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Low-Cost CdZnTe Devices for Cascade Cell Application

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PREFACE

This is the Final Technical Progress Report of a research program entitled "Low Cost Technique for Producing $Cd_{1-x}Zn_xTe$ Devices for Cascade Cell Application." The purpose of this project is to apply a two-stage process to the fabrication of $Cd_{1-x}Zn_xTe$ devices with a transparent contact and with a bandgap of around 1.7 eV. The proposed transparent contact is a low resistivity ZnTe layer.

The two-stage technique used in this project involves depositing thin films of the elemental components (i.e. Cd, Zn and Te) of $Cd_{1-x}Zn_xTe$ in the form of stacked layers, and then heating and reacting these layers to form the compound. We have used both electrodeposition and evaporation methods to prepare the metal stacks used in this program. During the first phase of the project we concentrated our efforts on the electrodeposition technique for the deposition of the elemental layers, and using this approach we successfully demonstrated the feasibility of the two-stage process for preparing $Cd_{1-x}Zn_xTe$ ($0 < x < 1$) thin films of various compositions. Extrinsic doping of these films with Cu was also achieved. The structural, optical and electrical characteristics of the films obtained by the two-stage process were determined. Transparent ZnTe films of low resistivity were obtained by a two-stage process for the first time. Preliminary solar cells using films with low Zn-content were demonstrated. Work during the second phase of the project concentrated on the films with higher Zn-content ($> 15\%$). These films were grown on CdS coated substrates for device fabrication. The effects of the solar cell processing steps on the $Cd_{1-x}Zn_xTe$ films and CdS/ $Cd_{1-x}Zn_xTe$ interfaces were studied. It was observed that the nature of the CdS/ $Cd_{1-x}Zn_xTe$ interface depended on the stoichiometry of the $Cd_{1-x}Zn_xTe$ film. A sharp interface was observed for CdS/CdTe structures. However, this interface got highly diffused as the Zn content in the absorber layer increased above 15%. The interaction between the window layer (CdS) and the absorber ($Cd_{1-x}Zn_xTe$) was found to result from an exchange reaction between Zn in the absorber layer and the thin CdS film.

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1.0 SUMMARY

1.1 Objective

This is the Final Technical Progress Report of a research effort entitled "Low Cost Technique for Producing $Cd_{1-x}Zn_xTe$ Devices for Cascade Cell Application." The research was supported by SERI under Contract XL-7-06074-2. The contract period was June 1, 1987 through May 15, 1990.

The objective of this research program is to demonstrate a $Cd_{1-x}Zn_xTe$ solar cell with a transparent ohmic contact. The proposed device structure is a TCO/ $Cd(Zn)S/Cd_{1-x}Zn_xTe/ZnTe/TCO$ configuration where the highly doped ZnTe film acts as an ohmic contact to both the $Cd_{1-x}Zn_xTe$ layer and the transparent conductive oxide (TCO) film. The targeted stoichiometry of the $Cd_{1-x}Zn_xTe$ film is $x = 0.25-0.4$ which is expected to give a bandgap value of 1.65-1.75 eV. This device, once developed, can be the top cell in a high efficiency tandem structure where the bottom cell may be a device with around 1 eV bandgap.

1.2 Discussion

A two-stage process has been developed during this research program for depositing $Cd_{1-x}Zn_xTe$ films of various stoichiometries including $x=1$. This process involves the deposition of the elemental components of a compound in the form of stacked layers, followed by the reaction of these stacked layers to form the desired compound.

In the case of $Cd_{1-x}Zn_xTe$, the elemental components are Cd, Zn and Te. Low-cost electrodeposition techniques have been used in the first phase of this research program for depositing the elemental components in the form of thin layers. The second phase concentrated more on the devices and the evaporation technique.

Important variables to be controlled during the deposition of the elemental layers in a two-stage process are the morphology, thickness and the thickness uniformity of the deposited films. For the case of evaporation approach, the control of the morphology of the films does not present any difficulty. For the electrodeposition technique, however, special plating baths containing additives (brighteners, surfactants, leveling agents) are necessary to obtain small-grained smooth deposits.

Reaction of the stacked elemental films was achieved by heating these layers in tube furnaces at temperatures ranging from 350 °C to 600 °C for times ranging from 30 minutes to 2 hours. Doping experiments were performed by including a p-type dopant such as Cu in the elemental layers before their reaction.

Doped ZnTe films with 0.1-0.5 ohm-cm resistivity and good optical transmission were thus obtained. Preliminary solar cells with Glass/CdS/Cd_{1-x}Zn_xTe (0<x<0.1)/Ni structure gave efficiency values of around 4%.

1.3 Conclusions

We have successfully demonstrated the use of the two-stage process for obtaining Cd_{1-x}Zn_xTe films of various stoichiometries on relatively inert substrates. We have developed plating electrolytes and plating conditions for depositing thin Te, Cd and Zn layers of proper morphology. These elemental layers and layers prepared by the evaporation technique have successfully been reacted to obtain Cd_{1-x}Zn_xTe films.

We have used the two-stage process to deposit highly transparent ZnTe films, and we have demonstrated effective extrinsic doping for such films. ZnTe layers with resistivities in the 0.1-0.5 ohm-cm range and optical transmission with over 65 % have been obtained by this technique. These layers can be used as buffer contact films in CdTe devices.

Cd_{1-x}Zn_xTe films have been grown on CdS coated substrates for device fabrication. CdS/Cd_{1-x}Zn_xTe heterojunction solar cells with around 4% efficiency have been fabricated using films with Zn concentrations of up to 10%. Films grown on CdS coated substrates showed quite different properties compared to those grown on inert substrates. It was observed that the nature of the CdS/Cd_{1-x}Zn_xTe interface was strongly dependent on the Cd_{1-x}Zn_xTe film stoichiometry. This interface was sharp for films containing small amounts of Zn, whereas, it became highly diffused for films with x>0.15. This was shown to be due to an exchange reaction between the CdS window layer and Zn which is a strong reducing agent.

2.0 INTRODUCTION

$Cd_{1-x}Zn_xTe$ is a variable bandgap II-VI compound semiconductor with possible application to thin film solar cells. The bandgap of this material can be tuned from 1.45 eV to 2.25 eV by controlling its stoichiometry. A $Cd_{1-x}Zn_xTe$ alloy cell with 1.65-1.75 eV bandgap is especially attractive as a top device in a high efficiency tandem solar cell structure. The bottom cell for such a device may be a CdS/CuInSe₂ solar cell or a Hg_yCd_{1-y}Te cell with around 1-1.1 eV bandgap.

The contact to the $Cd_{1-x}Zn_xTe$ top device in a tandem structure has to be transparent to sub-bandgap radiation. A highly conductive and transparent ZnTe thin film coupled with a transparent conductive oxide (TCO) is an ideal contact for such a device.

