

Structure and Properties of High Efficiency ZnO/CdZnS/CuInGaSe₂ Solar Cells

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Abstract—Thin-film polycrystalline solar cells with the structure ZnO/CdZnS/CuInGaSe₂ have been fabricated with total area efficiencies of up to 12.5 percent under AM1.5 equivalent illumination and 10.5 percent under AMO equivalent. These are among the highest total area efficiencies reported for polycrystalline thin-film solar cells. Current-voltage and quantum efficiency data for such a high efficiency cell are given. Described are the deposition of the CuInGaSe₂ by physical vapor deposition in vacuum, the CdZnS by chemical deposition from solution, and the ZnO by reactive sputtering. The electrical and optical properties of the individual layers have been inferred from measurements on complete devices and on separate witness layers. Optical constants and thicknesses obtained from these measurements for the device layers are presented and the requirements for optimizing the device efficiency discussed.

INTRODUCTION

THE USE of the ternary chalcopyrite compound CuInSe₂ as the p-type base absorber layer in a heterojunction solar cell with CdS or CdZnS as the n-type window layer has been well established [1]–[3]. Replacement of the ternary CuInSe₂ with its quaternary analog CuInGaSe₂ has been demonstrated to shift the bandgap of the absorber toward a better match with the incident solar spectrum and result in higher net AM1.5 and AMO efficiencies [4]. The bandgap of the CuInGaSe₂ increases with the gallium content, shifting from approximately 1.04 eV for pure CuInSe₂ to approximately 1.7 eV for pure CuGaSe₂. This range easily spans the calculated optimum bandgap for a single absorber for most solar cell related applications. Use of an intermediate composition CuInGaSe₂ therefore results in a higher voltage, higher efficiency device than is obtainable with CuInSe₂.

A fundamental limit on the efficiency of the CdS/CuInSe₂ cell is the low value of the bandgap of the CdS window layer. Absorption in the CdS window layer results in a light generated current loss of approximately 6 mA/cm² for the AM1.5 global spectrum at 100 mW/cm² equivalent intensity [5]. The replacement of the CdS with the higher bandgap ternary CdZnS has been normally considered as a means to lower the window absorption losses. However, shifting the bandgap of the CdZnS to higher energies has been limited by the lack of an ef-

fective dopant for high Zn content CdZnS layers. The simple CdZnS/CuInSe₂ devices have therefore been limited to Zn: Cd ratios in the sulfide of approximately 0.2:0.8 at the highest, with only small bandgap shifts resulting [2]. The CuInGaSe₂ based cells are higher bandgap, higher voltage, lower current devices and the efficiency penalty paid for the sulfide absorption is proportionately higher.

ZnO has the potential to be a much improved window layer for either CuInSe₂ or CuInGaSe₂. The bandgap is high enough to reduce the window absorption loss to less than 1 mA/cm². Doping with aluminum gives reasonable sheet resistivities (20–30 Ω/sq), comparable to that obtained in CdZnS layers. However, at these low sheet resistivities free carrier absorption in the infrared is much more of a problem with ZnO than with CdZnS.

While the fundamental limit on the transmission of the window layer can be circumvented by using ZnO, it has not yet been possible to form a good heterojunction between ZnO and either CuInSe₂ or CuInGaSe₂.

A system consisting of ZnO as the low resistivity current carrying layer but combined with CdS or occasionally CdZnS as the n-type layer has therefore been used [6]. In this case the CdZnS can now have higher resistivity and be very thin since it does not carry the lateral current flow. Appreciable transmission through the CdZnS or CdS can then be achieved if the thickness is less than the absorption length, which for CdS at 400 nm is typically several tens of nanometers.

We have pursued application of the ZnO/thin CdZnS window layers to both the CuInSe₂ and CuInGaSe₂ based devices. A device of the type ZnO/CdZnS/CuInGaSe₂ has the potential for exploiting both the better short wavelength response afforded by the ZnO conductive oxide and the optimum bandgap afforded by adjusting the gallium content in the CuInGaSe₂. In addition the considerable penalty in current paid in ZnO/CdS/CuInSe₂ devices due to the infrared absorption of the ZnO decreases significantly as the bandgap of the selenide is shifted to higher energy.

