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Investigation on the performance of Mo_2N thin film as barrier layer against Fe in the flexible $Cu(In,Ga)Se_2$ solar cells on stainless steel substrates

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ABSTRACT

In the present work, flexible $Cu(In,Ga)Se_2$ (CIGS) solar cells were prepared from annealing and post-selenization of electrodeposited Cu/In/Ga precursor layers on stainless steel (SS) substrates. The Mo_2N thin film was fabricated by radio-frequency (RF) reactive magnetron sputtering deposition and was proposed as a barrier layer to restrain the diffusion of Fe into the CIGS film. It was observed that the insertion of a Mo_2N barrier layer had no influence on the crystal structure nor the morphology of the Mo and CIGS films, as identified and confirmed by X-ray diffraction (XRD) analysis and field emission scanning electron microscopy (FESEM). In addition, secondary ion mass spectrometry (SIMS) analysis indicated that the Mo_2N barrier layer significantly reduced the diffusion of Fe into the CIGS film. The performance of the flexible CIGS solar cell was dramatically improved due to the reduced Fe concentration in the CIGS film. Finally, the flexible CIGS solar cell with a Mo_2N barrier layer demonstrated an enhanced conversion efficiency of 6.86%, compared to that of a solar cell (3.45%) without a Mo_2N barrier layer.

1. Introduction

Among all of the thin film solar cells reported to date, Cu(In, Ga)Se_2 (CIGS) solar cells deposited on a rigid glass substrate have the highest conversion efficiency (22.6%) [1]. However, CIGS solar cells fabricated on glass substrates have several drawbacks including fragileness, increased mass and high cost [2]. Recent research has focused on flexible substrates [3–11] including polyimide (PI) [3,4], stainless steel (SS) [5–9] and metallic foils [10,11]. Deposition of CIGS films on such flexible substrates can significantly decrease production costs by employing roll-to-roll process manufacturing and monolithic integration of solar cells to develop modules [12].

Flexible CIGS solar cells with high efficiencies of up to 20.4% on PI substrates [13] and 17.7% [14] on SS substrates have been reported in laboratory conditions. Although the solar cells on PI substrates have achieved the highest efficiencies among all flexible CIGS solar cells, the PI substrate is not suited to temperatures above 500 °C whereas high quality CIGS films are usually manufactured at temperatures exceeding 500 °C. Thus, SS substrates are regarded as promising substrates for fabricating high quality CIGS thin films due to their low cost, light weight and high thermal stability [15]. However, some detrimental elements such as Fe from the SS substrates can diffuse through molybdenum (Mo) back contacts into the CIGS films during high temperature processing of CIGS films, which would decrease the open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}) and fill factor (FF), resulting in reduced efficiency of the solar cells [15,16]. This likely results from the fact that the deep level acceptor defects of Fe_{In} and Fe_{Ga} substitutions can result in carrier recombination [16,17]. Therefore, it is essential to control the diffusion of Fe into the CIGS film for solar cells on SS substrates.

To solve this problem, an additional layer acting as a diffusion barrier was proposed to restrain Fe diffusion from the SS substrate. Cho et al. [18] studied the effect of direct-current (DC) magnetron sputtered Cr barrier thickness on the performance of solar cells. A direct correlation between Fe concentration in the CIGS film and Cr barrier thickness was discovered, where a thicker barrier could achieve better blocking capacity. Additionally, the conversion efficiency of the cell was found to increase with the increase of Cr barrier thickness. Wuerz et al. [19] reported a similar direct

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correlation between Fe content in the CIGS film and corresponding solar cell performance for a Mo barrier layer of varying thickness. Shi et al. [20] deposited a ZnO diffusion barrier by DC magnetron sputtering in order to strongly reduce the diffusion of Fe from SS substrate into the CIGS film. With such a barrier layer, a dramatic enhancement of V_{oc}, FF and efficiency was observed. Kim et al. [21] fabricated intrinsic ZnO (i-ZnO) diffusion barriers by radio-frequency (RF) magnetron sputtering to improve the flexible cell efficiency from 5.9% to 9.06% without doping Na in the CIGS film. Lee et al. [22] successfully fabricated flexible solar cells on SS substrate with high efficiency comparable to the reference cell on SLG substrate by introducing a Mo:Na layer and an RF sputtered i-ZnO barrier layer. Bae et al. [23] deposited an Al_2O_3 diffusion barrier layer via atomic layer deposition (ALD) on the SS substrate. Due to the Al_2O_3 barrier layer's amorphous characteristic forming a complex diffusion path to significantly restrain the diffusion of Fe and decrease the number of defects in the CIGS film, the solar cells with such barrier layers were found to achieve better conversion efficiency and uniformity compared to those with ZnO barrier layers fabricated by sputtering. Moriwaki et al. [24] developed a newly flexible substrate to prepare high efficiency CIGS solar cells. The newly developed substrate has a laminated structure with an Al_2O_3 dielectric surface layer formed by anodization, where the Fe impurity did not diffuse into the CIGS film. Tseng et al. [25] fabricated amorphous SiO_x diffusion barriers by aerosol spraying and showed that such a SiO_x barrier of 200 nm could suppress the diffusion of impurities from the SS substrate into the Mo back contact. Kim et al. [26] developed a solution-based SiO_2 (sol-SiO_2) using silk screen printing techniques to perform as an insulation diffusion barrier for the fabrication of an integrated module. The flexible CIGS solar cells on this sol-SiO_2-coated SS substrate yielded a high conversion efficiency of 14% with external Na incorporation, which was higher than those obtained from reference cells on SLG substrates (12.8%). Liu et al. [27] developed a flexible CIGS solar cell on an SS substrate by using a Ti/TiN composited structure as a diffusion barrier layer. Li et al. [28] reported that AlN film with specific thickness could function as an efficient insulation barrier as well as a barrier layer in flexible CIGS solar cells. Sim et al. [29] improved the efficiency of cells using a nanoscale homomorphic thin Cr_2O_3 barrier formed by thermal oxidation on the surface of SS substrates in an oxygen atmosphere. In summary, these barrier layers help to significantly improve the performance of CIGS solar cells on SS substrates by decreasing the Fe concentration in the CIGS films. However, from the viewpoint of enhancing efficiency of the flexible solar cell, it is still of great importance to develop new materials functioning as diffusion barrier layer.

