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CdSiAs₂ THIN FILMS FOR SOLAR
CELL APPLICATIONS

REPORT NO. DOE/ET/23007-3

THIRD QUARTER REPORT: 10/1/79 - 12/31/79

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ABSTRACT

Sputtering studies (single composite target; $\text{CdAs}_2 + \text{Si}$) of CdSiAs_2 films have continued. An improved substrate has been developed (Ta film on 7059 glass) for post-deposition heat treatments, although films still have mechanical defects. High resistivity ($\rho > 10^6 \Omega \text{ cm}$) polycrystalline p-type films with optical cutoff at 1.53 eV and absorption coefficient of $\sim 2 \times 10^4 \text{ cm}^{-1}$ at $0.6 \mu\text{m}$ have been obtained.

CdS/CdSiAs_2 and In/CdSiAs_2 junctions have been formed on heat treated CdSiAs_2 films. Both junction types exhibit rectifying behavior, although with little photovoltaic response. Poor yield and unstable characteristics are attributed to mechanical defects in the CdSiAs_2 films.

The new multi-target sputtering unit is now installed and operating. It is planned to begin the transfer of the sputtering studies over to this unit during the next reporting period.

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1. INTRODUCTION

This is the Third Quarter Report for DOE Contract DE AC04 79ET23007, "CdSiAs₂ Thin Films for Solar Cell Applications." In this section, a brief review of the program is presented. Program tasks are then summarized, with emphasis on those treated during this reporting period.

1.1 Background

The major reasons for studying CdSiAs₂ as a potential photovoltaic material have been discussed previously in some detail.⁽¹⁾ Over the first two reporting periods, the work emphasized bulk growth of required materials, and sputtered and evaporated film studies.^(1,2) Over the first quarter, bulk polycrystalline CdSiAs₂ was synthesized by direct fusion of the elements and by direct fusion of the binaries SiAs, Cd₃As₂ and CdAs₂. The latter material resulted in denser ternary material with good homogeneity.

Evaporation studies related to CdSiAs₂ formation were completed during the second quarter. The decomposition of CdSiAs₂ was found to be preferential toward Cd between 570°C and 710°C, and toward As in the 710 - 1010°C range. It was concluded that evaporation of the ternary is not a suitable method for forming CdSiAs₂ films. Evaporation studies related to CdAs₂ were also completed. Stoichiometric CdAs₂ films could not be formed by means of single-source evaporation of CdAs₂ bulk. Following this study, the evaporation experiments were discontinued, and all emphasis placed on sputtering.

Sputtered ternary films were formed by using a bulk CdSiAs₂ target, and several "composite" targets, formed by imbedding CdAs₂ discs into Si backing plates. All films deposited from those targets were amorphous and off-stoichiometry. It was found that post-deposition heat treatments in

As + Cd ambients could improve both the composition and crystallinity of the films. It was also found that sputtering power and target geometry (CdAs_2 to Si area ratio) were important sputtering parameters which could be used to some extent to control film properties.

No thin film junctions were formed over the first two quarters of the program.

1.2 Program Objectives

The major objective of the program is the formation of CdSiAs_2 thin films suitable for heterojunction solar cells. The research effort is broken down into the following tasks⁽³⁾:

Task 1: Thin Film Growth

Task 1.1 - Preparation of bulk material for sputtering and evaporation. This includes CdSiAs_2 , CdAs_2 , Cd_3As_2 , SiAs and SiAs_2 as required to form targets and charges.

Task 1.2 - Sputter deposition of CdSiAs_2 films. Single and multi-target techniques will be used.

Task 1.3 - Evaporation of CdSiAs_2 films. Single and multi-source techniques will be used.

Task 1.4 - Film optimization.

Task 2: Film Characterization

Task 2.1 - Mechanical and electrical film characterization, including morphology, x-ray diffraction, average composition, composition profiles, resistivity and mobility measurements.

Task 2.2 - Wavelength dependence of absorption coefficient between 0.4 and 1.0 μm .

Task 2.3 - Minority carrier diffusion length measurement.

Task 2.4 - Determine film thickness for absorption of 50% and 90% of incident light as function of wavelength; optimize film thickness.

Task 3: Solar Cell Fabrication

Task 3.1 - Fabrication of $\text{CdSiAs}_2/\text{CdS}$ thin film heterojunction solar cells, using CdS as the collector material.

Task 3.2 - Evaluation of $\text{CdSiAs}_2/\text{CdS}$ solar cells by taking I-V curves under solar or simulated radiation.

Most of the research effort during the third three month period of the contract was directed toward tasks 1.2, 1.4, 2.1 and 3.1, i.e. toward sputtered film deposition and heat treatments, film measurements, and initial thin film junction formation. These items are discussed in more detail in the following section.

2. TECHNICAL NARRATIVE

The research conducted over the third quarter was directed mostly toward single target sputtering and heat treatments, and toward initial thin film junction formation.