In previous work on CdZnS/CuInGaSe₂ devices [7] we have shown that gallium contents significantly above 0.25 (CuIn_{0.75}Ga_{0.25}Se₂) result in devices with poor current-voltage (*I-V*) characteristics and low efficiencies. Therefore the present work utilizes CuInGaSe₂ with compositions no higher than CuIn_{0.72}Ga_{0.28}Se₂ for all the devices

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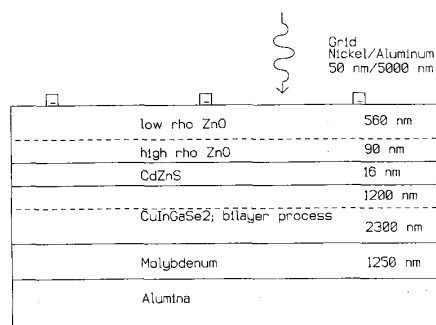


Fig. 1. Structure of ZnO/CdZnS/CuInGaSe₂ solar cell.

fabricated. Neither the nature of this problem nor the exact upper limit to the usable composition were explored in this work. The compositions used are in any case near the optimum for the unfiltered AM1.5 solar spectrum.

DEVICE STRUCTURE

Fig. 1 shows the cross section through the ZnO/CdZnS/CuInGaSe₂ device. The layers are not presented to scale but estimates of the layer thicknesses are given.

All devices reported here were single cells of approximately 1 cm² in total area fabricated using the photoresist and patterning technology already described for CuInSe₂ [8]. The present device is essentially one cell of a monolithically interconnected series string design which has already given CdZnS/CuInSe₂ 4 cell strings of area 91 cm² with an efficiency of 9.5 percent [8].

The optical characteristics of the complete device are dominated by the roughness of the original CuInSe₂ or CuInGaSe₂ surface. While the ZnO and CdZnS layers as deposited can be optically coherent, the CuInGaSe₂ layer has a rough surface with lateral features with dimensions of approximately 1 μm. This results in reflection from the selenide film far below that expected from a bare CuInGaSe₂ surface. Therefore the complete device shows some optical interference in the reflectance and quantum efficiency but much less than would be predicted from a coherent thin-film model.

DEPOSITION AND CHARACTERISTICS OF THE CuInGaSe₂ LAYER

The preparation of the CuInGaSe₂ layer for these devices is essentially unchanged from the described in [7]. The CuInGaSe₂ layers are prepared on molybdenum coated alumina substrates by simultaneous vacuum evaporation of the four elements from resistively heated crucibles.

The selenide is a bilayer as deposited, with the initial 2.3 μm of the 3.5-μm film deliberately deposited copper rich relative to the indium plus gallium total and the remaining 1.2 μm deposited highly copper poor. Examina-

tion of CuInSe₂ layers grown using this same bilayer process has shown that extensive homogenization between the two layers of the bilayer occurs during the growth process. No detectable gradient in element composition has been detected in the finished layers. No deliberate gradient in the Gallium:Indium ratio is built into the layers. For the best device the CuInGaSe₂ layer was determined by EDX analysis to have composition 23.8-percent Cu : 19.4-percent In : 7.4-percent Ga : 49.4-percent Se (atomic percent). Thermoelectric potential (hot probe) measurements showed this film to be slightly p type as deposited.

In almost all respects the growth process and film properties of the CuInGaSe₂ are closely analogous to those of the CuInSe₂. The deposition process is, of course, considerably more complex due to the additional elemental source. Substrate temperatures required to produce good film morphology are also higher for the CuInGaSe₂, 450° and 550° C during the first and second layer depositions, respectively, compared to 350° and 450° C for the CuInSe₂.

