



# Multi-Junction Thin-Film Solar Cells on Flexible Substrates for Space Power

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# MULTI-JUNCTION THIN-FILM SOLAR CELLS ON FLEXIBLE SUBSTRATES FOR SPACE POWER

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## ABSTRACT

The ultimate objective of the thin-film program at NASA GRC is development of a 20% AM0 thin-film device technology with high power/weight ratio. Several approaches are outlined to improve overall device efficiency and power/weight ratio. One approach involves the use of very lightweight flexible substrates such as polyimides (i.e. Kapton<sup>TM</sup>) or metal foil. Also, a compound semiconductor tandem device structure that can meet this objective is proposed and simulated using Analysis of Microelectronic and Photonic Structures (AMPS). AMPS modeling of current devices in tandem format indicate that AM0 efficiencies near 20 % can be achieved. And with improvements in materials, efficiencies approaching 25% are achievable. Several important technical issues need to be resolved to realize these complex devices: development of a wide bandgap material with good electronic properties, development of transparent contacts, and targeting a 2-terminal device structure (with more complicated processing and tunnel junction) or 4-terminal device. Recent progress in the NASA GRC program is outlined.

## INTRODUCTION

Concepts for future space platforms include very large satellites such as solar power satellite (SPS) down to very small satellites;<sup>1,2</sup> long-term plans envisage swarms of distributed, autonomous, small

satellites termed microsats or even nanosats. Solar electric propulsion (SEP) technology that uses propulsion by accelerated ions has been successfully demonstrated in Deep Space 1.<sup>2</sup>

Photovoltaic (PV) arrays will continue to be a key source for power generation in space. While Si and GaAs PV technologies continue to play a vital role in space, there are two areas in which improvement is sought: mass-specific power (MSP) or power/weight ratio and radiation hardness. Both materials suffer in this regard because they are based upon bulk materials, and Si is limited to single junction efficiencies. Solar cells based on thin-film materials offer the promise of much higher MSP and much lower cost. However, for space applications, a 15% or greater AM0 efficiency ( $\eta$ ) may be required.<sup>3</sup> The leading thin-film materials - amorphous Si, CuInSe<sub>2</sub> and CdTe have seen significant advances in efficiency over the last decade but may not achieve the required efficiency in the foreseeable future. The ultimate objective of the thin-film program at NASA GRC is development of a 20% AM0 thin-film device technology with high power/weight ratio.

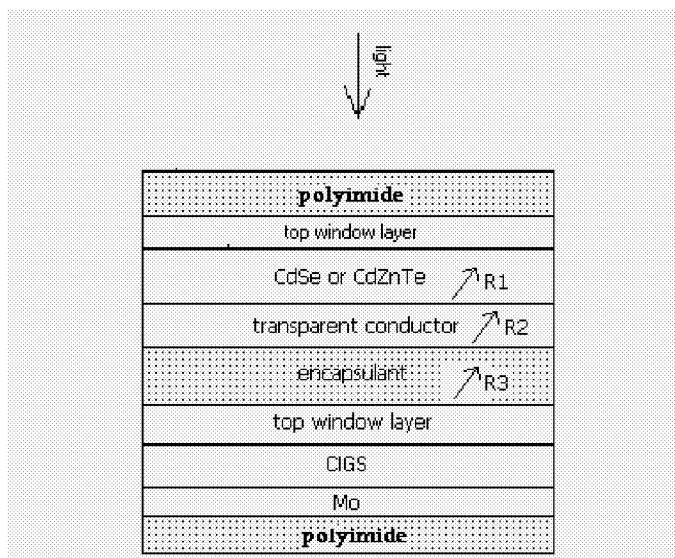
While current thin-film single-junction efficiencies rival those of silicon, tandem devices that offer significantly higher efficiencies are in production. These tandem devices more effectively utilize solar radiation by converting shorter wavelength radiation in the upper wide-bandgap layer and passing through

non-absorbed longer wavelength light to a narrow-bandgap bottom cell material. MSP can be further enhanced by use of thin, lightweight, metal foils, or even high-temperature plastics such as polyimides. Thin-film devices are fundamentally more radiation hard simply because of their reduced thickness, this should also apply to thin-film tandems.

