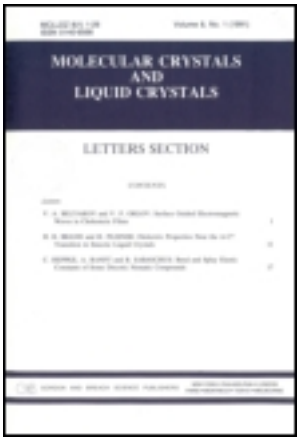

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Ju-Young Baek [a], Soon-Rok Park [a], Tae-Young Yun [a], Hye-Jin Han [a], Kyoung-Bo Kim [b] & Chan-Wook Jeon [a]

[a] Department of Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk, 712-749, Korea

[b] Surface Technology Research Group, POSCO Technical Research Laboratories, Incheon, Korea

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Effects of the Modified TCO Sputtering Condition on ZnS/CIGS Solar Cell

JU-YOUNG BAEK,[1] SOON-ROK PARK,[1] TAE-YOUNG YUN,[1] HYE-JIN HAN,[1] KYOUNG-BO KIM,[2] AND CHAN-WOOK JEON[1,*]

[1]Department of Chemical Engineering, Yeungnam University, Gyeongsan, Gyeongbuk 712-749, Korea
[2]Surface Technology Research Group, POSCO Technical Research Laboratories, Incheon, Korea

The Cu(In,Ga)Se_2 (CIGS) thin film solar cells were fabricated using ZnS buffer layer deposited by chemical bath deposition and ZnO/Al-doped ZnO transparent conducting layers deposited by magnetron sputtering with two different configurations of target-to-substrate angle and distance in order to evaluate the effect of plasma damage on device performance. The higher efficiency was obtained from the configuration of the substrate being far away from the target center than face-to-face configuration, suggesting that the excessive bombardment of high energy particles from the plasma on the film surface is responsible for the solar cell performance degradation. It is suggested that the improved open-circuit voltage is ascribed to the increased recombination barrier height.

Keywords CIGS solar cell; Cd-free buffer layer; ZnS buffer; plasma damage

Introduction

The efficiency of Cu(In,Ga)Se_2 (CIGS) solar cells has reached 20% in laboratory. It was fabricated using a cadmium sulfide (CdS) buffer layer grown by chemical bath deposition (CBD). But these CdS/CIGS solar cells have an optical absorption loss at short-wavelength, because of the low bandgap energy of CdS, which is about 2.4 eV. Cadmium also causes environmental safety problems. Many groups are trying to implement ZnS instead of CdS for the buffer layer of CIGS solar cell[1–3]. The best ZnO/CIGS solar cells fabricated using ZnS buffer in an active area showed the efficiency as high as 18.6 %[4]. The bandgap energy of ZnS is 3.8 eV which is much larger than that of CdS. Hence, the ZnS buffer layer is expected to improve the quantum efficiency at short wavelengths and result in an increase in the short circuit current density (J_{sc}) of the solar cells.

On the other hand, there are several disadvantages of using ZnS as buffer layer for ZnO/CIGS solar cell. Formation of ZnS by CBD normally takes a long deposition time and ZnS is well known to be sensitive to plasma damage during subsequent sputtering process of ZnO layer[5,6]. While 50 nm of CdS layer is generally accepted to be enough

*Address correspondence to Prof. Chan-Wook Jeon Department of Chemical Engineering Yeungnam University Dae-dong, Gyeongsan-si, Gyeongbuk, 712-749, Korea (ROK). Tel: (+82)53-810-3860, Fax: (+82)53-810-4631. E-mail: cwjeon@ynu.ac.kr