CHEMICALLY DEPOSITED THIN CdZnS LAYERS

The allowable thickness for the CdZnS, assuming bulk properties for such a very thin film, can be calculated from the literature values for absorption constants. The basic requirement for high (> 80 percent) transmission through a CdS layer at a wavelength of 400 nm is a thickness of less than 20 nm. Physical vapor deposition, as used for the 3-μm-thick CdZnS layers in CdZnS/CuInSe₂ devices, cannot produce layers with reasonably continuous coverage on the present CuInGaSe₂ films at even many times this thickness.

The thin CdZnS layer is therefore chemically deposited onto the CuInGaSe₂ using a modification of the process described by Danaher *et al.* [9].

Deposition occurs by placing the substrate in a freshly prepared solution of 0.01M(CdCl₂ + ZnCl₂) + 0.026M NH₄Cl + 0.26M NH₄OH and 0.083M thiourea. The solution is maintained at 85°C and vigorously stirred. For these concentrations the reaction in the solution goes to completion in approximately 30 min during which time deposition of a film of 40–50 nm thickness occurs. The Zn content in the deposited film is varied by adjusting the ratio of ZnCl₂ to CdCl₂. Film thickness is varied by adjusting the overall concentrations in the solution.

This process has been found to give conformal, reasonably uniform coverage even on the rough CuInGaSe₂ surfaces with controllable thickness down to approximately 10 nm. Optimization of the CdZnS layer was primarily a matter of determining optimal values for the Zn content and for the layer thickness.

Decrease in the sulfide thickness much below approximately 20 nm was found unnecessary since this thickness leaves the short wavelength response dominated by the ZnO absorption edge. For the same reason, use of high Zn content sulfide results in no net current gain with these thin layers.

The Zn fractional contents of the films used in the best devices are approximately 15–20 percent ($[Zn]/([Zn] + [Cd])$) from AUGER microprobe measurements. The films were not intentionally doped. Both the dark and light lateral resistivity is high, unmeasurable on our equipment ($> 5 \times 10^5 \Omega\text{-cm}$). This could be due either to the witness films used for the measurement being discontinuous or to the bulk resistivity of the films.

The optical constants and electrical resistivity of the thin solution deposited CdZnS were determined from optical measurements of witness layers on glass substrates. From a set of measurements of transmittance and reflectance it is possible to extract the real index of refraction n , the absorption constant α , and a best fit value for the film thickness [10]. The best fit to the optical data for the CdZnS film witness to the highest efficiency devices gave a film thickness of 16 nm, values of n somewhat below bulk, and α as shown in Fig. 2.

These n and α values are consistent with a simple model for the CdZnS of a thin, nearly or completely continuous film with optical constants somewhat below bulk due to film porosity.

ZnO DEPOSITION AND FILM CHARACTERISTICS

The ZnO layer functions as a high conductivity lateral current collector. As such it must make ohmic contact to the thin CdZnS layer. A more stringent requirement is that the contact between the ZnO and the CuInGaSe₂ be blocking or of high resistance in order to make the structure tolerant to defects in the thin CdZnS layer which allow direct contact between the ZnO and the CuInGaSe₂.

The ZnO films are deposited by RF magnetron sputtering in an Ar or O₂/Ar atmosphere from a ZnO target doped with 2 percent by weight Al₂O₃. The ZnO is deposited in two steps to form a high resistivity/low resistivity bilayer. First a thin (90 nm) high resistivity layer is deposited using a relatively high oxygen content ambient. A thick (560 nm typically) low resistivity layer is then deposited using pure Argon as the ambient. The target is preconditioned in the high oxygen ambient before either deposition.

The ZnO optimization involves a complex tradeoff among grid spacing, ZnO thickness, ZnO sheet resistance, ZnO infrared absorption, and ZnO reflection. Such a complete optimization was not attempted in this work. Using a reasonable grid geometry and a standard set of ZnO process parameters, the ZnO thickness was varied to optimize the tradeoff between sheet resistance and transmission. The grid metallization used to contact the ZnO is nickel/aluminum with thicknesses as given in Fig. 1.

