Post-treatment effects on ZnS(O,OH)/Cu(In,Ga)Se$_2$ solar cells deposited using thioacetamide-ammonia based solution

Taizo Kobayashi [a,*], Toyokazu Kumazawa [b], Zacharie Jehl Li Kao [a], Tokio Nakada [a]

[a] Research Institute for Science & Technology, Photovoltaic Science and Technology Research Division, Tokyo University of Science, SIC-2-206, 5-4-30 Nishihashimoto, Sagamihara, Kanagawa 252-0131, Japan
[b] Department of Electrical Engineering and Electronics, Aoyama Gakuin University, 5-10-1 Fuchinobe, Sagamihara, Kanagawa 229-8558, Japan

ARTICLE INFO

ABSTRACT

The impact of post-treatments such as annealing, light-soaking and heat-light soaking on film properties and cell performance of ZnS(O,OH)/Cu(In,Ga)Se$_2$ solar cells were investigated, when ZnS(O,OH) buffer layer was deposited using a thioacetamide (TAA)-ammonia based chemical solution. Chemical bath deposition (CBD) time was shortened to one seventh by combination of a thinner buffer layer and TAA-ammonia based high-rate CBD, as compared to conventional thiourea (TU)-ammonia based CBD process. The ZnO:B window layer was deposited by metal organic chemical vapor deposition (MOCVD) in order to avoid plasma-damage during subsequent sputtering process. An optimum CIGS solar cell fabricated using 50 nm-thick ZnS(O,OH) buffer layer yielded a total area efficiency of 18.8% after heat-light soaking treatment for 80 min at 130 °C under AM1.5, 100 mW/cm^2 illumination. The influence of post-treatments on the compositional changes of the ZnS(O,OH) buffer layer, which affect the conduction band offset (CBO) at the CIGS/ZnS(O,OH) interface, are also discussed on the basis of X-ray photoelectron spectroscopy(XPS) analysis.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Zinc-compounds are very promising candidates for cadmium free buffer materials for Cu(In,Ga)Se$_2$(CIGS) solar cells, being both environmental friendly and highly transparent materials at short wavelengths as compared to commonly used CdS buffer [1]. Zn-compound buffer layers such as ZnS(O,OH) deposited by chemical bath deposition(CBD) [1–7] and Zn(O,S) deposited by atomic layer deposition(ALD) [8–14] are typically used for high efficiency CIGS solar cells and modules, and efficiencies of 19.7% have recently been obtained on small solar cells [6], while 30 × 30 cm^2 sub-module reached 17.8% [5].

In our previous work, high-efficiency cadmium-free CIGS solar cells were obtained using a ZnS(O,OH) (120 nm) buffer layer deposited by two runs of thiourea(TU)–ammonia based CBD process for 120 min [2]. However, shorter CBD process by high-rate deposition and/or thinner thickness is desired to increase the throughput of module′s manufacturing. Since a thinner-ZnS(O,OH)/CIGS interface is weak against plasma damage during subsequent sputtering process, damage-reduced process such as metal organic chemical vapor deposition (MOCVD) is required for deposition of the window layer. We have also reported that ZnO:B window layer deposited by MOCVD was more suitable for CIGS solar cells than sputter-deposited ZnO:Al

window layer, even when very thin ZnS(O,OH) (10 nm) buffer layer was used [8]. The ZnS(O,OH)/CIGS solar cells with MOCVD-ZnO:B window layer showed different behavior from that with sputter-deposited ZnO:Al window layer, and were drastically improved and stabilized by combination of light-soaking (LS) and thermal annealing at 130 °C (heat-soaking, HS), namely heat light-soaking (HLS) [15–18]. Since the sputtering process itself provides the light illumination and the thermal radiation for the device during the film growth, it is suggested that an as-fabricated device with sputter-deposited window layer has already been influenced by a HLS-like effect. Actually, ZnS(O,OH)/CIGS solar cells with sputter-deposited ZnO:Al did not need LS or HLS post-treatment to reach high efficiencies (> 15%) in the previous work [19]. In contrast, MOCVD does not provide light illumination during film growth. Therefore all ZnS(O,OH)/CIGS solar cells with MOCVD-ZnO:B always showed very low efficiency (5–10%) regardless of CBD conditions before the HLS post-treatment in our previous works [17–19]. Hariskos et al. reported a high-rate CBD process for ZnS(O,OH) buffer layer using thioacetoamide (TAA) which can be dehydrolyzed faster than TU, and showed high efficiency Cd-free CIGS solar cells with the following device configuration of sputter-deposited-ZnO:Al/ZnMgO/CBD-ZnS(O,OH)/CIGS/Mo/SLG [4]. However, the influence of HLS post-treatment on our specific device configuration of MOCVD-ZnO:B/CBD-ZnS(O,OH)(TAA-based recipe)/CIGS/Mo/SLG has never been investigated.

