CdTe Solar Cells with Iron Pyrite Thin Film Back Contacts Fabricated by a Hybrid Sputtering/Co-evaporation Process

Khagendra P. Bhandari, Xinxuan Tan, Peymon Zereshki, Robert W. Collins, and Randy J. Ellingson

Wright Center for Photovoltaic Innovation and Commercialization, Department of Physics and Astronomy, The University of Toledo, 2801 Bancroft Street, Toledo, OH 43606

Abstract — **We report the properties of sputtered/co-evaporated thin film iron pyrite as the back contact interface layer of CdS/CdTe solar cells. In our study we have compared the performance of sputter-deposited CdTe devices which utilized either a Cu/Au contact, or an FeS_2/Cu/Au contact. Comparing our best devices of each type, the FeS_2 contact layer has improved the V_{OC} by ~16 mV, to 816 mV, and improved the FF by ~4.7% absolute to 73.7%, with respect to devices omitting the FeS_2 layer. Under Standard Test Conditions of 100 mW/cm^2 and 25 °C, devices utilizing the FeS_2 back contact have shown a relative increase in the power conversion efficiency by ~7.5%, with a best device efficiency of 12.9%.**

Index Terms – sputtered, co-evaporated, iron pyrite, FeS_2, CdTe

I. INTRODUCTION

Iron pyrite (FeS_2) is an earth-abundant, low cost, and non-toxic sulfide mineral that has been identified as a promising candidate material for large-scale deployment of solar-to-electricity generation.[1, 2] FeS_2 has an indirect bandgap at ~0.95 eV and also displays high absorption in the visible and near infra-red spectral region, enabling relatively thin absorber layers that minimize materials cost.[3, 4] Indeed, iron pyrite has been extensively researched for photovoltaic (PV) applications since the mid-1980s.[2] With a record conversion efficiency of 2.8%, FeS_2 has not yet been successfully implemented as an absorber for high efficiency PV cells.[2, 5, 6] However, we recently discovered that the high free hole (p+) density and the relatively deep work function (~5 eV) exhibited by most polycrystalline and nanocrystalline FeS_2 thin films support these materials as good candidates for low-resistance back contacts for CdS/CdTe solar cells.[7] Initial promising results using a solution process based on colloidal FeS_2 nanocrystals (NCs), deposited and chemically modified using hydrazine to improve conductivity, showed an improvement in solar conversion efficiency of at least 5% when compared with test cells using our laboratory standard Cu/Au back contact.

Since the cubic FeS_2 NCs synthesized here have an average edge length of ~100 nm, thin films prepared with this material are porous.[8] To minimize the adverse effect of porosity of the FeS_2 NC film at the CdTe back contact, and to enhance the performance of the solar cells, an FeS_2-NC film of ~1.0 μm thickness is required.[9] In addition, when preparing the FeS_2-NC film by the LbL method, treatment by hydrazine solution is applied to remove the NC surfactant molecules to improve the film's conductivity. Solution-based fabrication of thin films even though cost-effective, is not generally considered as an economically viable route for large scale production. In addition, the use of hydrazine is highly undesirable due to concerns of volatility and toxicity. Keeping these facts in mind, we describe here the development and demonstration of a hybrid vacuum deposition method for making iron pyrite polycrystalline thin films on CdTe. This method relies on sputtering and concurrently evaporating sulfur onto a heated CdS/CdTe film-stack to form a polycrystalline iron pyrite back contact. Our investigations have revealed favorable initial results, with CdS/CdTe/FeS_2 devices showing improvements in the open circuit voltage (V_{OC}), fill-factor (FF), and the power conversion efficiency under AM1.5G simulated solar illumination.

