Cadmium Sulfide/Copper Ternary Heterojunction Cell Research

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1.0 Abstract

Dual source, Se and CuInSe_2 , coevaporation and flash evaporation of stoichiometric CuInSe_2 powder were investigated to develop a process of fabricating large area CdS/CuInSe_2 heterojunction solar cells.

CuInSe_2 was seen to decompose upon evaporation, producing layered films in the dual source system. Annealing of these films and alternative dual sources have been considered. Single phase p type films have been produced but no devices have been made from such films.

Flash evaporation circumvents the decomposition problem, and if one bakes the powder to obtain a small Cu excess as well as getting a Se excess in the film, p type CuInSe_2 films can be obtained.

A 11% efficient device of 6 cm^2 area was made using a flash evaporated CuInSe_2 film. Annealing studies and measurements of spatial uniformity of this device are reported.

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4.0 Discussion

4.1 Introduction

A number of copper ternary semiconductors have been investigated and their properties reported in the literature. A review of much of this work is given in Shay & Wernick, "Ternary Chalcopyrite Semiconductors/Growth, Electronic Properties and Applications," Pergamon Press, 1975. Of these, CuInSe_2 is the preeminent candidate for a heterojunction cell with CdS. Preliminary investigations of this system, both single-crystal^{1,2,3} and polycrystalline^{4,5} have been encouraging. CuInSe_2 has a band gap of 1.0 eV which is within the range of 1-2 eV expected to give best efficiency⁶ in solar photovoltaic devices. CuInSe_2 has a smaller lattice mismatch with CdS (~1%) than any other copper ternary. This leads to a smaller defect density at the junction, which in turn reduces the junction current and makes the external current larger, all other things being equal. Single crystal $\text{CuInSe}_2/\text{CdS}$ cells have achieved 12% efficiency⁷, and polycrystalline cells have achieved an efficiency of 6% to 8%.^{8,10} Analysis⁹ of device physics has indicated that 11% devices should be achievable from obtainable polycrystalline CuInSe_2 films.

In order to develop a Cadmium Sulfide/Copper Ternary heterojunction solar cell which can be reproducibly manufactured with an air mass-1 conversion efficiency of no less than 8% (as measured between 20°C and 30°C over cell areas of at least 4 cm²), with a maximum electrical output degradation of 5% over 20 years, this research program has been undertaken. The

program involves physical vapor deposition of CdS and CuInSe₂ films and fabrication of devices. The dependence of material parameters on deposition conditions is being investigated along with the effect of fabrication procedures on device efficiency and stability so as to establish a technology capable of producing cells meeting the above goal.

Several methods of depositing p type CuInSe₂ films were investigated. Flash evaporation of p-type (Se rich) CuInSe₂ powder and a dual source, CuInSe₂ and Se coevaporation process utilizing Electron Impact Emission Spectroscopy (EIES) to monitor and control the deposition process, were the principal methods studied. Flash evaporation is an attractive process for depositing compound semiconductors. It is a simple procedure having few process parameters to control. By keeping the source sufficiently hot, any tendency for the CuInSe₂ to decompose can be ameliorated. The deposition of p-type CuInSe₂ films using flash evaporation has been reported.⁵ The dual source deposition of CuInSe₂ for photovoltaic applications has been used to fabricate efficient devices. Utilizing EIES to monitor and control the deposition was expected to provide the process control required to turn it in to a reliable manufacturing process.

4.2 Dual Source Evaporation

Dual source, Se and CuInSe₂, coevaporation has been shown capable of fabricating CuInSe₂ films useful for devices.⁸ As envisioned the dual source system, see Figure 1, would consist of a CuInSe₂

Figure 1. EIES DUAL SOURCE SYSTEM

source and a Se source which would be controlled separately using an Electron Impact Emission Spectroscope to monitor the vapor stream. Cu rates would be observed to control the CuInSe₂ rate and the added Se would be controlled by observing the Se rate. Thus the added Se required to control the film electrical properties could be regulated and reproducible device quality films obtained. There have been a number of problems in implementing this system including the EIES monitor¹¹ and CuInSe₂ melt.

