Applied Surface Science 320 (2014) 519–523

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Formation of Me–O–Si covalent bonds at the interface between polysilazane and stainless steel

Dodji Amouzou[a,*], Lionel Fourdrinier[b], Fabrizio Maseri[b], Robert Sporken[a]

[a] *Research Centre in Physics of Matter and Radiation (PMR), University of Namur, Rue de Bruxelles 61, 5000 Namur, Belgium*
[b] *CRM-Group, Boulevard de Colonster, B 57, 4000 Liège, Belgium*

ARTICLE INFO

Article history:
Received 16 May 2014
Received in revised form 21 August 2014
Accepted 18 September 2014
Available online 28 September 2014

Keywords:
Polysilazane
Oxide
Hydroxide
Cr–O–Si
Fe–O–Si
Stainless steel

ABSTRACT

In earlier works, we demonstrated the potential of polysilazane (PSZ) coatings for a use as insulating layers in Cu(In,Ga)Se_2 (CIGS) solar cells prepared on steels substrates and showed a good adhesion between PSZ coatings and both AISI316 and AISI430 steels. In the present paper, spectroscopic techniques are used to elucidate the reason of such adhesion. X-ray Photoelectron Spectroscopy (XPS) was used to investigate surfaces for the two steel substrates and showed the presence of metal oxides and metal hydroxides at the top surface. XPS has been also used to probe interfaces between substrates and PSZ, and metallosiloxane (Me–O–Si) covalent bonds have been detected. These results were confirmed by Infra-Red Reflection Absorption Spectroscopy (IRRAS) analyses since vibrations related to Cr–O–Si and Fe–O–Si compounds were detected. Thus, the good adhesion between steel substrates and PSZ coatings was explained by covalent bonding through chemical reactions between PSZ precursors and hydroxide functional groups present on top surface of the two types of steel. Based on these results, an adhesion mechanism between steel substrates and PSZ coatings is proposed.

1. Introduction

Thin films optoelectronic devices such as Cu(In,Ga)Se_2 (CIGS) solar cells [1,2] and organic light emitting diodes [3,4] are attractive due to their potential for fabricating flexible modules. Monolithic manufacturing on a large area remains the best way for reducing the cost of such modules. On steel foils, devices have to be scribed into single cells and then interconnected to form modules [5]. Thus, an insulating layer on steel substrates is needed [6] and a good adhesion between active stacks and the insulating layer is required.

Here, polysilazane (PSZ) coatings were prepared on both AISI316 and AISI430 stainless steels (SS) following a procedure that was reported earlier [7]. All samples passed the ASTM D3359-07 standard adhesion test. The key question in this study is to understand how PSZ adheres to steel substrates. For this purpose, we probed the interface of the two SS substrates and PSZ coatings using spectroscopic techniques in order to investigate chemical interactions between different materials. The top surface of SS substrates was analyzed to determine which functional groups are present before the deposition of PSZ coatings. Then, we analyzed SS substrates that we had functionalized beforehand with PSZ precursors. By comparing the two types of samples (uncoated steel and modified steel), we determined the chemical interactions between steel and PSZ coatings.

2. Experimental

2.1. Sample preparation

Chemical compositions of the two SS substrates are summarized in Table 1. Substrates are systematically cleaned to remove contaminants such as grease and dust commonly present on commercial steel sheets. The cleaning is usually performed in successive ultrasonic baths using appropriate degreasing solvents: classically, a sequence of acetone, water and ethanol with 600 s of duration in each bath is applied. Substrates are then dried by blowing with filtered nitrogen before being analyzed.

For some investigations, substrates were coated with PSZ using a bar coating technique. In this work, the bar coating process consists in depositing the PSZ coating by manually moving a wet solution of PSZ precursors with a coating bar onto the surface of the substrate. As-deposited PSZ coatings are then annealed at 270 °C in air using a convection oven during 1 min for crosslinking. This technique allows us to obtain PSZ coatings that are thick enough to be analyzed in X-ray Photoelectron Spectroscopy (XPS) and Infra-Red

---

* Corresponding author. Tel.: +32 475 59 24 77.
E-mail address: adodji@gmail.com (D. Amouzou).

http://dx.doi.org/10.1016/j.apsusc.2014.09.109

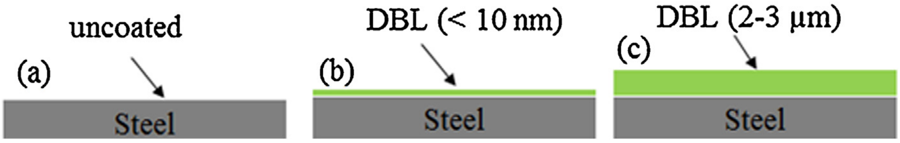

Fig. 1. Schematic illustration of samples tested for each SS substrate: (a) uncoated SS substrate, (b) steel coated with an ultra-thin PSZ to probe directly the interface and (c) SS substrate coated with a thick PSZ.

Table 1
Composition of AISI316 [8] and AISI430 [9] (wt. %).

Stainless steel	Fe	C	Cr	Ni	Mn	Si
ASI316	65	0.03	16.85	11.75	1.66	0.45
AISI430	80	0.4	16.3	0.5	0.36	1.0

Reflection Absorption Spectroscopy (IRRAS) with no signal from the substrate being recorded. To probe the interface between PSZ and steel foils directly by using XPS or IRRAS, an ultra-thin PSZ film with thickness below 10 nm is deposited onto the used stainless steel substrates. Ultra-thin films were obtained by dipping substrates into PSZ solution diluted thousand times in an appropriate solvent and crosslinked using the same procedure as for thicker films.