II. EXPERIMENTAL METHODS

Cadmium sulfide (CdS) and CdTe layers were deposited by RF magnetron sputtering onto TEC^{TM} 15 glass substrates (Pilkington N. A.). The thicknesses of CdS and CdTe films were ~80 nm and ~2 μm respectively. For characterization purposes, polycrystalline iron pyrite (FeS_2) films were prepared on soda lime glass and silicon wafers for structural and optical characterization. In addition, FeS_2 was deposited onto the $CdCl_2$-treated CdTe layers of CdS/CdTe solar cells for completion into working PV devices. These cells were completed by evaporation of a Cu/Au metal layer stack, followed by thermal treatment to drive Cu diffusion into the CdTe/FeS_2 filmstack. The FeS_2 films were prepared by hybrid DC sputtering of iron with co-evaporation of elemental sulfur. The FeS_2 film was deposited at 165 °C to 340 °C calibrated substrate temperatures, 4 mT Ar pressure and 70 W DC power, respectively. Another important parameter found to determine crystalline properties of the iron sulfide was the sulfur evaporation rate (SER). Several SER values were investigated, and high quality iron pyrite was obtained when the SER was within the range of ~2 Å/s to ~3.75 Å/s. Depending on the purpose of FeS_2 film, the deposition time was varied from 5 to 60 minutes which produce films of thickness from ~30 nm to ~750 nm, respectively, depending also on the SER. When an FeS_2 film was deposited as the

interface layer for CdS/CdTe solar cells, film thicknesses of < 100 nm were preferred. Although a complete study of the dependence of device performance on FeS_2 film thickness study has not yet been performed, a reduced thickness reduces (i) the deposition time, (ii) the required amount of Cu, and (iii) the time and temperature required for Cu diffusion during processing. For the standard back contact deposition, ~3 nm Cu and ~40 nm Au are thermally evaporated, sequentially, onto the $CdCl_2$-treated CdTe layer. Subsequently, Cu is diffused into the CdTe by annealing at 150 °C in dry air. The identical Cu/Au evaporation and thermally-driven diffusion steps were followed to complete metal back contact on top of thin FeS_2 film fabricated on CdTe.

For both types of back contacts, the cell areas (0.085 cm^2) were defined by laser scribing. Quantum efficiency (QE) measurements were used to confirm J_{SC} values. Current density vs. voltage measurements were performed in the dark, and under 1 Sun AM1.5G illumination.

The crystal structure of FeS_2 films was found by X-ray diffraction spectroscopy (XRD) and Raman spectroscopy measurements; surface morphology was determined using scanning electron microscopy (SEM); and the material composition was measured via energy dispersive X-ray (EDX) spectroscopy.

III. RESULTS AND DISCUSSION

Current density vs. voltage (J-V) curves for the best device using each of the two back contact designs are shown in Fig. 1, and the average J-V characteristic parameters for 20 devices prepared for each type of contact are shown in Table 1. As mentioned, we use Cu/Au as our reference back contact. To minimize the back barrier effect, for which a Schottky barrier forms an opposing diode at the CdTe/metal interface, a high work function metal (Au, $\phi \approx 5.0$ eV) is chosen. In Fig. 1, solid lines represent the light J-V measurements and dashed lines represent the dark measurements. From the J-V curves shown in Fig. 1 and the parameter values in Table I, it can be seen that adding a thin layer of FeS_2 as an interface layer improved the device performance. While the J_{SC} appears similar for both back contact types, increases in V_{OC} and FF result in increased device efficiency when using the FeS_2/Cu/Au back contact. The relative increase in V_{OC} is 2% and the relative increase in FF is 7% for the CdTe solar cells shown in Fig. 1.

The improvement in device performance observed here for the hybrid deposition process for FeS_2 approximately replicates the improvement seen when using nanocrystalline FeS_2 (FeS_2-NC) as an interface layer.[7] In addition to the significantly different method of FeS_2 preparation (solution processing vs. hybrid sputtering/co-evaporation), the results reported here result from introducing the Cu at a different point in the process. In the case of the solution-processed

