Adjustment of alkali element incorporations in Cu(In,Ga)Se$_2$ thin films with wet chemistry Mo oxide as a hosting reservoir

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ABSTRACT

Thin film Cu(In,Ga)Se$_2$ solar cells remain one of the most promising devices for commercial photovoltaic panels. Aimed at high quality absorber film, alkali elements such as sodium and potassium incorporation can improve the crystal structure and electrical properties of the Cu(In,Ga)Se$_2$ film. However, the precise control on sodium content as well as the incorporation mechanisms is yet comprehensively understood. We propose a facile wet chemistry oxidation approach for large area homogeneous Mo oxidation and allow for uniform sodium incorporation in a controllable manner. Eventually the oxidized Mo substrate in an optimal condition leads to a relative increase of 8% of conversion efficiency in the final solar device compared with the non-oxidized sample. We thoroughly examine the surface chemistry of the Mo substrate with X-ray photoelectron spectroscopy after a systematic H$_2$O$_2$ oxidation treatment. A qualitative analysis show that the predominant Mo trioxides as a reservoir can adjust alkali elements contents in Cu(in,Ga)Se$_2$ films. Upon oxidation, the narrowing down of Mo grain boundaries has now suppressed the over sufficient sodium incorporation compared to uncontrolled diffusion from soda lime glass. Also, the emergence of potassium element in the thin film improves the electrical properties. Thermodynamic calculation indicate that the K$_2$MoO$_4$ as an intermediate from K$_2$O and MoO$_3$ reaction is a preferable reaction path compared the Na$_2$O reaction and thus enhanced potassium ion diffusion. We have correlate the sodium contents by simply adjusting the H$_2$O$_2$ treatment time to improved Cu(InGa)Se$_2$ film qualities, e.g., crystal structures, grain sizes, charge carrier concentrations and defect densities.

1. Introduction

Thin film Cu(In,Ga)Se$_2$ (CIGS) solar cell has attracted intensive interests from both laboratories and industries due to its high conversion efficiency, long life time and low fabrication cost [1–10]. Recently Cu(In,Ga)Se$_2$ solar cells has a refreshed record efficiency of 22.6% [11], which satisfies the requirements of photovoltaic electricity plant and household solar panels. In the Cu(In,Ga)Se$_2$ solar cell, a multi-layer thin film device, optimizations have been done on all functional layer films. As we know, Mo back contact layer plays an important role in Cu(In,Ga)Se$_2$ solar cells. So Researchers have done some work on the relationship between the preparation parameters of Mo layer and its morphology [12,13] as well as absorber characteristics [14]. And other groups also investigate the formation condition of MoSe$_2$ during absorber deposition [15–19].

Moreover, sodium-rich glass substrate, e.g., soda lime glass, can greatly enhance the structural and electrical properties of Cu(In,Ga)Se$_2$ absorber materials in comparison to the sodium-free glass. Tiwari [20] and Schock [21] determined that this electrical improvement is attributed to the incorporated alkali elements which diffuse in the Cu(In,Ga)Se$_2$ films from the sodium-rich glass through Mo grain boundaries [22]. Moreover, sodium incorporation have other advantages, such as improving the CIGS/Mo interface for an ohmic contact [23], increasing charge carrier concentration [24] as well as decreasing defect density [25]. However, the excess sodium diffusion [26] from the soda lime glass not only hinders the Cu(In,Ga)Se$_2$ structures with smaller grains and undesired Ga distribution profile but also degrades their electrical properties as well device performances with higher defect density, which causes severe recombination of photo-generated electron-hole pairs. In addition, it is necessary for another cation to maintain charge balance during diffusion process. So H$^+$ is suggested to be the essential cation to exchange with Na$^+$ from SLG substrate [21].

Early studies show the influences of surface treatments over Mo substrates like morphology modification [12,27], deposition of thin layers on Mo surface [28–31] and surface sulfurization [32] or oxidation [33]. These treatments are aimed at reducing back-interface recombination or improving the back ohmic-contact. Meanwhile, the sodium diffusion is also influenced by these surface modifications as they will introduce diffusion barriers or increase oxygen contents which has strong affinity for sodium [34] to the CIGS/Mo interface. In fact, the role of oxygen contents in Mo substrates remain an open question for sodium diffusions in $Cu(In,Ga)Se_2$ thin films [27,33–36].

In order to adjust the incorporation of sodium, we develop a non-vacuum facile aqueous H_2O_2 soaking method to modify the Mo surface morphology and oxygen content. With systematic H_2O_2 treatment studies, we provide an optimal protocol for both increasing the electrical performance and avoiding degradation in grain sizes and Ga gradient. Indeed, the crystalline structure, grain sizes, Ga distribution gradient of the $Cu(In,Ga)Se_2$ films have been improved with the optimal alkali element diffusion. This high quality of the $Cu(In,Ga)Se_2$ thin films have been reflected in the final higher efficiency solar cells with larger open circuit voltages and greater filled factors.

2. Experimental

The Mo layer was deposited by DC-sputtering with commonly adopted double-layer process onto DI water rinsed and ultrasonic cleaned 24 cm × 24 cm soda lime glass. The first layer was sputtered with high Ar pressure to form low density Mo layer which has good adhesion to the SLG surface and the second layer was deposited with low Ar pressure to form high density Mo layer which has good conductivity and compact surface [37]. The final film thickness is about 900 nm and the sheet resistance is about 0.3 Ω/□. After the Mo layer deposition, the whole Mo/SLG substrate was cut into small ones with size of 42 mm × 44 mm to be applied in the subsequent procedures. To ensure the substrate identical for all samples in our work, all small Mo/SLG substrates were taken from the same large one.

