Materials Research Bulletin 85 (2017) 168–175

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Copper indium gallium selenide (CIGS) solar cell devices on steel substrates coated with thick SiO_2-based insulating material

Kyoung-Bo Kim[a], Moojin Kim[b,*], Hong-Chan Lee[b], Sang-Wook Park[c], Chan-Wook Jeon[c,*]

[a] Department of Metallurgical & Materials Engineering, Inha Technical College, Incheon, 402-752, Republic of Korea
[b] Department of Renewable Energy, Jungwon University, Goesan-gun, Chungbuk, 367-805, Republic of Korea
[c] School of Chemical Engineering, Yeungnam University, Gyeongsan, 712-749, Republic of Korea

ARTICLE INFO

Article history:
Received 20 August 2015
Received in revised form 13 June 2016
Accepted 16 September 2016
Available online 17 September 2016

Keywords:
A. Chalcogenide
A. Oxides
A. Metals
A. Inorganic compounds
D. Electrical properties

ABSTRACT

Flexible copper indium gallium selenide (CIGS)-based solar cells were developed on stainless steel (STS) substrates covered with an insulating layer. The properties of the CIGS films fabricated on STS foils coated with SiO_2-based soluble material ("sol-SiO_2") were compared with those on plasma enhanced chemical vapor-deposited silicon oxide ("PE-SiO_2")/MoNa/STS and SLG substrates. The decrease in compensating donor due to sufficient Na doping from the insulating layer was attributed to higher open-circuit voltage and fill factor. Furthermore, the double graded Ga composition in the CIGS films grown on the STS substrates was preserved, and the open-circuit voltage was enhanced with a minor decrease in the short-circuit current. As a result, solar cells with 14% efficiency were produced on sol-SiO_2/STS samples with a Fe atom diffusion barrier and external Na incorporation. This was far higher than the 9.5% and 12.8% obtained from the solar cells on PE-SiO_2/MoNa/STS and SLG, respectively.

1. Introduction

The development of flexible substrates for producing electronic devices, such as solar cells and displays using roll-to-roll processes, has recently attracted considerable interest [1,2]. In contrast to general processes using rigid substrates, these technologies offer opportunities to substantially reduce production costs. Stainless steel (STS) and polymer substrates are commonly used in flexible substrates in roll-to-roll processes [3–6]. STS substrates have many advantages over polymer substrates, such as enhanced chemical stability and lower thermal expansion coefficients. Furthermore, a high temperature process is possible due to the higher thermal stability of STS compared to that of polymers, and a passivation layer is not required to prevent water vapor and oxygen migrating through the substrate. On the other hand, impurities from the substrate and surface roughness are significant issues impeding electronic applications. Device performance may deteriorate due to out-diffusion of detrimental elements from the STS substrate, such as Fe atoms, and/or electrical short circuits (i.e. direct contact of the anode and cathode electrodes in solar cell devices) due to severe surface roughness [7–9]. Therefore, these types of impurities and levels of roughness must be reduced before STS substrates can be utilized in electronic devices. The out-diffusion of impurities is especially critical because the deposition of copper indium gallium selenide (CIGS) thin films is performed at substrate temperatures greater than 550 °C in a co-evaporation method [7,9].

In this study, a solution-based SiO_2 material ("sol-SiO_2"), which is more adaptable to roll-to-roll processes than dry vacuum coating, was adopted as an insulating diffusion barrier layer and a planarization layer for the fabrication of an integrated module. For the majority of the applications described, for the fabrication of CIGS solar cells, the insulating material was deposited on the STS substrates by silk screen printing methods [10]. The CIGS films on those substrates were compared with CIGS/Mo/SLG structures. The performance of the solar cells is also discussed in terms of the SiO_2-based layer.

2. Experimental details

To fabricate the CIGS solar cells, STS (Cr steel) with a thickness of 127 μm, which has already been commercialized for use in thin film solar cells by POSCO, was used as a substrate because the thermal expansion coefficient of Cr steel (10.5 ppm/K) is lower than that of nickel (Ni)-Cr steel (15.0 ppm/K). First, the STS substrates were prepared for the deposition of the contact layers by cleaning the organic contaminations using acetic acid and

* Corresponding authors.
E-mail addresses: moojinkim7@jwu.ac.kr (M. Kim), cwjeon@ynu.ac.kr (C.-W. Jeon).

