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Enhancement of dielectric barrier layer properties by sol-gel and PECVD stacks

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ABSTRACT

Thin-film PV modules grown on flexible, light weight, thermally stable and low cost substrates such as stainless steel foil, are an attractive product for solar market applications. When metal foils are used as substrate, it is essential to deposit a dielectric barrier layer to isolate electrically and chemically the thin-film solar cells from the substrate. In this work, SiO_x stacks deposited on 'rough' stainless steel by a combination of a new sol-gel formulation and a Plasma Enhanced Chemical Vapor Deposition (PECVD) deposition step are reported as a suitable dielectric barrier layer candidate. Using these SiO_x multilayers, a smooth and homogeneous film was achieved. X-ray diffraction (XRD) analysis showed that back contact of the solar cell (based on Molybdenum) is not affected by the presence of the barrier layer. Moreover, according to X-ray photoelectron spectroscopy (XPS) and Secondary Ion Mass Spectrometry (SIMS) measurements, this approach led to excellent barrier layer properties against the diffusion of impurities from the stainless steel. A complete electrical characterization of these dielectric barrier layers was also carried out showing good electrical insulation.

1. Introduction

One of the challenges for photovoltaic (PV) market applications is to be able to manufacture efficient optoelectronic devices based on suitable low cost materials and processes. Therefore, there is an industrial interest to transfer conventional manufacturing process from thin film PV technologies (CIGS and CZTS) based on glass to alternative low cost materials [1–7]. Furthermore, these new substrates for thin-film PV devices will open new market opportunities and features such as flexibility, low weight, low cost, roll-to-roll manufacturing, etc. It is believed that these PV modules are the ideal candidates for PV markets such as Building Integrated Photovoltaic Applications (BIPV) and distributed generation in rooftops. Stainless steel is often identified as one of the best alternative candidate to rigid glass substrates traditionally used for thin-film PV modules [8,9]. However, an extra layer must be added to the stainless steel, named dielectric barrier layer, to make it compatible with the thin-film PV modules, guaranteeing their performance and their electrical interconnection through the so-called monolithic integration process.

The dielectric barrier layer and its application on the metallic substrate must be designed with the following functions: (i) inhibit diffusion of detrimental transition metallic elements (Fe, Cr, Ni) from the stainless steel substrate to the semiconductor structure of the solar cell; (ii) reduce the surface roughness of the substrate as much as possible in order to reduce inhomogeneities or defects formation during thin-film deposition and to minimize the pinholes creation; (iii) keep mechanically stable to avoid failures during the subsequent thermal annealing like delamination or presence of cracks. This goal is achieved by designing the layer with a coefficient of thermal expansion (CTE) similar to those materials in contact with it; (iv) provide electrical insulation between the metallic substrate and the back contact of the solar cell. This feature is critical in order to monolithically integrate the neighboring solar cells to build the thin-film PV module [3]. Numerous examples consisting of Al_2O_3, ZnO, SiO_2 or enameled layer, deposited by sputtering, sol-gel, PECVD or spray techniques have been previously investigated [10–14]. Nevertheless, few of them report on the electrical properties of these layers and the effect of surface roughness on the dielectric function. It is well documented that one of the most common failures in this barrier layer is the mechanical stability, during and after the post-thermal annealing which is the process responsible for the formation of the CIGS or CZTS semiconductor [8].

Abbreviations: PECVD, Plasma Enhanced Chemical Vapor Deposition; CTE, coefficient of thermal expansion; R_t, peak-to-valley roughness; TOF-SIMS, Time-of-Flight Secondary Ion Mass Spectrometry; SEM, Scanning Electron Microscopy; SIMS, Secondary Ion Mass Spectrometry; XRD, X-ray diffraction; XPS, X-ray photoelectron spectroscopy.

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Table 1
Density, coefficient of thermal expansion (CTE), and peak-to-valley (R_t) of soda lime glass (SLG) and alternative foils.

	SLG	Ti	Kapton	Stainless steel
Density [g/cm^3]	2.5	4.5	1.42	7.7
Tmax [°C]	600	>600	<500	>600
CTE [10^{-6} K^{-1}]	9	8.6	17–44	10–11
R_t [nm]	10–15	1400	540	1600

The aim of this work was to develop and integrate dielectric barrier layers on commercially available stainless steel foils with high surface roughness and low cost. In the present work, the feasibility of dielectric barrier layers based on SiO_x stacks has been studied. These SiO_x stacks were grown by a combination of sol-gel and Plasma Enhanced Chemical Vapor Deposition (PECVD). The processed samples were 100×100 mm^2, which shows the scalability of the proposed process technology.

2. Experimental

2.1. Material selection

In the recent years, several related works have shown that flexible metals such as Al [15], Ti [16], and steel [9] can yield performances close to soda lime glass (SLG). Steel is a competitive material against Ti or Al in terms of both cost and physical properties (mechanical, thermal and coefficient of thermal expansion). Moreover, steel meets requirements of a PV substrate since it is a very good barrier to oxygen and water, and is robust against external shocks thanks to its good weight/stiffness ratio. Table 1 presents some technical data for potential candidates to substitute glass, such as density, CTE and maximum surface roughness [2].

To replace soda lime glass ensuring similar CTE and low cost, the selected substrate was stainless steel AISI430, 0.2 mm in thickness and 100×100 mm^2 active area (average roughness ($R_a = 0.23 \pm 0.04$ μm) and peak-to-valley roughness ($R_t = 1.51 \pm 0.33$ μm)).

