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CdSiAs₂ THIN FILMS FOR SOLAR CELL APPLICATIONS

First Quarter Report for April 9—June 30, 1979

By
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July 25, 1979

Work Performed Under Contract No. AC04-79ET23007

Virginia Polytechnic Institute and State University
Blacksburg, Virginia

MASTER

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FIRST QUARTER REPORT: 4/9/79 - 6/30/79

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ABSTRACT

Near stoichiometric bulk polycrystalline CdSiAs_2 has been synthesized by two techniques: (1) direct fusion of the elements and (2) direct fusion of the binaries SiAs , Cd_3As_2 and CdAs_2 . The latter technique resulted in denser ternary material with good homogeneity. The above binaries melt congruently and were also formed by direct fusion.

Sputtered ternary films were formed using a bulk CdSiAs_2 target, and a composite target of CdAs_2 discs in a Si plate. Composition of the CdSiAs_2 target changed with sputtering time. Amorphous films deposited from that target were heat treated, and became crystalline and near stoichiometric but with poor mechanical properties. It appears that films deposited from the composite target ($\text{Si} + \text{CdAs}_2$) can be adjusted to stoichiometry by means of sputtering power and target geometry. As deposited, these films also were amorphous.

With respect to evaporated films, the study of thermal decomposition of CdSiAs_2 in vacuum was completed. The decomposition is preferential toward Cd between 570° and 710°C , and toward As in the 710 – 1010°C range. It is concluded that evaporation of the ternary is not a suitable method for forming CdSiAs_2 films.

Plans for the next reporting period include continued sputtering studies with the composite target, constructing a two-source setup for evaporated films, expanded film characterization and fabrication of bulk $\text{CdSiAs}_2/\text{CdS}$ solar cells.

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1. INTRODUCTION

This is the First Quarter Report for DOE Grant DE AC04 79ET23007, "CdSiAs₂ Thin Films for Solar Cell Applications." In this section, we first discuss the reasons why this material is being studied. Program tasks are then summarized, with emphasis on those treated during this reporting period.

1.1 BACKGROUND

Several of the II-IV-V₂ chalcopyrite compounds have been studied and reported upon in sufficient detail that their applicability to photovoltaics is readily apparent. These compounds can be viewed as ternary analogs of the III-V compounds⁽¹⁾, with the group III atom (ex. Ga) being replaced by one atom each from groups II and IV (ex. Cd and Si). These materials are appealing for photovoltaics due to their similarity with III-V compounds.

The most important prerequisites for a photovoltaic absorber are that the energy gap be direct and in the 1-2 eV range⁽²⁻⁴⁾. Parameters for several II-IV-V₂ compounds satisfying these conditions are shown in Table 1 (E_g = energy gap, a = lattice parameter, χ = electron affinity, MP = melting point).

In single crystal form to which the table pertains, the compounds are most commonly found to be p-type, with electrical properties dominated by electrically active native defects due to deviations from stoichiometric compositions. The reported p-type behavior of CdSiAs₂ allows CdS to be used as the wide-gap collector in a heterojunction solar cell.

Another consideration in selecting the collector material is the lattice match with the absorber. As seen in Table 1, the lattice parameter mismatch between CdS and CdSiAs₂ is only about 0.6%.

TABLE 1

Data for Several II-IV-V₂ Compounds (From Ref. 1,
Except χ Values, which are from Ref. 5)

CdS values are also shown for comparison.

<u>Material</u>	<u>Type</u>	<u>E_g(eV)</u>	<u>a(Å)</u>	<u>χ(ev)</u>	<u>MP(°C)</u>
CdSiAs ₂	p	1.55	5.884	3.85	>850
ZnSnP ₂	p	1.66	5.651	4.25	930
CdSnP ₂	p,n	1.17	5.900	4.41	570
ZnGeAs ₂	p	1.15	5.672	4.20	860
CdGeP ₂	p,n	1.72	5.741	3.98	790
CdS	n	2.42	5.851	4.50	-

Using values given in Table 1, a tentative band diagram was constructed for the CdSiAs₂/CdS heterojunction and is shown in Figure 1. Carrier concentrations of 10^{16} and 10^{18} cm^{-3} were assumed for the CdSiAs₂ and CdS, respectively. Due to the low electron affinity of the CdSiAs₂, no energy spike exists at the interface.