Our work has shown that such a scheme is not feasible. Figure 2 shows schematically the total deposition rate as determined by a crystal rate monitor and the Cu deposition rate as determined by the EIES monitor during the rf evaporation of a CuInSe₂ melt. The decomposition of the CuInSe₂ is clearly evidenced and nothing can be gained by controlling the CuInSe₂ source using Cu rate monitoring.

In order to characterize further the composition of evaporating CuInSe₂, sequential samples of the vapor stream have been taken. This was accomplished by depositing through a small aperture mask onto an unheated glass substrate and moving the substrate several times as the melt was depleted. Several such runs have been carried out and the deposits have been analyzed using x-ray fluorescence.

Figure 2. Deposition Rate and Cu Rate vs. Time

X-ray fluorescence spectra of one such CuInSe_2 deposition are shown in Figure 3. These photos confirm the EIES results that the Cu is deposited during the last part of the deposition and further show that the In comes off before the Cu with Se being a component throughout the deposition. Thus when evaporating a melt of CuInSe_2 one has In-Se compounds in the vapor stream during the initial phase of the deposition followed by Cu-Se compounds upon depletion of In in the melt. One would expect to see multiple phases in a layered structure in films deposited from such a system.

The Photovoltaic Program Office of SERI (PVPO) has profiled by means of Auger Electron Spectroscopy some of our films, which were deposited in the dual source system. The calculated atomic percentages for one of these samples are shown in Figure 4. These films are clearly layered in the order we would expect from the melt decomposition that has been seen.

If layered at all, films useful for devices must have controlled compositional gradations that are thermodynamically stable. We have begun to study the affect of annealing on film compositional gradations. A CuInSe_2 film was deposited onto quartz substrates at 200°C using the dual source system. The film was divided into several samples; as deposited, annealed for 1 hr. in 1000 ppm H_2Se in Ar. at 400°C , 500°C , and 600°C . X-ray diffraction data and x-ray fluorescence data were taken of these films. The

a) First Quarter Melt

b) Second Quarter Melt

c) Third Quarter Melt

d) Last Quarter Melt

Figure 3. X-ray Fluorescence CuInSe_2
 Sequential Vapor Samples

Figure 4. Auger Profile of Dual Source CuInSe_2 Film

diffraction data indicated the reduction of extraneous diffraction peaks with the higher temperature anneals. X-ray fluorescence of the as-deposited sample appeared In deficient while the annealed films appeared stoichiometric indicating that annealing may be effective in redistributing the Cu, In and Se in the deposited films.

Another approach to improving compositional uniformity in the dual source system was also studied. A variety of In-Se and Cu-Se compounds were synthesized and deposited onto cold glass substrates which were moved during deposition to give sequential time samples of the vapor stream. These samples were examined using x-ray fluorescence. The copper compounds CuSe_2 and CuSe evaporated Se first becoming more copper rich during the run and finally approaching the composition of Cu_2Se , which appeared to evaporate without decomposition. In_2Se_3 and InSe were the indium selenium compounds investigated. Their behavior on evaporation was more erratic than the copper selenium compounds with no clear trend for the In/Se ratio. However In_2Se_3 did show less variation in the In/Se ratio throughout the melt. Representative fluorescence data for Cu_2Se and In_2Se_3 are shown in Figure 5.

A number of films have been deposited in the dual source system using a Cu_2Se source and an In_2Se_3 source. P type single phased films have been obtained by this procedure but no devices

a) Early In_2Se_3 Melt

b) Late In_2Se_3 Melt

c) Early Cu_2Se Melt

d) Late Cu_2Se Melt

Figure 5. X-ray Fluorescence In_2Se_3 and Cu_2Se Vapor Samples

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have been made. Thus the suitability of these films for efficient devices and the ability to control film properties remain undemonstrated at this time.

4.3 Flash Evaporation System

In the flash evaporation system, small grains of CuInSe_2 powder are dropped from a hopper into a heated crucible. By continually evaporating the powder to completion, uniform stoichiometry during the deposition is promoted. We had found that single phased, stoichiometric CuInSe_2 films are readily deposited using flash evaporation.¹¹ However these films were probably small grained and had n type conductivity.