FeS_2 contact layer, Cu is introduced and diffused into the CdTe *prior to* deposition of the FeS_2-NC and evaporated Au layers (no thermal processing is used during or subsequent to the FeS_2-NC/Au processing). However, we found generally poor performance for devices prepared with Cu prior to the hybrid vacuum deposition of FeS_2; we attributed this to over-diffusion of Cu associated with the elevated substrate temperature present during vacuum deposition of the FeS_2. Therefore, the hybrid sputtered/co-evaporated thin film of FeS_2 is first deposited onto the CdTe surface, and the device is then completed by evaporation of Cu/Au and subsequently annealing the device to drive Cu diffusion.
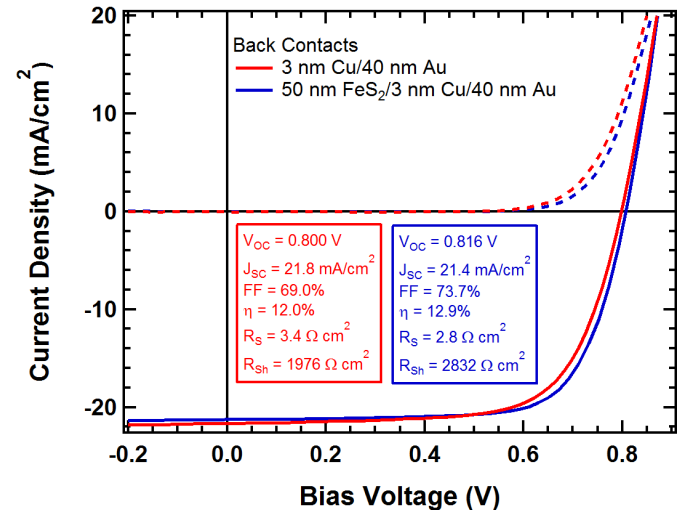

Fig. 1. Current voltage characteristics for sputtered CdTe solar cells using two different back contacts; the approximate thicknesses of each back contact type are shown in the graph. J_{SC} was verified by using external quantum efficiency.

Unlike the FeS_2-NC film, the FeS_2 film prepared by using the sputtered/co-evaporated method is more uniform and compact and the film strongly adheres to the substrate. Due to the improved FeS_2 film density, CdTe devices using a sub-100 nm thick hybrid-deposited back contact perform at a level equal to the performance of devices utilizing a ~1 μm thick FeS_2-NC back contact. The hybrid-deposited FeS_2 films have the same cubic crystal structure and pyrite phase, but according to the peak intensity of XRD spectra, the films appear smaller-grained crystalline than FeS_2-NC films.[8] This may be due to the relatively low substrate temperature (260 °C) which yields a high nucleation density. We evaluated several substrate temperatures starting from 165 °C to 340 °C, and found that the pure iron pyrite phase FeS_2 was best obtained at 265°C. The lattice constant is calculated from the various FeS_2 films deposited at 265 °C and is found to be ~5.423Å. Scanning electron microscopy (SEM) shows that the average grain size of FeS_2 is smaller than the size of NCs. The average atomic percentage of S to Fe was found to be 2.08 when the substrate temperature was 265 °C, but the ratio was higher when the film was fabricated at lower substrate

temperatures. Hall measurements indicated that the FeS_2 film is p-type with carrier density of the order of 10^{20} cm^{-3} and mobility of ~8 cm^2/Vs. Higher mobility is expected to be beneficial for improved back contact performance.

TABLE I

AVERAGE PARAMETERS OF CDTE SOLAR CELLS PREPARED USING TWO DIFFERENT BACK CONTACTS FOR SPUTTERED CDTE SOLAR CELLS; AVERAGE VALUES WERE CALCULATED FOR 20 CELLS OF EACH CONTACT TYPE. J_{SC} VALUES ARE THOSE OBTAINED FROM THE J-V MEASUREMENT SYSTEM.

Back Contact Type	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	η (%)	R_S (Ω cm^2)	R_{Sh} (Ω cm^2)
Cu/Au (20)	0.793 ± 0.010	21.7 ± 0.2	68.4 ± 0.9	11.8 ± 0.2	3.7 ± 0.4	1619 ± 212
FeS_2/Cu/Au (20)	0.812 ± 0.002	21.4 ± 0.3	72.8 ± 0.9	12.7 ± 0.3	3.1 ± 0.3	2580 ± 556

Typical external quantum efficiency (EQE) curves of CdTe devices with and without the FeS_2 interface layer are shown in Fig. 2. The EQE spectra show that current collection improves slightly in the wavelength range of ~700 nm to 860 nm. Electron-hole pairs generated away from the CdS/CdTe p-n junction, due principally to these long wavelength photons, benefit from the lower barrier potential present within the CdTe/FeS_2/Au contact. Since the Cu is deposited and diffused after FeS_2 deposition, the conductivities of both FeS_2 and CdTe films may have been increased as a result.

Fig. 2. Typical external quantum efficiency of cells with and without FeS_2 as an interface layer for CdTe solar cells.