We have proposed and simulated a thin-film tandem device structure that can meet program objectives. The bottom cell is a 1.0 eV CIGS device (efficiency requirements for this device have been demonstrated).<sup>4</sup> However, there is no known device that meets the requirements of the top cell. The key requirements are: a band gap in the range 1.6–2.0 eV, an efficiency of 16–18%, and transparency to transfer longer wavelengths to the bottom cell. An immediate objective is development of such a cell. Modeling and device-processing results of NASA GRC's multijunction thin-film program are highlighted.

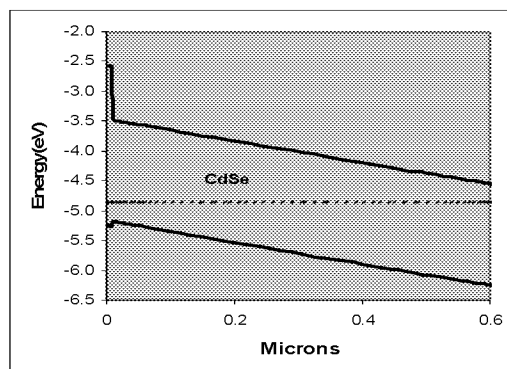
### AMPS MODELLING

Specifically the proposed structure is a 4-terminal tandem as shown in figure 1. The thickness of the active layers is expected to be about 10  $\mu\text{m}$ . The bottom polyimide can be as thick as needed for structural support, and the top polyimide (or other) layer will be designed to minimize radiation damage.



**Figure 1.** 4-terminal tandem device schematic.

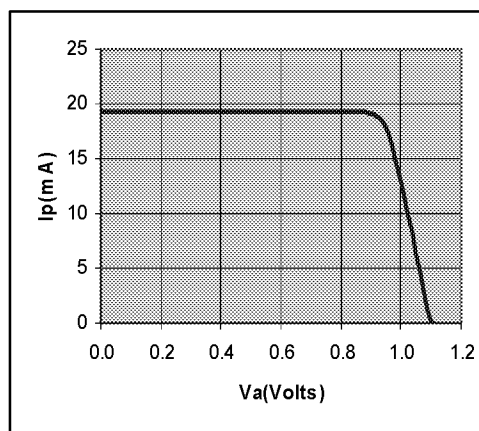
The best CdSe cells to date have been in the MIS configuration with ZnSe as the insulating (I) layer.<sup>5</sup> AMPS was used to model this structure.<sup>6</sup> Typical values for the key parameters were taken from the literature, or by analogy to similar materials. An example of the latter is the density of states (DOS) for the conduction and valence bands that were chosen to be  $1 \times 10^{18}$  and  $1 \times 10^{19}$ , respectively. A donor doping concentration of  $1 \times 10^{14}$  was used for the



**Figure 2.** Equilibrium band diagram for a ZnSe/CdSe MIS structure.

CdSe, while  $1 \times 10^{14}$  was used for ZnSe to make it an insulator. No defects in either layer were included. The equilibrium band diagram is shown in figure 2. As expected, the CdSe layer is completely depleted. The electron affinities used for ZnSe and CdSe were 3.67 and 4.56, respectively. The conduction band offset acts as a good electron mirror, while the offset in the valence band does not impede hole flow.

The light IV curve is shown in figure 3 and is near ideal. The parameters are  $V_{oc}$ : 1.11 volts,  $J_{sc}$ : 19.3  $\text{mA}/\text{cm}^2$  (assumed 5% reflection loss at front), FF: 0.81, and  $\eta$ : 17.4%. This is highly encouraging in that it indicates that a MIS structure can meet our performance requirements. A key to getting this to work is finding external contacts at the right energies. In this case the rear contact was at 0.3 eV from the CdSe conduction band, and the front contact at 0.3 eV from the CdSe valence band. Thus the achieved  $V_{oc}$  is essentially the band gap of the CdSe (1.7) minus the sum of these two contact voltages. Experimentally the rear contact should not pose a problem, while finding a front contact with such a high energy will be difficult. The highest  $V_{oc}$ 's reported for these devices were indeed for Pt and Au contacts (up to 0.85 volts, but with low  $J_{sc}$  and FF) which have the



**Figure 3.** Simulated light IV for the ZnSe/CdSe MIS structure with 17.4% efficiency.

highest work functions. Also reported was a dependence of  $V_{oc}$  on work function.<sup>5</sup> Post-deposition treatment of the interface with metal was critical to achieving this; getting higher efficiencies with these structures has yet to be proven.