2.1 Sputtered Thin Films

The work over the last period concentrated on the following:

- 1) RF sputtering of Cd-Si-As from single composite targets,
- 2) Heat treatments of films in inert ambients, with characterization measurements (x-ray, thickness, composition, optical, electrical) being made before and after.

In order to be able to accommodate the high annealing temperatures ($> 400^{\circ}\text{C}$), suitable substrate materials were sought. Suitability was determined by the following prerequisites:

- 1) Chemically inert with respect to CdSiAs_2 under heat treatment conditions (relates both to cross diffusion of components across film substrate interface and negligible chemical reaction).
- 2) Able to withstand heat treatment temperatures.
- 3) Thermal compatibility between film and substrate (i.e. no thermal cracking).
- 4) Transparent for optical film measurements, and electrically conductive and ohmic to CdSiAs_2 for electrical and junction measurements.

Sputtering parameters and various substrates used are listed in Table 1 along with other variables for several Cd-Si-As films. Electron microprobe data for one sample from each run are also shown. The sputtering parameters were adjusted in an effort to obtain films near stoichiometric CdSiAs_2 . Only as deposited compositions are indicated in the table. Effects of post-

Table 1. Sputtering Parameters for Different Substrates

RUN	SUBSTRATES	POWER (w)	PRESSURE (mT)	TIME (min.)	THICKNESS RANGE (μm)	COMPOSITION (%)		
						Cd	As	Si
2-4	7059 Moly	200	8	250	6.8-7.8 1.8-2.7	23.7	24.8	51.5
2-5	SiO ₂ 7059 Moly SS	110	14	305	4.1-5.2 4.4-4.9 2.8-3.7 1.3-2.6	18.4 18.5 27.9	29.0 28.8 23.4	52.6 52.7 48.7
2-6	SS	150	13	255	0.88-1.97	5.4	37.9	56.7
2-7	SS	125	13	300	1.59-2.14	8.3	36.7	56.0
2-8	Mo	90	13	240	0.65-1.32			
2-9	SiO ₂	90	13	195	2.43-3.34	19.3	28.9	51.8
2-10	Mo/SiO ₂ SiO ₂	100	13	185	1.9-2.7	21.6	27.3	51.1
2-11	Ta/SiO ₂ 7059	85	13	143	1.4-1.8	20.8	29.6	49.4
2-12	7059	95	13	220	2.43-3.33	21.3	32.1	46.6
2-13	Ta/7059	100	13	255	2.1-2.7	21.8	28.4	49.8
3-4	SS	170	12	250	1.7-3.8	40.7	5.1	54.2
3-5	Mo	100	13	210	1.8-8.7	26.2	13.7	60.1

description heat treatments are discussed below.

Work during December concentrated on metallic substrates (1 and 2 mil thick moly and stainless) in an effort to fabricate junctions. Post-deposition heat treatments at temperatures of 400 - 600°C were used. For heat treatment times of ~ 24 hrs, no substantial film crystallization (films as deposited are amorphous) occurred below ~ 450°C. Above this temperature, x-ray patterns indicated the onset of crystallization, but a reaction between the CdSiAs_2 and substrate in addition. X-ray and microprobe analyses both indicated significant reactions with the substrate occurred at ~ 600°C, which appeared to be roughly the minimum temperature needed. The substrates were therefore modified, as follows.

Transparent (SiO_2 and 7059) and conducting (Mo and Ta on SiO_2 and 7059) were employed.

Films deposited onto moly/glass were of immediate poor quality, with very poor adherence and exhibiting reaction with the moly. Similar problems were not encountered for the Ta on glass substrates. X-ray diffraction of the films on Ta heat treated for 6, 24 or 48 hrs. at 550°C showed the CdSiAs_2 chalcopyrite structure in all cases. Eight Cd-Si-As films on Ta coated silica were heat treated for six hours in a Cd/As_4 atmosphere. The films were crystalline CdSiAs_2 via x-ray diffraction. The peaks were not shifted from their theoretical positions, indicating stoichiometric CdSiAs_2 . However, the microprobe analyses indicated compositions close to 23% Cd, 29% Si and 48% As. This point is discussed later, when the microprobe analysis is considered in more detail.

SEM studies of films heat treated for up to 48 hours reveal no perceptible grain structure. A series of 1 week and 2 week heat treatment studies were therefore conducted. Subsequent x-ray diffraction indicated

a large Ta peak in one case, which had previously been quite small. This indicated the possibility of Ta diffusion or reaction with the film during the prolonged heat treatment. No grain structure was evident in subsequent SEM examinations, although a larger ($\sim$ mm) pattern was evident, which was attributed to cracks.

Thin CdSiAs_2 films were also sputter coated onto Ta on 7059 glass. The objective was to obtain a better thermal match to the CdSiAs_2 in order to prevent the cracking of films during heat treatments. Although films were improved over the Ta/silica case, cracking of CdSiAs_2 was still visible.