$Cd_{1-x}Zn_xTe$ films have most commonly been prepared by the vacuum evaporation technique [1,2]. The source material used in the evaporation method is typically the compound itself. Vacuum evaporated and doped ZnTe films with low resistivity have also been reported in the literature [3,4]. These films were obtained by co-evaporating the ZnTe source material and the dopants (Cu or Sb) onto heated substrates. The stoichiometry and the optical transmission of the evaporated ZnTe films are highly dependent on the substrate temperature and the evaporation rate. Therefore, it is essential that these variables be closely controlled during deposition. Direct combination of Cd, Zn and Te vapors in a hydrogen or helium atmosphere has also been used to prepare $Cd_{1-x}Zn_xTe$ films of various compositions [5]. Recently, MBE technique was successfully applied to the preparation of $Cd_{1-x}Zn_xTe$ films and devices were demonstrated using these layers [6].

The two-stage process is a relatively new technique which has been successfully employed for the preparation of semi-conducting films. In this method the individual elements of a compound are deposited in the form of stacked layers. They are then reacted to form the desired material. One of the elements of the compound may also be introduced from the vapor phase. This is the case for CuInSe₂ which is formed by reacting Cu/In stacked layers in an annealing atmosphere containing H₂Se.

In the two-stage process the individual elements of the compound can be deposited by various techniques such as electrodeposition, vacuum evaporation or sputtering. The stoichiometry of the compound is primarily determined by the relative thicknesses of the elemental layers in the stack. Therefore, it is essential that these thicknesses are well controlled during the deposition step. Thickness control for the electrodeposited films can be achieved by experimentally determining the plating efficiencies of each element and then by monitoring and controlling the total charge passed through the circuit during plating. Conventional methods can be used for thickness monitoring for the

evaporated or sputtered layers. Reaction of the elemental layers in a two-stage process is generally achieved by heating these layers in a controlled atmosphere in a furnace. In this report we present our results on the preparation of $Cd_{1-x}Zn_xTe$ thin films and devices by a two-stage process utilizing electrodeposition or evaporation [7,8,9,10]. The ultimate aim of the project is to obtain a wide-bandgap $Cd_{1-x}Zn_xTe$ solar cell with a transparent contact, to be used as the top device in a tandem structure.

3.0 TECHNICAL DISCUSSION

3.1 Deposition of the Elemental Layers

The first important step of the present process is to deposit thin films of Te, Cd and Zn, in the form of stacked layers, on a substrate. Our work during the first phase of this project has focused on the electrodeposition technique as the method of deposition for these elemental layers. Vacuum evaporation was used during the second phase of the program.

Four types of substrates were used in this work. Highly conductive glass/Mo substrates were employed in the early deposition studies for the ZnTe films [7]. Glass/Mo substrate was then replaced by the glass/TCO structure to be able to evaluate the ZnTe/TCO contact quality and to be able to make optical transmission measurements. Glass/TCO/CdS substrates were used in the fabrication of CdS/Cd_{1-x}Zn_xTe heterojunction devices. Glass substrates were utilized for preparing films for in-plane resistivity measurements. Both ITO and SnO₂ were used as the TCO layers. CdS films were either evaporated (1-2 microns) or chemically deposited (0.1-0.2 microns).

There are three important variables to be controlled during the deposition of Te, Cd and Zn layers:

- i) thickness
- ii) thickness uniformity
- iii) morphology

The first variable determines the compound stoichiometry. Thickness uniformity determines the uniformity of the stoichiometry in a given film sample. The morphologies of the elemental layers affect the micro-scale stoichiometric uniformity and also the morphology of the compound film as will be described below.

In the electrodeposition technique, the total charge passed through the plating circuit during the deposition step gives a good measure of the amount of material deposited. Once the plating efficiencies of individual elements are experimentally determined, then the average thicknesses of the corresponding elemental layers can be directly controlled by controlling the plating current and the plating time. Thickness uniformity was adequate in the electrodeposition technique for the 1.5 cm x 1.5 cm substrates we typically worked with. We have designed a special plating fixture for this purpose where the I-R drops were minimized by making electrical contact all around the plated area on the conductive substrate.

Morphologies of the electroplated elemental films are extremely important in the two-stage process. Smooth and continuous elemental films are necessary to obtain smooth and continuous

compound films after the reaction step. If, for example, Cd or Zn films deposited over Te layers were discontinuous, then the areas of the sample with exposed Te would evaporate during the annealing process due to the high vapor pressure of elemental Te, and the resulting film would also be discontinuous. Even if the coverage of the Te film by the Cd and/or Zn layers were good, but the morphology of these layers were very rough, one would get stoichiometric differences, on the micro scale, in the compound film after the reaction step. For the electroplated films it is essential to use electrolytes and electrodeposition parameters that yield smooth, continuous and uniform films. The details of our work on the development of electroplated elemental layers for the two-stage process have been published previously and they will not be repeated here [8,9,10,11]. Only a summary will be presented below.

Tellurium electrodeposition was carried out using an acidic aqueous solution containing HTeO_2^+ (TeO_2 powder dissolved into 1M H_2SO_4 solution). The anode consisted of a Te block. Morphology of the Te film was found to be a strong function of the plating current density. Best results were obtained at low current densities ($0.5\text{-}3 \text{ mA/cm}^2$).

Cadmium films were electrodeposited using acidic CdSO_4 electrolytes without any stirring or circulation. Plating was carried out at room temperature and a Cd plate was used as the anode. To break the dendritic growth and to obtain small grained smooth deposits, additives had to be employed in the Cd plating electrolytes. Plating current densities were typically 20 mA/cm^2 .

Morphology is of prime concern in electroplated Zn layers. Just like Cd, Zn tends to grow in dendrites when electroplated out of simple acidic electrolytes. Therefore, brighteners and levelling agents have to be included in the formulation of the plating solution to obtain smooth and shiny deposits.

Evaporation of Te, Cd and Zn layers was carried out at a pressure of about 4×10^{-5} torr. All of the elemental source materials were 4 N's pure and the substrates were not intentionally heated during evaporations. Morphologies of the evaporated layers were smooth and their thicknesses were monitored using a crystal oscillator.