Studies of CdSiAs₂ film growth and of the CdSiAs₂/CdS heterojunction solar cell are therefore being conducted for the following reasons:

- a) The CdSiAs₂ energy gap is direct and close to the predicted efficiency maximum;
- b) The lattice mismatch with CdS is less than 0.6%;
- c) The wide gap of CdS allows the backwall configuration to also be investigated;
- d) Electron affinity values indicate that there is no energy spike at the interface;

Figure 1. Energy band diagram for the CdSiAs₂/CdS heterojunction. CdS electron affinity value is assumed to be 4.5 eV (4.8 eV for dashed curve).

e) For possible long term terrestrial applications, availability of materials should not pose a problem⁽⁶⁾, and several less expensive technologies already exist for the formation of CdS films⁽⁷⁾.

1.2 PROGRAM OBJECTIVES

The major objective of the program is the formation of CdSiAs₂ thin films suitable for heterojunction solar cells. The research effort is broken down into the following tasks⁽⁸⁾:

Task 1: Thin Film Growth

Task 1.1 - Preparation of bulk material for sputtering and evaporation. This includes CdSiAs₂, CdAs₂, Cd₃As₂, SiAs and SiAs₂ as required to form targets and charges.

Task 1.2 - Sputter deposition of CdSiAs₂ films. Single and multi-target techniques will be used.

Task 1.3 - Evaporation of CdSiAs₂ 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 irradiation.

Most of the research effort during the first three month period of the contract was directed toward Tasks 1.1, 1.2, 1.3 and 2.1, i.e. toward material (bulk and thin film) growth and characterization. These items are discussed in more detail in the following section.

2. TECHNICAL NARRATIVE

Most of the work performed over this reporting period was related to bulk synthesis, and to initial sputtering and evaporation studies of CdSiAs_2 films. For single sputtering target or thermal source film formation, CdSiAs_2 bulk was required. For multi-target or multi-source techniques, binary compounds can be employed. For these techniques CdAs_2 , Cd_3As_2 , SiAs and SiAs_2 are being studied.

This section therefore deals first with bulk material synthesis, and then with thin film studies. Characterization measurements are discussed along the way wherever appropriate.

2.1 BULK MATERIALS SYNTHESIS

2.1.1 Background The object of the chemical synthesis task is to prepare materials for the formation of CdSiAs_2 thin films by RF sputtering and thermal evaporation. The thin films are then to be further processed into $\text{CdSiAs}_2/\text{CdS}$ heterojunction solar cells. The bulk growth task is made necessary by the lack of supply of suitable binary and ternary materials from outside vendors.

Since it is projected to arrive at thin films by evaporation from multiple sources using elemental or binary sources, it is necessary to arrive at processes which will yield binary compounds of high quality. These binaries may also be necessary as intermediate compounds in the synthesis of the CdSiAs_2 ternary compound. Detailed descriptions of the lines of attack on the synthesis problem follow, but here it will be useful to comment upon some general problems and techniques applying to the preparation of all the compounds that are under consideration. Some pertinent data on these elements and compounds are included in Table 2. There

TABLE 2: Properties of Some Compositions in the Cd-Si-As Ternary System

<u>Composition</u>	<u>Density (g/cm³)</u>	<u>Melting Point (°C)</u>	<u>Melting Behavior</u>	<u>Vapor Species</u>	<u>Vapor Pressure (Torr)</u>		
					<u>740°C</u>	<u>820°C</u>	<u>1100°C</u>
Cd	8.64	321	simple	Cd	6×10^2	2×10^3	2×10^4
As	5.73	817 (28 atm)	sublimes 613°C	As ₂ /As ₄	10^4	3×10^4	8×10^4
Si	2.33	1420	simple	Si ₂			2×10^{-6}
Cd ₃ As ₂	6.31	721	congruent	Cd, As ₂ /As ₄	80 71	2×10^2 1.7×10^2	1.1×10^3 7×10^2
CdAs ₂	5.88	621	congruent		Approx. same as for Cd ₃ As ₂		
SiAs	3.82	1083	congruent	As ₂ /As ₄	-	-	-
SiAs ₂	-	944-1040	incongruent	As ₂ /As ₄	-	-	-
CdSiAs ₂	5.12	821-943	incongruent sublimes 620- 800	Cd, As ₂ /As ₄	- -	- -	$\sim 10^3$ $\sim 8 \times 10^2$

are three factors which greatly affect the experimental design: (1) The high vapor pressures of cadmium and arsenic; (2) the high melting point and low vapor pressure of silicon; and (3) the incongruent melting behavior of CdSiAs_2 .

