



Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl20>

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Version of record first published: 18 Oct 2011

To cite this article: Hyeonwook Park, Sung Cheol Kim, Hae Chul Bae, Taehoon Cheon, Soo-Hyun Kim & Woo Kyoung Kim (2011): ALD-Grown Al_2O_3 as a Diffusion Barrier for Stainless Steel Substrates for Flexible $\text{Cu}(\text{InGa})\text{Se}_2$ Solar Cells, *Molecular Crystals and Liquid Crystals*, 551:1, 147-153

To link to this article: <http://dx.doi.org/10.1080/15421406.2011.600634>

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ALD-Grown Al_2O_3 as a Diffusion Barrier for Stainless Steel Substrates for Flexible $\text{Cu}(\text{InGa})\text{Se}_2$ Solar Cells

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Al_2O_3 layer deposited by atomic layer deposition was successfully used as a diffusion barrier and insulator for the stainless steel substrate of a $\text{Cu}(\text{InGa})\text{Se}_2$ thin film solar cell. The 100–300 nm-thick Al_2O_3 coating on stainless steel improved the surface smoothness and presented reliable resistance. More importantly, the diffusion of detrimental impurities, such as Fe and Ni, was significantly reduced during CuInSe_2 deposition at the substrate temperature of 550°C.

Keywords: atomic layer deposition; diffusion barrier; flexible CIGS solar cells

Introduction

Chalcopyrite $\text{Cu}(\text{InGa})\text{Se}_2$ (CIGS)-based solar cells have demonstrated attractive high efficiencies of around 20%.¹ They have the added advantage of being able to form flexible cells when incorporated with flexible substrates, such as lightweight polymers (e.g., polyimide) and metal foils (e.g., stainless steel, Ti, Al).^{2–4}

The properties required of flexible substrates include vacuum compatibility, thermal stability, suitable thermal expansion coefficient, chemical inertness and surface smoothness.² Polyimide has been widely used as a flexible substrate for CIGS cells despite its thermal instability which limits the temperature of CIGS deposition to less than 450°C with a subsequent reduction of conversion efficiency. Metal foils such as stainless steel, Ti and Al are hoped to be alternative high-temperature flexible substrates. A stainless steel foil substrate requires an additional layer acting as both a diffusion barrier against possible impurities within the substrate and an insulator to realize monolithic integration. Several oxides, such as SiO_2 , Al_2O_3 and ZnO , have been studied as possible candidates for these diffusion barriers.^{5–7} Herz et al.⁶ deposited Al_2O_3 layers of 1–3 μm by RF sputtering onto three metal foils: Ti, Kovar[®] and Cr steel; and fabricated flexible CIGS cells of 0.25 cm^2 with 10–11% efficiencies without any Na doping. Their work suggested effective thicknesses of Al_2O_3 to be $\geq 2 \mu\text{m}$ on Cr steel and $\geq 1 \mu\text{m}$ on Kovar[®].

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While it is not well established how and which impurities degrade cells' efficiencies, there are reports that Ni and Fe may be detrimental.^{3,8}

In this paper, Al_2O_3 layers with thicknesses of 100 and 300 nm were deposited onto stainless steel 430 (SS) substrates by atomic layer deposition (ALD). The properties of the Al_2O_3 layers and the diffusion of impurities were characterized by several techniques.

Experimental

The Al_2O_3 diffusion barriers with a thickness of 100 nm and 300 nm were deposited on SS substrates using a travelling-wave type thermal atomic layer deposition (ALD) reactor. The thickness range of 100–300 nm was selected as an initial thickness of ALD-grown Al_2O_3 layer, considering the slow growth rate (~ 0.1 nm/cycle) and excellent conformality of Al_2O_3 ALD, even though Herz et al.⁶ employed the thickness of 1–3 μm for sputter-grown Al_2O_3 on Cr steel. Tri-methyl-aluminum (TMA, $\text{Al}(\text{CH}_3)_3$) was used as a precursor for Al. De-ionized (DI) water vapor and nitrogen (99.9999%) were used as reactant and purge gases, respectively. During the deposition, the chamber was maintained at a pressure of 1 Torr with the substrate kept at 225°C. Each deposition cycle consisted of four steps: Al_2O_3 injection, purge/pumping, H_2O injection and purge/pumping producing around 1.2 Å/cycle (Fig. 1). Repeated cycles formed the 100 nm and 300 nm-thick layers. Areal resistances (Ohm/cm^2) of each Al_2O_3 layer were measured by a HIOKI 3256–50 Digital Tester after an indium contact was added to its top and bottom. Surface roughnesses of the as-deposited barriers were estimated at room temperature and 30–35% relative humidity by a Pacific Nanotechnology atomic force microscope (AFM) (Model: NanoR2) with Si_3N_4 tip. To investigate the diffusion of impurities during the deposition of the CuInSe_2 layer at substrate temperatures of 500–550°C, a 500 nm-thick Mo layer was sputter-deposited on to the Al_2O_3 -coated SS substrate, followed by the elemental co-evaporation of Cu, In and Se at the substrate temperature of 550°C, yielding a SS/ Al_2O_3 /Mo/ CuInSe_2 (CIS) structure.

