

RECENT PROGRESS IN CuInS_2 THIN FILM SOLAR CELL RESEARCH AT NASA GLENN

M. H.-C. Jin, K. K. Banger, and C. V. Kelly
Ohio Aerospace Institute, Brook Park, OH 44142

J. H. Scofield
Oberlin College, Oberlin, OH 44074

J. S. McNatt, J. E. Dickman, and A. F. Hepp
NASA Glenn Research Center, Cleveland, OH 44135

INTRODUCTION

The National Aeronautics and Space Administration (NASA) is interested in developing low-cost highly efficient solar cells on light-weight flexible substrates, which will ultimately lower the mass-specific power (W/kg) of the cell allowing extra payload for missions in space as well as cost reduction (1). In addition, thin film cells are anticipated to have greater resistance to radiation damage in space, prolonging their lifetime (2). The flexibility of the substrate has the added benefit of enabling roll-to-roll processing (3).

The first major thin film solar cell was the "CdS solar cell" – a heterojunction between p-type Cu_xS and n-type CdS (4). The research on CdS cells started in the late 1950s and the efficiency in the laboratory was up to about 10 % in the 1980s (5). Today, three different thin film materials are leading the field. They include amorphous Si, CdTe, and $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) (6). The best thin film solar cell efficiency of 19.2 % was recently set by CIGS on glass (7). Typical module efficiencies, however, remain below 15 % (8).

Several groups have attempted to fabricate thin film solar cells on metal foils and polymers. Efficiencies up to 12.8 % on polyimide (9) and 17.1 % on stainless steel (10) have been reported. Polymer substrates cannot tolerate temperatures as high as those allowed by metal foils. Cell fabrication and absorber layer synthesis on polymer substrates must be accomplished at temperatures below 450 °C (11). This low-temperature constraint introduces challenges for achieving high-quality absorber layers and high-efficiency solar cells. To facilitate low temperature deposition, single-source organometallic precursors with low decomposition temperatures (< 250 °C) were synthesized and used in an aerosol-assisted chemical vapor deposition (AACVD) setup to create chalcopyrite thin films (12,13). This paper gives a brief description of the first systematic effort at NASA Glenn Research Center (GRC) to fabricate CuInS_2 thin film solar cells.

EXPERIMENTAL

As previously reported, CuInS_2 SSP, $(\text{PPh}_3)_2\text{CuIn}(\text{SEt})_4$ was synthesized following a modified version (12) of the procedure reported by Kanatzidis (14). Because of their sensitivity to O_2 and H_2O , all reagents were handled in an argon-filled glove box. The precursor was dissolved in toluene and the solution was delivered to the heated substrate in the form of sprayed aerosol in a horizontal, atmospheric-pressure, hot-wall AACVD reactor equipped with a plate-type ultrasonic nebulizer (Sonaer Ultrasonics, 2.5 MHz). A detailed description of the film growth process with a schematic of the reactor can be found elsewhere (13,15). For this study, (112)-oriented CuInS_2 films were deposited using 0.01 M precursor solution under 4 L/min of Ar flow. The evaporation and hot zone temperatures were 120 °C and 395 °C respectively. Typical film thickness was around 0.7 μm and Cu/In ratio was 1.0 ± 0.1 . The detailed characterizations of the films were reported previously (13,16).

The solar cell structure used in this study was Al/ZnO:F/CdS/ CuInS_2 /Mo/glass. Prior to CuInS_2 film growth, molybdenum (bottom metal contact) was deposited on glass substrates (Fisher catalogue no. 12-550A) at room temperature using radio-frequency (RF) magnetron sputtering. After CuInS_2 film was grown by AACVD, the film

was etched in 1.5 M KCN solution for 1 min at room temperature prior to the CdS chemical bath deposition (CBD). CBD was performed with a solution consisting of 0.001M CdSO₄, 1.5M NH₄OH, and 0.0075M thiourea. The bath was heated to 70 °C then the sample was immersed. After the CBD, the particulates on the surface of the sample were removed in an ultrasonic bath. Subsequently a ZnO:F layer was deposited from a 6.5" (16.5 cm)-diameter F-doped ZnO target in an RF sputter system. The sputter gas was pure Ar for both Mo and ZnO:F deposition. Following ZnO:F growth, a 0.2 μm thick Al top metal contact was deposited by thermal evaporation through a shadow mask. The cell area was defined by mechanical scribing after Al deposition with a typical cell area of 0.4 cm². A solar simulator at GRC (Spectrolab X-25 Mark II) was used to characterize the solar cells under AM0 radiation, calibrated using either a standard GaAs single-junction cell or a Si single-junction cell.

