SOLAR CELLS FABRICATED WTH CuInS$_2$ FILMS DEPOSITED USING SINGLE-SOURCE PRECURSORS

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We report a chalcopyrite thin film solar cell fabrication process established at NASA Glenn Research Center. The process was validated by fabricating a Al/ZnO:F/CdS/PVD-deposited chalcopyrite solar cell with an efficiency of 5.3 % under AM0 illumination. 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 %. Solar cells were also prepared with CuInS$_2$ thin films deposited by aerosol-assisted chemical vapor deposition using a single-source precursor, (PPh$_3$)$_2$CuIn(SEt)$_4$. The best solar cell parameters collected respectively from a series of the solar cells are V$_{oc}$=412 mV, I$_{sc}$=12.5 mA/cm^2, and FF=0.45.
Keywords: Solar Cell, Chalcopyrite, CuInS$_2$

1 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$_x$S and n-type CdS [4]. Research on CdS cells began in the late 1950s; laboratory efficiency was 10 % by the early 1980s [5]. Today, three different thin film materials are leading the field.   They include amorphous Si, CdTe, and Cu(In,Ga)Se$_2$ (CIGS) [6]. The best thin film solar cell efficiency of 19.2 % was recently set by CIGS on glass [7]. 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 and thus cell fabrication and absorber layer synthesis on them must be accomplished at temperatures below 450 °C [11].

This low-temperature constraint of the polymer substrates 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]. AACVD gained momentum in the early 1980s due to its success in the preparation of several oxides [14] and has been constantly examined as a low-cost, large-area, thin film deposition method for preparing solar cell materials [13]. The characteristics of the solar cells fabricated with chalcopyrite absorber layers prepared by AACVD were compiled in Table I.   They typically show a low efficiency (η) primarily due to low open-circuit voltage (V$_{oc}$) and fill factor (FF).   However, the short-circuit current (I$_{sc}$) of a CuInSe$_2$ (CISe$_2$) solar cell [18] was comparable to the world-record CIGS solar cell [7].

This paper gives a brief description of the first systematic effort at NASA Glenn Research Center (GRC) to fabricate CuInS$_2$ (CIS) thin film solar cells.

Table I: Output characteristics of solar cells prepared with AACVD-deposited chalcopyrite absorber layers

Solar cell structure	V$_{oc}$(mV)	I$_{sc}$(mA/cm^2)	FF	η(%)
CIS/CdS/ZnO [15]	443	5.5	0.37	
CIS/CdS/ZnO/ZnO:In[16]	430	8.1		
CIS/TiO$_2$ [16]	373	3.5		
CIS/ZnO [17]	280	13.3	0.38	2.03
CIS/Cd(Zn)S/ITO [18]	440	21.7	0.28	2.66
CISe$_2$/Cd(Zn)S/ITO [18]	305	32.0	0.32	3.15
ZnO:F/CdS/CIS [13]	304	10.5	0.29	0.68

2 EXPERIMENTAL

2.1 Film preparation and characterizations

A solid CIS-SSP, (PPh$_3$)$_2$CuIn(SEt)$_4$ was synthesized as outlined in a literature [19].   Because of their sensitivity to O$_2$ and H$_2$O, 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 [13,20].

Ex-situ post-deposition sulfur-annealing was often performed in the same AACVD reactor. For sulfur annealing, a crucible with a powder of pure elemental sulfur (STREM 93-1618, 99+%) was placed inside evaporation zone of the reactor and heated at 120 °C. S$_2$ gas was swept by Ar and delivered to the sample in the hot zone. Hot zone temperature was varied from 450 °C to 580 °C for the maximum duration of 17 hours.

The film thickness was determined using a profiler (Sloan Dektak IIA) and the optical transmittance was

measured by a UV/VIS spectrophotometer (Perkin-Elmer Lamda-19). The electrical measurements were performed with a four-point probe system (Bio-Rad HL5500PC) operated in the van der Pauw configuration. X-ray diffraction (XRD) (PANalytical X'Pert Pro) was used for phase identification. Film morphology was examined using scanning electron microscopes (SEM) (Hitachi S-3000N) and the composition of the films was analyzed by energy dispersive spectroscopy (EDS) (EDAX) built into the Hitachi S-3000N. The Cu/In ratio was calculated by quantifying Cu K and In L lines by the ZAF standardless method.

