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Cu-accumulation at the interface between sputter-(Zn,Mg)O and $Cu(In,Ga)(S,Se)_2$ — A key to understanding the need for buffer layers?

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Abstract

$Zn_{0.85}Mg_{0.15}O$ buffer layers can replace both i-ZnO and CdS in n-ZnO/i-ZnO/CdS/$Cu(In_xGa_{1-x})(S_ySe_{1-y})_2$/Mo/glass (CIGSSe) solar cells without significant loss of efficiency. We found that the efficiency of $Zn_{0.85}Mg_{0.15}O$ buffered solar cells decreased with increasing sample temperature when we sputter-deposited $Zn_{0.85}Mg_{0.15}O$ directly onto the CIGSSe absorber surface, e.g. from 9.5% without deliberate heating to 6.5% at 240 °C. To find an explanation for this behavior we sputter-coated bare, KCN-etched CIGSSe absorbers with about 420 nm of $Zn_{0.85}Mg_{0.15}O$ at different sample temperatures and subsequently removed the $Zn_{0.85}Mg_{0.15}O$ layers by wet-chemical etching with dilute acetic acid. The exposed CIGSSe surfaces were examined by surface-sensitive X-ray photoelectron spectroscopy (XPS) and X-ray excited Auger electron spectroscopy (XAES). We found a strong increase in the [Cu]/([In]+[Cu]) ratio compared to a bare, Acetic-acid-etched CIGSSe reference. The surface of samples that had been sputter-coated at 150 °C changed from being initially Cu-poor to Cu-rich. The chemical shift of Cu Auger peaks from the same surface confirmed this finding. The increased Cu/In ratio and the chemical shift were reversed after KCN etch. These findings are discussed in the context of the model of a Cu-depleted, wide-band gap surface region in CIGSSe solar cells as a prerequisite for high efficiency.

Keywords: Chalcopyrite; Solar cells; Cu-depletion; Sputter-coating; (Zn,Mg)O; Cd-free buffer; CIGSSe

1. Introduction

Thin film solar cells based on the chalcopyrite absorber material $Cu(In_xGa_{1-x})(S_ySe_{1-y})_2$ ("CIGSSe") have reached cell efficiencies close to 20% on a laboratory scale [1]. A current research challenge is the replacement of the conventionally used CdS buffer layer in the standard cell structure n-ZnO/i-ZnO/CdS/CIGSSe/Mo/glass. Recently, it was shown that the replacement of the i-ZnO/CdS-double layer by an rf-sputtered single layer of $Zn_{0.85}Mg_{0.15}O$ (120 nm) directly on a CIGSSe absorber from the Shell Solar pilot line (Munich) without any surface treatment led to a solar cell efficiency of 12.5% (compared to 13.2% with the conventional double layer and 6.3% solely with i-ZnO on the same absorber) [2]. In this paper we describe the effect of the sample temperature during sputter deposition on the solar cell efficiency and the interface composition.

2. Experimental

CIGSSe absorber layers on Mo-coated glass were supplied by Shell Solar, Munich. Immediately prior to use they were etched in an aqueous solution of KCN (10%) and KOH (approx. 1%) for 5 min at room temperature, rinsed several times with purified water and blown dry with nitrogen. Rf-sputter coating with $Zn_{0.85}Mg_{0.15}O$ was performed in a UHV-compatible sputter chamber equipped with two water-cooled magnetron sources. The ceramic sputter target consisted of a mixture of 85% i-ZnO and 15% MgO and was purchased from W.C. Heraeus GmbH &

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Co. KG. The sputter gas was argon with a purity of 99.9999 (grade 6.0, Air Liquide) which was used without further purification. For further details on the setup see [3].

The samples were heated to the desired temperature with a ceramic resistive heater placed in the back of the sample holder before sputter coating. The sample temperature was measured using a Ni/CrNi thermocouple mounted between sample and sample holder. It should be noted that the sample temperature indicated in this paper was measured before the sputter deposition started. Due to the unavoidable heating by the argon plasma during the sputter process, however, all samples experienced additional heating. This effect was especially pronounced in the case of the "room temperature" sample, where no external heating was used. After 10 min, which is the duration of the sputter process, the temperature had risen to about 100 °C. At higher initial temperatures the difference between desired and final temperature was smaller, i.e. around +60 °C at nominal 50 °C and +20 °C at nominal 150 °C. The thickness of the resulting layers was approximately 420 nm. Removal of the $Zn_{0.85}Mg_{0.15}O$ was achieved by etching in a 20% (v/v) solution of acetic acid (Baker, 99–100%, "Baker Analyzed" grade) in 2-propanol (Merck, p.A.) at room temperature for 2 h. The samples were then rinsed three times, each time with about 5 ml of 20% acetic acid in 2-propanol to avoid precipitation of $Zn(OH)_2$, then rinsed with purified water and blown dry with nitrogen.