In order to validate the fabrication procedure, a chalcopyrite thin film deposited by physical vapor deposition (PVD) on Mo-coated glass substrate was acquired and a solar cell was fabricated through the same procedure described. In an effort to improve the cell performance, GRC collaborated with Oberlin College to try a double window layer scheme (n-type ZnO/intrinsic ZnO) after CdS deposition. In addition, a Ni/Al double metal top contact was also used instead of a single Al contact. The intrinsic and the Al-doped ZnO layers were deposited using a reactive DC magnetron sputter process (Sloan) in a mixture of O₂ and Ar gases. The Ni was evaporated from an alumina-coated tungsten boat and the Al from a single-hearth e-gun (Sloan) mounted in a 24-in. diffusion-pumped bell jar. The GRC and Oberlin cell structures are illustrated in Figure 1.

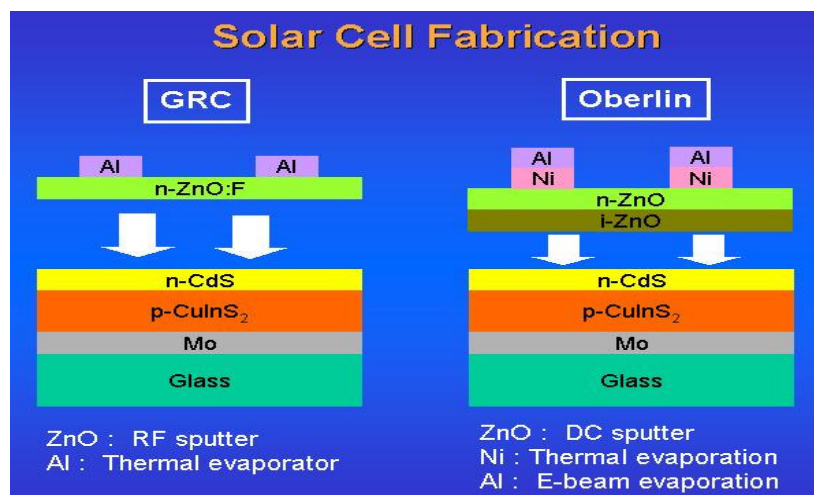


Figure 1. Schematic of the solar cell structures made at GRC and Oberlin College.

The film thickness was determined using a profiler (Sloan Dektak IIA) and the optical transmittance was measured by a UV/VIS spectrophotometer (Perkin-Elmer Lambda-19). The electrical measurements were performed with a four-point probe system (Bio-Rad HL5500PC) operated in the Van der Pauw configuration. For the CdS film, X-ray diffraction (XRD) (PANalytical X'Pert Pro) was used to identify phases and glancing-angle X-ray diffraction (GAXRD) was further performed to probe phases in the film and on the surface of the film separately.

RESULTS AND DISCUSSION

The surface resistance of Mo bottom contact was about 0.5 ohm/sq. with a typical thickness of 0.7 μm. XRD confirmed that the Mo had a body-centered cubic phase with a (110) texture showing the strongest diffraction at 2θ = 40.5°. The optical transmittance of CBD-grown CdS was 65 % at a photon energy of 1.5 eV and it had a strong signature of cubic phase with CdO as an impurity phase (Figure 2). GAXRD confirmed that the CdO phase was present both in the bulk and the surface of the film (not shown). There have been many reports regarding secondary phase formation including CdO in the CdS CBD (17,18), but no XRD was reported to support the CdO formation in as-deposited CdS prepared by CBD. A typical 1 μm-thick GRC n-type ZnO:F layer had a sheet resistance of about 200 ohm/sq and a transmittance of 85 % at a photon energy of 1.5 eV. In comparison, a 560 nm thick n-type ZnO layer deposited at Oberlin College had a sheet resistance of about 46 ohm/sq. with a transmittance of about 70 % at a photon energy of 1.5 eV. The transmittance of the 70 nm thick intrinsic ZnO was

over 90 % at photon energy of 1.5 eV and the sheet resistance of the double window layer, n-ZnO/i-ZnO was about 200 ohm/sq. Typical thickness of single Al top contact deposited at GRC was about 700 nm and the sheet resistance of the double top contact layer (2 μm Al/50 nm Ni) made was about 0.18 ohm/sq.