To further our understanding of these structures, several parameters were varied. Using electron affinities for ZnSe and CdSe of 3.67 and 4.56 respectively, the following observations were made. Changing the thickness of the ZnSe layer has no effect on performance. There is some disagreement in the literature on the values of electron affinities, so it is appropriate to vary this parameter.  $J_{sc}$  is found to be independent of the ZnSe affinity, while the  $V_{oc}$  and FF dependence is shown in figure 4.

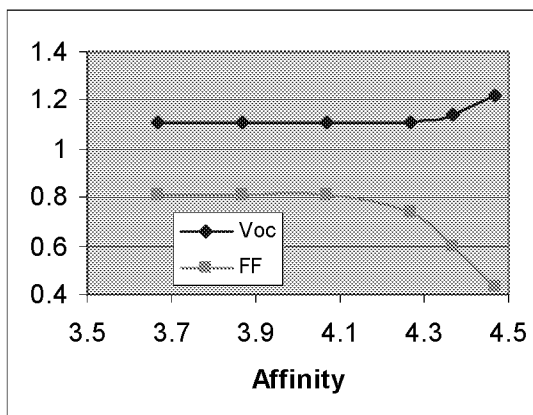


Figure 4.  $V_{oc}$  and FF dependence on ZnSe affinity.

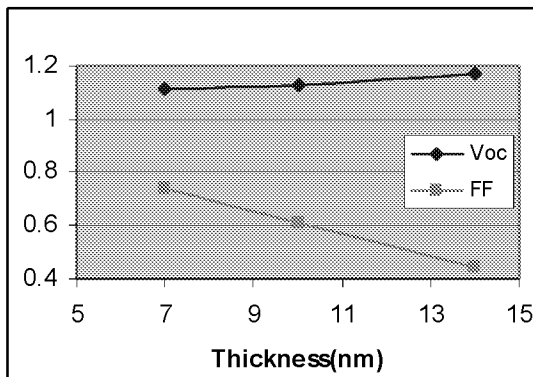


Figure 5. Dependence of  $V_{oc}$  and FF on ZnSe thickness for a ZnSe affinity of 4.27.

As ZnSe affinity is increased, increasing valence band offset occurs which results in poor hole transport across the interface and declining FF. This results in a small increase in  $V_{oc}$ . With ZnSe affinity in the transition range (4.27) (see figure 5), there is now a strong ZnSe thickness correlation with FF and a weak dependence for  $V_{oc}$ . At a ZnSe affinity of 4.27 the

valence and conduction bands each have an offset of about 0.3 eV; interference with collection begins. It is apparent that having the right band gap and electron affinity for the I layer is important. It is noteworthy that there is quite a large range of acceptable values.

It is interesting that in none of the above simulations was there a reduction in  $J_{sc}$ . To find the limits here we go back to the base case and systematically increase the band gap of the I layer while keeping everything else constant. Not until the I layer band gap reaches 3.37 eV is there an effect on  $J_{sc}$ . The light and dark IV's for this case are shown in figure 6. As can be seen, forward dark current is severely restricted.  $J_{sc}$  has just dropped down a bit to 18.6, but the curve shape has plummeted. Any further increase in the band gap will result in similar losses in  $J_{sc}$ . The saturation of the dark current at  $1 \times 10^{-12}$  in figure 6 is due to the large band gap of the ZnSe. In figure 7 is shown the effect of the I layer band gap on dark current.

