Properties of Ga_2O_3/Ga_2O_3:Sn/CIGS for visible light sensors

K Kikuchi[1], S Imura, K Miyakawa, H Ohtake, M Kubota

NHK Science and Technology Research Laboratories
1-10-11, Kinuta, Setagaya-ku, Tokyo, 157–8510, Japan

E-mail: kikuchi.k-oa@nhk.or.jp

Abstract. A Ga_2O_3/Ga_2O_3:Sn/$CuIn_{1-x}Ga_x(Se_{1-y}S_y)_2$(CIGS) structure is proposed for use in visible light sensors. CIGS thin films have been investigated for high efficiency thin-film solar cells. The typical structure of CIGS solar cells consists of ZnO/CdS/CIGS. However, the quantum efficiency of this structure at short wavelengths is decreased due to optical absorption loss from the CdS layer. In this study, a Ga_2O_3 layer was adopted instead of a CdS layer. Ga_2O_3 has a wide band gap and high transmittance in the visible region. Furthermore, it was assumed that it could function as a hole-blocking layer to suppress hole injection from the anode. Additionally, a Ga_2O_3:Sn thin layer was laid on the CIGS layer to spread the depletion region to the CIGS layer, because the carrier density of the undoped Ga_2O_3 layer was much lower than that of the CIGS layer. In this structure, signal current multiplication and quantum efficiency greater than unity were observed at applied voltages over 3.5 V.

1. Introduction

$CuIn_{1-x}Ga_x(Se_{1-y}S_y)_2$ (CIGS) chalcopyrite thin films have been used for thin film solar cells with very high energy conversion efficiency of over 20 % [1, 2]. They have high quantum efficiencies and high absorption coefficients. Moreover, the band gap is adjustable by varying the composition ratios [3, 4]. CIGS films have great potential for improving the sensitivity of image sensors. For solar cells, a cadmium sulfide (CdS) buffer layer is usually applied to a CIGS film. However, cadmium is undesirable from the viewpoint of environmental safety. Also, this structure has low sensitivity to blue light, because the band gap of CdS is 2.4 eV [5]. This is especially a problem for solar cells and visible light sensors. For these reasons, much effort has been expended on finding a Cd-free replacement material for solar cells [6, 7]. Another problem is that the dark currents of CIGS films are high because of their low resistivities [8]. We used gallium oxide (Ga_2O_3) instead of CdS, as Ga_2O_3 has a wide band gap of 4.9 eV and high transmittance of visible light [9]. Higher short-wavelength quantum efficiency can be expected by widening the band gap beyond that of CdS. Moreover, we assumed that the Ga_2O_3 thin film would function as a hole-blocking layer for CIGS films and suppress the injection of holes from the electrode [10]. A Sn-doped Ga_2O_3 (Ga_2O_3:Sn) layer was layered between the CIGS and Ga_2O_3 layers to spread the depletion region to the CIGS layer, because the carrier density of the undoped Ga_2O_3 layer was much lower than that of CIGS layer. In this study, the electric characteristics of Ga_2O_3/Ga_2O_3:Sn/CIGS structure were investigated.

[1] To whom any correspondence should be addressed.

Journal of Physics: Conference Series **619** (2015) 012009 doi:10.1088/1742-6596/619/1/012009

2. Experimental

The Ga_2O_3:Sn (50 nm)/CIGS (1μm) structures were formed on Mo (1μm)-coated alkali-free Corning glass substrates (EAGLE-XG) in a procedure similar to those in our previous studies [11, 12]. Then, Ga_2O_3 films (100 nm) were deposited by pulsed laser deposition (PLD) from a Ga_2O_3 target using an Nd:YAG laser (wavelength of 213 nm; repetition rate of 1.0 Hz). The substrate temperature during PLD was 295 K. Finally, a front contact 30-nm ITO film was deposited by direct current (DC) magnetron sputtering onto each sample in Ar/O2 1% atmosphere. The optical transmittance and reflectance of the CIGS and Ga_2O_3 films were measured with a spectrophotometer to estimate their optical band gaps. The energy difference between the Fermi level and valence band for each film was analyzed by X-ray photoelectron spectroscopy (XPS).