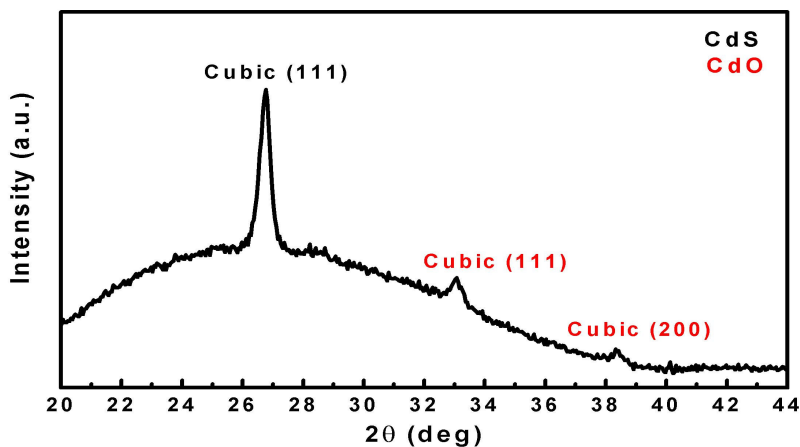


Figure 2. XRD of CdS film deposited by chemical bath deposition.

Figure 3 shows the characteristics of the reference solar cells completed with both the GRC and Oberlin College window/contact layers. The chalcopyrite absorber layer deposited by PVD was used for this validation process of the device fabrication at GRC. The AM0 efficiencies of 5.3 % and 6.7 % were obtained with minimum device optimization. The use of intrinsic ZnO and Ni/Al top contact layers, which is known to improve the quality of this type of solar cell (6), lowered the series resistance and improved the fill factor (FF) as shown in the Figure 3. Although the short circuit current (I_{sc}) was comparable to that of any other reported chalcopyrite solar cells (7,8), open circuit voltage (V_{oc}) and FF have to be further improved. Further optimization of the fabrication process will be performed in the future.

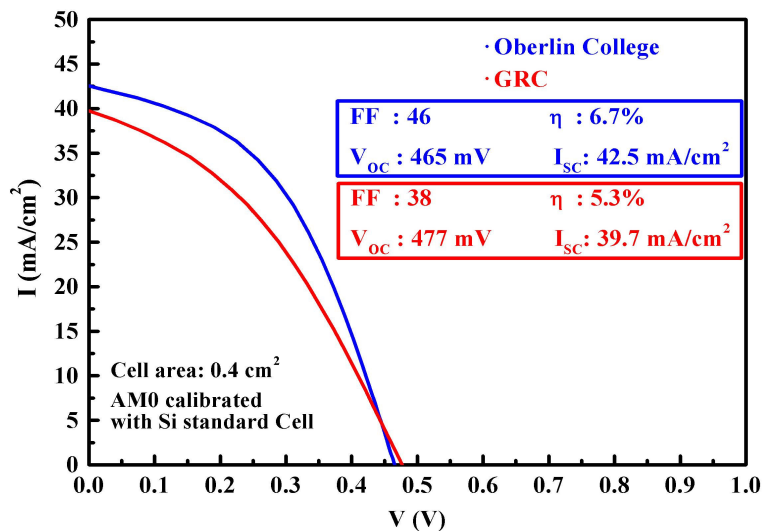


Figure 3. Characteristics of the reference solar cells made at GRC and Oberlin College.

A solar cell with a structure of Al/ZnO:F/CdS/CuInS₂/Mo/glass was fabricated with a CuInS₂ thin film deposited by AACVD at GRC and its output characteristics were shown in Figure 4. The cell had both low shunt resistance and high series resistance. The intrinsic ZnO and Ni/Al top contact will be incorporated for further improvement in the future. In addition, further increase of CuInS₂ film thickness from 0.7 μm should minimize the optical loss. It should be noted that the best efficiency reported for a solar cell prepared from AACVD-made CuInS₂ was 2.66 % (20). However, the cell had a superstrate structure – Cd(Zn)S was deposited on the glass substrate first and light

passes through from the glass side - and there was no report of a working device with a typical chalcopyrite solar cell structure, CdS/CuInS₂ except for the authors' previous results (13).