3.2 Reaction of the Elemental Layers

Reaction of the elemental stacked layers to form the compounds was carried out in a tube furnace in Ar, or N_2 atmosphere. Reaction times ranged from 30 minutes to 2 hours. Reaction temperatures varied from 350°C to 600°C . At the end of the reaction period, the tube was cooled down to room temperature and the samples were removed for analysis. Since in-plane resistivity measurements were not possible for films on conducting

substrates, a set of samples were also prepared by vacuum evaporating Cd, Zn and Te layers onto glass substrates. These films were similarly reacted in a tube furnace. Cu doping experiments involved inclusion of the dopant atoms in the elemental stacked layers before the reaction step. The relationships between the thicknesses of the elemental layers and the resulting compound films after the reaction step are as follows:

- a) A 100 Å thick Cd layer reacting with a 157 Å thick Te film is expected to yield a 298 Å thick layer of CdTe.
- b) A 100 Å thick Zn layer reacting with a 223 Å thick Te film is expected to yield a 331 Å thick layer of ZnTe.
- c) In a $Cd_{1-x}Zn_xTe$ alloy film the composition parameter, x , is related to the individual thicknesses of the CdTe (t_{CdTe}) and the ZnTe (t_{ZnTe}) components of the film by the equation,

$$t_{CdTe}/t_{ZnTe} = 1.27 (1-x)^{-1}x$$

where t_{CdTe} and t_{ZnTe} can be calculated using the relationships given in a) and b).

3.3 Measurements on Reacted Films and Solar Cells

3.3.1 Films grown on glass or ITO/glass substrates

X-ray diffraction data taken from a series of films with varying compositions is given in Fig. 1. The substrates for these films were ITO coated glass, and the reacted film thicknesses were in the range of 1 micron. The reaction temperature and time used in processing these films were 550°C and 1 hour, respectively. The data in Fig. 1 clearly demonstrates the compositional change in the $Cd_{1-x}Zn_xTe$ alloy films. The position and the intensity of the diffraction peaks at $2\theta = 21.45, 30.5, 35.4, 37.7, 51$ and 60.6 degrees are similar for all the samples. These peaks are associated with the ITO substrate. The remaining major peaks are all associated with cubic $Cd_{1-x}Zn_xTe$. As expected, these peak positions shift in the direction of smaller diffraction angles as the film stoichiometry becomes more and more Cd-rich. Also, again as expected, the 200 peak ($2\theta = 29.3$), which is prominent in the ZnTe film, gets diffused as the stoichiometry approaches CdTe. The 400 peak, which can be observed in the CdTe sample, overlaps with the ITO diffraction peak in the Zn-rich compositions, and thus it can not be resolved in those samples. The "a" values for the measured films were graphically determined and the film compositions were estimated as shown in Fig. 1. The "a" values for the ZnTe and CdTe films agree very well with the values given in the ASTM cards (6.1026 Å for ZnTe and 6.481 Å for CdTe).

A low-resistivity ZnTe film is needed as the contact material to the $Cd_{1-x}Zn_xTe$ device in a cascade structure. There-

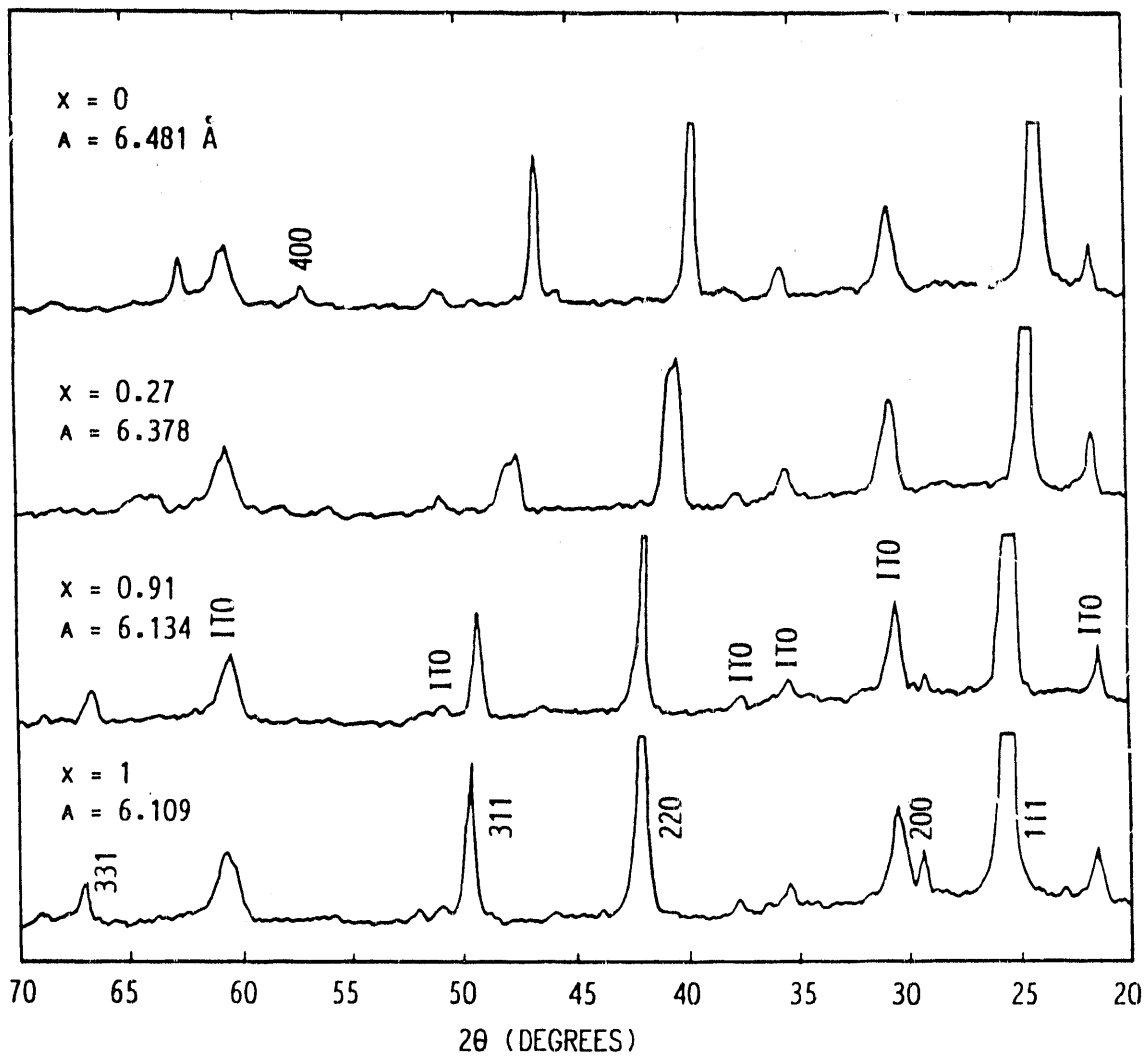


Fig. 1. X-ray diffraction data obtained from $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ films of various stoichiometries.

fore, we carried out Cu doping experiments and demonstrated the feasibility of doping in the two-stage process. The resistivities of Zn-rich films were found to be generally lower than that of Cd-rich compositions. Undoped film resistivities changed from 3000 ohm-cm to over 10^5 ohm-cm going from ZnTe to CdTe. Corresponding resistivities for the doped layers changed from 0.6 ohm-cm to higher than 10^5 ohm-cm. This result is in accordance with the general experience that it is more difficult to obtain low-resistivity p-type CdTe polycrystalline thin films than to obtain low resistivity p-type ZnTe films. For the undoped samples this is due to the fact that the native acceptors in ZnTe (i.e. Zn vacancies) occupy shallower states than the Cd-vacancies in CdTe. For the doped samples the ionization energy for the Cu-acceptor level is lower in ZnTe than in CdTe.

