1995114096

N95-20512

STATUS OF FLEXIBLE CIS RESEARCH AT ISET[1]

B.M. Basol, V.K. Kapur, A. Minnick, A. Halani, and C.R. Leidholm
International Solar Electric Technology (ISET)
Inglewood, California

SUMMARY

Polycrystalline thin film solar cells fabricated on light-weight, flexible substrates are very attractive for space applications. In this work $CuInSe_2$ (CIS) based thin film devices were processed on metallic foil substrates using the selenization technique. CIS deposition method involved reaction of electron-beam evaporated Cu-In precursor layers with a selenizing atmosphere at around 400 °C. Several metallic foils such as Mo, Ti, Al, Ni and Cu were evaluated as possible substrates for these devices. Solar cells with AM1.5 efficiencies of 9.0-9.34 % and good mechanical integrity were demonstrated on Mo and Ti foils. Monolithic integration of these devices was also demonstrated up to 4"x4" size.

INTRODUCTION

Great advances have been made in polycrystalline thin film terrestrial solar cell technologies since early 1980's when the first promising laboratory devices with high efficiencies were demonstrated. These cells were fabricated on polycrystalline CdTe and $CuInSe_2$ (CIS) layers and they had AM1.5 conversion efficiencies of around 10%. During the last decade, the polycrystalline thin film solar cell efficiencies have improved to over 15% range and the stability data obtained from these devices has been very encouraging.

As the efficiency and the stability of the polycrystalline thin film solar cells have improved through the years, these devices have become more and more attractive for space applications where a reliable power source with high specific power is needed (refs. 1 and 2). Cells and modules fabricated on foil substrates also appeal to some specific terrestrial markets where flexibility is either required or preferred.

CIS and related compound thin film solar cells have already demonstrated terrestrial conversion efficiencies of over 16% (the highest efficiency reported is 16.4% by NREL for a Cu (In,Ga) Se_2 device). Preliminary tests also indicated that the radiation tolerance of CIS thin film cells was superior to that of single crystalline devices under high energy electron and proton irradiation.

Besides their radiation resistance and promise of high efficiency, CIS thin film devices also offer to the space power market a high specific power and low cost. If these devices could be fabricated on light-weight substrates and if they could be monolithically integrated to form modules, they would become very competitive with the existing single crystal technologies even if their beginning-of-life efficiencies were lower than those of the single crystalline cells (ref. 3). The typical substrate for a high efficiency terrestrial CIS solar cell is a 0.3 cm thick soda lime glass sheet. The main thrust of our effort in this program was the

[1] Work funded by NASA SBIR II contract No. NAS3-26615

fabrication of these devices on thin metal foil substrates using the selenization method.

EXPERIMENTAL

A "substrate" device structure with Foil/Mo/CIS/CdS/ZnO configuration was employed in this work. The 1-2 micron thick Mo layer was sputter deposited on the 1-2 mil thick foil substrate. CIS and CIGS ($Cu(In,Ga)Se_2$) layers were grown by the selenization technique (refs. 4 and 5). In the first step of this process thin layers of Cu and In, and in some cases Ga, were deposited on the metallic foils by e-beam evaporation. Thicknesses of the Cu and In layers in these precursors were typically 0.2 microns and 0.47 microns, respectively. Ga content was varied from 0% to 20%. During the second step of the process the precursors were reacted in a selenizing atmosphere containing H_2Se gas at 400 °C to form the selenide compounds. The selenization profile and the selenization period were varied to optimize conditions so that films of good electrical and mechanical properties could be obtained.

Devices were completed by CdS and ZnO depositions. CdS layer was obtained using the chemical dip method. This technique utilizes a meta-stable solution containing a Cd source such as Cd-acetate, a sulfur source such as thiourea, and a complexing agent that controls the rate of release of the Cd^{2+} ions into the electrolyte. ZnO films were deposited by the MOCVD technique to a thickness of 1-1.8 microns. Further details of the processing steps can be found in our previous publications (refs. 4 and 5).

RESULTS AND DISCUSSION

Flexible Substrate Selection

We have evaluated various metallic foils as possible substrates for the growth of CIS layers. Some of the factors that were taken into consideration in these evaluations are indicated in Table I and they will be reviewed here.