The material proposed in this work as dielectric barrier multilayer is SiO_x, which CTE ($1–9 \cdot 10^{-6}$ K^{-1}) is similar to the AISI430 stainless steel substrate ($10–11 \cdot 10^{-6}$ K^{-1}) and the Mo back contact ($5–6 \cdot 10^{-6}$ K^{-1}) of the solar cell [2]. Moreover, the SiO_x, due to its strong ionic interatomic bonding, allows the impurity blocking. Finally, its dielectric character provides suitable electrical insulation between the stainless steel substrate and the electrode of the solar cells.

2.2. Processing

In order to analyze the barrier layer properties of the SiO_x stacks, two alternative structures based on PECVD and sol-gel have been deposited on the AISI430 stainless steel substrate, shown in Fig. 1: a SiO_x bilayer structure [Steel/PECVD/sol-gel] [BL-01] (Fig. 1A), and a three-layer SiO_x structure [Steel/sol-gel/PECVD/sol-gel] [BL-02] (Fig. 1B). A full description of the sample preparation is presented below. Afterwards the Mo layer to serve as the solar cell back contact was deposited by DC-sputtering on both structures. This Mo layer is needed to evaluate the electrical insulation provided by the dielectric barrier layer.

Before film deposition, the stainless steel surface was cleaned with soapy water, acetone and dried with nitrogen to remove any grease contamination which may have hindered the SiO_x adhesion.

A novel SiO_x sol-gel process [17] based on acid catalysis was formulated to reduce the appearance of cracks during high temperature (ca. 550 °C) thermal annealing. The coating sols were prepared from a 2 mL of tetraethylorthosilicate (TEOS), 8 mL of Methyltriethoxysilane (MTES) and 3 mL of 2,4,*N*,*N*′-Dimethylformamide (2,4,*N*,*N*′-DMF) which were mixed at room temperature under vigorous stirring during 15 min. After, 5 mL of polyethylene glycol 400 (PEG), 2 mL of deionized water and 250 μL of H_3PO_4 were added in different steps waiting 15 min between each one. The so-obtained solution was finally aged for 1 h before its use. After the addition of H_3PO_4, the temperature of the solution increased about 5 to 8 °C and became transparent. To achieve the suitable solution for being spin-coated, the molar ratios were adjusted as follows: 4.9 MTES/TEOS, 2.4 DI H_2O/(MTES + TEOS), 0.8 *N*,*N*′-DMF/(MTES + TEOS) and 0.3 PEG-400/(MTES + TEOS). The resulting sol-gel precursor had a pH between 5.0 and 5.5 and a viscosity of 14 and 18 cP (22 °C).

Then, 2 mL of precursor solution was deposited on the steel substrate by spin-coating (Spin coater SUS Microtec Delta 6RCTT) working at 1750 rpm for 20 s. A dense SiO_x film was formed by sintering the sol-gel film in a hot plate (Titan 5P) following this thermal profile: 60 °C for 15 min in order to remove the solvents, 150 °C for 60 min, 300 °C for 30 min and 550 °C for 30 min, finally the coated substrates were taken out form the hot plate after cooling at room temperature.

The PECVD SiO_x layer was deposited by radiofrequency (13.56 MHz) in a cluster tool from Elettrorava (model V0714) with a ratio of SiH_4 to N_2O of 6:80. The applied power density was 20.8 mW/cm^2 at 500 mTorr pressure and substrate temperature was 480 °C, which resulted in a deposition rate of 6.25 Å/s.

The final thicknesses of the SiO_x stacks for both BL-01 and BL-02 were 3 and 5 μm ca, respectively. Previous experiments showed that thinner SiO_x stacks presented a higher probability for pinhole formation whereas thicker SiO_x stacks led to mechanical failures such as delamination or cracks formation [2,18,19].

To measure the dielectric properties and the impurity diffusion through the SiO_x stack a Molybdenum bilayer structure, suggested by Scofield et al. [20], was deposited by magnetron sputtering, with a surface area of 90×90 mm^2 and a total thickness of 800 nm to ensure good mechanical and electrical properties of the back contact.

2.3. Characterization

Surface roughness of all samples was characterized with a mechanical profilometer (model Ambios XP1, Ambios Technology), following the ISO 4287 protocol. Scotch adhesion tests were performed based on ISO 2409 protocol. Depth profiling of the barrier layers and potential diffusion of metallic elements from the metallic substrate was performed by Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) from

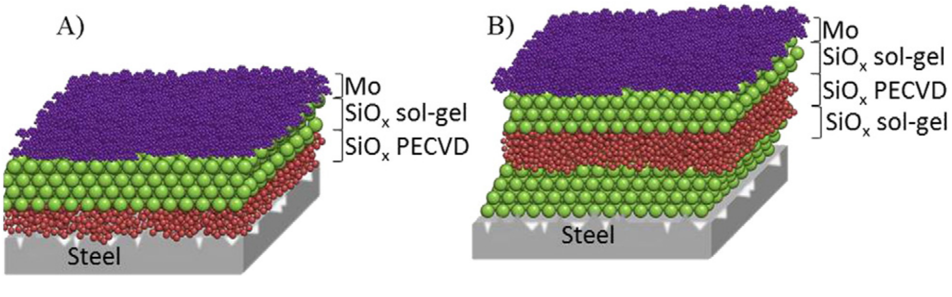

Fig. 1. Barrier multilayer scheme integrated in thin-film solar cell structure. A) BL-01: Steel/PECVD/sol-gel, B) BL-02: Steel/sol-gel/PECVD/sol-gel.