The first and most obvious problem to be dealt with is the volatility of Cd and As. Figures 2 and 3 show the temperature variation of pressure of Cd and As and their binaries, according to information available from the literature⁽⁹⁻¹¹⁾. It is seen that the maximum pressure is from elemental As at high temperatures. For synthesis temperatures of 1100°C , the As pressure can be as high as 80 atmospheres. In the synthesis of the ternary compound, the graphs show that one may expect a total combined pressure at 1100°C on the order of 3 atmospheres.

It is clear that in all cases, the synthesis should be conducted in a closed capsule to avoid loss of reactants by volatilization; and that in some cases, the capsule must be of high strength to contain the high pressures. The most convenient method for containment of the small batches required in this work is to seal off the reactants in an evacuated fused silica or vycor tube. It is also sometimes desired to have an inner crucible of graphite to ensure a reducing atmosphere and to provide for stress relief on cooling.

One problem in achieving stoichiometry with this kind of vessel can be the volatilization of the elements into the free space in the tube. A problem arises when the Cd or As volatilizes from the inner graphite container and enters the space between that container and the silica ampoule. Condensation on tube walls (in cooler regions, if they exist) will result in disproportionation on cooling below the freezing point of the compound being synthesized.

Figure 2. Vaporization equilibrium for cadmium

Figure 3. Vaporization equilibrium for arsenic

This problem can be aggravated in quenching when a sharp temperature gradient exists, such that the gas condenses out on tube walls, causing the still-hot unrecrystallized inner portion of an ingot to attempt to restore vapor pressure equilibrium by boiling, thus leading to void formation.

A milder form of dehomogenization occurs when on cooling, an axial temperature gradient is established across the tube, leading to vapor phase transport of the cadmium and arsenic away from the ingot and condensation at the tube ends. To prevent this, it is necessary to utilize a furnace which can maintain a uniform temperature across the ampoule.

Assuming that the Cd and As vapors behave as ideal gases, calculations indicate that excesses of 8×10^{-3} g and 11×10^{-3} g will fill the free space in the silica ampoule (4 cm^3) at a reaction temperature of 1100°C . This technique has alleviated stoichiometry problems initially encountered in the synthesis of these compounds.

2.1.2 CdSiAs₂ Synthesis The preparation of homogeneous CdSiAs₂ is complicated by the fact that the compound melts incongruently⁽¹²⁾. Thus, if a direct fusion technique is used, the peritectic decomposition products must be eliminated from the resulting solid. Various other methods for bulk formation are solution growth from molten tin⁽¹³⁾, closed tube chemical transport^(13, 14) and solution growth from SiAs contained in molten CdAs_x, with $0.67 < x < 2$ ⁽¹⁵⁾. These latter methods have been used to produce small samples of p-type single crystals, but are of questionable feasibility for the production of large polycrystalline ingots.

A major problem in the formation of CdSiAs₂ is the lack of phase equilibria information. While this information for the binary system is quite well developed, there has been no comprehensive investigation reported

of the three phase region. The most detailed work available is that of Houserova and Hruby⁽¹²⁾, who have prepared and examined a number of compositions in the arsenic rich region in attempting to establish the limits of the glass forming region by means of differential thermal analysis. They establish the liquidus and solidus temperatures for the CdSiAs_2 composition.

There has been no phase diagram reported for this compound, but one does exist for the CdP_2 -Sn system containing CdSnP_2 ⁽¹⁾. This compound is similar to CdSiAs_2 , and was therefore used for guidance in the preparation of the latter. A better understanding of the direct fusion method is facilitated by examining the tentative phase diagrams of Figures 4 and 5. The diagrams allow an estimate of the temperature range over which the peritectic decomposition can occur.