In this work, the impacts of HLS post-treatment on the film properties and cell performance of the above-mentioned device

* Corresponding author. Tel.: +81 42 770 9607.
E-mail address: t.koba.t1977@gmail.com (T. Kobayashi).

were investigated. The influence of TAA concentration and the post-treatment effects on the film properties and cell performance of ZnS(O,OH)/CIGS solar cells are also discussed in connection with the conduction band offset(CBO) at the CIGS/ZnS(O,OH) interface.

2. Experimental

CIGS thin-film solar cells with a ZnO:B/ZnS(O,OH)/CIGS/Mo/ soda lime glass (SLG) structure were fabricated as follows. A 1-μm-thick Mo back-contact film was deposited by DC-magnetron sputtering on SLG substrates at room temperature. A 2.4-μm-thick CIGS absorber layer was deposited by a three-stage process using a molecular beam epitaxy system at a maximum substrate temperature of 560 °C. The average film composition was measured using inductively coupled plasma spectroscopy (ICP). A 50 nm-thick ZnS(O,OH) buffer layer was deposited onto the CIGS layer by CBD using a $ZnSO_4$ (0.16 M)/ammonia (7.5 M)/TAA aqueous solution. The TAA concentration was varied from 0.03 M to 0.3 M. The temperature of the $ZnSO_4$/ammonia/TAA aqueous solution was increased from room temperature to 67 °C. The ZnS(O,OH)/CIGS stacked layers were air-annealed immediately after the CBD process at 200 °C for 10 min in order to enhance Zn diffusion into CIGS layer and thus promote the formation of shallow junction [20]. Subsequently, 0.9-μm-thick ZnO:B thin-films were deposited by metal organic chemical vapor deposition (MOCVD) at a substrate temperature of 185 °C for 15 min under ultraviolet light irradiation($\lambda = 172$ nm) [8,16]. The impact of heat soaking (HS), LS, and HLS was investigated for a set of completed solar cells. These post-treatments were as follows:

HS: the solar cells were annealed on a heating stage at 130 °C for 80 min in the air, LS: light-soaking under AM1.5, 100 mW/cm^2 illumination using a solar simulator for 80 min without intentional heating, the device temperature was increased from 25 °C to the saturated temperature of 40 °C in 10 min by the radiation during light soaking, HLS: a combination of one-sun LS and annealing on a heating stage at 130 °C for 80 min in the air.

The J–V characteristics of the solar cells with a ZnO:B/ZnS (O,OH)/CIGS/Mo/SLG structure were measured using a solar simulator (Class A for spectrum match, YSS-80, Yamashita Denso Corporation) calibrated with a Si standard cell under AM1.5, 100 mW/cm^2 illumination at 25 °C. The data of our in-house measurement are very close to those measured at NREL.

The film compositions as a function of TAA concentration before and after the post-treatments were also investigated for ZnS(O,OH)/CIGS stacked layers. XPS measurements were carried out using an AXIS-ULTRA (KRATOS) with monochromatic Al K$\alpha_{1,2}$ (15 keV) X-ray radiation under a base pressure of 2×10^{-9} Torr. Ar ion-beam sputter etching was carried out using a differentially pumped ion gun operating at 0.5 keV at a pressure of 5×10^{-8} Torr. The accuracy of the XPS measurements was estimated to be within ± 0.1 eV. In order to avoid peak shifting as a result of specimen charge-up, the surface of the specimen was grounded. The chemical shifts of the core-level emissions such as In 3d and Zn 2p are indistinguishable, and are suitable to serve as a monitor for peak-shifts as a result of charge-up. No significant peak-shifts caused by charge-up were observed in any of the measurements.