In cascade cell applications, the optical transmission of ZnTe film is as important as its resistivity. As a contact layer, ZnTe must be highly transparent to sub-bandgap light so that a large portion of this radiation can reach the bottom cell. Optical transmission and reflection of the ZnTe films were measured using a double beam spectrophotometer. Evaporated samples were always found to be more specular than the films obtained by the electroplating technique. This is due to the fact that evaporated elemental layers have smoother morphologies compared to the electroplated ones. Fig. 2 shows the optical transmission data taken from a ZnTe film (curve A) and a $\text{Cd}_{0.25}\text{Zn}_{0.75}\text{Te}$ (curve B) layer. The average transmission value for the ZnTe film is over 65%. The band edge is sharp and it is at 0.55 microns. The bandgap values extrapolated from α^2 versus energy data for the films A and B of Fig. 2 are 2.25 and 2.04 eV respectively. These band gap values are in good agreement with the given stoichiometries of these films.

3.3.2. Films grown on CdS coated substrates, and solar cells

As presented in the previous sections of this report, $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ films of various compositions have been successfully deposited by the two-stage method on glass and ITO coated glass substrates. However, these films need to be grown on CdS coated surfaces for solar cell application. The device processing steps include; the deposition of Te, Cd and Zn layers over CdS/ITO/glass substrates, the reaction of these layers to form $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$, annealing of the whole structure in air at around 400 C and the completion of the devices by evaporating gold contacts after a mild Br-methanol etch. In this section we will discuss the effects of such solar cell processing procedures on the properties of $\text{Cd}_{1-x}\text{Zn}_x\text{Te}$ films deposited by the two-stage technique.

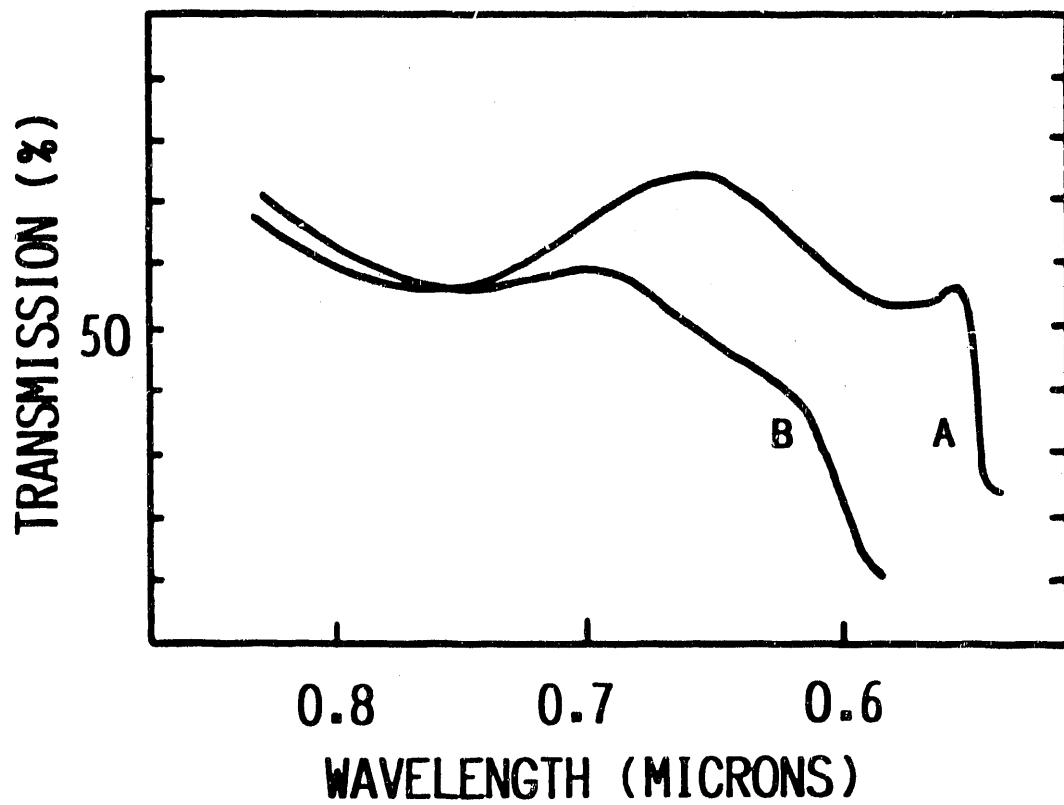


Fig. 2. Optical transmission of a ZnTe (curve A) and a Cd_{0.25}Zn_{0.75}Te film (curve B) obtained by the two-stage process.

CdTe Films

CdTe films obtained by reacting evaporated Cd and Te layers were shiny, adherent and compact on both ITO/glass and CdS/ITO/glass substrates. Figure 3 is a cross-sectional SEM of a CdTe/CdS/ITO/glass structure showing a dense 2.0 μm thick CdTe film grown by the two-stage process. This film was obtained reacting the Te and Cd films at 400°C for 30 minutes. The grain structure of this film can not be readily seen in this micrograph. However, the surface features suggest a grain size of $< 1 \mu\text{m}$ for this film. Auger depth profile of a 0.8 μm thick CdTe film grown on a CdS/ITO/glass substrate at 500°C is shown in Fig. 4. It is observed that the distribution of Cd and Te through this film is quite uniform except for the oxidized surface region which is estimated to be less than 500 Å thick. The CdTe/CdS interface is clearly marked by a sharp sulfur peak in Fig. 4. We have found that the CdTe/CdS interface was relatively sharp for the whole range of reaction temperatures (350-600) employed in this work. This is due to the fact that the Te film deposited directly over the CdS layer does not react with CdS. The reaction of elemental layers of Te and Cd, on the other hand, does get initiated for temperatures higher than 350°C.

CdTe Devices

Solar cells were fabricated by evaporating gold contacts over CdTe films grown on CdS/ITO/glass substrates. Devices made on as-deposited films yielded low current density values (1.0-2.0 mA/cm²) and low open circuit voltages (0.3-0.4 V). Spectral response measurements made on these cells revealed that they were Au/CdTe Schottky barriers rather than the intended CdTe/CdS heterojunctions. Curve A in Fig. 5 shows the spectral response data taken through the glass substrate of such a device. It is clear from the high long-wavelength response that the carrier collection in this cell takes place at the Au/CdTe interface.