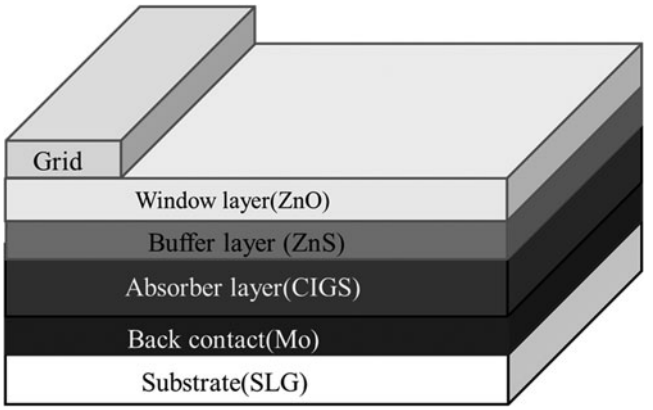

Figure 1. The structure of the CIGS solar cell.

for preventing plasma damage, ZnS is required to be thicker than 100 nm[7]. However, it is hard to deposit ZnS layer thicker than 30 nm from one batch of CBD.

In this study, we performed a comparative study on the effect of ZnO sputtering conditions on device performance of ZnO/ZnS/CIGS solar cells with only 30 nm thick ZnS buffer layer in an effort to find a way to reduce the plasma damage.

Experimental

The structure of the CIGS solar cell is shown in Figure1. The CIGS absorbers were deposited by three stage co-evaporation process using a molecular beam epitaxy (MBE) system on the Mo-coated soda-lime glass (SLG) substrate. The detailed deposition method of CIGS has been reported previously[8]. Subsequently the ZnS thin films were deposited by CBD on the CIGS absorber with 0.4 M zinc acetate, 0.16 M thiourea and 4M ammonia aqueous

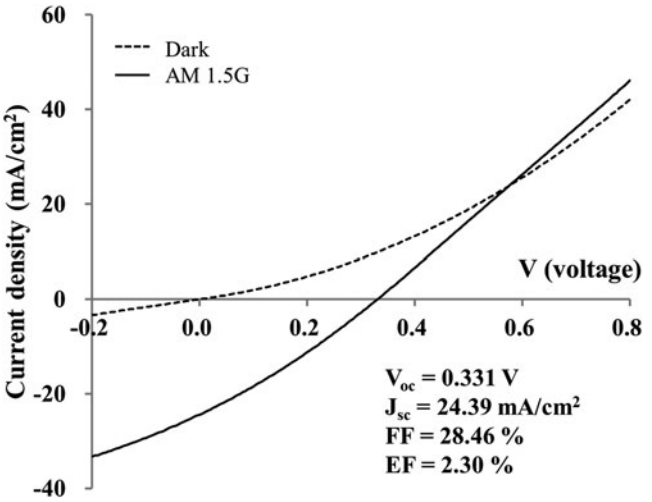

Figure 2. I-V characteristics of standard ZnS/CIGS device.

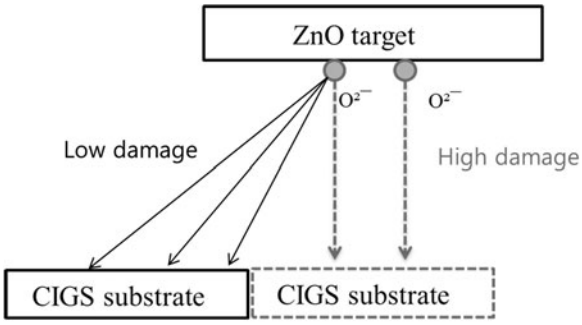

Figure 3. Schematic diagram of the modified sputtering system.

solution. After 20 min, a ZnS layer of approximately 30 nm was grown on the CIGS absorber.