By quenching a melt of the CdSiAs_2 composition rapidly along $x_1-x'_1$ (see Fig. 5) it is possible to retain a homogeneous chemical composition in the vitreous form^(12, 16). The material thus obtained may then be reheated to a temperature just below the solidus to recrystallization of the glassy material at a point where the ternary phase is in equilibrium. This was the method that we used in the preliminary work related to the fabrication of polycrystalline bulk samples. X-ray analysis indicated a homogeneous CdSiAs_2 crystalline composition, but subsequent electron microprobe measurements revealed the presence of minor amounts of phases identified as SiAs , Cd_3As_2 and As of quantities too small to appear in the x-ray analysis.

Another problem occurring during the quenching process was the generation of voids due to condensation of the vapor species on the cold tube walls, with the hotter inner material trying to reestablish the equilibrium vapor pressure by volatilization of Cd and As from the bulk. This often resulted in the formation of a spongy mass sometimes filling the containment vessel.

Figure 4. Phase information related to the Cd-Si-As system (ref. 12).

Figure 5. A very tentative phase diagram for Si-CdAs₂ compositions

The subsequent heat treatment caused conversion of the material to the ternary compound, but obviously could not effect densification. Therefore, the further steps of grinding the material, re-encapsulation, and reheating to sinter the powder was employed to obtain more dense shapes for sputtering target and bulk device fabrication.

With respect to void elimination, one approach suggested was a modified quench program conducted directly in the furnace. This consisted of opening the top and bottom ends of a vertical tube furnace in which the ampoule was being heat treated such that quenching was by air convection at a slower rate. Furthermore, the temperature of the ampoule was not allowed to drop below the condensation temperature of the arsenic vapor. In this way, the reaction vessel temperature was dropped to 815 - 820°C in 5 to 10 minutes, then the furnace ends were closed, and the temperature allowed to equilibrate at a holding temperature. This holding temperature was maintained for roughly a week in an attempt to achieve recombination of the unwanted phases.

In our initial work, this solidus temperature was thought to be 850°C, according to Averkieva, et al⁽¹⁷⁾. Therefore, heat treatments for homogenization of the quenched material were carried out at 835 - 840°C for times of about a week. More accurate work on the differential thermal analysis for this ternary mentioned earlier⁽¹²⁾ has indicated a solidus temperature at 821°C. Thus, subsequent homogenization was carried out at a temperature between 816°C (condensation of As) and 821°C (ternary solidus).

Fairly high quality p-type ternary material has been achieved by this method, particularly when the graphite crucible was omitted to diminish the quartz envelope length and reduce temperature gradient effects.

We have also initiated an alternate technique, based on the relation

The attractiveness of this process is in the greater ease of fabrication of the binaries by virtue of their congruent melting characteristics, the lowered equilibrium vapor pressure over the reactants as compared to direct fusion from elements, and the ability to achieve complete reaction at temperatures below the solidus of the ternary.

In this method, it is necessary to obtain intimate mixing of fine starting powers in order to decrease the path length in diffusion-controlled reaction processes. Upon heatup of the binary mixtures, the following behavior might occur:

- (1) The vapor pressure of Cd and As in the tube is kept in equilibrium by volatilization of Cd from Cd_3As_2 and of As from CdAs_2 (SiAs being stable to approximately 800°C)
- (2) At 610°C localized melting takes place at points of contact between CdAs_2 and Cd_3As_2 .
- (3) At 621°C the CdAs_2 melts, filling the void space, attacking and dissolving more Cd_3As_2 . In sufficient time, all the Cd_3As_2 and CdAs_2 would equilibrate as a liquid of composition CdAs (m.p. - 618°C).
- (4) As the temperature is raised, the arsenic-silicon bonds will become very weak, permitting atomic rearrangements in the SiAs .

The Si-Si bonds of SiAs must be altered to form the basic tetrahedral structure of the chalcopyrite. The alteration takes the form of replacing the Si-Si bond by two Si-As bonds. The structure of SiAs here is fortuitous in that Cd and As can diffuse along the SiAs interlaminar planes and be

within a very few atomic diameters of the reaction site, thus promoting rapid reactivity.

Thus, the mixed binary powders should be heated in the reaction ampoule to just above the As condensation point at 815°C but below the ternary solidus at 821°C. After completion of the reaction, the cooling rate must be slow to prevent disproportionation by low melting point constituents.