This finding is similar to the results previously reported on electrodeposited CdTe solar cells. In the electrodeposited CdTe device fabrication process, a "type-conversion, junction-formation" step was developed [12,13,14] that involved heat treatment of the as-deposited n-type CdTe films at around 400°C in air. This annealing step was shown to convert the n-CdTe films into high resistivity p-type material, and thus allow fabrication of high efficiency CdTe/CdS solar cells.

We have applied the same approach to the CdTe films of the present work. Curve B of Fig. 5 shows the spectral response data for a Au/CdTe/CdS device fabricated on a CdTe film which was annealed in air for 15 minutes at 400°C. It is observed that, as a result of the annealing step, the rectifying junction of the device has moved from the Au/CdTe interface to the CdTe/CdS interface. The short circuit current density and the open circuit voltage values of the device have also improved. By using

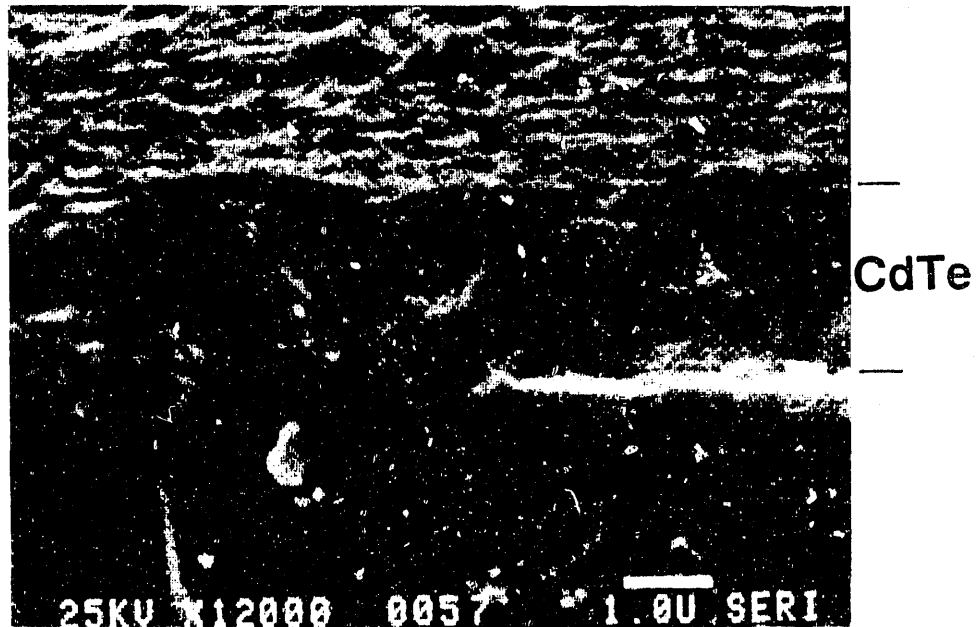


Fig. 3. Cross-sectional SEM of a CdTe film grown on a glass/ITO/CdS substrate by the two-stage process.

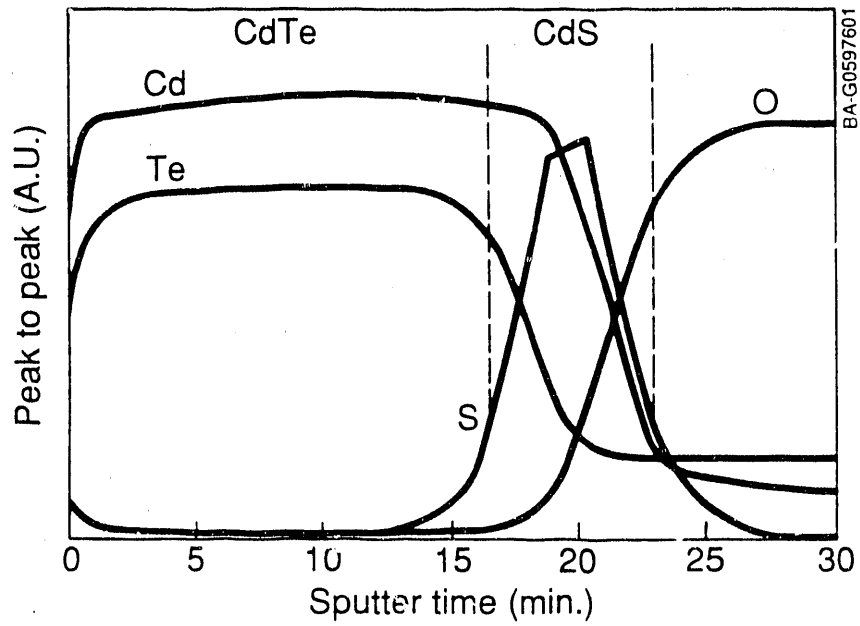


Fig. 4. Auger depth profile of a CdTe/CdS/ITO/glass structure.

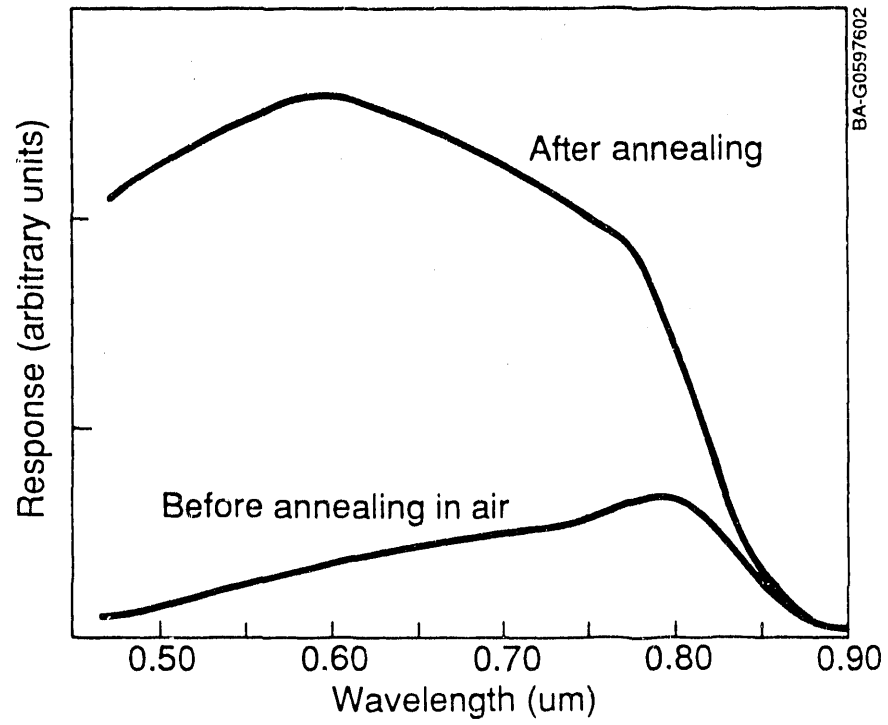


Fig. 5. Spectral response of a Au/CdTe/CdS/ITO/glass structure before heat treatment (A) and after annealing at 400 °C in air (B).

this approach and optimizing the heat treatment step, we fabricated cells with J_{sc} and V_{oc} values as high as 15 mA/cm² and 0.65 V respectively.