The selenization technique for CIS film formation involves a reaction step during which the Cu-In precursor layer is annealed in a reactive atmosphere containing H_2Se gas. It is, therefore, essential that the substrates selected for CIS cells do not participate in the reaction between the Cu-In layers and the H_2Se gas and/or they do not themselves react extensively with the H_2Se atmosphere at elevated temperatures. We found Mo and Ti foils to be the best in terms of chemical stability in the reactive atmosphere of our selenization chamber. However, we also determined that Al and Ni foils could be utilized provided that a Mo layer of good mechanical integrity was interposed between the foil surface and the growing CIS film. This thin Mo layer was found to act as an effective diffusion barrier between the foil surface and the CIS film and between the foil and the selenization atmosphere. Any pinholes present in the thin Mo inter-layer deposited on the highly reactive foils of Al and Ni, however, would allow an interaction between the CIS film and the foil substrate through these defects. Such an interaction would give rise to the formation of areas in the growing film which were associated with undesirable Cu-In-Al-Se, or Cu-In-Ni-Se compounds. The parts of the CIS film with a defect free Mo inter-layer, however, were highly uniform suggesting that the Mo layer deposited over the Al and Ni surfaces was an effective barrier to selenization at 400 °C. The defect density of the Mo layers deposited on Ti and Mo foils was not a critical factor in determining the stoichiometric uniformity of the CIS films grown on such substrates with limited reactivity. The main requirement for the Mo inter-layer in these cases was "good adhesion to the foil surface". Cu foils were extremely reactive and they could not be utilized in our application even if they were covered on both of their surfaces by Mo layers. Mo/Cu/Mo structures tested under selenization conditions quickly inter-diffused and Cu reacted with H_2Se forming copper selenides. More details of our studies on the reactivity of foil substrates can be found in references 4 and 5.

Handling of the thin foil substrates during processing is a practical factor that needs to be considered. Our experience showed that 1 mil thick Mo, Ti and Ni foils could easily be handled and they kept their mechanical integrity throughout the device fabrication steps. Al foils, on the other hand, tended to crease easily. Specially drawn "annealed" Al foils were better in terms of handling during the precursor deposition, but these substrates lost their "springy" nature after the high temperature selenization step and they again became susceptible to creasing.

In terms of specific power, Al and Ti are the two attractive choices as indicated in Table I. Both of these foils would contribute only 0.6-1 kg/kW to the overall specific power of CIS modules with 10W/ft^2 output. Thermal expansion coefficient match between the CIS film and the substrate is best for Ti and, to a certain degree, Mo foils.

Based on these factors and the experimental results, we first adapted Mo foil as the substrate because of our familiarity with this material as the back contact to CIS devices. Later we initiated work on Ti foil substrates which are more attractive in terms of their light weight and near-ideal coefficient of thermal expansion.

CIS Films and Solar Cells

It is very important to control the nature of the Cu-In precursor layers in the first stage of our CIS deposition process. The thickness uniformity, the degree of alloying between the Cu and In layers and the morphology of the resulting Cu-In precursor film are all factors that determine the quality of the CIS layer obtained after the selenization step. In films containing Ga, the place of this element in the precursor stack also affects the morphology of the resulting compound film. Adhesion is of utmost importance for CIS layers, especially for those deposited on flexible substrates. An important source of poor adhesion between a film prepared by the two-stage technique and its Mo coated substrate is the stresses generated in the CIS layer during the selenization process. We have eliminated this problem by carefully engineering the precursor layers (ref. 4) and have successfully deposited well adhering CIS layers on 6"x6" flexible Mo and Ti foil substrates.

Figure 1 shows the I-V characteristics of two CIS cells fabricated on flexible Mo (fig. 1a) and Ti (fig. 1b) foils. The area of these devices was 0.09-0.1 cm^2 and their AM1.5 efficiencies were 9% (active area), and 9.34% (total area) respectively. Witness cells fabricated on glass substrates utilizing the same Mo layers, the same Cu-In precursors and the same selenization procedures yielded efficiencies in the 11-12% range. Study of the flexible cell parameters indicated that these devices, on the average, gave 30-40 mV lower V_{oc} values compared to the glass based cells. The J_{sc} values were also lower but only by 1-2 mA/cm^2. However, the parameter that was consistently low in flexible solar cells was the fill factor. While the FF values of the glass based cells were typically in the 0.65-0.75 range, this range was only 0.5-0.6 for the flexible devices.