2.2. Characterization

A Thermo VG-Scientific Sigma Probe spectrometer with an Al Kα source ($h\nu = 1486.6$ eV) was used for XPS analysis. The photoelectron take-off angle is 45°. Thermo Avantage 4.7 V data acquisition and analysis software was used to record XPS spectra and to process data. The energy resolution was 1 eV at pass energy of 200 eV for survey scans and 0.5 eV at pass energy of 50 eV for high resolution scans. XPS depth profiles of uncoated substrates were recorded by alternating cycles of XPS analysis and sputtering using an argon ion beam (3 keV, 1 µA) incident at 45° with a spot size of 200 µm × 200 µm.

IRRAS analyses were performed from 400 to 2000 cm^{-1} using NEXUS spectrometer. Adhesion was evaluated using ASTM D3359-07 adhesion standard test also called cross-cut-test.

3. Results and discussions

3.1. XPS analysis

Three samples were prepared for each type of steel substrate as shown in Fig. 1. XPS depth profiles have been performed on uncoated SS substrates to obtain the relative atomic concentration of species in each SS substrate. The depth scales are calibrated using sputter rate of iron. The conventional method (84–16%) [10] is used to estimate the thickness of the native oxide layer present on the top surface of each steel substrate. Fig. 2 shows the atomic concentration of main atoms in AISI316 and AISI430. As can be checked, the thickness of the native oxide layer on both substrates is around of 2–3 nm/eq.Fe. These results are in accordance with values currently reported for Fe–Cr alloys [11,12].

To evaluate the distribution of the main oxides in the passivation layer, concentrations of iron, chromium and nickel were recorded and Fig. 3 illustrates the case of AISI316 substrate. A concentration gradient is clearly observed. The outer region of the passivation layer is iron-rich; a strong enrichment of chromium is observed in the center of the passivation layer while enrichment in Ni is found for the region close to the interface. This is in agreement with published reports [3,13] and could be attributed to a double-oxide stratification of Fe_xO_y/Cr_xO_y oxides at the top surface of steel.

In some previous studies [14,15], Cr enrichment was observed however at the top surface of stainless steels. To try understanding

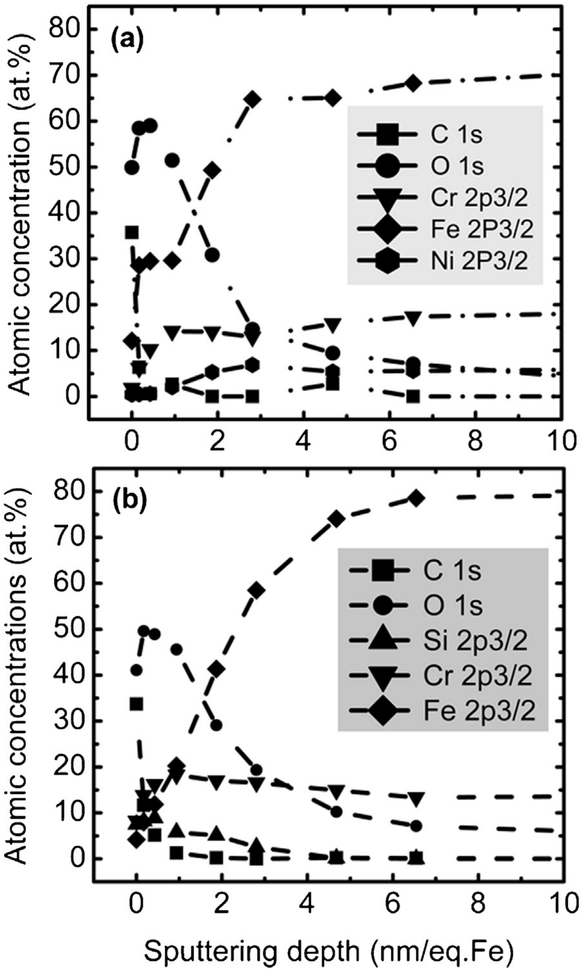

Fig. 2. Atomic concentration in uncoated (a) AISI316, and (b) AISI430 stainless steels.

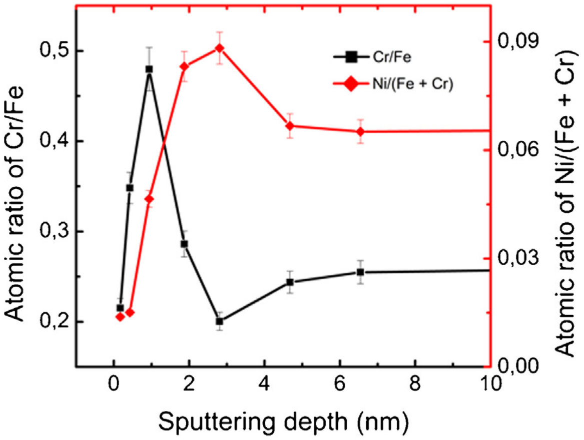

Fig. 3. Enrichment of Cr, Fe and Ni in the passivation layer calculated from raw data for AISI316.