The substrate was rinsed in a 2.5 % ammonia aqueous solution to prevent from aggregating $Zn(OH)_2$ on the surface. Once the sample was washed and dried, CBD-ZnS/CIGS was heat-treated at 200°C in air for 10 min. The intrinsic ZnO layer was deposited using a sputtering system equipped with a tilted sputter gun. The "standard" deposition was done by facing the sample surface to the sputtering target. The "modified" deposition was carried out by positioning the sample away from the target center so that the possible high energy ions from the target would not impinge on the sample directly. The thickness of ZnO was controlled to be 80 nm by adjusting the deposition time since the deposition rates were different with the sample-to-target configuration. Al-doped ZnO film (500 nm) was then deposited via magnetron sputtering, and Ag grid electrodes were formed by E-beam deposition.

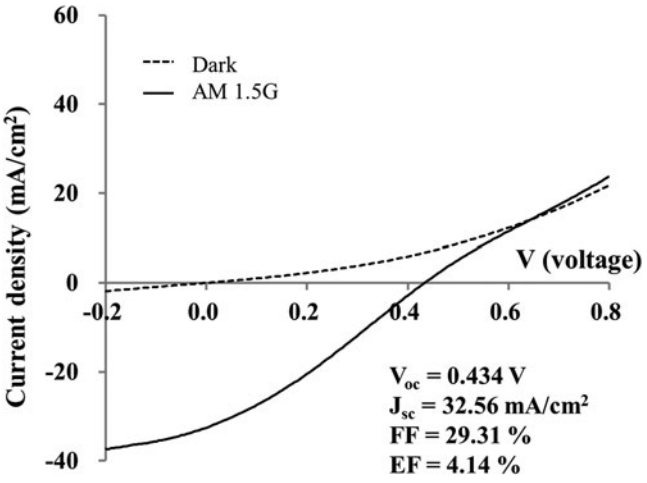

Figure 4. I-V characteristics ZnS/CIGS device manufactured by low damage TCO sputtering system.

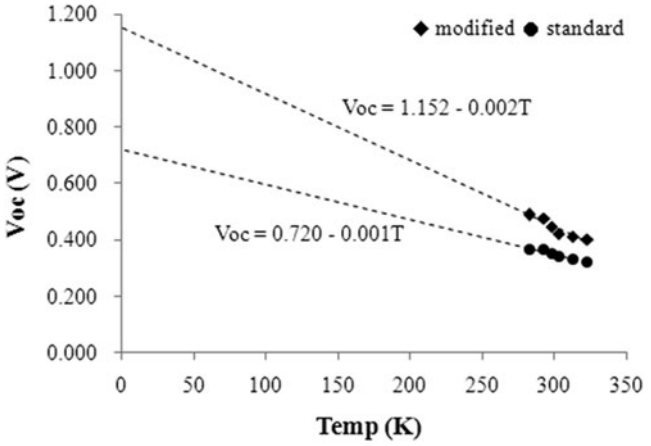

Figure 5. IV-T characteristics of CIGS device.

Measurements

The evaluation of photovoltaic performance of CBD-ZnS/CIGS solar cells have been performed using a solar simulator under AM1.5, 100 mW/cm^2 illumination at 25°C or from 10°C to 50°C. The spectral response was measured using an IPCE (Incident-Photon-to-electron Conversion Efficiency) measurement system at 25°C.

Results and Discussion

The current density-voltage (J-V) curve of standard ZnS/CIGS solar cell is shown in Figure 2. The conversion efficiency (EF) was 2.3 % (aperture area of 0.4 cm^2) with open circuit voltage (V_{oc}) = 0.331 V, short circuit current density (J_{sc}) = 24.39 mA/cm^2, and fill factor (FF) = 28.46 %. In general, the efficiency of ZnS/CIGS solar cell was lower than that of CdS/CIGS solar cell mainly due to much lower open circuit voltage and fill factor. The poor V_{oc} and FF of ZnS-device can be attributed to the higher interface recombination due to lower degree of surface inversion and plasma damage of the absorber surface[9,10]. It is suggested that the Zn ion is hard to substitute with Cu ion compared to the Cd ion so that the formation of buried junction is less prominent[11]. The higher conduction band offset of ZnS/CIGS (> 0.4 eV) than that of CdS/CIGS (0.2∼0.3 eV) is also responsible for lower fill factor and short-circuit current density[12]. In order to overcome the major issues subjected to the sputtered-ZnO/ZnS/CIGS structure, we modified the sputtering process in a way to reduce the plasma damage as shown in Figure 3. In general, the high energy oxygen ions, supplied from the target element or the environment and accelerated from the cathode sheath, are responsible for the plasma damage[13]. The sputter deposition is performed away from the cathode face in the modified system, therefore, the high energy oxygen ions have very little chance to arrive at the film surface.