In an effort to establish deposition conditions to give p type films having repeatable electrical properties, a series of films were deposited at fixed substrate temperature of 200°C and a range of excess added Se from 0% to 60%. Because of mechanical problems with the powder feed mechanism and insufficient capacity to give thicker CuInSe_2 films for the higher percentages of added Se, the flash evaporated films were then deposited with the added Se in a second resistance heated crucible whose rate was monitored with a second quartz crystal monitor. No p-type films resulted from this series.

Two other series of CuInSe_2 films were flash evaporated. These involved either 5% or 10% excess Se deposited at substrate temperatures of 50°C to 600°C . Like the previous series, no reproducible conditions for obtaining p-type conductivity in the

films were found.

We have however been able to obtain p type films in the flash evaporation system using residue CuInSe_2 for the starting powder. The residue material is taken from deposits that build up on the system tooling around the flash evaporation crucible. Likewise we have found that by heating stoichiometric CuInSe_2 powder to approximately 600°C for 10 min. and then flash evaporating it, p-type films can be obtained. N type films resulted if no excess Se were used but such films could be converted to p type conductivity through a one hour anneal at 400°C in a 1000 ppm H_2Se in Ar atmosphere, unlike previous n type CuInSe_2 films using the stoichiometric powder. The baked or residue CuInSe_2 powder should be Cu rich from the loss of In-Se compounds during the baking process. Both sufficient Cu and Se content are required to obtain p type films.

4.4 Film Electrical Characterization

In order to further characterize the electrical properties of the dual source and the flash evaporated CuInSe_2 films, the resistivity and Hall voltages of a number of samples were measured as a function of temperature. Sample temperatures of 100°K to 330°K were obtained by mounting the samples in a copper enclosure which was cooled by passing liquid nitrogen through an attached coil or heated with a hot air gun.

Though single phased, stoichiometric, p type CuInSe_2 films can be obtained from either system the electrical characteristics of

Figure 6. Dual Source CuInSe_2 Film
Electrical Properties

Figure 7. Flash Evaporated CuInSe_2 Film Electrical Properties

of the films from each system are quite distinct. Figure 6 shows the resistivity and Hall data for a typical film deposited by coevaporation of CuInSe_2 and Se in the dual source system. Resistivities of $1 \rightarrow .001 \text{ } \Omega\text{-cm}$ are common with room temperature carrier concentrations sometimes as high as 10^{20} cm^{-3} . The carriers are seen to arise from a range of energy levels above the valence band. The mobility shows no evidence of grain boundary scattering. Figure 7 shows similar data for a typical n type flash evaporated CuInSe_2 film. Room temperature resistivities of 10^3 to $10^4 \text{ } \Omega\text{-cm}$ are common with Hall voltages either undetectable at room temperature or shortly below due to the low carrier mobility. Activation energies of .03 ev to .3 ev for the conductivity of these films are common.

4.5 Device Studies

In addition to investigating methods of fabrication CuInSe_2 films, our second area of effort was in fabricating large area devices. These devices, see Figure 8, are deposited on 1" by 3" glass slides. The central square inch has approximately 1μ of CuInSe_2 deposited onto a Au electrode along with a sample at one end. In a later deposition approximately 4μ of CdS are deposited onto the central square inch of each slide along with test samples at the remaining end. An In grid consisting of a central busbar and perpendicular fingers of $\frac{1}{4}$ mm width on 1 mm spacing is deposited through a mask.

A number of devices have been fabricated using dual source CuInSe_2 films and flash evaporated CuInSe_2 films. The efficiencies of these devices have been low. Figure 9 shows the IV curve in the dark and with 100 mw/cm^2 simulated sunlight for the best device. This device is six square centimeters and has a conversion efficiency of 1%. The short circuit current density of 12 ma/cm^2 is much improved over other devices on the program while the open circuit voltage of .3 volts and fill factor of 30% are poorer than has been seen. The CuInSe_2 was deposited in the flash evaporation system using prebaked CuInSe_2 powder and annealed at 400°C in 1000 ppm H_2Se in Ar to obtain p type conductivity.

This device was subjected to a series of annealing steps. Efficiency changes produced by such processes are indicative of

(a)

(b)

(c)

Figure 8. CuInSe_2 DEVICES AND ASSOCIATED FILM SAMPLES

Figure 9. Flash $\text{CuInSe}_2/\text{CdS}$ Device IV Curve

the mechanisms governing cell efficiency, and efficiency improvements have been reported by others¹² through annealing. The annealing steps consisted of 2 minute heat treatments at 200°C in a variety of atmospheres. An Argon gas atmosphere was used for the first annealing steps. Then a reducing atmosphere (forming gas - 15% H₂) was used while the final annealing steps were carried out in air. IV curves were run in simulated sunlight and the dark between each annealing step.

