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Effect of Zn(O,S) buffer layer thickness on charge carrier relaxation dynamics of $CuInSe_2$ solar cell

Juan Sun [a,b], Venkatram Nalla [c], Mai Nguyen [a], Yi Ren [d], Sing Yang Chiam [d], Yue Wang [e], Kong Fai Tai [a,e], Handong Sun [c,e], Nikolay Zheludev [c], Sudip K. Batabyal [a,*], Lydia H. Wong [b,*]

[a] *Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, Research Techno Plaza, Singapore 637553, Singapore*
[b] *School of Materials Science & Engineering, Nanyang Technological University, Singapore 639798, Singapore*
[c] *Centre for Disruptive Photonic Technologies, Nanyang Technological University, Singapore 637371, Singapore*
[d] *Institute of Materials Research and Engineering, A*STAR (Agency for Science Technology and Research), 3 Research Link, Singapore 117602, Singapore*
[e] *Division of Physics and Applied Physics, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore*

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Abstract

A pinhole free Zn(O,S) buffer layer was deposited on $CuInSe_2$ (CIS) absorber by chemical bath deposition (CBD) method. Thin Zn(O,S) exhibits better power conversion efficiency (PCE) at lower thickness. Enhancement of PCE from 1.5% to 3.9% was observed for electrodeposited CIS photovoltaic device when the buffer layer thickness reduces from 50 nm to 20 nm. Although the conduction band offset (CBO) at Zn(O,S)/CIS interface are almost identical for both the 20 nm and 50 nm thick buffer layers, investigation on charge carrier dynamics reveals that the carrier lifetime for the 20 nm buffer is much longer than the 50 nm buffer. This offers a plausible explanation for the higher *J*sc of the device with 20 nm buffer layer compared to the device with 50 nm buffer layer.

Keywords: Solar cell; $CuInSe_2$; Buffer layer; Zn(O,S); Pump-probe; Charge carrier dynamics

1. Introduction

There has been considerable research interest for high efficiency $CuInGaSe_2$ (CIGS) based thin film solar cells because of promising material properties and outstanding performance. A variety of methods are used today for the fabrication of such cells and currently, the highest cell efficiency is reported as 21.7% (Jackson et al., 2015). Most of these cells are obtained using CdS buffer layer deposited by chemical bath deposition (CBD). However, there are some debates on the fundamental issues with this buffer layer, mainly because of the toxicity of Cd and the non-ideal band gap. CdS has band gap energy about 2.4–2.5 eV, which is non-optimal for cell performance especially in the short wavelength domain as it has considerable absorbance in these regions (Siebentritt, 2004; Hariskos et al., 2005). Hence, many research efforts in the realm of CIGS solar cells are focused on the development and implementation of Cd-free alternative buffer layer (Naghavi et al., 2010; Lee et al., 2014).

* Corresponding authors. Tel.: +65 6790 4626 (S.K. Batabyal), +65 6513 8292 (L.H. Wong).
E-mail addresses: Batabyal@gmail.com (S.K. Batabyal), lydiawong@ntu.edu.sg (L.H. Wong).

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To find out the best candidate many alternative materials have been tested in the past decade for a Cd-free buffer layer (Siebentritt, 2004; Cherian et al. 2012) in CIGS solar cells. ZnS-based buffer layer has emerged to be one of the most promising candidates for this purpose (Kushiya et al. 1996; Kushiya, 2004; Shin et al. 2011; Bhattacharya and Ramanathan, 2004). There are few reports to develop the ZnS based buffer layer as a promising alternative of CdS based buffer layer (Merdes et al. 2014; Kushiya et al. 1996; Nakamura et al. 2013; Spiering et al. 2006). It was reported that CIGS cells fabricated with chemical bath deposited (CBD) Zn–S buffer layer yielded 19.7% efficiency (Nakamura et al., 2013), comparable to the efficiency of CIGS cell with CdS buffer which was used as a control in that study. Initially very thick Zn(O,S) buffer layer were used, such as 120 nm Zn(O,S) achieved by 3 cycles of CBD deposition (Nakada et al., 2001; Bhattacharya and Ramanathan, 2004), Japanese CIGS manufacturing company showa Shell (Hariskos et al., 2005) deposited a Zn(O,S) buffer with a thickness of around 50 nm. While there were differences in the deposition methods used by the various groups, it is noted that most of the research groups used a Zn(O,S) buffer of about 50–100 nm (Nakada et al., 2001; Contreras et al., 2003; Hsieh et al., 2014). Recently, Very thin CBD grown Zn(O,S) buffer layer was reported as highly promising buffer layer (Kobayashi et al., 2013; Nguyen et al. 2014). This result was also echoed by reports from other research group (Wei-Tse et al., 2012) who compared the 15 nm CBD–Zn(O,S) with the control 50 nm CdS buffer layer for CIGS solar cell applications. The excellent performance of ultra thin Zn(O,S) buffers were reported either by CBD (Kobayashi et al., 2013; Wei-Tse et al., 2012) method or the atomic layer deposition (ALD) (Platzer-Björkman et al., 2006; Uhm et al., 2014). However, the results are largely empirical and the fundamental science to explain the reasons for the equivalent or better performance of the ultra thin buffer layer compared to the thicker one is still unclear.