Thus, in summary the situation is as follows: all Cd-Si-As films are amorphous and way off stoichiometry, as deposited. Heat treatments give the films a certain degree of crystallinity (grain sizes probably $\gtrsim 100^\circ\text{A}$), improved stoichiometry (within $\approx \pm 1\%$ of desired), but with mechanical properties not sufficiently good to permit detailed transport and junction studies. Resistivities of films have been measured to be $> 10^6 \Omega\text{-cm}$ (p-type) both before and after heat treatments. The large resistivity of films before heat treatment is due to their amorphous nature. The large resistivity after heat treatment could be an inherent property of the film bulk, due to heat treatment caused cracks, or both. Optical absorption measurements on one set of heat treated films indicated an absorption edge shift of from ~ 1.38 eV to 1.53 eV, the latter value being anticipated from the literature for crystalline CdSiAs_2 . Optical absorption coefficient for one of the mechanically better heat treated films was estimated to be $\approx 2 \times 10^4 \text{ cm}^{-1}$ at $0.6 \mu\text{m}$. This is only an approximate result, since reflection coefficient was estimated, and there were some microscopic pinholes detected in the film. The latter fact indicates that the actual film absorption coefficient is probably greater than $2 \times 10^4 \text{ cm}^{-1}$. This is consistent with the

fact that all CdSiAs_2 films are opaque to the eye, down to a fraction of a micron in thickness.

The microprobe analysis has been improved by changing from a GaAs to a SiAs standard. However, there is still some discrepancy between microprobe and x-ray determinations of film composition. In order to cross check the probe, a set of samples has recently been prepared (February) for analysis by atomic absorption spectroscopy. These results will be discussed in the next report.

2.2 Junction Fabrication

Due to the poor mechanical properties of the films following their post-deposition heat treatments, only a few junctions were fabricated. On most of the samples, shorts resulted after deposition of CdS and/or a metallic contact. Optical examination of the CdSiAs_2 films indicate two major reasons for shunting or shorting behavior: 1) Most films examined have at least some pinholes evident, prior to post-deposition heat treatment and 2) cracks are evident in post-heat treated films, sometimes quite severe.

For these initial junction studies, CdS/ CdSiAs_2 heterojunctions and In/ CdSiAs_2 Schottky diodes were made. An In grid was deposited onto the CdS in the former case; in the latter, the In was deposited thick ($> 0.5 \mu\text{m}$) and contact made directly to it, in order to first examine dark diodes only.

Due to the above mechanical problems, the best diodes had shunting problems. They (the CdS ones) exhibited only very poor photovoltaic response, with $V_{oc} < 20 \text{ mV}$ and $J_{sc} < 10 \mu\text{a}$. Dark I-V characteristics are shown in Figures 1 and 2 for a heterojunction and a Schottky barrier diode.

Even though the photoresponses are essentially zero, it should be noted on the positive side that rectification is obtained in both cases,

Figure 1. Dark current-voltage behavior for CdS/CdSiAs₂ thin film junction.

Figure 2. Dark current-voltage behavior for In/CdSiAs₂ thin film junction.

as anticipated. Poor shunt resistance ($< 500\Omega$ in all cases) is due to pinholes and cracks. High series resistance ($> 100\Omega$ in all cases) is attributed mainly to CdSiAs_2 resistivity. The low photoresponse for the heterojunction is attributed to low diffusion length in the CdSiAs_2 and perhaps to detrimental interface properties.

Due to the poor mechanical properties of these devices and their unstable characteristics, more detailed analyses were not attempted. However, such analyses will be performed as soon as more mechanically sound films are available.

2.3 Equipment Status

It is evident that improved procedures will be necessary if usable sputtered CdSiAs_2 films are to be made. Toward this end, even though its use was not required in the original contract, some mention should be made of the new sputtering unit since it will be used extensively in the future.

The multi-target sputtering unit (Perkin-Elmer Randex 2400 8-J, cryo-pumped, with stainless bell jar and three target capability) has now been installed. The J-arm, originally damaged during shipment, has been replaced. A Perkin-Elmer engineer has visited our facility three times, in order to de-bug the machine. It is now operational, with initial single target runs (Si target; stationary substrates) having been performed. Over roughly the next two months (into April 1980) all CdSiAs_2 sputtering studies will be shifted from the single target unit over to this new unit. It is anticipated that much improved control of all important deposition parameters, and subsequent films, will result.

3. NEXT QUARTER PLANS

Single target sputtering and optimization studies will continue until the targets are obtained for the new system. CdS/CdSiAs₂ and Schottky barrier junctions will continue to be fabricated, with more extensive studies being performed on mechanically improved samples. In the new sputtering system, parametric studies will be initiated, starting with Si and Cd targets. As these are performed the third target (of CdAs₂) will be fabricated.

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