Fabrication steps for the CdTe/CdS devices could not be successfully applied to the Cd_{1-x}Zn_xTe cells. Presence of a strong reducing agent, Zn, in the Cd_{1-x}Zn_xTe films changed the nature of the Cd_{1-x}Zn_xTe/CdS interface and also caused compositional non-uniformities in the annealed films. We will discuss these topics in the following section.

Cd_{1-x}Zn_xTe Films

Compositional uniformity: Figure 6 is an Auger depth profile taken from a Cd_{1-x}Zn_xTe film grown on an ITO coated glass substrate. The intended composition for this film was $x=0.2$ and it was reacted in nitrogen gas at 400 °C under static conditions. The striking feature of the Auger profile of Fig. 6 is the highly non-uniform distribution of Zn through the film. Specifically, it is observed that a high concentration of Zn is localized near the surface of the Cd_{1-x}Zn_xTe layer, most likely in the form of an oxide. The oxygen signal which was limited to a thin surface region on the CdTe film of Fig. 4, extends as deep as 2000 Å into the Cd_{1-x}Zn_xTe layer of Fig. 6. Furthermore, a Zn peak is observed at the Cd_{1-x}Zn_xTe/ITO interface.

Non-uniform Zn distribution in air-annealed Cd_{1-x}Zn_xTe films has been recently observed in layers deposited by the MBE technique [6]. The optical bandgap values of such layers were found to decrease as a result of a heat treatment at around 400 °C, further demonstrating the loss of Zn from the bulk of the film. Observation of the same phenomenon in our Cd_{1-x}Zn_xTe films suggest that the residual oxygen in the annealing furnace as well as on the elemental layers was high enough to cause formation of ZnO in a thick surface layer. It should be noted that the use of a reducing atmosphere in the annealing furnace decreases the thickness of the surface ZnO layer. However, the diffusion of Zn and the formation of ZnO at the surface commence once these films are heat treated in air for solar cell fabrication. Zn pile-up at the Cd_{1-x}Zn_xTe/ITO interface is a result of the reaction between Zn and the ITO surface at 400 °C.

Cd_{1-x}Zn_xTe/CdS interface: Unlike the relatively sharp CdTe/CdS interface, the nature of the Cd_{1-x}Zn_xTe/CdS interface was found to depend on the composition, x . Higher values of x promoted more intermixing between the Cd_{1-x}Zn_xTe and the CdS layers during the reaction step. Fig. 7 is an Auger depth profile of a Cd_{1-x}Zn_xTe/CdS/ITO structure that was heat treated in air at 400 °C after the reaction step which was carried out in nitrogen at 500 °C. The intended x value for this Cd_{1-x}Zn_xTe film was 0.3. The following observations can be made from the Auger data of Fig. 7.

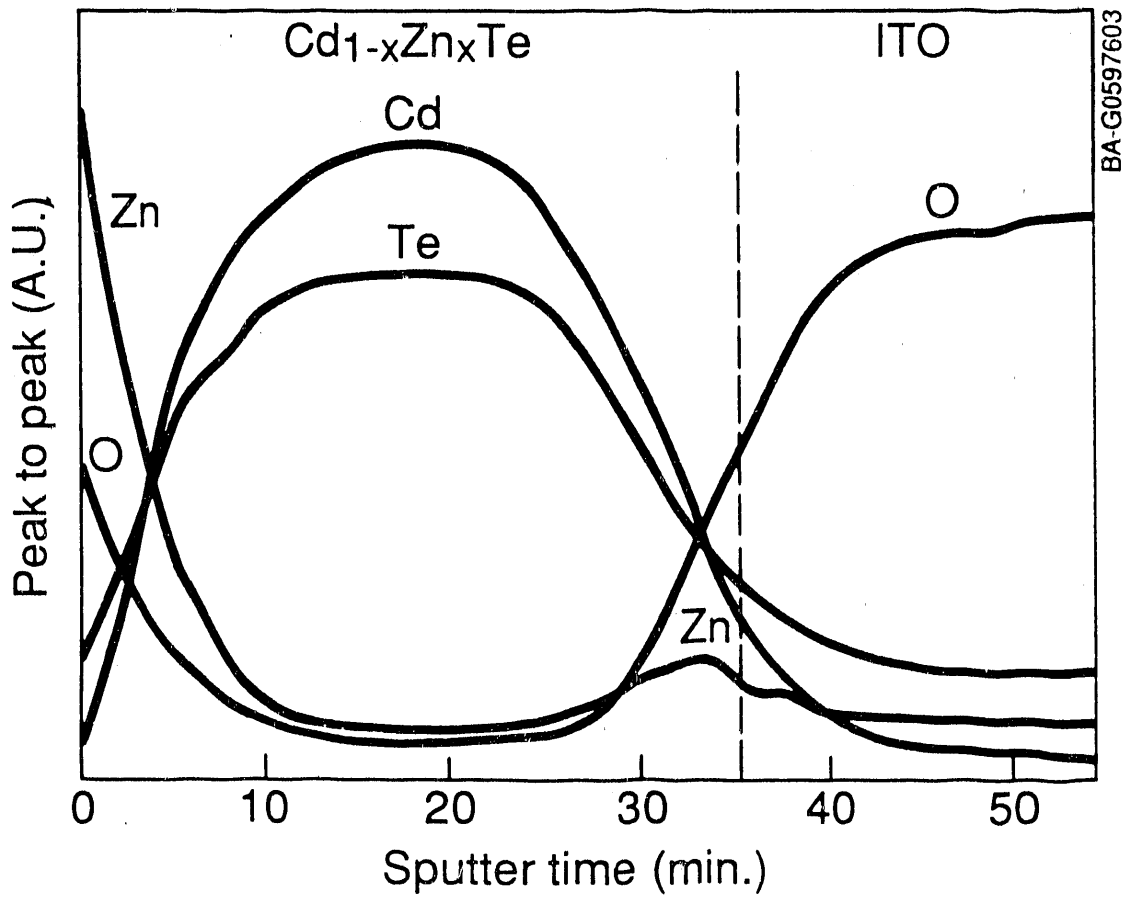
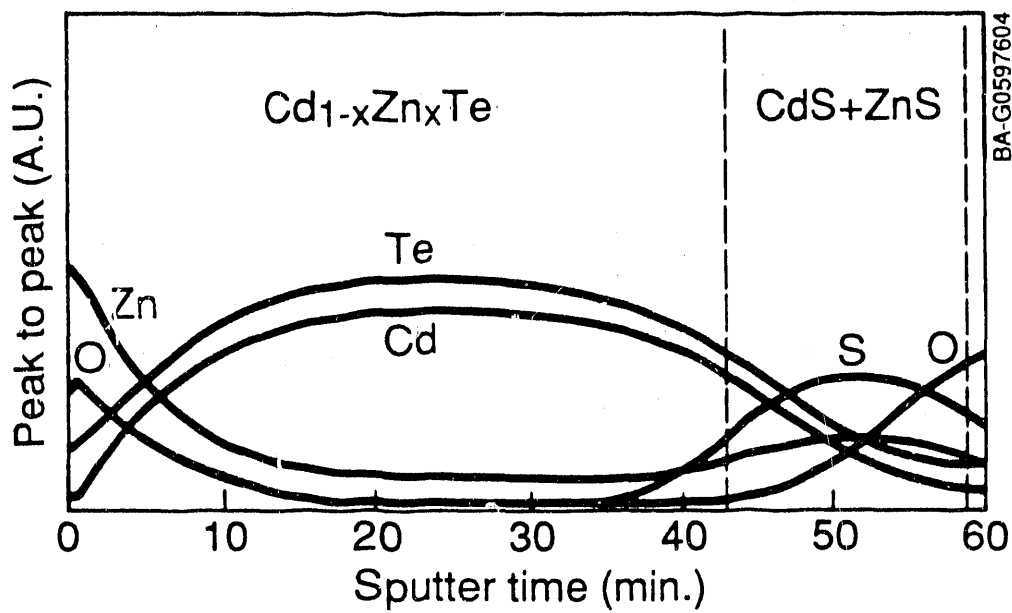