Independent of atmosphere, the annealing steps resulted in degradation of cell efficiency. The diode parameters (R_{S_1} - 3 ohms, R_{sh} - 500 ohms, nV_t - 75 mv, and I_o - .04 ma/cm²) were essentially unchanged through the course of the annealing. The annealing reduced the amount of hysteresis and improved the reverse breakdown voltage. The most dramatic effect was seen in the light generated current, $I_L(V)$ i.e. the difference between the dark and light IV curves. The annealing steadily reduced this curve in the fourth quadrant. In the third quadrant the $I_L(V)$ saturated at 19 ma/cm² independent of annealing. The annealing apparently did not affect the electron-hole pair production in the CuInSe₂ but does change the electric fields at the junction which lowers collection efficiency. The reduction of hysteresis can be due to annealing out of stress at the junction thereby eliminating trap states.

In an effort to assess cell spatial uniformity, a scan of cell short circuit current vs position was made. A 3 mw 6328 Å

He-Ne laser light focused to a spot was scanned over the cell at a spacing of 1 mm. A few of such scans are shown in Figure 10.

The 1 mm grid spacing is indicated there. The detail resolution is the order of 40μ. Averaging the short circuit current between grid lines and looking at a number of randomly selected scans across the cell area, a ± 10% standard deviation in short circuit current was seen.

Figure 10. J_{sc} vs Position, 6328 Å Illumination

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5.0 Summary

Two methods of fabricating CuInSe_2 films for large area CdS/ CuInSe_2 solar cells have been studied. Neither the flash evaporation of stoichiometric CuInSe_2 powder nor dual source, Se and CuInSe_2 , coevaporation has produced films which have demonstrated high efficiency devices. A number of factors relating to problems of making efficient devices have been identified.

Many of the methods applied to characterize the CuInSe_2 films have been discussed previously. In addition to these methods, principally x-ray diffraction and electrical characterization, characterization methods have been extended to include Hall voltage measurements for a range of temperatures. Device characterization including spatially-scanned response measurements were made.

Dual source coevaporation of Se and CuInSe_2 has been shown capable of producing single-phased, p-type films, with grain sizes approaching 1μ , however the control of the film electrical properties is difficult and the interpretation of some of the measured properties is uncertain. CuInSe_2 has been shown to decompose upon evaporation. In-Se compounds make up the initial stages of the vapor stream with Cu-Se compounds (ultimately Cu_2Se) dominant through the final stage of depletion of the melt. This leads to layered films whose properties are non uniform. Some preliminary work has been done on annealing the films to make the films uniform and on using a Cu_2Se and In_2Se_3 dual source system to deposit uniform stoichiometric films. Though single-phased films have been made by both of these techniques, neither

sufficient process control to obtain reproducible properties nor efficient devices have been demonstrated by these methods.

The CuInSe_2 films produced in the flash evaporation systems are generally single-phased, the decomposition problem having been circumvented. However obtaining p-type films only by the addition of Se to the vapor stream did not prove feasible. It was fortuitously discovered that by baking stoichiometric CuInSe_2 powder for 10 minutes at 600°C prior to flash evaporating it, p-type films could be obtained. These films are p-type when deposited if sufficient Se is added during deposition or can be annealed p-type in a H_2Se atmosphere at 400°C . Presumably sufficient Se and an excess of Cu are required to obtain p-type films. The highest efficiency of 1% was achieved with such a film.

Annealing of this 6 cm^2 area 1% efficient device degraded its efficiency. The annealing was carried out at 200°C in 2 minute steps. Inert, reducing, and oxidizing atmospheres made no difference. The diode parameters were essentially constant throughout the annealing, with a decrease in $I_L(V)$, the light generated current, in the 4th quadrant and reduction of hysteresis being the major effects caused by the annealing. A study of spatial uniformity of the devices indicated approximately a $\pm 10\%$ variation across the 6 cm^2 area.

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