The optical and electrical constants of the ZnO layers were studied using witness layers deposited on glass substrates. For the first, high resistivity ZnO layer the reflectance and transmittance were found to be well modeled using the literature values for $n(\lambda)$ along with $\alpha(\lambda)$ values found from the transmittance. These α values are shown

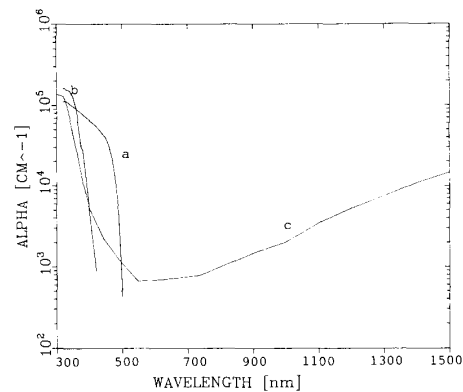


Fig. 2. Absorption constants of thin CdZnS (a), high resistivity ZnO (b), and low resistivity ZnO (c) layers as measured from witness layers on glass.

in Fig. 2. No detectable extrinsic absorption losses are present in this high resistivity layer.

The electrical characteristics of the high resistivity layers are highly unstable. As deposited the layers are typically 50 K Ω /sq. However, the sheet resistance changes drastically with any subsequent heat treatment: treatment at 225°C in O₂ results in films of >500 K Ω /sq, while treatment in a 10-percent H₂/90-percent Ar mixture results in 7 K Ω /sq. The final resistivity of the layers in the actual devices after heat treatment is therefore unknown.

The low resistivity ZnO layer is optically and electrically stable but complex. Transmittance and reflectance measurements on witness slides showed significant and rising absorption at wavelengths beyond 1 μm as expected. The layer, however, is heavily graded in both electrical and optical properties. The as-deposited bulk resistivity varied from approximately $4 \times 10^{-3} \Omega\text{-cm}$ in the first quarter of the film to $2.6 \times 10^{-4} \Omega\text{-cm}$ in the last quarter. We believe this grading to be simply due to the target preconditioning done before each deposition. The α values for the low resistivity ZnO shown in Fig. 2 are therefore average values for the layer.

ELECTRICAL CHARACTERISTICS OF THE ZnO/CdZnS/CuInGaSe₂ DEVICES

Fig. 3 shows the I - V characteristics of the highest efficiency cell under simulated global AM1.5 solar spectrum at 100 mW/cm² equivalent intensity as measured at the Solar Energy Research Institute (SERI). These measurements closely agree with those made in our own laboratory.

The total area efficiency of this 1 \cdot cm² device is 12.5 percent. The equivalent active area efficiency is 12.9 percent. Measurements under AMO spectrum, 137 mW/cm² equivalent intensity gave a total area efficiency of 10.5 percent. The AMO I - V characteristics as measured at Boeing are given in Fig. 4.

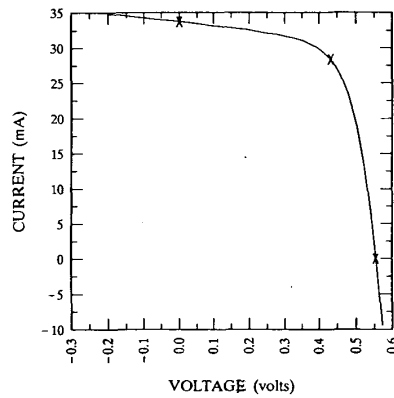


Fig. 3. I - V characteristics of high efficiency ZnO/CdZnS/CuInGaSe₂ solar cell under simulated AM1.5 global spectrum at 100-mW/cm² equivalent intensity as measured at the Solar Energy Research Institute. Sample: 1174H, temperature = 25°C, area = 0.987 cm². V_{oc} = 0.555 V, J_{sc} = 34.2 mA/cm², fill factor = 65.7 percent, efficiency = 12.5 percent, I_{sc} = 33.7 mA, I_{max} = 28.4 mA, V_{max} = 0.434 V.