3. Results and discussion

Figure 1 shows the energy band diagram of Ga_2O_3 and $CuIn_{0.5}Ga_{0.5}S_2$. The work function of Ga_2O_3 and electron affinity of CIGS was taken from other studies [13, 14]. As observed in the diagram, Ga_2O_3 should have a high potential barrier against holes from the anode.

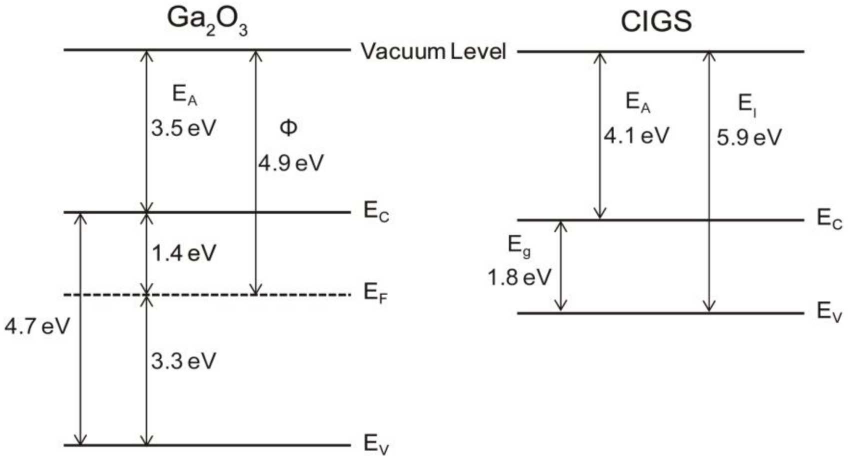

Figure 1. Energy band diagram of Ga_2O_3 and CIGS.

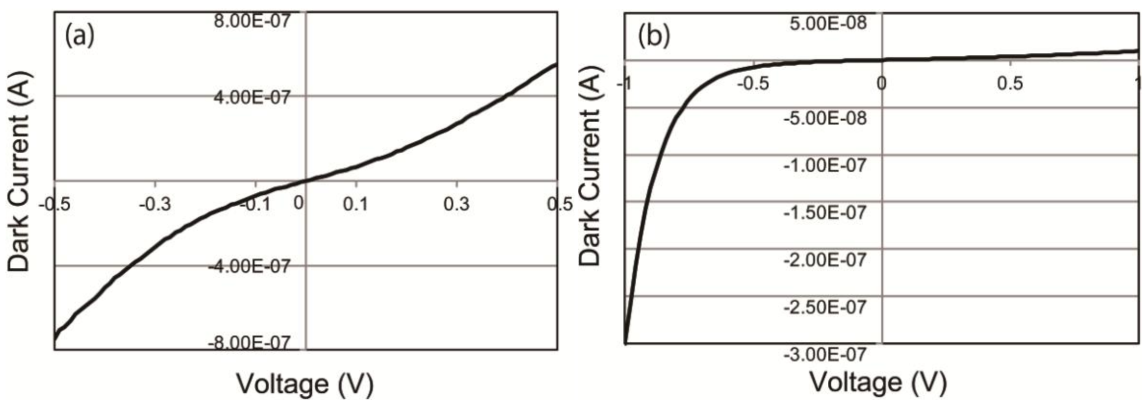

Figure 2. The dark current–voltage characteristics for the (a) Ga_2O_3:Sn/CIGS and (b) Ga_2O_3/Ga_2O_3:Sn/CIGS structures.

Figure 2 plots the dependence of the dark current on the voltage for the Ga_2O_3:Sn/CIGS and Ga_2O_3/Ga_2O_3:Sn/CIGS structures. These results indicate that the Ga_2O_3 layer improved the diode characteristics, because the Ga_2O_3 layer increased the resistance in the shunt path and decreased the leakage current.

The current–voltage characteristics and quantum efficiency of the Ga_2O_3/Ga_2O_3:Sn/CIGS structure is shown in Figure 3. The signal current from irradiated visible light (450 nm, 550 nm, and 650 nm) significantly increased at applied voltages over ~3.5 V. We consider this carrier multiplication was due to avalanche current or tunneling current. The quantum efficiency exceeded unity due to carrier multiplication at applied voltages over 3.5 V. These results indicate that the Ga_2O_3/Ga_2O_3:Sn/CIGS structure had a very high sensitivity to visible light. We deposited our CIGS films by one-step RF sputtering, which increased the number of sulfur vacancies, because the vapor pressure of sulfur is very high. We confirmed that there were many sulfur deficiencies in our CIGS film in a previous study [11]. This means that this structure could have a higher quantum efficiency and lower dark current if a higher quality CIGS film is used.