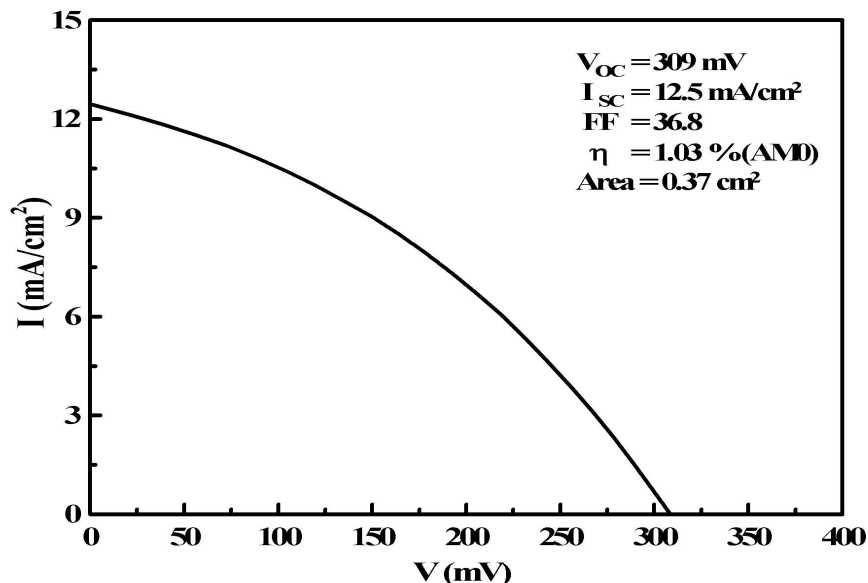


Figure 4. Characteristics of the CuInS₂ solar cell made at NASA GRC.

CONCLUSION

Chalcopyrite solar cell fabrication process has been established at NASA GRC. A reference solar cell with a cell structure of Al/ZnO:F/CdS/CuInS₂/Mo/glass was fabricated and an efficiency of 5.3 % under AM0 illumination was achieved. Further improvement was made by incorporating an intrinsic ZnO layer and Al/Ni top metal contact at Oberlin College, increasing the efficiency up to 6.7 %. The series resistance and fill factor were clearly improved. In addition, GRC has fabricated CuInS₂ thin films solar cells prepared from AACVD using the single source precursor, (PPh₃)₂CuIn(SEt)₄. Although the solar cell performance still needs to be improved, I_{sc} and FF were better than results reported previously (13). The major loss was due to the low V_{oc} and it remains as a challenge, which has been observed in solar cells prepared with AACVD deposited films (19,20).

REFERENCES

- (1) D. J. Hoffman, T. W. Kerslake, A. F. Hepp, M. K. Jacobs, and D. Ponnusamy, "Thin-Film Photovoltaic Solar Array Parametric Assessment," *Proc. of the AIAA 35th Intersociety Energy Conversion Engineering Conference*, pp. 670-680, Las Vegas, NV, 2000.
- (2) V. K. Kapur, M. Fisher, and R. Roe, "Fabrication of Light Weight Flexible CIGS Solar Cells for Space Power Applications," *Mat. Res. Soc. Symp. Proc.*, **668**, pp. H3.5.1-H3.5.6, 2001.
- (3) G. M. Hanket, U. P. Singh, E. Eser, W. N. Shafaran, and R. W. Birkmire, "Pilot-scale Manufacture of Cu(InGa)Se₂ Films on a Flexible Polymer Substrate," *Proc. of the 29th IEEE Photovoltaic Specialists Conference*, pp. 567-570, New Orleans, LA, 2002.
- (4) A. Rothwarf and A. M. Barnett, "Design analysis of the thin-film CdS-Cu₂S solar cell," *IEEE Trans. Electron Devices*, **ED-24**, pp. 381-387, 1977.
- (5) R. B. Hall, R. W. Birkmire, J. E. Phillips, and J. D. Meakin, "Thin-film polycrystalline Cu₂S/Cd_{1-x}Zn_xS solar cells of 10% efficiency," *Appl. Phys. Lett.*, **38**, pp. 925-926, 1981.
- (6) M. D. Archer and R. Hill, "Clean Electricity from Photovoltaics," Imperial College Press, London, 2001.
- (7) K. Ramanathan, M. A. Contreras, C. L. Perkins, S. Asher, F. S. Hasoon, J. Keane, D. Young, M. Romero, W. Metzger, R. Noufi, J. Ward, and A. Duda, "Properties of 19.2% Efficiency ZnO/CdS/CuInGaSe₂ Thin-film Solar Cells," *Prog. Photovolt: Res. Appl.*, **11**, pp. 225-230, 2003.
- (8) K. Kushiya, "Progress in Large-area Cu(InGa)Se₂-based Thin-film Modules with the Efficiency of over 13%," *Proc. of the 3rd World Conference on Photovoltaic Energy Conversion*, 2PL-C1-02, Osaka, Japan, 2003.