Fig. 6. Auger depth profile taken from a Cd_{1-x}Zn_xTe film grown on a ITO/glass substrate.



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Fig. 7. Auger depth profile of a Cd_{1-x}Zn_xTe/CdS/ITO/glass substrate. Intended composition, x, was 0.3.

a) Zn distribution through the film is non-uniform. A high concentration of Zn is observed within the top 2000 Å thick surface layer.

b) The $Cd_{1-x}Zn_xTe/CdS$ interface is highly diffused compared to the $CdTe/CdS$ interface of Fig. 4. A Zn peak is also observed near the ITO contact.

The diffused $Cd_{1-x}Zn_xTe/CdS$ interface and the Zn pile-up near the ITO surface are due to the exchange reaction between the CdS film and Zn. Zn, being a strong reducing agent, replaces Cd in the CdS layer at the elevated growth temperatures. As a result of this reaction the sharp interface observed between the CdTe layer and the CdS film of a CdTe/CdS structure is lost in a $Cd_{1-x}Zn_xTe/CdS$ junction.

We have carried out an experiment to further understand this reaction between Zn and the CdS. In this experiment a sample was prepared on a CdS/ITO/glass substrate where Te, and Zn layers were deposited through a shadow mask so that three distinct regions were obtained on the substrate (Fig. 8). Region 1 consisted of a Te film over the CdS/ITO layer, region 2 had only the Zn layer and region 3 had both the Te and Zn films. After the reaction step the Te film in region 1 had totally evaporated without reacting with the CdS/ITO film. Region 2 had a transparent layer, an Auger profile of which is given in Fig. 9. It is observed that the Zn layer in this region, instead of evaporating away, has reacted with the CdS/ITO substrate. Existence of Zn, O and S peaks suggest the formation of both ZnS and ZnO. In region 3, a film with a bandgap value smaller than that of ZnTe was obtained. This suggests that Cd from the CdS layer has moved into the ZnTe film and Zn has reacted with S giving rise to an intermixed layer.

Cd_{1-x}Zn_xTe Devices

Efficient $Cd_{1-x}Zn_xTe/CdS$ solar cells could not be fabricated using films with $x > 0.25$. The main reason for this was the reaction of Zn with CdS giving rise to a highly diffused $Cd_{1-x}Zn_xTe/CdS$ interface and poor morphology. Devices made on films with $x < 0.2$ yielded efficiency values of 3-4% (Fig. 10). However, the stoichiometry of these films are expected to be graded, i.e. the contact side more Zn-rich compared to the CdS side.

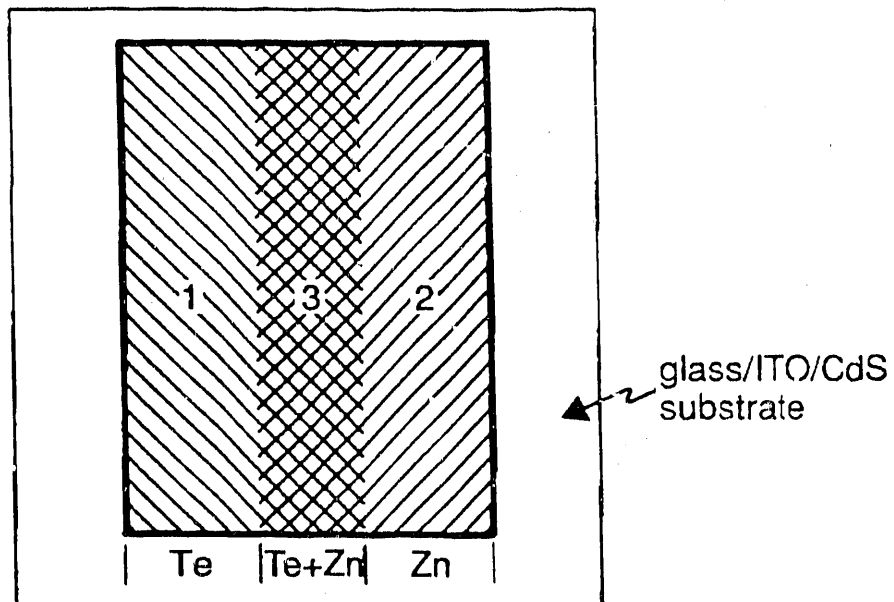


Fig. 8. The sample prepared for studying Zn/CdS reaction.