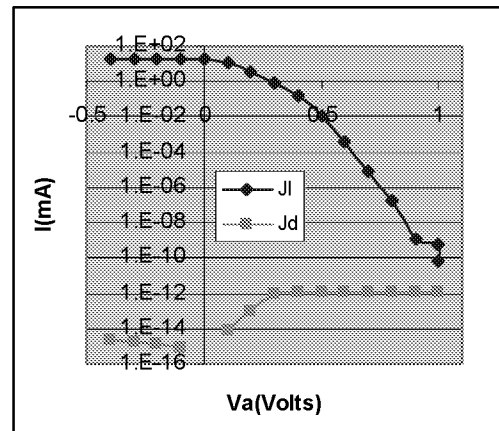


Figure 6. Light and dark IV for an I layer bandgap of 3.37 eV.

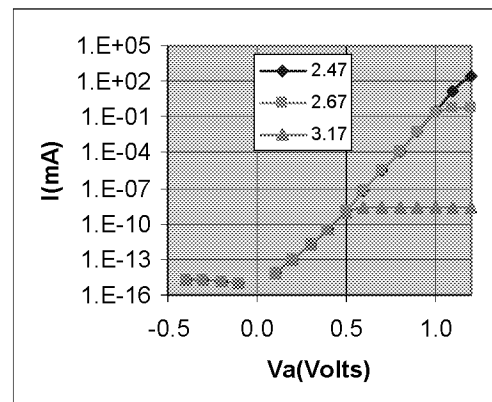


Figure 7. Dependence of dark current saturation on the energy gap of the I layer

As can be seen, dark current flow at just over one volt is affected for the ZnSe band gap of 2.67 eV. While this does not affect  $J_{sc}$ , FF is affected (Table 1). The small loss in FF for the 2.67 eV band gap of ZnSe is due to the band gap itself and not on the details of band alignment. As seen in figure 4, it takes a large change in affinity to start affecting FF. Modest increases in band gap, however, result in more substantial losses. While none of this suggests that ZnSe is not a good choice, the implications are that a smaller band gap material would be somewhat better. This would have to be weighed against the favorable interface defect control reported for ZnSe.<sup>7</sup> In this regard ZnTe would seem to have a band gap advantage over ZnSe as an I layer, although a disadvantage because of the toxicity of Te.

**Table 1.** MIS device properties as a function of Insulator-layer bandgap.

$E_g$	$J_{sc}$	$V_{oc}$	FF	Eff. ( $\eta$ )
2.47	19.3	1.11	.89	19.0
2.67	19.3	1.11	.81	17.4
3.17	19.3	1.11	.37	7.9

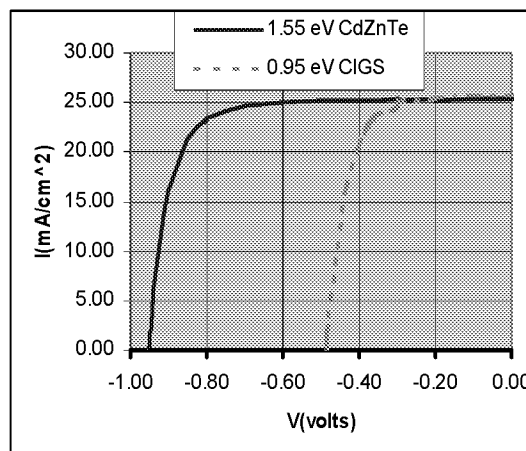
While there remain issues on details to be resolved for the MIS structure we are satisfied that good performance can be achieved under the right circumstances. At the outset we were concerned that sensitivity to the strong thickness dependence of tunneling for a true MIS structure would be troublesome, but these devices do not require tunneling to function well. ZnSe is not behaving as an I layer, but rather as a type of heterojunction contact to CdSe. Up to this point, we have ignored optical losses due to the metal contact. Metals have not been used as transparent conductors in solar cells for this reason. While this is a concern here, there may be mitigating circumstances that relax that concern. As will be discussed below, the "M" in the MIS structure may also be a misnomer. That is, the metal, particularly Cu may be reacting with the semiconductor layers. This may be its most important role, and once this is accomplished by a small quantity of metal, the top of the device could be finished with a standard transparent conductor such as ZnO with proper opto-electronic properties.

In fact this leads us back to our concept of a device structure *p-transparent contact/absorber/n-transparent contact*. Following up on what we have learned about the MIS structure, a metal/ZnSe structure would serve as our p-transparent contact. This should serve as a valid starting point for developing our devices, particularly the absorbers. Eventually, however, we will have to replace this p contact with one with larger effective contact energy to achieve high  $V_{oc}$ .