The SEM of figure 2 shows a cross sectional view of the CIS layer on a flexible Mo foil. There are certain characteristics of the flexible CIS films that we noted in studying such micrographs. The morphology of the CIS layers deposited on flexible foils are quite different than those grown on glass substrates. The dome-like features that are commonly observed in SEMs taken from the surfaces of flexible CIS layers originate from the dome-like pores that can be seen at the Mo/CIS interface in figure 2. The crystalline quality of the flexible films is also inferior to the crystalline quality of the glass based layers. This, we believe, is due to the different surface qualities of the two substrates. Foil substrate surfaces provide a large number of nucleation sites for grain growth and the resulting small crystals are not well oriented. CIS films grown on foil substrates do not show the columnar grain structure often observed in layers deposited on glass substrates. We have initiated work to address this issue and increase the flexible cell efficiencies to the 12-13% range.

Module Integration Studies

Monolithic integration of devices fabricated on metallic substrates requires deposition of an insulating layer over the metallic foil, and then a series of scribing steps to interconnect and isolate the adjacent cells (fig. 3). Glass based integration techniques which use mechanical scribers can not be utilized in the foil cell integration process because of the fragile nature of the thin insulator. Possible interaction of the insulating layer with the selenization environment is another factor that needs to be taken into account. We have carried out module integration work on 4"x4" size foils and monolithically integrated 16 cells on such a foil. Although these submodules demonstrated voltage addition the fill factor values are presently low and they limit the efficiency at this time to below 5%. Work is in progress to improve the efficiencies of these submodules to the 6-8% range by addressing the fill factor issue. It should be noted that the data reported in this paper represents the highest efficiency flexible CIS cells reported to date and the very first demonstration of monolithic integration of CIS cells on a flexible metal foil substrate.

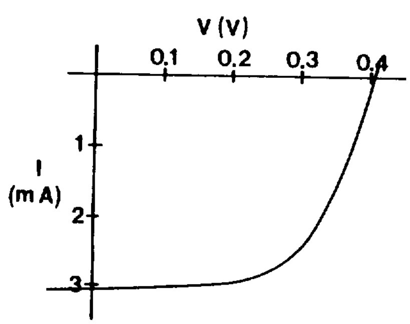
REFERENCES

1. Landis G.A.; and Hepp A.F.: Applications of Thin-Film Photovoltaics For Space. 26th Intersociety Energy Conversion Engineering Conf., 1991, vol. 2, pp.256-261.
2. Boswell J.; Anspaugh B.; and Mueller R.: Thin Film PV Development at Phillips Laboratory. Proc. 23rd IEEE PV Specialists Conf., 1993, pp. 1324-1329.
3. Armstrong J.H.; Pistole C.O.; Misra M.S.; Kapur V.K.; and Başol B.M.: Flexible CIS Films and Devices For Space Applications. Proc. Space PV Research and Technology Conf., May 7-9, 1991, NASA Lewis Center, Cleveland, Ohio, p. 19-1.
4. Basol B.M.; Kapur V.K.; Halani A.; and Leidholm C.: CIS Thin Film Solar Cells Fabricated on Flexible Foil Substrates. Solar Energy Materials and Solar Cells, vol. 29, 1993, pp. 163-173.
5. Başol B.M.; Kapur V.K.; Halani A.; Minnick A.; and Leidholm C.: Modules and flexible cells of CIS. Proc. 23rd IEEE Photovoltaic Specialists Conf., 1993, pp. 426-430.