Here we aim to understand the effect of thickness of Zn(O,S) buffer layer on CIS solar cell. The optical properties and PCE of CIS solar cells with different thicknesses of Zn(O,S) buffer layers were investigated. Details stoichiometries of the buffer layer were studied when the thickness increases by XPS analysis which helps to understand the charge carrier dynamics of the buffer layer for different thickness. We want to investigate how the thickness of the buffer layer effected the *Jsc* of the photovoltaic device depends on the buffer layer deposition condition and how the carrier life time in the buffer layer is depends on the thickness of the buffer layer. Although there were few reports on the utilization and optimization of Zn(O,S) buffer layer for CIGS solar cell, this paper is the first to correlate device data to charge carrier dynamics and investigate the effect of thickness of the buffer layer by optical probing.

2. Experimental

2.1. Materials

In order to prepare the deposition bath, zinc acetate dihydrate (Sigma Aldrich, ACS reagent grade, ⩾98%), Thiourea (Sigma Aldrich, ACS reagent grade, 99%) and Ammonia hydroxide (Sigma Aldrich, ACS reagent grade, 28–30%) were used as received without further purification.

2.2. Thin film growth and device fabrication

To study the optical properties of Zn(O,S) film, the film was deposited onto plasma cleaned UV-transparent quartz substrate by a CBD method. The chemical bath solution was comprised of 0.08 M $Zn(Ac)_2$, 5 M Thiourea (TU) and 7 M NH_3 in deionized (DI) water. $Zn(Ac)_2$ powder was first added into DI water then followed by TU powder. When the temperature of water bath reached close to 85 °C, concentrated NH_3 was added. The whole bottle of mixed precursor solution was placed into the water bath with stirring. And then the reaction started. The pH of the solution was maintained between 10 and 11. The NH_3 produced from the NH_4OH worked as a complexing agent to form complexation with Zn^{2+} and then control the growth of ZnS, through following reactions (Shin et al., 2013).

Complexation process:

$$Zn^{2+} + 4NH_3 \leftrightarrow Zn(NH_3)_4^{2+} \quad (1)$$

ZnS film growth

$$Zn(NH_3)_4^{2+} + (NH_2)_2CS + 2OH^- \leftrightarrow ZnS + 4NH_3 + CN_2H_2 + 2H_2O \quad (2)$$

Because the solution is basic, $Zn(OH)_2$ will also form through

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad (3)$$

The deposition time was varied from 12 min and 25 min to vary the thickness of Zn(O,S) film. The quartz substrate was then taken out from the chemical bath and washed in NH_3 solution (aqueous 2.5% solution) in order to clean out the uncontrollable precipitation of $Zn(OH)_2$ on the surface. At last, the quartz substrate was rinsed with DI water and dried under N_2 gun. Then the films were annealed at 200 °C for 20 min to convert $Zn(OH)_2$ inside Zn(O,S) film to ZnO.

To fabricate the CIS solar cell, a 500 nm-thick molybdenum (Mo) back contact was deposited by DC-magnetron sputtering on soda lime glass (SLG) substrates. To clarify the basic device structure a schematic representation of the device are provided in Supporting Information S1. The elemental Cu and In were deposited onto Mo substrate sequentially by electrodeposition method (Calixto and Sebastian, 1998; Bhattacharya, 2013). The Cu/In ratio