The  $CuIn_{1-x}Ga_xSe_2$  (CIGS) bottom cell technology already exists. This is certainly the case on glass substrates where efficiencies in excess of 15% are routine. Some effort has gone into

developing CIGS on metal foil and polyimide,<sup>8</sup> but performance is somewhat poorer. Nevertheless this can be improved upon with further effort, and we thus will focus our efforts under this project on the top cell. This is where innovation is needed because there is no known thin-film device with a high band gap and high efficiency. Below we report progress on development of this top cell. In addition to requiring high efficiency and light-weight there is the added requirement for a tandem device structure that it be transparent to longer wavelengths. Our approach is to break these down into individual components and address each technical issue in turn.

As shown in figure 8, performing these simulations at AM0 results in projected efficiencies in excess of 20%—13.8% is contributed by a top cell with band gap of 1.55 eV, and 6.3% is contributed by the underlying CIGS cell. In this case we argued that the top cell could be  $Cd_{1-x}Zn_xTe$  (CZT) with a small amount of zinc that should not change the electronic properties significantly from those of CdTe that were used in the simulation. As the band gap of the top cell is increased beyond 1.55 by adding more Zn, or using CdSe with its 1.7 eV band gap, the expected efficiency moves above 20%. Thus our primary objective is to demonstrate a top cell from either of these material options with an AM0 efficiency of 13% or more.



**Figure 8.** Simulated AM0 IV curves for a tandem device consisting of a 1.55 EV top cell and 0.95 eV bottom CIGS cell. Tandem efficiency is 20.1%.

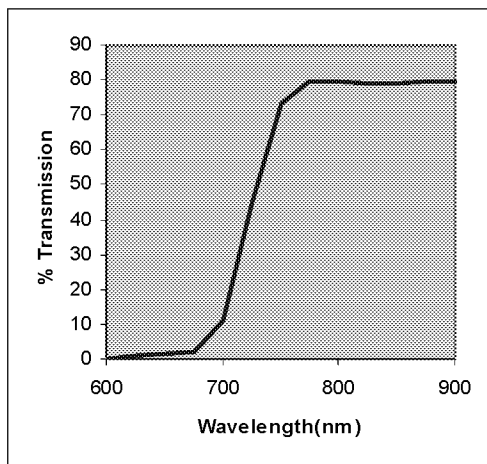
## PROCESSING OF TOP-CELL MATERIALS

We are pursuing  $CuIn_{1-x}Ga_xS_2$  (CIGS2) (FSEC), CdSe (USF), and CZT (USF) as candidate absorbers for the top cell. (CIGS2) thin films were prepared by sulfurization of DC magnetron-sputtered CuGa/In precursor on stainless steel foil substrates. The modeling and fabrication effort at USF is focused on CdSe and CZT as primary candidates. The progress that we discuss below will be for CdSe. Much of the effort thus far on CZT has been on material processing and characterization.



### **CdSe Fabrication**

To check the optical performance of our CdSe films we deposited a 1600 nm thick film on glass and measured its transmission profile. As seen in figure 9, ~80% is transmitted in the wavelength range above 750 nm that is the domain of the underlying CIGS cell. This is only 5% lower than the 85% figure assumed in the simulations for efficiency. This is very encouraging because this film is thicker than the CdSe film we expect to use; no attempt was made to reduce reflection losses. Much of the 20% loss is expected to be reflection that will be reduced when top layers are present. When suitable AR layers are determined, a further reduction of losses is expected.