Subsequently, 42 mm × 44 mm Mo/SLG substrates were oxidized in 5% H_2O_2 solution for different time at temperature of 12 °C before the deposition of $Cu(In,Ga)Se_2$ absorbers. Two batches of samples are prepared. One is 0 s, 20 s, 40 s and 60 s and the other is 0 s, 30 s, 60 s and 90 s. The samples will be named according to their oxidation time in latter descriptions. Then, the oxidized Mo substrates were introduced into the high vacuum chamber to start the absorber layer deposition. The absorber films were deposited with three-stage co-evaporation processes [38]. The substrate temperatures were 350 °C, 550 °C and 550 °C during three stages, respectively. After the absorber deposition, the samples were immersed into chemical bath deposition (CBD) solution to start the CdS film deposition with bath temperature of 77 °C. When the film thickness approached about 50 nm, the deposition process ended and the samples were rinsed in DI water before drying with N_2 flux. The following deposition of intrinsic ZnO and Al doped ZnO were finished with magnetic sputtering. Then the samples were

transferred to an electron beam evaporation equipment to finish the Ni/Al grid deposition with mask to define the grid shape. At last, the cells were defined with mechanical scribing. The final cells' total area is about 0.5 cm^2. The active area is about 97% of the total area. About 105 nm thick layer of MgF_2 is deposited by e-beam evaporation to act as anti-reflection coating.

XPS characterizations were done by PHI5000 Versa Probe on Mo/SLG substrate surface. The composition distributions of absorber layers were characterized by secondary ion mass spectrum (SIMS) on a CAMECA IMS-7F SIMS. The Mo morphology SEM pictures were taken on a HITACHI S-4800 Scanning Electron Microscope and device cross section images were taken on an FEI Nova NanoSEM 450. X-ray diffraction (XRD) measurements were performed on PANalytical X′Per Pro. Current density-Voltage (J-V) curves were obtained on a Keithley 2420 Source Meter under the illumination of SAN-EIXES-500T1 solar simulator generated AM1.5G spectrum. Capacitance-Voltage and Admittance Spectroscopy characterizations were both performed with an HP 4284A LCR meter. To obtain the data of low temperature range for admittance spectrum, an Accent HL5550 LN2 cryostat is used to cooperate with LCR meter.

3. Results and discussion

3.1. Optimization of Mo oxidation with H_2O_2

We first look at the H_2O_2 oxidation influence on the surface morphology. The SEM and XPS characterizations were applied to 0 s and 60 s oxidized Mo to analyze the morphology variation and chemical state. The SEM images were shown in Fig. S1 in Supplementary Material. Before oxidation, the Mo grains show clearly visible boundaries. However, after oxidation in H_2O_2, the boundary turned blurred with more compact surface. The compact Mo surface is caused by the addition of oxygen into the Mo surface which decrease porosity with the expansion of crystalline grains. The compact surface will play dual roles in the diffusion of alkali elements through Mo layers (discussed later). The first is to introduce a diffusion barrier on the Mo surface. The second is to introduce an oxygen-rich layer to act as an alkali reservoir. Both roles contribute to the differences of alkali element contents in the absorbers prepared on Mo substrates with different oxidation time.

We now look at the chemical states of Mo for H_2O_2 oxidized sample and the reference. X-ray photoelectron spectroscopy presents rich information for chemical environment such as valence state of an element in a compound. As seen in Fig. 1(a), the non-treated Mo shows some shift to the oxide peaks. Indeed, the quantitative XPS analysis shows the Mo surface consists of 49% Mo, 34% MoO_2 and 17% MoO_3. Our sample possesses a much larger portion of MoO_2 than literature [12], which may be caused by slow oxidation in air storage for days. This suggests that the main product by air nature oxidation is MoO_2 because the MoO_3 ratio does not change too much with storage time. However as shown in Fig. 1(b), the H_2O_2 treatment greatly enhanced the oxidation of the Mo surface with 98% oxide phase with negligible elemental Mo
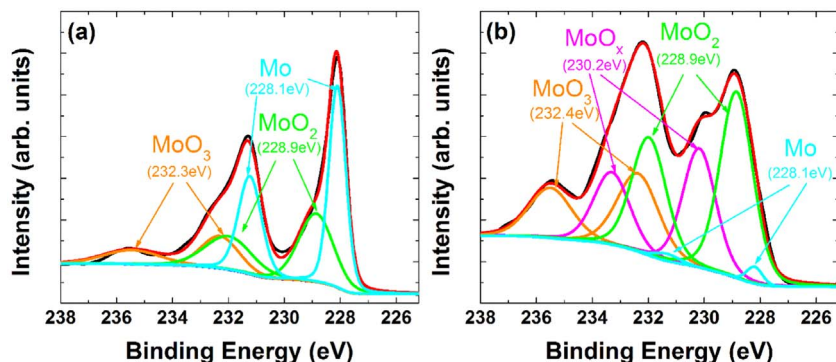

Fig. 1. XPS spectrum and Gaussian fitting of Mo 3d region for 0 s (a) and 60 s (b) H_2O_2 solution oxidized Mo/SLG samples.