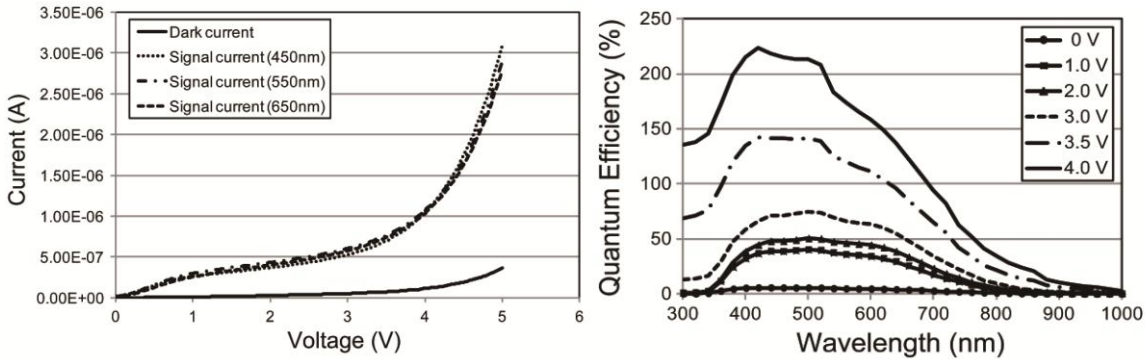

Figure 3. The current–voltage characteristics and quantum efficiency of the Ga_2O_3/Ga_2O_3:Sn/CIGS structure.

4. Conclusion

The electrical properties of Ga_2O_3/Ga_2O_3:Sn/CIGS heterojunctions were investigated. We succeeded in improving the pn characteristics by applying Ga_2O_3 onto the Ga_2O_3:Sn layer. The dark current of this structure was very low because of the high potential barrier of Ga_2O_3 against holes. The carrier multiplication phenomenon was observed, which is beneficial for high-sensitivity sensors. Further optimization in the fabrication of the CIGS film is needed for higher sensitivity.

5. Acknowledgments

This work was partly supported by the Foundation for Promotion of Material Science and Technology of Japan (MST Foundation).

6. References

[1] M. A. Green, K. Emery, Y. Hishikawa and W. Warta 2009 Prog. Photovolt. **17** 320
[2] N. Nakamura, N. Yoneyama, K. Horiguchi, Y. Iwata, K. Yamaguchi, H. Sugimoto and T. Kato 2014 Proc. 40th IEEE Photovolt. Specialist Conf. 0107
[3] Turcu M, Kotschau I M and Rau U 2001 *Appl. Phys.* A **73** 769
[4] Chirila A et al 2013 *Nature Materials* 12 1107
[5] Pudov A, Sites J, Nakada T 2002 *Jpn. K. Appl. Phys.* **41** L672
[6] Nakada T, Furumi K and Kunioka A 1999 *IEEE T. Electron Dev.* **46** 2093

[7] Hultqvist A, Platzer-Bjorkman C, Coronel E and Edoff M 2011 *Sol. Energy Mater. Sol. Cells* **95** 497
[8] Tanaka K, Kosugi M, Ando F, Ushiki T, Usui H and Sato K 1993 *Jpn. J. Appl. Phys. Suppl.* **32** 113
[9] Varley J B, Weber J R, Janotti A and Van de Walle C G 2010 *Appl. Phys. Lett. 97* 142106
[10] Kikuchi K, Ohkawa Y, Miyakawa K, Matsubara T, Tanioka K, Kubota M, Egami N 2011 *Phys. Stat. Sol.* C **8** 2800
[11] Kikuchi K, Imura S, Miyakawa K, Kubota M and Ohta E 2014 *Thin Solid Films* **550** 635
[12] Kikuchi K, Imura S, Miyakawa K, Ohtake H, Kubota M and Ohta E 2014 *2013 MRS Fall Meeting* 1635
[13] Minami T, Miyata T and Yamamoto T 1998 *Surf. Coat. Technol.* **108** 583
[14] Sugiyama M, Nakanishi H and Chichibu S 2001 *Jpn. J. Appl. Phys.* **40** L428