MASTER

Cadmium Sulfide/Copper Ternary Heterojunction Cell Research

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Abstract

Third quarter activities on a CdS/CuInSe₂ cell research program are discussed. Two methods of fabricating the thin film CuInSe₂ are being investigated, dual source evaporation and flash evaporation of CuInSe₂ powder.

A variety of measurements on the dual source system indicates that layered films are being produced due to decomposition of the CuInSe₂ in the melt. Alternative Cu-Se and In-Se melts have been studied for use in the dual source system. ~~_____~~

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P type films or films which can be annealed p type have been obtained ~~from the flash~~ evaporation system using CuInSe₂ powder that was prebaked to 550°C in vacuum. Indications are that both sufficient Cu and Se are required for p type conductivity.

1.0 Introduction

In order to achieve the goal of developing 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 cm^2), 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 CuInSe_2 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.

Thin film CdS or $(\text{CdZn})\text{S}/\text{CuInSe}_2$ devices of 6 → 8% have been demonstrated by several groups.^{1,2} Analysis of device physics has indicated that 11% devices³ should be achievable using CuInSe_2 . Two major factors, depositing stoichiometric CuInSe_2 films of controlled electrical properties and obtaining low resistivity CdS films on the CuInSe_2 , have been identified as essential to obtaining such performance.

Several methods of depositing p type CuInSe_2 films are being investigated. Principally these methods are the flash evaporation of p-type (Se rich) CuInSe_2 powder and a dual source, CuInSe_2 and Se, coevaporation process. Flash evaporation is an attractive process for depositing compound semiconductors. By keeping the source sufficiently hot, any tendency for the

CuInSe₂ to dissociate can be ameliorated. It is a simple procedure having few process parameters to control. The deposition of p type CuInSe₂ films using flash evaporation has been reported. The dual source deposition of CuInSe₂ for photovoltaic applications is likewise a proven technique requiring further development to understand the processes involved and how to control them.

2.0 Progress

Originally, it was planned that the dual source system would consist of a CuInSe_2 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 CuInSe_2 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 monitor⁴ and the CuInSe_2 melt.

CuInSe_2 decomposes upon being evaporated. Comparison of crystal rate monitoring of the total deposition rate and Cu rates as obtained from the EIES monitor indicate that the Cu is deposited during the second half of the run. Several sequential time samples of CuInSe_2 melt vapor streams were obtained by depositing onto cold glass substrates that were moved several times during the deposition process. X-ray Fluorescence analysis of these samples has indicated that the vapor stream initially consists of In-Se compounds followed by Cu-Se compounds till depletion.

The Photovoltaic Program Office of SERI (PVPO) has had some of our films, which were deposited in the dual source system, profiled using Auger Electron Spectroscopy. The calculated atomic percentages for one of these samples are shown in Figure 1. These films are clearly layered in the order we would expect from the melt decomposition that has

been observed.

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 films 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 flourescence data were taken before delivery of the samples to PVPO for Auger profiling. The diffraction data indicated the reduction of extra diffraction peaks with the higher temperature anneals. X-ray flourescence 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. The Auger data will give more exact information on elemental profiles.

Another approach to improving compositional uniformity in the dual source system is being investigated. A variety of In-Se and Cu-Se compounds were synthesized and deposited unto cold glass substrates which were moved during deposition to give sequential time samples of the vapor stream. These samples were examined using x-ray flourescence. 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 evaporated 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

Figure 1. Auger profile of dual source CuInSe_2 film

Figure 1. Auger profile of dual source CuInSe_2 film

a) Early Cu_2Se melt

b) Late Cu_2Se melt

c) Early In_2Se_3 melt

d) Late In_2Se_3 melt

Figure 2. X-ray Fluorescence of Vapor Stream Samples

trend for the In/Se ratio. However, In₂Se₃ did show less variation in the In/Se ratio throughout the melt. Representative fluorescence data for Cu₂Se and In₂Se₃ are shown in Figure 2. Preliminary attempts to deposit CuInSe₂ films from a dual source Cu₂Se and In₂Se₃ system have been made. A single phased CuInSe₂ film has been deposited but repeatability and good electrical properties have not yet been demonstrated. This work will be continued next quarter.

The flash evaporation of CuInSe₂ (dropping small pieces of CuInSe₂ into a heated crucible until the desired thickness of CuInSe₂ is deposited) should reduce the problems of decomposition during evaporation. A range of substrate temperatures and added amounts of Se have been unsuccessful at controlling film electrical properties, principally carrier type. However we have found that p type films can regularly be deposited using residue CuInSe₂ (CuInSe₂ that has built up, through operation, around our flash evaporation source). The residue is presumably Cu rich. We have been duplicating this material by heating the CuInSe₂ powder as synthesised to 550°C for 5 min in vacuum. This material gives either p type films or films which can be rendered p type by annealing at 400°C for 1 hr. in 1000 ppm H₂Se in Ar. Both sufficient Cu and Se content are required to obtain p type films. A number of devices have been fabricated in the flash evaporation system using CuInSe₂ residue deposited from the residue type starting material. They are very inefficient having fill factors of $\frac{1}{4}$, open circuit voltages of 150 mv and short circuit current densities of 1 ma/cm². We will continue to

investigate ways of controlling the copper content of our films to obtain p type films and achieve more efficient devices.

The final area of investigation this past quarter was an attempt to obtain quantitative results from the x-ray fluorescence measurements. The Ziebold⁵ correction procedure allows determination of fluorescence and absorption corrections to x-ray line intensity measurements. However the electron beam current in a field emission tip SEM is too nonuniform to allow the x-ray intensity measurements. We tried normalizing the intensity measurements to the total counts received but consistent data on a variety of Cu, In, and Se binary alloys could not be obtained. Additionally the method would not work on layered films. No further effort will be made in this area.

3.0 Summary

The dual source system yields layered films which are essentially In-Se phases in the first deposited layers and Cu-Se phases in the last deposited layers. The non uniformity of these films makes determination of their properties difficult and of questionable value. Cu_2Se and In_2Se_3 have been identified as the best combination of binary compounds to co-evaporate to obtain uniform CuInSe_2 films. A study of the effect of annealing on film layering was begun.

The flash evaporation system giving films which either are p type or can be annealed p type in a 1000 ppm H_2Se in Ar atmosphere by heating to 400°C for 1 hr. The CuInSe_2 powder is prebaked to 550°C for a few minutes, presumably rendering the powder Cu rich. Sufficient Cu and Se content are apparently required to obtain p type films. Very inefficient devices have been made using these films.

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