This method has been tried once, but the furnace temperature overshot the solidus limit by about 50°C for a short while, contrary to the planned schedule. However, subsequent equilibration at the desired holding temperature for seven days resulted in a ternary ingot with a homogeneity at least as good as anything produced to date, and with the additional quality of high density in the ingot form. Further tests will follow modifications being made in the furnace and fumehood setup.

In summary, p-type polycrystalline CdSiAs_2 ingots and chunks have been formed by the above direct fusion techniques. Minor phases by Cd_3As_2 and CdAs_2 have been detected by electron microprobe measurements, but not by x-ray analysis. These samples have been adequate for our initial studies related to sputtered and evaporated films (described below). A typical CdSiAs_2 sample, with single crystallites of several mm length evident, is shown in Figure 6.

2.1.3 Binary Compound Synthesis The binary compounds CdAs_2 , Cd_3As_3 , SiAs and SiAs_2 are also being synthesized as part of this program. This is because they (in addition to the ternary) also can be used in the formation of CdSiAs_2 thin films. Examples are the hybrid sputtering target, using Si and CdAs_2 (discussed below), and multi-source evaporation (also discussed

Figure 6. Polycrystalline CdSiAs₂ formed by direct fusion. Crystal length is about 1 cm.

below). In addition, these binaries could also be useful as intermediary compounds in the synthesis of CdSiAs_2 .

The major binaries of interest are CdAs_2 and SiAs_2 . In order to better understand the synthesis of these compounds, additional members of the family, Cd_3As_2 and SiAs , are also being studied.

Cadmium Arsenide, CdAs_2

Clark and Pistorius⁽¹⁸⁾ have summarized the phase equilibria of CdAs_2 , showing that: (1) the melting of this compound is accompanied by a decrease in volume; (2) that there are no solid/solid phase transformations below the freezing point at pressures up to 20 kilobars; (3) care must be taken to avoid formation of a metastable glassy phase on cooling; (4) it melts congruently.

While there is no published work available on the temperature dependence of vapor pressure over the CdAs_2 composition, it can be inferred⁽¹¹⁾ that the vapor constitution of cadmium is very nearly equal to that of arsenic. This behavior would tend to minimize disproportionation during the preparation by direct fusion. A rough calculation based on the graphs in reference 11 shows the cadmium and arsenic pressures at 730°C to be about 80 Torr and 70 Torr, respectively, with a very nearly equal temperature dependence.

The Cd-As phase relationships govern the reaction strategy. Important phase relationships are seen in Figure 7⁽¹⁰⁾. It is seen that Cd_3As_2 melts at 721°C , while the CdAs_2 melting point is 621°C . In the direct fusion of cadmium and arsenic, Cd_3As_2 would be formed first at the reaction boundary between liquid cadmium (m.p. 321°C) and solid arsenic (m.p. 816°C , 36 atm). Below 721°C this phase would also be solid, tending to inhibit the reaction. Raising the melting temp to just above 721°C would probably cause the reaction layer to be liquid and mobile, thus permitting enhanced diffusion of the cadmium to the solid/liquid reaction interface.

Figure 7. As-Cd phase relationships (from ref. 10)

Normally, the elemental vapor pressures would be about 10 atm for arsenic and 0.5 atm for Cd, but the total pressure in the reaction vessel is kept down by direct gas phase reaction between the cadmium and arsenic vapors. Therefore, the reaction mechanisms are seen to be complex.

During post-reaction cooling, the expansion of the material at the freezing point, 621°C, gives rise to stresses in the containment vessel, such that thinwalled quartz tubing is easily ruptured. This problem can be avoided by using an inner crucible of graphite and/or by employing a quartz tubing of about a 1:4 ratio of wall thickness to inner diameter.

Near the freezing point, some problems can develop because of the heat evolution accompanying freezing of the melt, as indicated by Hansen, et al⁽¹⁰⁾. A temperature rise will be experienced, the magnitude of which is dependent on the amount of material present and the rate of heat conduction away from the ingot. Recrystallization will proceed from the outside of the ingot toward the inside. In large ingots having minimum surface area, the evolved heat can cause such a temperature rise on the remaining contained melt that the vapor pressure is increased to the point of creating an internal void space. Furthermore, the vapor can exert a significant internal pressure which can cause rupture of the ingot. In our work, such problems were not experienced with small ingots of 5 or 10 grams, but became apparent in attempts to melt larger batches of 50 to 100 grams.