Surface characterization was performed in the "CISSY" UHV apparatus, consisting of several interconnected UHV chambers, a sputter-deposition chamber, and an attached glove box for sample preparation (for more details see [4]). A CLAM 4 electron analyser (Thermo VG Scientific) was used for XPS and XAES. The angle between sample normal and the electron spectrometer lens (the emission angle φ) in this setup was 25°.

MgK_α (1253.6 eV) and Al K_α (1486.6 eV) radiation from a SPECS XR 50 X-ray gun served as excitation sources. The electron spectrometer was calibrated according to Ref. [5] using XPS and Auger line positions of different metals (Cu 3p, Au $4f_{7/2}$, Cu L_3MM, and Cu $2p_{3/2}$).

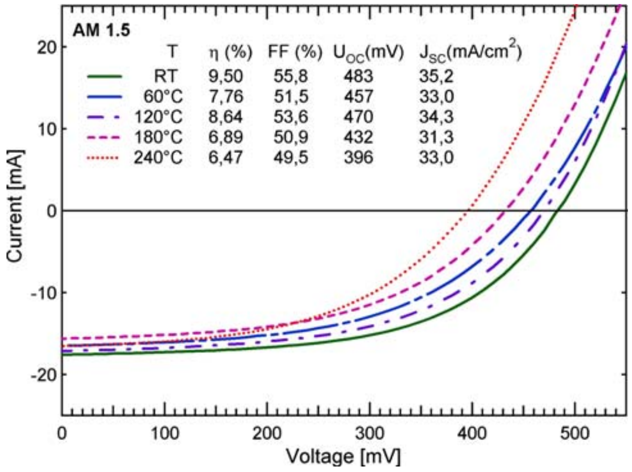

Fig. 1. Current–voltage curves from $Zn_{0.85}Mg_{0.15}O$-buffered CIGSSe solar cells, sputter-coated at different substrate temperatures as indicated in the insert. Solar cell parameters are also given in the insert.

3. Results and discussion

We observed a clear efficiency drop of solar devices of the structure n-ZnO/$Zn_{0.85}Mg_{0.15}O$/CIGSSe/Mo/glass with increasing substrate temperature during the sputter deposition of approx. 80 nm of $Zn_{0.85}Mg_{0.15}O$. This is shown in Fig. 1, where a steady decrease in V_{oc} with increasing substrate temperature, starting at (nominally) room temperature, is evident. Only the I/V curve at 60 °C does not fit the general pattern, however, here the serial resistance appears to be higher so that the slope of the curve is different. Since we had initially assumed a beneficial effect of a higher sample temperature due to the expected improvement in structural and electronic properties of the sputtered layer, we searched for an explanation. To examine possible temperature-dependent chemical changes that might account for the observed effects, we analyzed the interface between $Zn_{0.85}Mg_{0.15}O$, sputter deposited for 10 min (resulting in approximately 420 nm thick layers) at different substrate temperatures, and the CIGSSe absorber. In order to get access to the absorber surface we removed the $Zn_{0.85}Mg_{0.15}O$ cover layer by etching with dilute acetic acid and used surface-sensitive XPS and XAES to determine the surface composition. The following samples were examined:

- a KCN-etched CIGSSe absorber before and after heating in vacuum at 150 °C for 30 min
- a KCN-etched absorber after subsequent etching in dilute acetic acid as reference sample
- a KCN-etched absorber after sputter deposition of $Zn_{0.85}Mg_{0.15}O$ at room temperature for 10 min and subsequent removal of the $Zn_{0.85}Mg_{0.15}O$ with dilute acetic acid
- as above, but with sputter deposition of $Zn_{0.85}Mg_{0.15}O$ at 150 °C
- finally, the same "$Zn_{0.85}Mg_{0.15}O$ at 150 °C" sample after a second etching step in 10% aqueous KCN.

XPS overview spectra (not shown) revealed the presence of the expected absorber peaks from Cu, In, S, and Se. Additionally, O and C could be detected. Although the overall composition of the samples is $Cu(In_xGa_{1-x})(S_ySe_{1-y})_2$, Ga can normally not be observed on the surface of our samples because all the Ga is contained in Ga-rich chalcopyrite phases in the back contact region. In the case of the sputter-coated and etched samples also trace amounts of Zn, but no residual Mg could be detected. The relative amount of each absorber element was calculated by fitting the individual photoemission peaks Cu 3p, In 4d, S 2s and Se 3s, measured with high resolution (not shown), with the appropriate Voigt functions (including a linear base line) and integrating these. The values obtained were then divided by the photoemission cross-sections [6] and corrected for the different mean free paths using values calculated with the QUASES-IMFP-TPP2MTM Software Package [7]. It should be noted that due to uncertainties in both the mean free path and the