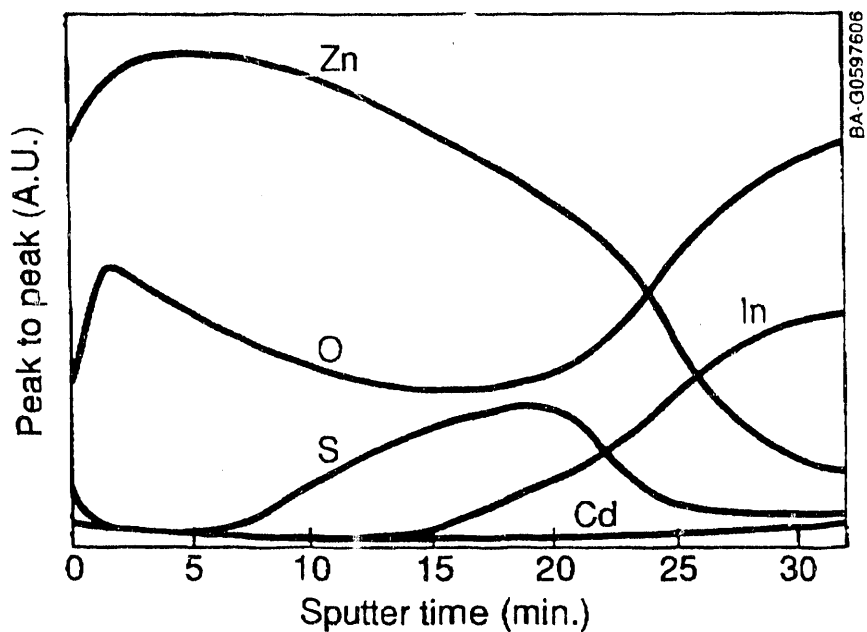


Fig. 9. Auger depth profile taken from region 2 of the sample of Fig. 8 after the reaction.

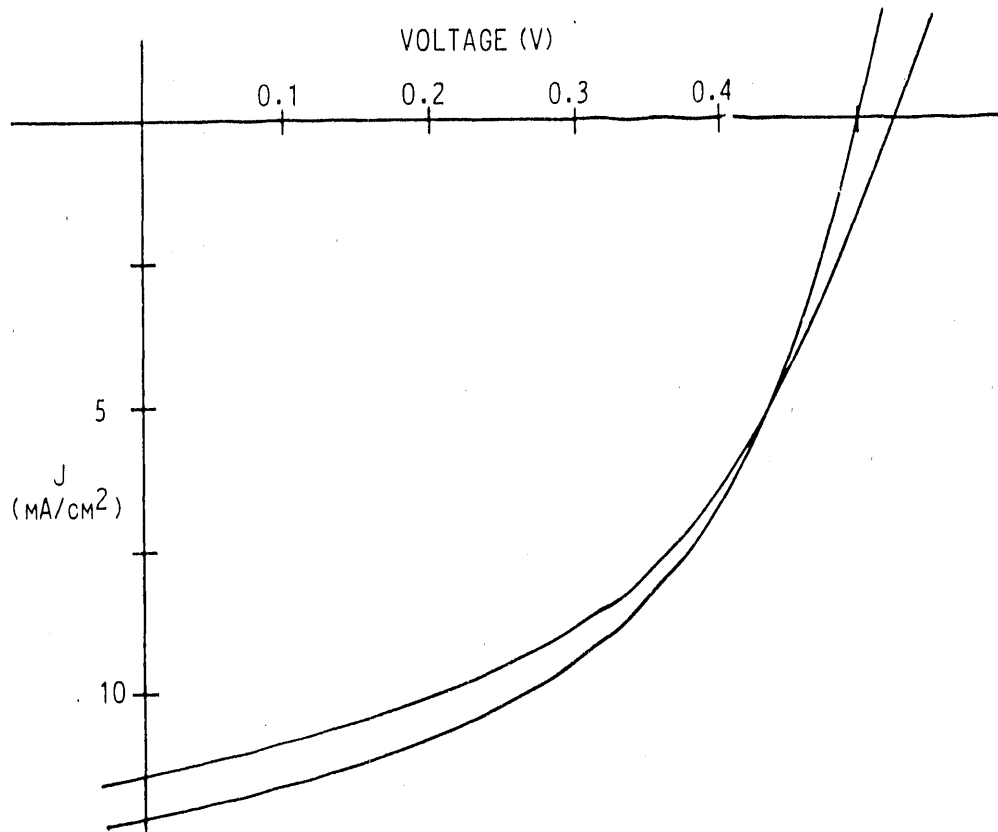


Fig. 10. Illuminated I-V characteristics of two $\text{Cd}_{0.9}\text{Zn}_{0.1}\text{Te}$ devices made by the two-stage process (100 mW/cm^2 ELH illumination).

4.0 CONCLUSIONS

In conclusion, we have demonstrated the successful use of the two-stage process for the preparation of $Cd_{1-x}Zn_xTe$ alloy films of all stoichiometries on inert substrates. We have demonstrated efficient doping of these films and good stoichiometric control. We have also demonstrated that cost effective electrodeposition steps can be used in the two-stage process to prepare alloy films once the chemistry of the plating solutions are optimized for depositing films with good morphology. We have prepared the first highly transparent and conducting ZnTe films by the two-stage process. Deposition of ZnTe films by the technique developed in this program is more attractive than the previously used evaporation methods which require substrate heating and deposition rate control during evaporation. The ZnTe films prepared by the two-stage process can be used as contact layers to high efficiency CdTe solar cells.

Use of $Cd_{1-x}Zn_xTe$ films for top cell application in a tandem device structure requires two key processing steps.

The first step is the deposition of a $Cd_{1-x}Zn_xTe$ film over a CdS coated transparent substrate. The CdS layer in such a structure needs to be thin ($<1000 \text{ \AA}$) to maximize the J_{sc} values. In this program we have discovered that thin CdS films, get reduced by Zn, a strong reducing agent, during the high temperature growth process. As a result, the CdS/ $Cd_{1-x}Zn_xTe$ interface gets diffused and the solar cell parameters deteriorate. This problem may be somewhat alleviated by replacing the thin CdS window layer of the present device structure with a thicker and more transparent CdZnS film.

In this project we have also discovered that an essential step in the fabrication process for a $Cd_{1-x}Zn_xTe/CdS$ device by the two-stage technique is the "type-conversion, junction-formation" step which involves heat treating this structure in an oxygen containing atmosphere at around 400°C . High reactivity of Zn with oxygen, however, causes this element to diffuse to the surface of the film during the annealing step and, therefore, the composition of the absorber layer changes. This problem may be overcome by including excess Zn into the film and etching away the Zn-rich surface before contact deposition or by developing techniques that yield solar cell grade as-deposited $Cd_{1-x}Zn_xTe$ films.

In conclusion, we can state that the two-stage process has proven to be successful for the deposition of $Cd_{1-x}Zn_xTe$ films. Specific requirements of device processing (such as deposition of films over thin CdS layers and the annealing step in air), however, present some challenges that need to be further addressed, especially for films with high Zn content.

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