Figure 4 shows current density-voltage (J-V) curve for the ZnS/CIGS device fabricated with the modified TCO sputtering process. Compared to the standard device, most of the performance parameters including V_{oc}, J_{sc}, fill factor and efficiency have been improved. However, the double diode behavior is still found in the modified device and therefore the fill factor increase is very marginal. The double diode characteristic may stem from the large conduction band offset between the ZnS/CIGS junction[14]. Both of the standard and

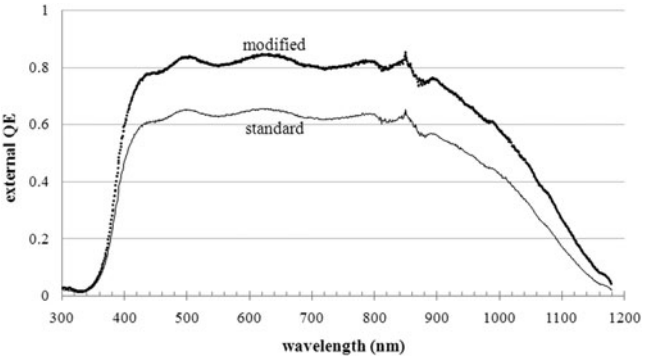

Figure 6. Quantum efficiency of CIGS device.

the modified device have identical absorber and buffer materials so that the conduction band offset remains same regardless of the TCO formation method. Nevertheless, the modified sputtering process was found to be successful in improving the open circuit voltage and short circuit current density due to the reduction of the plasma damage by avoiding the high energy ion impingement on either ZnS or CIGS itself.

Figure 5 shows the dependence of V_{oc} on measuring temperature (V_{oc}-T) for the two devices. The values of V_{oc} were extracted from a series of I-V measurements at different temperature ranging from 10°C to 50°C. At T = 0, V_{oc} equals to Φ_b^p/q, where Φ_b^p is the recombination barrier height defined by the energy difference between the Fermi level of TCO and the valence band edge of the absorber[15].

It is obvious that the barrier height in the ZnS/CIGS device fabricated by a modified sputtering system is much larger than that of the device fabricated by a standard system.

In the standard system, the surface of the CIGS layer is heavily damaged by the plasma during the i-ZnO sputter deposition, so that the Fermi level of CIGS surface could be pinned near the midgap and hence the barrier height will decrease. The Fermi level pinning near the midgap will substantially decrease the band bending so as to degrade V_{oc}. This result proves that even the absorbers of identical quality could yield totally different V_{oc} by simply changing the surface defect state.

The decreased barrier height also is responsible for the low J_{sc} as shown in Figure 6. The standard device shows significantly low quantum efficiency all over the spectral range due to the increased recombination loss of the photo-generated excess carrier.

Conclusions

In an effort to reduce the plasma damage on ZnS/CIGS device during the subsequent i-ZnO sputter deposition, a modified TCO sputter deposition was carried out by positioning the substrate off the normal of the cathode. The modified TCO resulted in improved performance by two times higher compared to the standard TCO deposited under face-to-face sputter geometry, especially the open circuit voltage. The increased recombination barrier height was found to be responsible for the performance improvement. It is believed that the Fermi level of CIGS surface was not pinned, or pinned away from the midgap at least, by avoiding the direct impingement of high energy ions accelerated from the cathode sheath.

Acknowledgments

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