This particular problem can be minimized not only by restricting the size of the batch, but also by very slow cooling through the melting point. The typical furnace cooling rate in the region of concern was 10°C per hour.

To avoid the development of a glassy phase, the furnace may be held at a temperature just below freezing point for some time to permit recrystallization. In our case, this was 600°C for three hours. The cooldown

may then occur faster, at say 50°C per hour, since there are no phase transformations below the freezing point.

A typical temperature program used for CdAs₂ fabrication is as follows:

- (1) Initial heatup of reactants at 150°C/hr. to 740°C.
- (2) Hold at 740°C for 4 to 5 days to ensure complete reaction.
- (3) Cool at 10°C/hr. to 640°C.
- (4) Cool at 5°C/hr. from 640°C to 600°C.
- (5) Hold at 600°C for 3 hours
- (6) Cool at 50°C/hr. or at lower furnace-limited rate to room temperature.

The first 10 gram batch of CdAs₂ made according to this schedule, examined by electron microprobe analysis, was found to be of a homogenous CdAs₂ composition both axially and radially. However, further attempts with larger batches were unsuccessful because of disproportionation accompanied by ampoule and/or ingot rupture from the lack of furnaces capable of handling the larger ampoule assemblies. Therefore, synthesis was continued with 10 gram batches and consistently good results, as indicated by x-ray and microprobe analysis. Thus, stoichiometric CdAs₂, to within the accuracy of the microprobe, can be made on a routine basis.

Cadmium Arsenide, Cd₃As₂

The compound Cd₃As₂ is more complex in the temperature dependence of structural behavior than CdAs₂. Pietraszko et al⁽¹⁹⁾ show four solid phases up to the melting point:

The α phases are tetragonal and the β phase is cubic. There is no indication from the literature as to the relative densities of the liquid and solid phases at the melting point. However, the work above shows that the successively higher temperature forms are also successively more dense. Because of this characteristic, fabrication of uncracked polycrystalline ingots of Cd_3As_2 is very difficult. In addition, the α'' - α' transformation can be suppressed, with the retention of the α phase to room temperatures. This room temperature allotropism complicates the interpretation of x-ray diffraction analyses. Fortunately, the compound melts congruently and has little tendency to disproportionate in the solid state.

One may expect from Roenkov's summary⁽¹¹⁾ that the pressures of Cd and As above the compound are about the same in the vicinity of the melting point. At lower temperatures, Cd pressure seems to be higher than that of As, as indicated by the work of Lovett⁽²⁰⁾.

As in the case of CdAs_2 , cooling through the freezing point should be slow to minimize the effects of the heat evolution during solidification. Cooling through the β - α'' transformation range at 578°C should also be at a slow rate to permit a full transformation. In subsequent cooling to room temperature, it is difficult to prevent the retention of the α'' phase.

A suitable heat treatment schedule for direct fusion is as follows:

- (1) Initial heatup of reactants to 740°C at 150°C/hr .
- (2) A holding period of 4-5 days at 740°C to insure complete reaction.
- (3) Cooling through the freezing point (721°C) at 5°C per hour to 700°C .
- (4) Cooling from 700°C to 600°C at 50°C/hr .
- (5) Cooling through the 578°C inversion at 5°C/hr . to 550°C .
- (6) Cooling at 50°C/hr . or at the furnace-limited rate to room temperature.

We have used this schedule to form Cd_3As_2 samples. It was found necessary to perform the heat treatment in a box furnace to obtain more uniform temperatures, and to produce material of uniform Cd_3As_2 chemical composition, as confirmed by electron microprobe analysis. However, x-ray diffraction analysis shows the persistence of varying amounts of α'' phase in the resultant material. This is of little consequence for the purposes of this project, except that the x-ray patterns are harder to analyze for possible phases of other chemical constitution.

Silicon Arsenide, SiAs

This congruently melting compound (1083°C) is different in structure, being monoclinic with a sheet-like habit, very much like mica. This is discussed by Wadsten⁽²¹⁾, whose results show that the fundamental structure consists of Si_2As_6 molecular groups.