http://dx.doi.org/10.1016/j.materresbull.2016.09.018
0025-5408/

deionized water. A radio frequency (RF) plasma pre-treatment was performed to improve the adhesion of the deposited films on the STS substrate. The plasma pretreatment was conducted at an RF power of 80 W and a pressure of 800 mTorr using an Ar flow. In this study, the STS foils were separated into two groups. One group was coated with sol-SiO_2 using a silk screen printing technique and then dried in a furnace, whereas the other group was coated with a 1000 nm-thick silicon oxide ("PE-SiO_2") layer by plasma-enhanced chemical vapor deposition after sputtering a 10 nm thin layer of Mo:Na (See Fig. 1). To discover the effect of the diffusion barrier of PE-SiO_2, we investigated the electrical insulation and bending properties of SiO_2 barriers prepared by different thicknesses. The results showed that the best electrical insulation and bending properties of the barrier layers were achieved with 1 μm-thick SiO_2 barrier layers. Based on the above results and considering the blocking effect, 1 μm-thick SiO_2 film was considered as a barrier. A commercially available sputtering target with a Na concentration of 5 at.% was used. Na was incorporated in the Mo target material in the form of sodium molybdate (Na_2MoO_4). Therefore, the amount of oxygen in the MoNa target increased as Na content increased. The use of sputtered MoNa layers offers two distinct advantages over the Na source: (i) a defined amount of Na can be homogeneously distributed over large areas, and (ii) it is applicable on different substrates, such as glass, metal and polymer foils. The Na out-diffusion capacity of MoNa depends on the sputtering conditions applied during the deposition process. For deposition conditions with low particle energies, a significant increase in the Na out-diffusion performance was obtained. This observation is explained by the microstructure of the MoNa film, where the low energy sputtering condition leads to higher film porosity and thus to more grain boundaries. As Na is stored within the MoNa layer in a complex of Mo and sodium molybdate, it may not easily diffuse within the grain itself, owing to the high amount of Mo in the crystal structure. However, it is expected that Na is very diffusive at oxygen rich grain boundaries and internal interfaces. The MoNa layer therefore represents an efficient Na source for CIGS processes. Soda-lime glass (SLG) without a coating was also used as a reference substrate. A Mo back contact with a thickness of approximately 500 nm was deposited on all substrates (including STS and SLG) by DC sputtering. To achieve low resistivity and good adhesion, a two-pressure deposition process was used for the Mo thin films. A CIGS absorber layer with a thickness of 2 μm was deposited by a co-evaporation system using a "3-stage" process at the highest temperature of approximately 580 °C. The substrate was rotated during deposition to improve film uniformity. A 90 nm CdS layer was then deposited using a chemical bath, followed by a sputter deposition of a 150 nm i-ZnO layer and a 200 nm aluminum doped ZnO layer. A contact grid of 1 μm of aluminum, employing a 10 nm adhesion layer of Ni, was deposited by e-beam evaporation to complete the fabrication of the solar cell devices. The effective area of the active layer for the solar cell prepared using this approach was 0.4 cm^2, which was determined using a shadow mask.

The structural and chemical properties of the insulating films were examined by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) using a Su-70 Hitachi system with a Rontec EDS and an acceleration voltage of 15 kV. The X-ray diffraction (XRD) measurements were conducted using Cu Kα radiation (λ = 1.54 Å) with a Ni filter to remove Cu Kβ reflections, a powder diffractometer that scanned over the range 0–90° 2θ at 0.01° steps (collection time = 3 s per step), a 0.5° divergence slit, and a 0.2° receiving slit. An Atomika 4500 was used for the secondary-ion mass spectroscopy (SIMS) measurements. The condition included a 15 keV Cs+ primary ion beam. The beam current was 50 nA, and the beam was rastered over an area of 200 × 200 μm. The specimens used in the transmission electron microscopy (TEM) investigations were prepared using a focused ion beam milling technique. The TEM analyses were conducted in a HRTEM JEOL 2200FS (JEOL, Japan) with a Cs corrector at a primary beam energy of 200 keV. In order to analyze the coating effects of the insulating layer on the steel substrates, non-contact 3D profiler measurements were performed on the fabricated samples using a Veeco 500-L X-ray diffractometer with a 532 nm green laser.

The electrical characteristics of the films were measured using an HP4145B semiconductor parameter analyzer at room temperature. The solar cells were characterized by standard current density-voltage (J-V) under standard test conditions (1000 W/m^2, 25 °C, AM1.5 equivalent illumination) and external quantum efficiency (EQE) measurements. The capacitance-voltage (C-V) profiles were recorded using a HP4192 ALF Impedance Analyzer at 100 kHz in the dark.

3. Results

3.1. Film characterization

Cross sections of the resulting films were analyzed via SEM and EDS. The thickness of the sol-SiO_2 layer annealed at 650 °C for 300 min was approximately 10 μm, as shown in Fig. 2(a). The coating layer showed good adhesion to the steel foils. No cracking

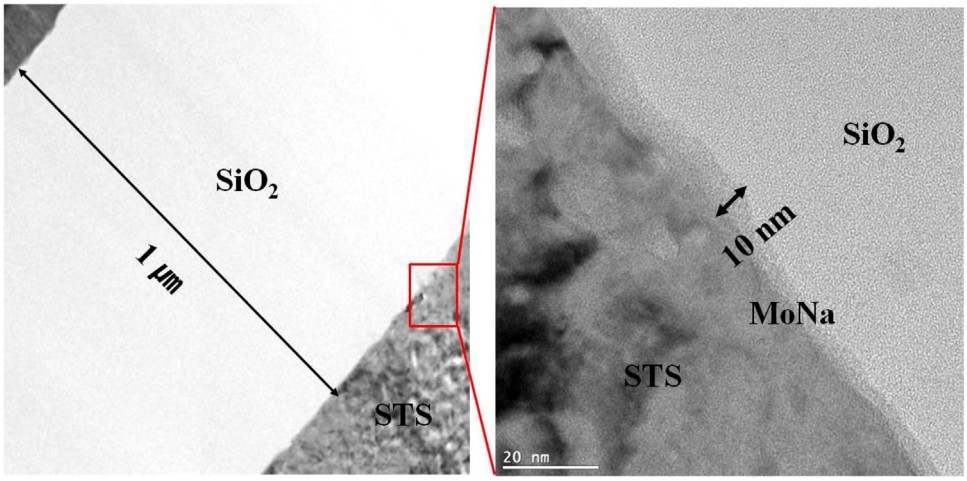

Fig. 1. Bright field TEM image showing the cross section of the PE-SiO_2/MoNa/STS structure. The figure on the right side shows a detailed image of the MoNa layer.