3. Results and discussion

Fig. 1 shows the ZnS(O,OH) layer thickness as a function of CBD processing time. The growth rate of ZnS(O,OH) films was successfully increased from 1 to 4 nm/min by replacing TU (0.6 M) with TAA (0.03 M). TAA-based CBD process can supply faster S atoms
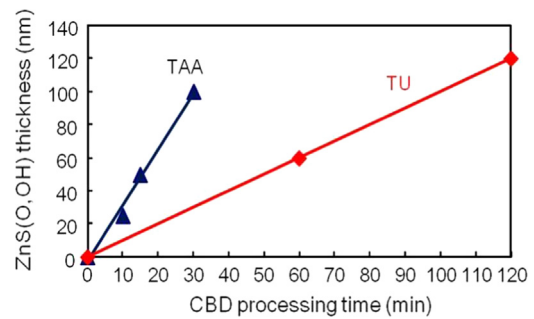

Fig. 1. ZnS(O,OH) layer thickness as a function of CBD processing time.
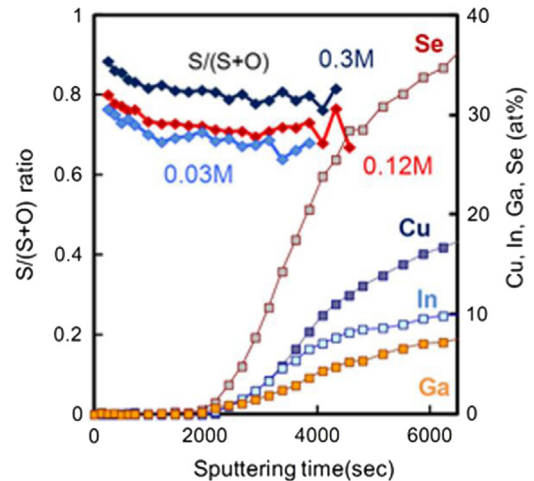

Fig. 2. XPS depth profiles of the S/(S+O) atomic ratios of ZnS(O,OH) buffer layers deposited using 0.03 M, 0.12 M and 0.3 M TAA concentrations

into the solution due to the higher hydrolysis rate of TAA as compared to TU [4]. Other than that, the deposition route and compositionof the ZnS(O,OH) buffer layers are suggested to be unchanged between the TAA- and TU-based CBD processes. Fig. 2 shows the XPS depth profiles of the S/(S+O) atomic ratios of ZnS (O,OH) buffer layers deposited using 0.03 M, 0.12 M and 0.3 M concentrations. The S/(S+O) atomic ratio in Fig. 2 are the values excluding the Zn(OH)$_2$ in the ZnS(O,OH) buffer layer. We see from Fig. 2 that the S/(S+O) atomic ratio increased with increasing the TAA concentration. TAA concentration was roughly optimized based on the composition of ZnS(O,OH) buffer layer. The S/(S+O) atomic ratio in ZnS(O,OH) film deposited using 0.03 M TAA showed almost the same value (S/(S+O)=0.6–0.7) as in our baseline ZnS(O,OH) buffer layer using 0.6 M TU [17,18].Therefore, the TAA concentration used in the latter experiments was fixed to 0.03 M. Fig. 3 shows (a) a SEM top-view and (b) a SEM cross sectional view of a 50 nm-thick ZnS(O,OH) buffer layer deposited onto CIGS layer. In the preliminary experiments, CIGS solar cells with 30 nm- and 50 nm-thick ZnS(O,OH) buffer layers were compared. The device with 50 nm-thick ZnS(O,OH) buffer layer showed higher cell parameters (V_{oc}=0.640 V, J_{sc}=34.8 mA/cm^2, FF 0.688, Eff. 15.4%) than that of the device with 30 nm-thick ZnS(O, OH) buffer layer(V_{oc}=0.603 V, J_{sc}=32.4 mA/cm^2, FF 0.455, Eff. 8.9%). The reason for the lower cell efficiency of the device with 30 nm-thick ZnS(O,OH) buffer layer is probably due to cliff nature of the CBO at the ZnS(O,OH)/CIGS interface and the insufficient coverage of the ZnS(O,OH) layer on the CIGS layer. Actually, the S/ (S+O) atomic ratio in ZnS(O,OH) buffer layer decreased with decreasing the film thickness, when the ZnS(O,OH) buffer layer was deposited by the TU-based CBD process [17]. Even while