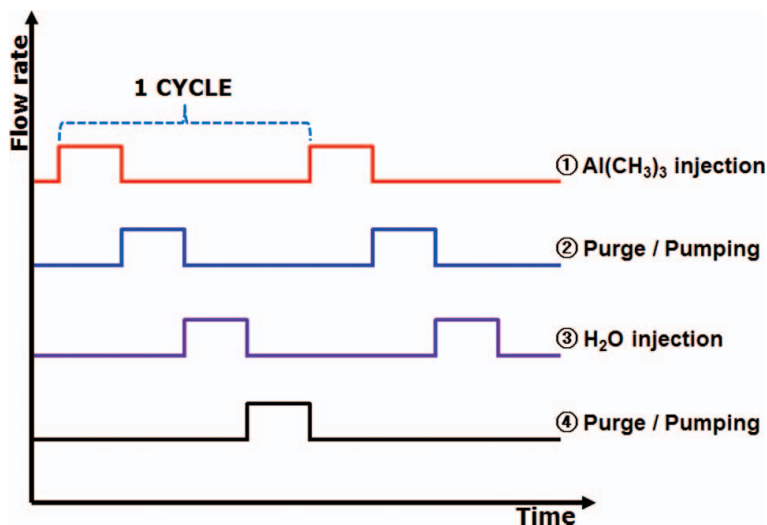


Figure 1. Schematic of Al_2O_3 atomic layer deposition (ALD) procedure.