TABLE I. EVALUATION OF VARIOUS METALLIC FOILS AS A SUBSTRATE FOR FLEXIBLE CIS SOLAR CELLS

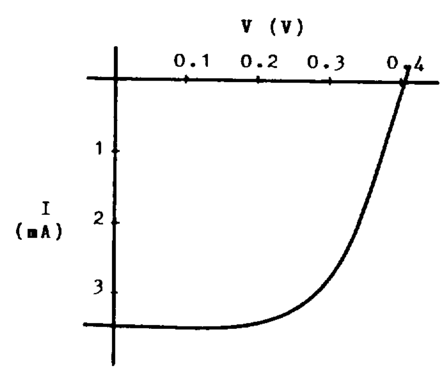
Foil Substrate	Reactivity with H_2Se	Ease of handling through process	Coeff. of thermal expansion* (x 10^6/°C)	Contribution to specific power** (kg/kW)
Mo	low	very good	4.8	2.29
Ti	moderate	very good	8.6	1.01
Al	high	poor (creases)	2.3	0.60
Ni	high	good	13.4	2.00
Cu	very high	very poor (reacts and becomes brittle)	16.5	2.01

* CTE for CIS ~ 7-9 ppm/°C
** Assuming $10 W/ft^2$ modules on 1 mil thick foils



V_{oc} = 0.405 V
J_{sc} = 37.5 mA/cm²
FF = 0.597
η = 9.0%
Area = 0.1 cm²

(a)



V_{oc} = 0.4 V
J_{sc} = 38.9 mA/cm²
FF. = 0.6
η = 9.34 %
Area = 0.09 cm²

(b)

Figure 1. Illuminated I-V characteristics of two flexible cells fabricated on a) Mo foil, b) Ti foil. Measurements were made under AM1.5 illumination.

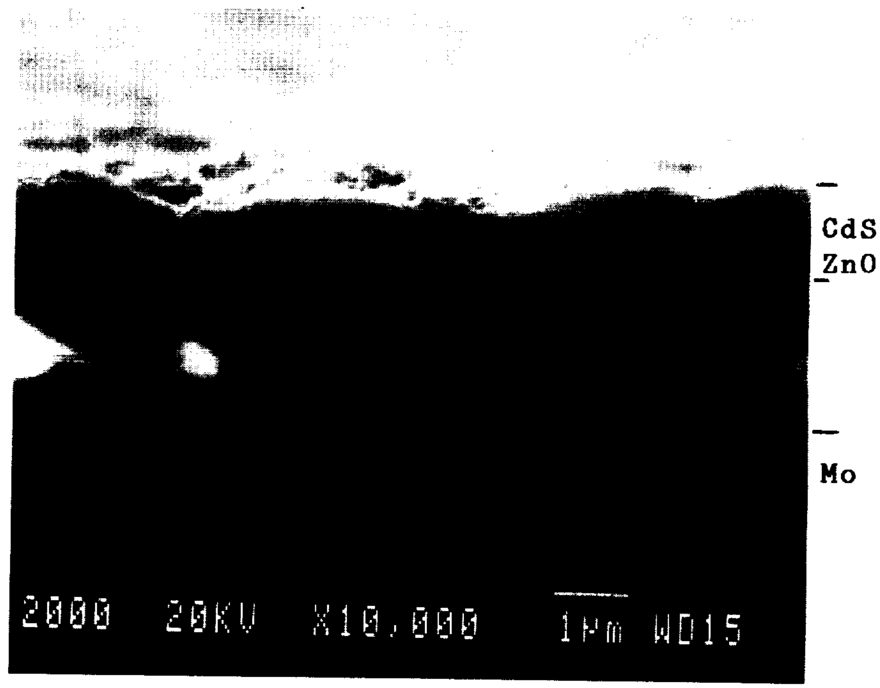


Figure 2. Cross sectional SEM of a foil/Mo/CIS/CdS/ZnO structure.

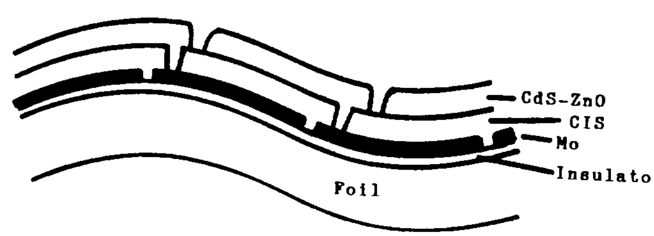


Figure 3. Structure of a monolithically integrated flexible CIS submodule.