As indicated in Fig. 8, this material exhibits no allotropism up to its melting point. The preparation by direct fusion of the elements is achieved by heating to 1100°C at 150°C/hr. , reacting at that temperature for 4-7 days, cooling through the melting point at 5°C/hr. , then lowering the temperature at 50°C/hr. to the furnace-limited cooling region, and then to room temperature. Due to the high As vapor pressure, thick walled ampoules are necessary.

In our work, the elements were first placed in a graphite crucible insert, in a manner similar to the cadmium arsenides. In the first attempt, the reaction time at 1100°C was only 24 hours, and resulted in incomplete combination. The second attempt resulted in the production of SiAs as determined by x-ray diffraction analysis, but with a fine brown powder at the graphite/ingot interface. Since this powder was thought to be unreacted silicon, the

Figure 8. As-Si phase relationships (from ref. 10)

reaction time was lengthened in subsequent trials. Contrary to expectations, the amount of fine brown powder increased. X-ray diffraction analysis showed the emergence of reflections not due to silicon, arsenic, or either of the silicon arsenides. A search of the diffraction file data showed that the extra reflections could be entirely accounted for in both appearance and relative intensity by β -SiC (cubic). The conclusion is that graphite may not be used as a containment for this reaction at the temperature required. Fortunately, the crucible is not necessary, since not only does SiAs have no crystalline inversions on cooling; but also stress development on solidification would be nearly impossible because of the weakness of the crystalline material under shearing stress. Further direct fusions will be performed using the fused quartz alone as the containment vessel.

It should be noted that even though there were problems in these initial trials, the SiAs thus formed exhibited well developed crystallinity with sheet faces as large as 1/2 cm x 1-2 cm in dimension, as shown in Fig. 9, a photograph of a typical 5 gram ingot.

Silicon Arsenide, SiAs₂

Silicon diarsenide was found to be orthorhombic, and to melt incongruently⁽²²⁾. Attempts were made to fabricate the compound by direct fusion at 1090°C for 7 days followed by furnace cooling to 930°C in 10 minutes, holding at that temperature for another week, then cooling at 50°C per hour or less to room temperature. Because the graphite crucible insert was used as a containment vessel within the silica ampoule, the same problem of competing reaction of silicon with carbon was experienced. In view of the expected difficulty in fabrication due to the incongruent melting, and since a need for the compound in project objectives was not immediate, the work has been discontinued for the time being.

Figure 9. Ingot of SiAs, polished on one side. Dimensions are 0.85 cm. dia, 3.5 cm. length.

Equipment Improvements

A control system has been obtained whereby temperature schedules of five furnaces can be programmed independently. This consists of five Leeds and Northrup Trend-Trak optical program followers, each driving a Halmar Model LN-1 SCR power controller capable of handling 50 amps at 240 volts. The furnace temperatures are recorded on an L & N Speedomax H multipoint recorder.

We have recently acquired a new muffle furnace and three tube furnaces whose temperature profiles can be varied. The tube furnaces are Norton Vacuum Equipment Model 1000 two zone units capable of $\pm 5^{\circ}\text{C}$ flat 8 inches long at 1100°C . The muffle furnace is a Lindberg Mod. 51442 with a $5\frac{1}{4}'' \times 7\frac{1}{2}'' \times 14''$ hot zone.

2.2 SPUTTERED THIN FILMS

The sputtered films were made in an RF sputtering system (RD Mathis 5P310) mounted on a turbomolecular pump capable of about 10^{-6} Torr. The sputtering module is equipped with a substrate heater and two controlled leaks.

2.2.1 Using CdSiAs_2 Target One bulk CdSiAs_2 target has been fabricated and used. The CdSiAs_2 was synthesized as follows: the mixed elements were melted at 950°C and held there for one day; ampoule was water quenched; homogenization occurred for seven days at 840°C . The ingot was then fragmented and inserted into a target ampoule (diagrammed in Figure 10). The ampoule was evacuated, sealed and heated to 950°C until the fragments were melted and coalesced into a disc. The ampoule was then removed from the furnace and cooled to room temperature. The target was removed from the ampoule and graphite disc, and was epoxied to an aluminum plate for installation in the sputtering chamber.

Figure 10. Silica ampoule arrangement for formation of bulk CdSiAs₂ sputtering target.

Films have been sputtered from the above target onto glass (Corning 7059) and polished aluminum substrates. The film parameter of primary initial interest was composition, which was determined by electron probe microanalysis. The aluminum substrates were in order to facilitate microprobe measurements free of silicon and oxygen pickup.