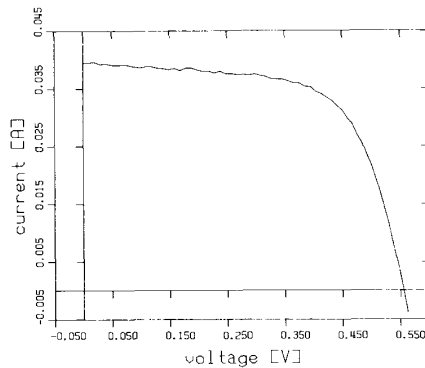


Fig. 4. I - V characteristics of high efficiency ZnO/CdZnS/CuInGaSe₂ solar cell under simulated AM0 spectrum at 137-mW/cm² equivalent intensity as measured at Boeing. Temperature = 28°C, Spectrolab XT-10, AM0 spectrum, 137.2 mW/cm². Area = 0.987 cm² assumed, V_{oc} = 0.556 V, I_{sc} = 39.5 mA, ff = 0.646, efficiency = 10.5 percent.

Measurements of forward and reverse I - V characteristics in the dark show that the shunt leakage seen in the I - V characteristics is light independent. Log I - V measurements made by SERI indicate much higher diode A factors in the dark than in the light, consistent with the behavior normally seen in CdZnS/CuInSe₂ cells.

Fig. 5 shows the quantum efficiency of the same ZnO/CdZnS/CuInGaSe₂ cell as in Figs. 3 and 4. Response with and without broadband ("white") light bias is shown. With the cell at short circuit loading there is little change in the quantum efficiency at any wavelength with and without the bias light.

The quantum efficiency was measured using a chopped monochromatic beam, therefore the measurement is actually of differential quantum yield (electrons/photon).

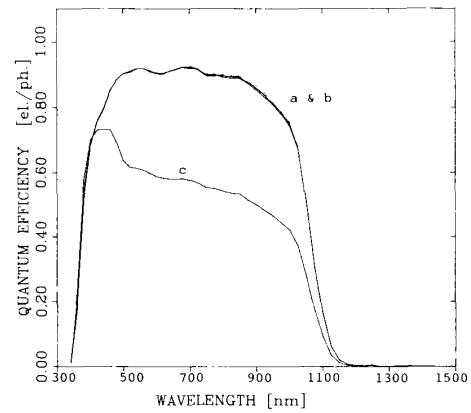


Fig. 5. Quantum efficiency of same ZnO/CdZnS/CuInGaSe₂ cell as in Figs. 3 and 4. Response is shown at (a) short circuit without bias light, (b) short circuit with bias light, I_{dc} = +15 mA, (c) V = 0.5 V forward bias with bias light, J_{dc} = -3 mA. Bias light intensity approximately 50-mW/cm² equivalent. Multiple data sets are shown for both (a) and (b).

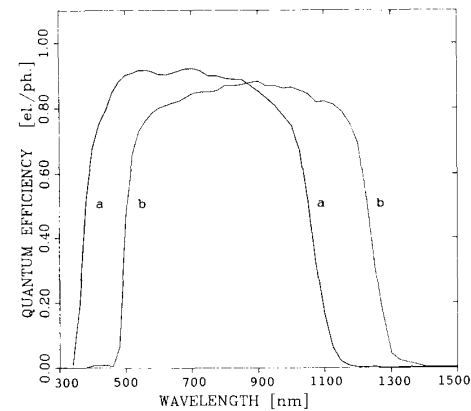


Fig. 6. Comparison of quantum efficiency of high efficiency ZnO/CdZnS/CuInGaSe₂ cell a, and high efficiency CdZnS/CuInSe₂ cell b.

The demonstrated lack of light intensity dependence of this quantity proves that the collected current is linear with light intensity at all wavelengths at short circuit loading.

The short circuit biased quantum efficiency shown can be explained with a simple linear model including only ZnO absorption, CdZnS absorption, and collection only from the CuInGaSe₂ with a finite bulk diffusion length, plus grid and reflection losses. Interference fringes are present in the quantum efficiency as expected from the thin ZnO layer but are strongly attenuated by the effects of the rough surface. Response at 400 nm is consistent with the 16 nm thickness for the CdZnS determined from the witness layers.