IV. CONCLUSION

This work illustrates the demonstration and application of a hybrid sputter/co-evaporation method for preparing thin film iron pyrite as the interface layer at the back contact of CdS/CdTe solar cells. Initial results indicate that devices including a pyrite FeS_2 back contact layer perform well, showing improvements in V_{OC}, FF, and PCE as compared with a Cu/Au contact. The FeS_2 back contact may ultimately benefit from further optimization to attain increased CdTe solar cell efficiency. Open-circuit light soak tests are underway to test the stability of the modified back contact design.

REFERENCES

[1] C. Wadia, A. P. Alivisatos, and D. M. Kammen, "Materials availability expands the opportunity for large-scale photovoltaics deployment," *Environmental Science & Technology,* vol. 43, pp. 2072-2077, 2009.

[2] A. Ennaoui, S. Fiechter, C. Pettenkofer, N. Alonso-Vante, K. Büker, M. Bronold, Ch. Hopfner and H. Tributsch, "Iron disulfide for solar energy conversion," *Solar Energy Materials and Solar Cells,* vol. 29, pp. 289-370, 5// 1993.

[3] P. P. Altermatt, T. Kiesewetter, K. Ellmer, and H. Tributsch, "Specifying targets of future research in photovoltaic devices containing pyrite (FeS_2) by numerical modelling," *Solar Energy Materials and Solar Cells,* vol. 71, pp. 181-195, 2/1/ 2002.

[4] J. Puthussery, S. Seefeld, N. Berry, M. Gibbs, and M. Law, "Colloidal Iron Pyrite (FeS_2) Nanocrystal Inks for Thin-Film Photovoltaics," *Journal of the American Chemical Society,* vol. 133, pp. 716-719, 2011/02/02 2010.

[5] A. Kirkeminde, R. Scott, and S. Ren, "All inorganic iron pyrite nano-heterojunction solar cells," *Nanoscale,* vol. 4, pp. 7649-7654, 2012.

[6] B. J. Richardson, L. Zhu, and Q. Yu, "Inverted hybrid solar cells based on pyrite FeS_2 nanocrystals in P3HT:PCBM with enhanced photocurrent and air-stability," *Solar Energy Materials and Solar Cells,* vol. 116, pp. 252-261, 9// 2013.

[7] K. P. Bhandari, P. Koirala, N. R. Paudel, R. R. Khanal, A. B. Phillips, Y. Yan, R. W. Collins, M. J. Heben and R. J. Ellingson, "Iron pyrite nanocrystal film serves as a copper-free back contact for polycrystalline CdTe thin film solar cells," *Solar Energy Materials and Solar Cells,* vol. 140, pp. 108-114, 2015.

[8] K. P. Bhandari, P. J. Roland, T. Kinner, Y. Cao, H. Choi, S. Jeong, and R. J. Ellingson, "Analysis and characterization of iron pyrite nanocrystals and nanocrystalline thin films derived
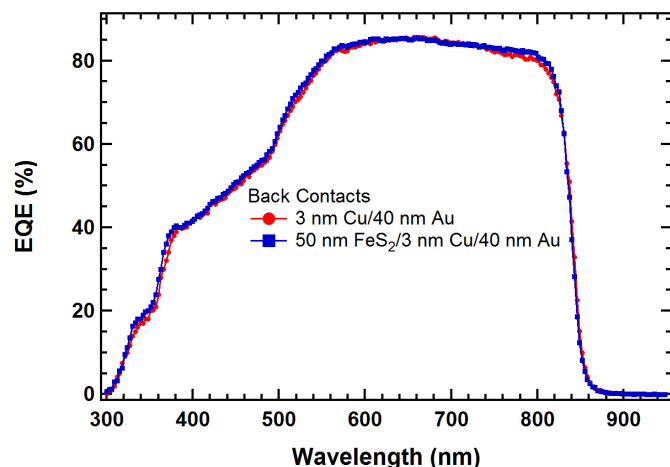
from bromide anion synthesis," *Journal of Materials Chemistry A,* vol. 3, pp. 6853-6861, 2015.

[9] K. P. Bhandari, P. J. Roland, P. Koirala, R. R. Khanal, N. R. Paudel, R. Collins, Y. Yan, M. J. Heben and R. J. Ellingson, "Enhancing the efficiency of CdTe solar cells using a nanocrystalline iron pyrite film as an interface layer," in *Photovoltaic Specialist Conference (PVSC), 2015 IEEE 42nd,* 2015, pp. 1-4.