CPV applications.

2. Experimental procedure

2.1. Materials

Absolute ethanol (purity 99.9%) was purchased from Scharlau and