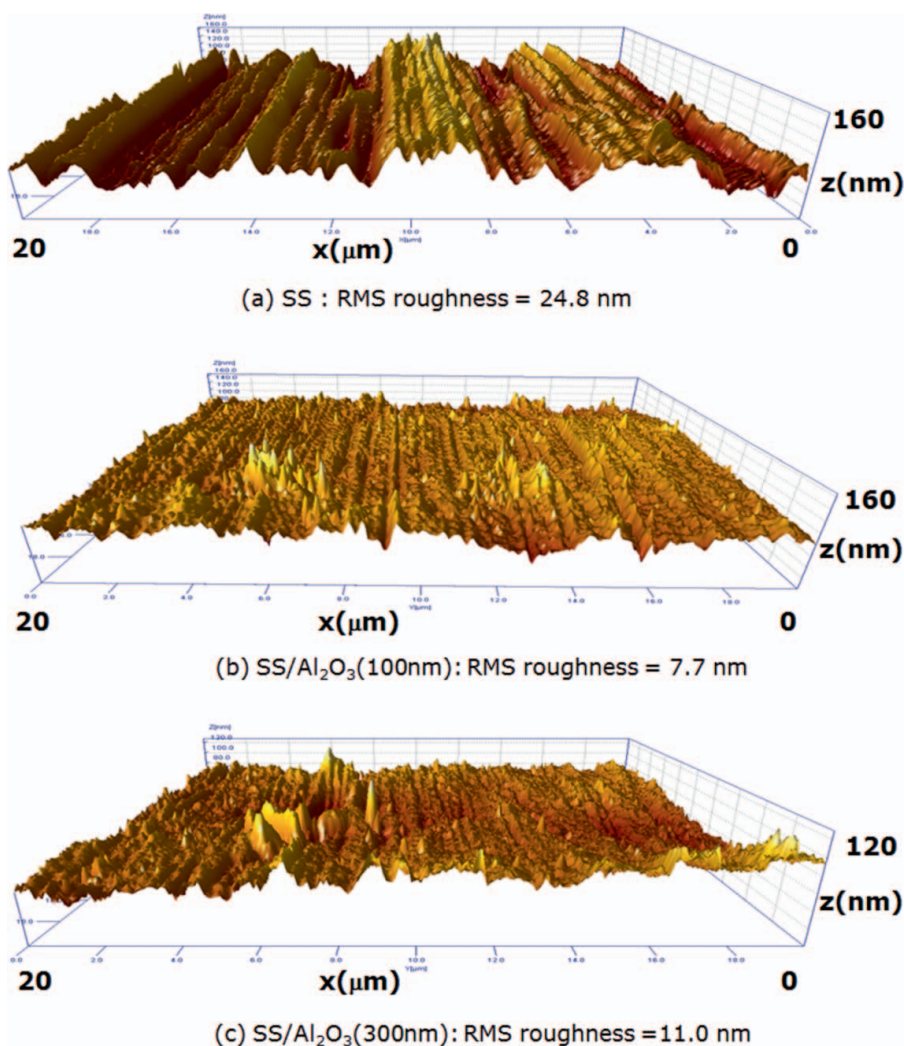


Figure 2. AFM surface scan and values of RMS roughness: (a) SS substrate, (b) SS/ Al_2O_3 (100 nm) and (c) SS/ Al_2O_3 (300 nm).

Secondary ion mass spectrometry (SIMS) was then performed to characterize the relative amounts of the impurities diffused out of the SS substrate.

Results and Discussion

Metal-insulator-metal (MIM) structures were constructed by the addition of indium contacts to the tops and bottoms of the insulated SS, yielding In/SS/ Al_2O_3 /In structures. Their resistances were measured by a digital tester. The sizes of the indium contacts for each sample were carefully controlled for consistency of resistance measurement. Resistances were divided by contact area to yield resistance per unit area [Ohm/cm^2], independent of the size of the indium contacts. The measured resistances had contributions from both

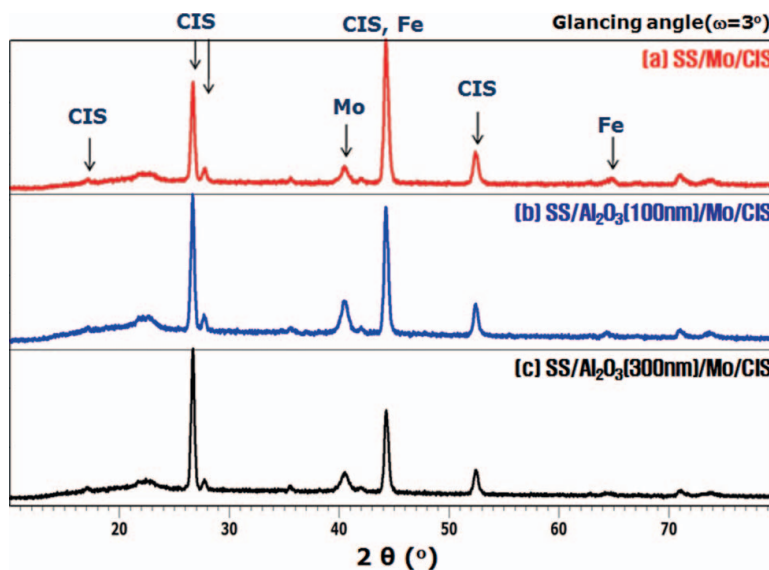


Figure 3. Grazing angle x-ray diffraction scans with $\text{CuK}\alpha_1$ incident radiation and $\omega = 3^\circ$ for (a) SS/Mo/CuInSe₂, (b) SS/Mo/Al₂O₃(100 nm)/CuInSe₂, and (c) SS/Mo/ Al₂O₃ (300 nm)/ CuInSe₂.

the SS substrate and the Al₂O₃ layer; however, SS substrate's contribution is likely to be much smaller than that of the Al₂O₃ insulating layer and can be considered negligible. The resistances of both the 100 nm- and 300 nm-thick Al₂O₃ layers were larger than 10 Mohm/cm², high enough to be used as insulating layers in the monolithic structures of flexible CIGS solar cells.