2.2 Solar cell fabrication at GRC

Prior to CIS film growth, molybdenum (bottom metal contact) was deposited on glass substrates (Fisher, 12-550A) at room temperature using radio-frequency (RF) magnetron sputtering.

After $CuInS_2$ film was deposited by AACVD, the film was etched in a 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 $CdSO_4$, 1.5M NH_4OH, 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 16.5 cm (6.5")-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. Using a shadow mask from the National Renewable Energy Laboratory (NREL), the cell area was defined by mechanical scribing after Al deposition with a typical cell area of 0.4 cm^2.

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.

2.3 Fabrication of test solar cells

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 at GRC through the same procedure described in the section 2.2.

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 thicker Ni/Al double metal top contact was also used instead of a single Al contact. The intrinsic and the n-type ZnO layers were deposited using a reactive DC magnetron sputter process (Sloan) in a mixture of O_2 and Ar gases [21]. 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.

2.4 Fabrication of CIS solar cells

(112)-oriented $CuInS_2$ films were deposited using the 0.01M ~ 0.04M SSP 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 [13,22].

Solar cells were fabricated both at GRC and IEC in order to isolate issues with AACVD-deposited CIS films from those associated with the solar cell fabrication at GRC by making solar cells with a well-established fabrication process at IEC [23].

For the solar cells fabricated at IEC, GRC deposited only CIS films on top of Mo-coated soda-lime glass substrates prepared at IEC. The rest of cell fabrication including mechanical scribing was performed at IEC. The cell area was 0.45 cm^2. Post-fabrication air-annealing was often performed on a hot plate (Cimarec 2) at 150 °C for up to 24 hours.

3 RESULTS AND DISCUSSION

The sheet resistance of the Mo bottom contact layer was about 0.5 Ω/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.

A typical 1 μm-thick GRC n-type ZnO:F layer had a sheet resistance of about 200 Ω/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 Ω/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 Ω/sq. Typical thickness of single Al top contact deposited at GRC was about 200 nm and the sheet resistance of the double top contact layer (2 μm Al/50 nm Ni) made was about 0.18 Ω/sq.

3.1 Post-deposition S-annealing

The crystalline structure of CIS often varies between two common polymorphs, chalcopyrite and sphalerite, depending on its preparation. They differ in the degree of order for the Cu and In atoms within the zinc-blende structure. This can be identified through characteristic XRD peaks and peak splitting which is only observed for the more ordered chalcopyrite structure [24].

As-deposited CIS films prepared by AACVD were previously characterized as having disordered chalcopyrite phase – weak peak splitting was only observed [22]. Post-deposition sulfur-annealing of CIS films increases the ordering of the metal atoms within the structure and changes it to well-ordered chalcopyrite. The chalcopyrite structure was clearly confirmed in a film annealed at 580 °C for 5 hours in a S-rich Ar atmosphere, as shown in Figure 1. The (101) and (211) diffraction peaks only allowed in the chalcopyrite structure at 17.9 and 37.3° are particularly clear. Peak splittings were stronger after annealing.

During a 5 hour, 580 °C anneal in a S-rich atmosphere, the CIS film's elemental composition of S, In, and Cu changed from 51.5, 24.5, and 24.0%, respectively, to 52.0, 23.5, and 24.5% making Cu and S rich film.
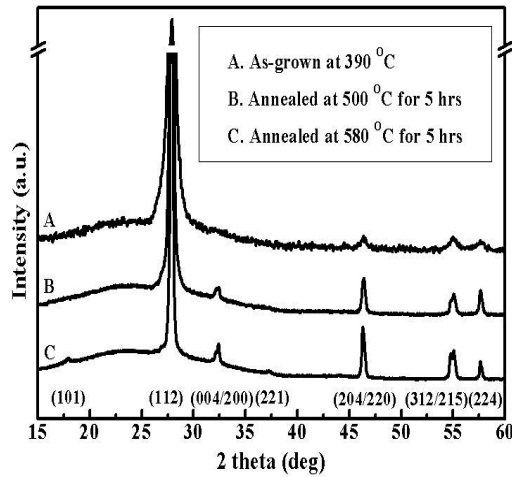
Figure 1: Graph of typical XRD patterns from as-deposited (A) and annealed CuInS$_2$ films (B and C)