In this paper, we proposed Mo_2N thin film as a barrier layer to reduce the Fe diffusion into CIGS films for its excellent barrier properties for semiconductor metallization [30,31], as well as its high chemical and thermal stabilities with high melting points [31,32]. The Mo_2N thin film was deposited on the SS substrate by RF reactive magnetron sputtering with an N_2/Ar gas mixture and its barrier effect on the diffusion of Fe was investigated. Flexible CIGS solar cells with and without a Mo_2N barrier layer were fabricated successfully by annealing and post-selenization of electrodeposited Cu/In/Ga precursors on SS substrates.

2. Experimental details

The CIGS solar cells were processed on flexible 430 SS substrates with a thickness of 50 μm. Before the deposition process, the SS substrates were first cleaned in an ultrasonic bath beginning with a soap solution, then followed by acetone, ethanol absolute and deionized water baths. Next, the SS substrates were dried with N_2 gas and mounted on the substrate holder. The Mo target used in the deposition process was 72.6 mm in diameter with a purity of 99.95%. Prior to deposition, the target was pre-sputtered to remove the surface oxide layer. An initial vacuum was maintained at below 1×10^{-4} Pa. No external heating was applied to the substrate during deposition.

Fig. 1 shows the structure of the flexible CIGS solar cell in this paper. As shown in Fig. 1, a 30-nm-thick Mo_A layer with tensile stress was first deposited by pulsed DC on the SS substrates at 0.3 Pa as an adhesion layer. Next, a 600-nm-thick Mo_2N thin film was deposited by RF reactive magnetron sputtering with N_2/Ar (9/30 sccm) gas mixture at room temperature as a barrier layer, followed by the sputtering of the Mo back contact. The Mo back contact was sputtered using two different processes: Mo_B (500 nm) and Mo_C (10 nm). The Mo_B was sputtered at low pressure for lower resistivity of the back contact, while the Mo_C was sputtered at high pressure to obtain a rough surface in order to improve the adhesion between the Cu layer and Mo back contact. Table 1 lists the detailed parameters of the sputtering deposition process for Mo and Mo_2N films. In addition, a $Mo_C/Mo_B/Mo_A$/SS substrate without Mo_2N barrier layer was also prepared for comparison.

The 2-μm-thick CIGS films were prepared from annealing and post-selenization of electrodeposited Cu/In/Ga precursor layers from aqueous solutions at room temperature. The precursor layers were electrodeposited in a two-electrode cell in which the counter electrode was the corresponding metal foils and the working electrode was the previously mentioned Mo-coated SS substrates with and without a Mo_2N barrier layer. The first Cu layer was electrodeposited from a 0.75 M copper sulfate based solution using a pulsed DC method with a duty cycle of 50% and a constant current density of 62.5 mA/cm^2 for 8 s. The second In layer was electrodeposited from a 0.106 M indium chloride based solution using a pulsed DC method with a duty cycle of 5% and a constant current density of 5 mA/cm^2 for 144 s. The third Ga layer was electrodeposited from a 0.106 M gallium chloride based solution using a DC method with a constant current density of 187.5 mA/cm^2 for 19 s. Next, the Cu/In/Ga precursor layers were annealed at 350 °C for 30 min in a vacuum chamber under a background pressure of ~5×10^{-4} Pa. Finally, the annealed Cu/In/Ga precursor layers were selenized at 550 °C for 30 min in a thermal evaporation system and naturally cooled to room temperature. A 50 nm CdS buffer layer was deposited by a chemical bath deposition and a window layer composed of 50 nm i-ZnO and 300 nm ZnO:Al was deposited using

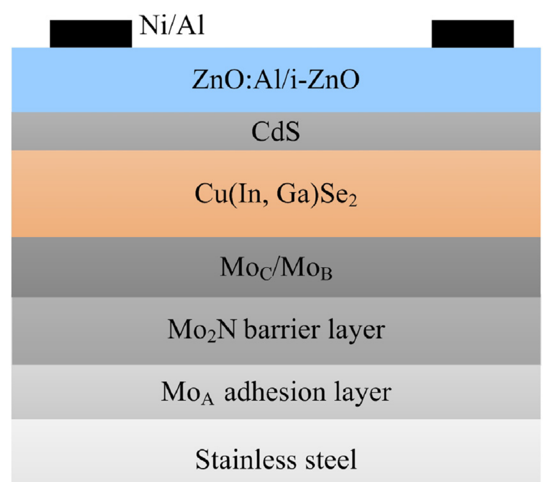

Fig. 1. Schematic structure of CIGS solar cell with the Mo_2N barrier layer on SS substrate.