Development of a New Double Buffer Layer for $Cu(In,Ga)Se_2$ Solar Cells

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Abstract: The new approach to buffer layer design for CIGS solar cells that permitted to reduce the buffer absorption losses in the short wavelength range and to overcome the disadvantages inherent to Cd-free CIGS solar cells was proposed. A chemical bath deposition method has been used to produce a high quality buffer layer that comprises thin film of CdS and Zn-based film. The double layer was grown on either ITO or CIGS substrates and its morphological, structural and optical properties were characterized. The Zn-based film was described as the ternary compound $ZnS_x(OH)_y$. The composition of the $ZnS_x(OH)_y$ layer was not uniform throughout its thickness. $ZnS_x(OH)_y$/CdS/substrate region was a highly intermixed region with gradually changing composition. The short wavelength cut-off of double layer was shifted to shorter wavelength (400 nm) compared to that (520 nm) for the standard CdS by optimization of the double buffer design. The results show the way to improve the light energy collection efficiency of the nearly cadmium-free CIGS-based solar cells.

1. Introduction

At the moment solar cells based on $Cu(In,Ga)Se_2$ (CIGS) provided a world record power conversion efficiency of 18.8% [1]. These cells employed a chemical bath deposited (CBD) CdS buffer layer. One of the perplexing problems faced by designers of CIGS solar cells has involved the need to improve the light energy collection efficiency of the cell. The short wavelength response of CIGS solar cell is limited by CdS absorption end (E_g.=2.4 eV). In general this problem can be decided by utilizing the n-type material having band gap energy of greater than 2.4 eV.

Therefore, our efforts have been directed to the reducing the buffer absorption losses in the short wavelength range. The foregoing objective is attained by forming a buffer layer that was comprised of CB depositing a very thin CdS layer and, CB depositing thereon Zn-based layer.

2. Experimental

A buffer layer that was comprised of a very thin CdS layer and, depositing thereon Zn-based layer was formed on either ITO or CIGS substrates. The experimental chemical bath conditions for CdS and Zn-based film growth were reported previously [2]. In such double buffer layer it is preferred that there be a first CdS film ranging in thickness from about 15 nm to about 40 nm, and a superimposed Zn-based film ranging in thickness from about 40 nm to 150nm.

To growth a high quality Zn-based layer the two very thin Zn-based films were sequentially applied on the substrate covered by CdS. The thickness of each film was varied from 40 to 60 nm. The deposition time was varied from 15 to 25 min.

3. Results and Discussion

Fig. 1 shows the cross section and surface SEM images of the CdS/Zn-based double buffer layers grown on ITO substrates. CdS and Zn-based films were deposited for 4 and 17 min, and their thicknesses in this case were found to be 14 and 60 nm, respectively (Fig. 1a). Zn-based film with 60 nm thickness shows uniform covering with grain structure. Grain size ranges from about 6 nm to about 11nm. Early we reported that the increased thickness over 100 nm results in defective films with cracks [2].

SEM studies have shown that a high quality double buffer layer can be grown by using sequentially deposition of two thin Zn-based films on either ITO or CIGS substrates covered by CdS film (Fig. 1b).

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Buffer layer (CdS/Zn-based/Zn-based) produced by using the foregoing method has an overall thickness about 130 nm. The double deposition of Zn-based film results in uniform film with grain structure. Grain size ranges from about 9 nm to about 11 nm (Fig. 1b).

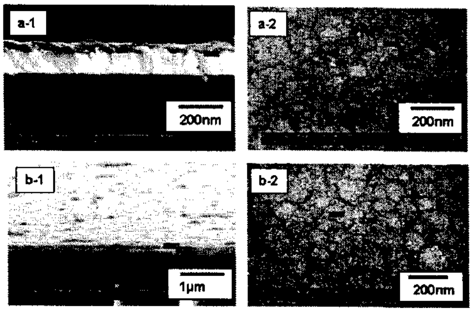

Fig. 1 Cross section and surface SEM images of $CdS/ZnS_x(OH)_y$ double layers on ITO substrates. CdS and $ZnS_x(OH)_y$ film thicknesses: 14 and 60 nm (a), $CdS/ZnS_x(OH)_y/ZnS_x(OH)_y$ layer thickness: 130 nm (b).

XPS analysis revealed that Zn based layer contains ZnS and $Zn(OH)_2$ compounds. An overall the chemical formula can be written as $ZnS_x(OH)_y$. The composition of the $ZnS_x(OH)_y$ layer was not uniform throughout its thickness. Auger sputter depth profile studies revealed the variation of the ratio of ZnS and $Zn(OH)_2$ with the profile depth of Zn based layer. Zinc sulfide content ranges in the film from about 83% to about 12% and zinc hydroxide content ranges from about 17% to about 88%. The maximum content of ZnS was found on the surface of the buffer layer while the minimum on the buffer/ITO interface.

Auger data showed the strong interdiffusion effect in a buffer/substrate region. Buffer/ substrate region does not consist of two abrupt interfaces; it is a highly intermixed region with gradually changing composition.

We believe that a high interdiffusion will strongly influence the conduction-band offset (CBO) and Cd impact will decrease CBO at the double buffer/CIGS interface compared to the large CBO for a pure ZnS buffer.

The thicknesses of both CdS and $ZnS_x(OH)_y$ films of the buffer layer were varied in order to form controlled transmittance of buffer layer to best suit the purpose of solar cell application. Fig. 2 shows the optical transmittance of the CdS films and $CdS/ZnS_x(OH)_y$ double films deposited on ITO substrates. The short wavelength cut-off corresponds to the band gap of the buffer layer. The short wavelength cut-off of double layer is governed by $ZnS_x(OH)_y$ absorption edge if the thickness of CdS film does not exceed 20 – 25 nm and was located at about 400 nm (Fig. 2). The optical transmittance of the double layer is higher than that of the CdS film with the same overall thickness, approaching on the order of 90% in the spectral range of 500 nm to 900 nm (Fig. 2).

The results have shown that by properly choosing the thickness of CdS film and overall thickness of $ZnS_x(OH)_y$ film, buffer layer can be matched to the solar spectrum where the photovoltaic conversion efficiency is maximum.

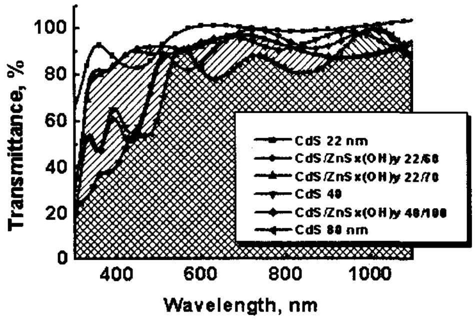

Fig. 2 Optical transmittance spectra of the $CdS/ZnS_x(OH)_y$ double films and CdS films deposited on ITO substrates.

4. Conclusion

The double layers that comprise thin film of CdS and $ZnS_x(OH)_y$ film were grown on either ITO or CIGS substrates. By optimizing the growth procedure it is possible to control of defect structure of the double buffer that is critical to the successful manufacture of CIGS solar cell.

By properly choosing the double layer design the short wavelength cut-off can be shift from about 520 nm for standard CdS buffer to about 400 nm. Solar cell can be matched to the solar spectrum and effectively collect incident light

We believe that interdiffusion of elements in buffer/CIGS region will effect on the CBO and Cd impact will decrease CBO at the interface compared to the large CBO for single ZnS buffer.

CIGS solar cells that employed the newly developed buffer layer utilize minimal amounts of hazard material and capable to keep the positive impact of the CdS/CIGS interface on the electronic structure of device.

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