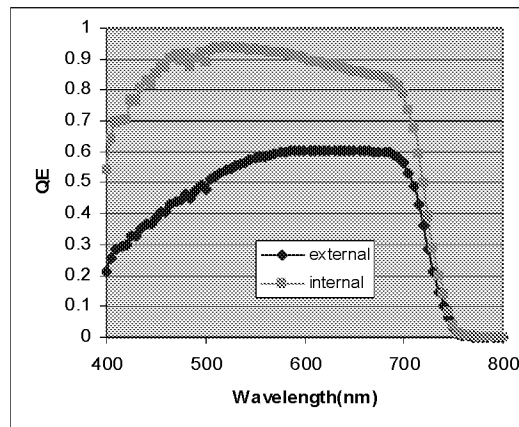


**Figure 9.** Transmission profile of a 1600 nm CdSe film on glass.

Our initial fabrication efforts centered upon the metal-insulator-semiconductor (MIS) structure. We used a transparent conductor as the growth surface. The device structure is Cu/ZnSe/CdSe/TC. The CdSe substrate temperature was varied over the 450–600 °C range while the substrate temperature for ZnSe deposition was 200 °C. The ZnSe and Cu layers are deposited sequentially by PVD without breaking vacuum between. However, they are deposited in a different system from the CdSe, and thus the CdSe surface is exposed to ambient prior to deposition of the MI contact layers. The ZnSe is a continuous layer, while the metal is deposited through a shadow mask.

Since our primary concern is to demonstrate high electronic quality CdSe, we have focused our efforts on demonstrating high short circuit currents in devices.  $J_{sc}$  is typically an indicator of bulk properties, while  $V_{oc}$  and FF in thin film devices are often more affected by interface properties and contact properties. For example, we expect that the low  $V_{oc}$ 's in these devices are primarily the result of the effective contact energies of the contacts and have little to do with the CdSe. This is more likely to be the case if we are seeing good  $J_{sc}$ 's indicating good properties for the CdSe bulk. Using  $J_{sc}$  as our

figure-of-merit we proceeded to vary the CdSe deposition parameters to optimize its electronic properties, specifically  $J_{sc}$ . In figure 10 we show QE spectral response of a device with the highest  $J_{sc}$  that we have achieved to date. Calibration of QE is accomplished by calibrating our light source against a Si reference cell.  $J_{sc}$  is determined by integrating the external QE spectrum and is found to be 14.7 mA/cm<sup>2</sup>. This is the actually measured  $J_{sc}$  of the device.



**Figure 10.** External and internal QE of a Cu/ZnSe/CdSe/TC device.

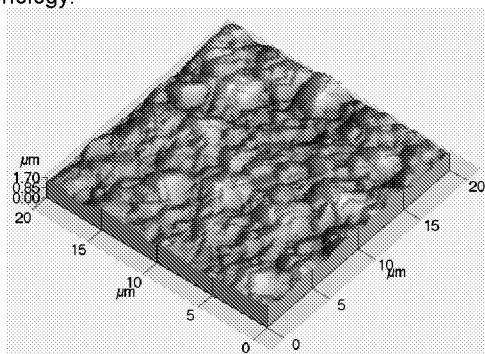
When the external QE spectrum in figure 10 is normalized against the transmission of the Cu/ZnSe layer, the internal QE spectrum shown in figure 10 results. Integration of this spectrum results in an equivalent internally generated  $J_{sc}$  of 18.3 mA/cm<sup>2</sup>. This is within one mA/cm<sup>2</sup> of the  $J_{sc}$  for the simulated 17.4% MIS device in Table 1. As such this result is a strong indication that we are making very good electronic quality CdSe. Since the CdSe is on a transparent conductor this represents a big step forward toward achieving our overall objectives. The next focus of our efforts is development of top contact layers. This is where higher  $V_{oc}$ 's will come from; higher  $V_{oc}$ 's will increase the internal fields that should further tweak  $J_{sc}$  values as well as FF's.

### **CIGS2 Thin Films on Metal Foil**

Substrates used in this study included 127 μm and 20 μm thick bright-annealed stainless steel (SS) foils and 25 μm thick titanium foils. The results discussed herein are for samples on 127 μm thick SS foils. CuGa and In precursor layers were DC magnetron-sputter deposited on Mo-coated SS foils with elemental ratio Cu/(In+Ga) of ~1.4. Metallic precursors were homogenized by heating the samples to 135 °C for 25 minutes in argon gas flow.  $CuIn_{1-x}Ga_xS_2$  (CIGS2) thin films were prepared by sulfurization of the CuGa/In precursor films in Ar:H<sub>2</sub>S (4%) gas mixture at 475 °C. CIGS2 thin films grew with a chalcopyrite  $CuIn_{0.7}Ga_{0.3}S_2$  phase with  $a = 5.67$  Å and  $c = 11.34$  Å and preferred {112} orientation.