The AFM results of the as-deposited barriers are shown in Fig. 2 (a)–(c). The root-mean-square (RMS) roughnesses of the Al₂O₃ coated substrates (7.7–11.0 nm) were significantly reduced, compared with that of SS with no barrier (24.8 nm). Increasing the Al₂O₃ thickness from 100 nm to 300 nm did not further improve the surface smoothness. In general, the smooth surface of substrates is preferred to prevent shunts between the front and back contacts of CIGS cells presumably resulting from rough surface morphology.

The diffusion of possible impurities within the SS substrate through the ALD grown Al₂O₃ layer was investigated by Mo and CuInSe₂ layers being deposited on to the SS/Al₂O₃, yielding structures of SS/Al₂O₃/Mo/CuInSe₂. A Mo layer of 0.5 μm was deposited by RF

Table 1. Relative amounts of impurities within CuInSe₂ layer

| Element | Reference (No barrier) | ALD-Al ₂ O ₃ (100nm) | ALD-Al ₂ O ₃ (300nm) |
|---------|---------------------------|---|---|
| Fe | 100 | 1 | 1 |
| Cr | 100 | 100 | 60 |
| Mn | 100 | 20 | 20 |
| Ni | 100 | 2~3 | 1~2 |
| Mg | 100 | 100 | 50~80 |

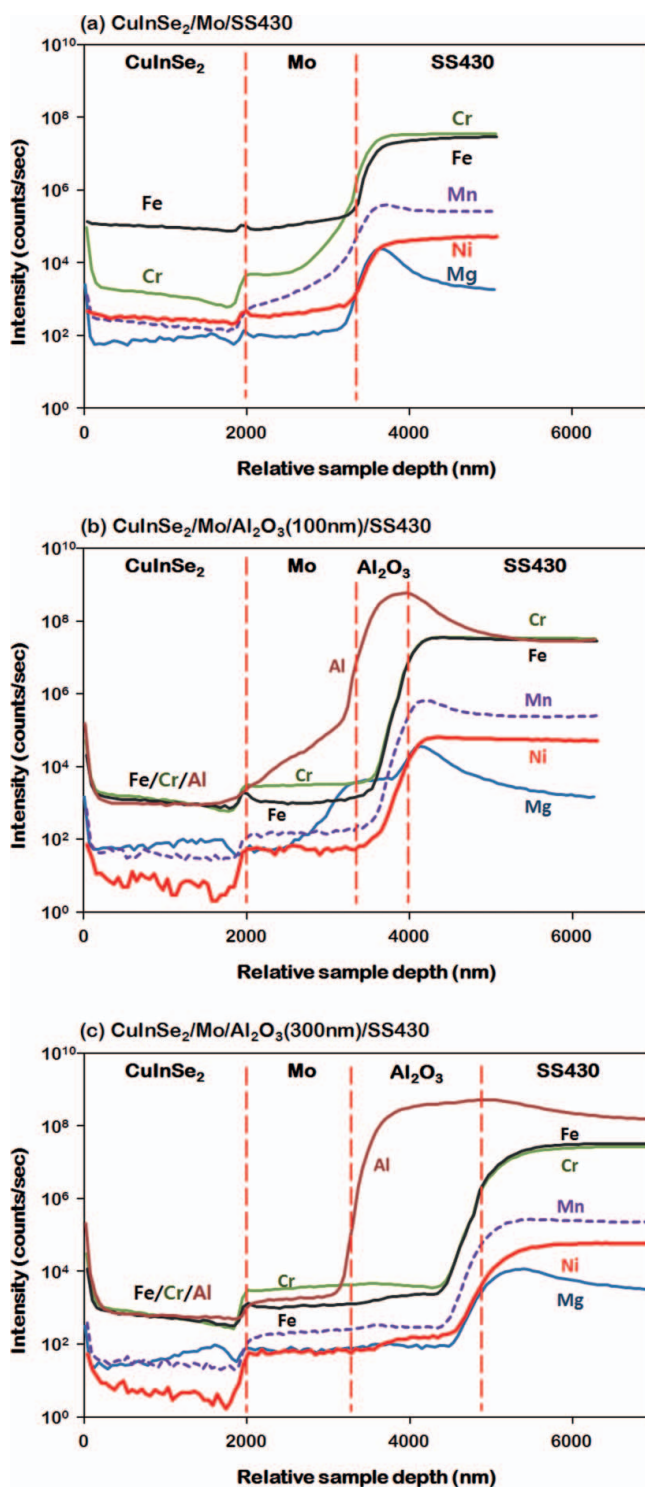


Figure 4. SIMS analysis results for (a) SS/Mo/CuInSe₂, (b) SS/Mo/Al₂O₃(100 nm)/CuInSe₂, and (c) SS/Mo/ Al₂O₃ (300 nm)/ CuInSe₂.

sputtering under the operating conditions of 250 W RF power, 40 sccm Ar flowrate and room temperature. A 2 μm CuInSe₂ layer was prepared by co-evaporating elemental Cu, In and Se at a substrate temperature of 550°C with deposition for approximately 30 min in a Molecular Beam Epitaxy (MBE) system.