Also shown in Fig. 5 is the quantum efficiency under white light bias at 0.5 V forward bias. At the light intensity used this is slightly above open circuit voltage. To

explain the features of this forward biased quantum efficiency it is necessary to include several effects which are voltage dependent. The known lumped series resistance of the cell causes an overall wavelength independent drop in the magnitude of the quantum efficiency [11]. The increased long wavelength falloff with forward voltage bias can be explained by any of several voltage dependent collection mechanisms in the CuInGaSe_2 . Measurements on CuInSe_2 devices indicate that a voltage dependent bulk diffusion length model best fits the present cells.

The shoulder at the sulfide band edge indicates photoconductive effects in the thin CdZnS , through either a field or conductivity modulation mechanism [11]. In either case we are seeing a majority carrier effect in the high resistivity sulfide. The existence of the strong photoconductivity shows intrinsic or lightly doped CdZnS , indicating little or no *in situ* doping of the CdZnS films.

Fig. 6 compares the quantum efficiency of the highest efficiency $\text{ZnO}/\text{CdZnS}/\text{CuInGaSe}_2$ cell with a high efficiency $\text{CdZnS}/\text{CuInSe}_2$ cell. The offset in bandgap of the CuInGaSe_2 relative to the CuInSe_2 is clearly evident, the bandgap of the CuInGaSe_2 from the intercept is 1.16 eV. This is consistent with the value predicted for this gallium fraction using the bandgap versus composition data given in [7].

The short wavelength response edge of the $\text{ZnO}/\text{CdZnS}/\text{CuInGaSe}_2$ as shown in Fig. 6 is essentially limited by the absorption edge of the ZnO , absorption in the CdZnS is not an important loss. The long wavelength decrease of the quantum efficiency is due to both absorption in the ZnO and to finite diffusion length effects in the CuInGaSe_2 .

SUMMARY AND CONCLUSIONS

Solar cells with the structure $\text{ZnO}/\text{CdZnS}/\text{CuInGaSe}_2$ have yielded significant improvements in efficiency over previous CuInSe_2 based devices under both AM1.5 and AM0 illumination conditions. Measurements on devices and on witness layers have yielded a consistent and relatively straightforward model of the cell structure.

The efficiency increase has been shown to be due to several improvements. The $\text{ZnO}/\text{thin CdZnS}/\text{CuInGaSe}_2$ structure exploits the higher bandgap of the quaternary CuInGaSe_2 to both increase voltage and minimize the infrared absorption losses in the ZnO . The CdZnS layer on the best cells has been found to be very thin, approximately 16 nm, resulting in little sulfide absorption.

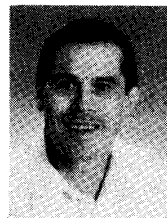
The major identifiable fill factor losses in the devices are shunt leakage, probably due to $\text{ZnO}/\text{CuInGaSe}_2$ contact associated with defects in the thin CdZnS layer, and the effective lumped series resistance of the devices. Reduction of these two to the values already seen in $\text{CdZnS}/\text{CuInSe}_2$ devices should be possible and would result in total area efficiencies of over 14 percent under AM1.5 illumination.

The short wavelength limit to the cell quantum efficiency has been identified as the absorption edge of the ZnO layer. Quantum efficiency measurements have identified the major long wavelength quantum efficiency loss mechanisms as ZnO absorption and the effect of finite bulk diffusion length in the CuInGaSe_2 . Reduction of the ZnO absorption losses and increased CuInGaSe_2 bulk minority carrier diffusion length should both be possible and would result in further efficiency increases.

The mechanisms controlling V_{oc} are not presently understood and no estimates of the possible improvements there can be made.

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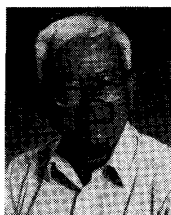
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John M. Stewart, photograph and biography not available at time of publication.



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