- (9) A. N. Tiwari, M. Krejci, F. J. Haug, and H. Zogg, "12.8% Efficiency Cu(In,Ga)Se₂ solar cell on a flexible polymer sheet," *Prog. Photovolt: Res. Appl.*, **7**, pp. 393-397, 1999.
- (10) M. Contreras, B. Egas, K. Ramanatan, J. Hiltner, F. Hasoon, and R. Noufi, "Progress toward 20% efficiency in Cu(In,Ga)Se₂ polycrystalline thin-film solar cells," *Prog. Photovolt: Res. Appl.*, **7**, pp. 311-316, 1999.
- (11) F. Kessler, K. Herz, M. Powalla, M. Hartmann, M. Schmidt, A. Jasenek, and H. W. Schock, "Flexible and monolithically integrated CIGS-Modules," *Mat. Res. Soc. Symp. Proc.*, **668**, pp. H3.6.1-H3.6.6, 2001.
- (12) K. K. Banger, J. Cowen, and A. F. Hepp, "Synthesis and Characterization of the First Liquid Single-Source Precursors for the Deposition of Ternary Chalcopyrite (CuInS₂) Thin Film Materials" *Chem. Mater.*, **13**, pp. 3827-3829, 2001.
- (13) J. D. Harris, K. K. Banger, D. A. Scheiman, M. A. Smith, M. H.-C. Jin, and A. F. Hepp, "Characterization of CuInS₂ films prepared by atmospheric pressure spray chemical vapor deposition," *Mat. Sci. & Engr.*, **B98**, pp. 150-155, 2003.
- (14) W. Hirpo, S. Dhingra, A. C. Sutorik, and M. G. Kanatzidis, "Synthesis of Mixed Copper-Indium Chalcogenolates. Single Source Precursors for the Photovoltaic Materials CuInQ₂ (Q = S, Se)," *J. Am. Chem. Soc.*, **115**, pp. 1597-1599, 1993.
- (15) J. A. Hollingsworth, K. K. Banger, M. H.-C. Jin, J. D. Harris, J. E. Cowen, E. W. Bohannon, J. A. Switzer, W. E. Buhro, and A. F. Hepp, "Single source precursors for fabrication of I-III-VI₂ thin-film solar cells via spray CVD," *Thin Solid Films*, **431-432**, pp. 63-67, 1993.
- (16) M. H.-C. Jin, K. K. Banger, J. D. Harris, and A. F. Hepp, "The Effect of Film Composition on the Texture and Grain Size of CuInS₂ Prepared by Chemical Spray Pyrolysis," *Mat. Res. Soc. Symp. Proc.*, **763**, pp. B8.23.1-B8.23.6, 2003.
- (17) P. J. Sebastian and H. Hu, "Identification of the Impurity Phase in Chemically Deposited CdS Thin Films," *Adv. Mater. Opt. Electron.*, **4**, pp. 407-412, 1994.
- (18) T. Nakada, H. Fukuda, A. Kunioka, and S. Niki, "XPS analysis of chemically deposited CdS films on polycrystalline CIS surface and glass substrates," *Proc. of the 13th European Photovoltaic Solar Energy Conference*, pp.1597-1600, Nice, France, 1995.
- (19) P. R. Ram, R. Thangaraj, A. K. Sharma, and O. P. Agnihotri, "Totally sprayed CuInSe₂/Cd(Zn)S and CuInS₂/Cd(Zn)S solar cells," *Solar Cells*, **14**, pp. 123-131, 1985.
- (20) O. Kijatkina, M. Krunk, A. Mere, B. Mahrov, and L. Dloczik, "CuInS₂ sprayed films on different metal oxide underlayers," *Thin Solid Films*, **431-432**, pp. 105-109, 2003.