To evaluate the adhesion strength at the interfaces of the SS/Al₂O₃/Mo layers, SS/Al₂O₃/Mo/CuInSe₂ samples were subjected to CdS chemical bath deposition (CBD) at 60–65°C for 150 sec. The results showed that each layer remained firm with no delamination.

Glancing angle XRD (GIXRD) analysis with CuK α_1 incident radiation and glancing angle of $\omega = 3^\circ$ on SS/Al₂O₃(0, 100, 300 nm)/Mo/CuInSe₂ samples are displayed in Fig. 3. The glancing angle of $\omega = 3^\circ$ was used to investigate the contribution from the thin layers of Al₂O₃/Mo/CuInSe₂ more precisely, while minimizing the interference of reflections from the SS substrate. No reflection peaks corresponding to Al₂O₃ were detected, implying amorphous Al₂O₃ films which did not crystallize during the deposition of the CuInSe₂ layer. The formation of polycrystalline chalcopyrite CuInSe₂ phases was clearly evidenced by major reflection peaks of (112) and (220) orientation.

The diffusion behavior of possible impurities within the SS substrate through the Al₂O₃ diffusion barrier and the Mo back contact to the CuInSe₂ layer was investigated by SIMS. Possible impurities in the SS substrate include Cr, Mn, Ni and Mg. Sufficient thermal energy and mobility were expected to be provided for impurities during the deposition of the CuInSe₂ absorber layer at 550°C for 30 min.

The results of SIMS analysis on the SS/Al₂O₃(0, 100, 300 nm)/Mo/CuInSe₂ samples are shown in Fig. 4(a)–(c). The diffusion of Ni and Fe was found to be restricted by the Al₂O₃ layer, while Cr and Mg were not affected. It is probably because the Al₂O₃ thickness of 100–300 nm is not thick enough to effectively block the diffusion of Cr and Mg atoms, which are lighter than Ni and Fe atoms. The results are promising as Ni and Fe are reported to reduce the efficiencies of CIGS cells^{3,8}. Both the 100 nm and the 300 nm Al₂O₃ displayed similar results in the impurity diffusion tests. As shown in Table 1, the relative amounts of impurities in the CuInSe₂ layers were estimated by assuming linearly proportional SIMS intensity with impurity amount.

Herz et al.⁶ reported that the diffusion of Fe from Cr steel could be restricted to 10% (i.e., 100 \rightarrow 10 cps) and 1% (100 \rightarrow 1 cps) by respectively applying 1 μm and 3 μm sputter-deposited Al₂O₃ diffusion barriers. This work, however, found that a 0.1 μm ALD-grown Al₂O₃ layer successfully reduced the diffusion of Fe from the SS substrate to 1% (100 \rightarrow 1 cps), as shown in Table 1, something possibly attributable to differences between sputter and atomic layer depositions. An ALD-grown Al₂O₃ layer has better conformality and uniformity of thickness compared with a sputter-deposited one, making it more able to mitigate the diffusion of impurities effectively. The comparison of Herz's results and ours for the diffusion of Cr suggests that, unlike the diffusion of Fe, the diffusion of Cr should be affected by the thickness of Al₂O₃ layer rather than the process of its formation.

Conclusions

ALD-grown Al₂O₃ layers of 100–300 nm demonstrated strong potential for use as diffusion barriers for SS substrates in CIGS-based thin film solar cells. These thicknesses are relatively thin compared with results (1–3 μm) from other reports using a sputter process. Further optimization of thickness, however, is necessary while satisfying the required properties of electrical resistance, smoothness, and prevention of impurity out-diffusion.

Acknowledgment

This work was supported by the New & Renewable Energy of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy (No. 20103010010011). Authors also thank T.E. Hong (Busan Center, Korea Basic Science Institute) for his help on the SIMS characterization.

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