3.2 Solar cells made with PVD-deposited films

Figure 2 shows the current-voltage characteristics of the test solar cells completed with both the GRC and Oberlin College window/contact layers. Table II lists the solar cell parameters of two cells measured. The chalopyrite 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 FF as shown in the Figure 2. Although I$_{sc}$ was comparable to that of any other reported chalcopyrite solar cells [7,8], V$_{oc}$ and FF need to be further improved.
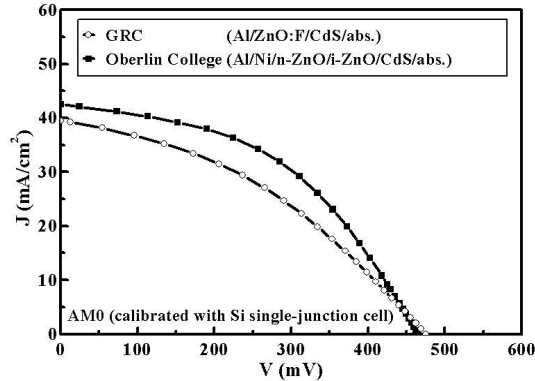

Figure 2: Light J-V characteristics of solar cells fabricated with PVD-deposited chalcopyrite films

Table II: Output characteristics of solar cells fabricated with PVD-deposited chalcopyrite films

Fabricator	V$_{oc}$(mV)	I$_{sc}$(mA/cm^2)	FF	η(%)
GRC	477	39.7	0.38	5.3
Oberlin College	465	42.5	0.46	6.7

3.3 Solar cells made with AACVD-deposited CIS films

The current-voltage characteristics of the solar cells prepared with AACVD-deposited CIS films are shown in Figure 3 and the solar cell parameters are listed in Table III. A series of solar cell were fabricated at GRC and the best cell, which is shown in Figure 3 was made with a film deposited using a 0.01M solution. The film was annealed under sulfur at 450 °C for 17 hours after deposition. There was no post-fabrication annealing.

The cell fabricated at IEC was prepared with a film deposited using a 0.04M solution and the film was annealed under sulfur at 450 °C for 6 hours 40 minutes. After fabrication, the solar cell was annealed under air at 150 °C for about 24 hours.

Although the efficiencies of the solar cells made at both GRC and IEC were comparable, the cell made at IEC clearly had a higher shunt resistance improving FF. V$_{oc}$ over 400 mV was obtained, but I$_{sc}$ was lower than that of the GRC-made cell indicating a possible difference in a minority carrier diffusion length. The major loss was due to low V$_{oc}$.

The increase of CIS film thickness from 0.7 μm should minimize the optical loss and the intrinsic ZnO and Ni/Al top contact will be incorporated for further improvement.

It should be noted that most solar cells prepared with AACVD method had a superstrate structure as seen in Table I and there has been no report of a working device with a typical chalcopyrite solar cell structure, top contact/window layer/CdS/CuInS$_2$ except for the authors' previous results [13].
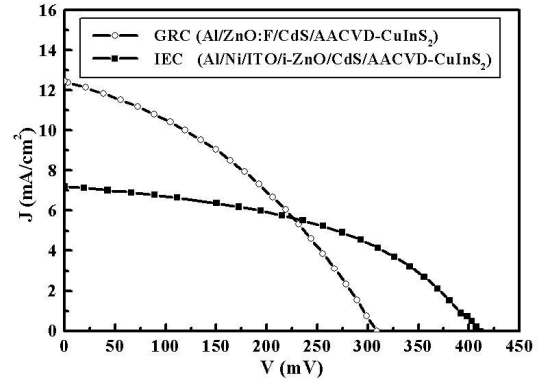

Figure 3: Light J-V characteristics of solar cells fabricated with AACVD-deposited CuInS$_2$ films

Table III: Output characteristics of solar cells fabricated with AACVD-deposited CuInS$_2$ films

Fabricator	V$_{oc}$(mV)	I$_{sc}$(mA/cm^2)	FF	η(%)
GRC	309	12.5	0.37	1.0
IEC	412	7.2	0.45	1.0

4 CONCLUSIONS

Chalcopyrite solar cell fabrication process has been established at NASA GRC. A test solar cell with a structure of Al/ZnO:F/CdS/PVD-deposited chalcopyrite film 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.

CIS thin films were prepared from AACVD using the

single source precursor, $(PPh_3)_2CuIn(SEt)_4$ and solar cells were fabricated both at GRC and IEC using the films deposited. The best solar cell parameters obtained were V_{oc} of 412 mV and FF of 0.45 from the IEC-cell and I_{sc} of 12.5 mA/cm^2 from the GRC-cell. 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 [16,18].

5 ACKNOWLEDGEMENTS

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