Cu<sub>x</sub>S phase segregating at the surface was etched away with a 10% aqueous KCN solution. CIGS2 solar cells were completed by deposition of CdS heterojunctions by chemical bath deposition, transparent-conducting ZnO/ZnO:Al window bilayer by RF sputtering, and vacuum deposition of Ni/Al contact fingers through metal mask. CIGS2 thin films and solar cells were characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray diffraction (XRD), C-V, I-V, micro-photoluminescence (micro-PL) and QE techniques.

Non-contact AFM image showed the unetched CIGS2 films to consist of compactly packed, well faceted grains having size ranging from 1–3  $\mu\text{m}$  with a roughness of 0.19  $\mu\text{m}$  (Fig. 11). SEM image of unetched sample also showed large, well faceted grains. Thus the Cu-rich stoichiometry during the growth of CIGS2 films resulted in an improved morphology.



**Figure 11.** Non-contact AFM image of an unetched CIGS2 film.

SEM of etched CIGS2 films display a considerably rougher surface with protrusions and valleys. XRD and EPMA analysis do not show evidence of compositional or structural fluctuations. Inhomogeneous broadening, and variation of peak position and amplitude of micro-PL signal variations may therefore be attributed to the rough morphology of the etched films. The CIGS2 carrier density extracted from the CV data was found to vary in the mid- $10^{16} \text{ cm}^{-3}$  range and relatively constant between 80 and 180 nm from the junction. PV parameters of the best CIGS2 solar cell on SS flexible foil measured at NASA GRC under AM0 conditions were  $V_{oc} = 802.9 \text{ mV}$ ,  $J_{sc} = 25.07 \text{ mA/cm}^2$ ,  $FF = 60.06\%$ , and  $\eta = 8.84\%$ . Quantum efficiency characteristics gave a band gap of 1.50 eV and only a modest CdS loss.

## CONCLUSIONS

Considerable progress has been made with CdSe using a MIS structure. We have modeled this structure and demonstrated that this structure can

meet our efficiency objectives. Guided by these results we have utilized a metal/ZnSe/CdSe/TC structure as our device format for evaluating CdSe. External and internal  $J_{sc}$ 's of 14.7 and 18.3  $\text{mA/cm}^2$  respectively have been demonstrated. This is a significant result in that it is on a transparent contact and indicates that we are able to deposit high electronic-quality CdSe on transparent conductors. We have demonstrated 80% transmission of light for the bottom cell through 1600 nm CdSe films. This is within reach of our target of 85% through use of AR coatings.

Unetched (CIGS2) thin films, prepared by sulfurization of DC magnetron-sputtered CuGa/In precursor on stainless steel foil substrates, consisted of compactly packed, well faceted grains having size ranging from 1–3  $\mu\text{m}$  with a roughness of 0.19  $\mu\text{m}$ . The etched CIGS2 films showed a considerably rougher surface with protrusions and valleys. The best efficiency of CIGS2 solar cell on SS flexible foil measured at NASA GRC was 8.84% AM0.

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13. ABSTRACT (Maximum 200 words)  The ultimate objective of the thin-film program at NASA GRC is development of a 20 percent AM0 thin-film device technology with high power/weight ratio. Several approaches are outlined to improve overall device efficiency and power/weight ratio. One approach involves the use of very lightweight flexible substrates such as polyimides (i.e., Kapton™) or metal foil. Also, a compound semiconductor tandem device structure that can meet this objective is proposed and simulated using Analysis of Microelectronic and Photonic Structures (AMPS). AMPS modeling of current devices in tandem format indicate that AM0 efficiencies near 20 percent can be achieved. And with improvements in materials, efficiencies approaching 25 percent are achievable. Several important technical issues need to be resolved to realize these complex devices: development of a wide bandgap material with good electronic properties, development of transparent contacts, and targeting a 2-terminal device structure (with more complicated processing and tunnel junction) or 4-terminal device. Recent progress in the NASA GRC program is outlined.				
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