The power level during sputtering was maintained at 150-200W, and the argon pressure at 7m Torr.

Since the target was slightly deficient in Cd, so are the films. After several runs the target became even more Cd deficient. Approximate changes in target composition over the course of roughly 20 runs are shown in Table 3.

TABLE 3: Ageing Effects of CdSiAs_2 Sputtering Target
(Composition in Atomic Percent)

	<u>Cd</u>	<u>Si</u>	<u>As</u>
Initial	21	27	51
Final	11	35	53

One apparent cause for the loss of Cd in the target is thermal interaction with the substrate. Following runs at substrate temperatures of 300°C and 540°C the Cd content of substrate and films was seen to noticeably decrease. At this point, the modified substrate design was initiated (discussed below).

The strong effect of substrate temperature on film composition is seen in Figure 11. One potentially troublesome trend is apparent in this figure. This is the loss of Cd, and eventually of As, as the substrate temperature is increased. This result should be

Figure 11. Dependence of sputtered CdSiAs_2 film composition on substrate temperature. Solid CdSiAs_2 target, 150-200W power; 7mTorr pressure.

viewed as only preliminary, since the target itself was Cd deficient, and other deposition variables have not yet been systematically studied.

Initial films sputtered onto glass had roughly the target composition (Cd deficient) and were amorphous as evidenced by x-ray diffraction. It has been found that both film composition and crystallinity can be improved by heat treatments with Cd and As vapor ambients. Some of these heat treatment results are shown below in Table 4.

TABLE 4: Sputtered CdSiAs₂ Film Heat Treatments

<u>Temp</u>	<u>Time</u>	<u>Ambient</u>	Composition (%)		
			<u>Cd</u>	<u>Si</u>	<u>As</u>
615°C	17 hrs	Cd vapor	23	28	48
615	19	Cd	42	17	42
615	7	Cd	38	19	44
610	13	Cd+As	25	26	49
610	24	Cd+As	25	27	48
610	5	Cd+As	25	27	48
585	24	Cd+As	24	28	47

Initial film compositions were roughly 18% Cd, 27% Si and 55% As. X-ray diffraction analysis reveals that all of the above films have some degree of crystallinity, although grain sizes could not be determined due to cracks and pores in the films. Micrographs of films before and after heat treatment are shown in Figure 12. X-ray patterns for amorphous (before heat treatment) and crystalline (following heat treatment) films are shown in Figure 13 for Cd and Cd+As ambients.

The following conclusions related to these heat treatments can be made:

1. Heat treatment in an ambient of Cd and As at $\approx 600^\circ\text{C}$ can bring non-stoichiometric films up to near stoichiometry.

Figure 12. Micrographs of sputtered films before (upper) and after (lower) heat treatments.

Figure 13. X-ray diffraction patterns of CdSiAs_2 films (a) as sputtered, (b) heat treated in vacuum at 615°C for 17 hrs. and (c) heat treated in vacuum at 610°C for 24 hrs.

2. The resulting films change in structure from amorphous to crystalline.

3. The mechanical integrity of the films is severely degraded.

Thus, even though the resultant films are crystalline and near stoichiometric, they are unsuitable for p-n junctions or even transport measurements. However, as the sputtering program improves, heat treatments such as this might be useful for making finer adjustments in stoichiometry and for improving crystallinity, assuming that the as-deposited films are not amorphous. Variations of heat treatments of this type will continue in an effort to better understand and optimize them as the films improve.

2.2.2 Using Si + CdAs₂ Composite Targets Two sputtering targets were fabricated by attaching CdAs₂ discs into Si plates. Holes were formed into 1/8" thick x 4" dia. Si plates by means of a core drill. CdAs₂ ingots 0.9 cm in diameter were prepared as described previously. The ingots were cut into slices so as to fit flush into the Si plate and were attached with epoxy.

Two configurations have been fabricated. In the first, mainly for an initial feasibility study, a single CdAs₂ disc was inserted into the center of a Si plate. In the second, 30 CdAs₂ discs were imbedded in a Si plate in a hexagonal array. These configurations are shown in Figure 14.

Only two runs were made using the "bulls-eye" (single CdAs₂ disc) target. This is because the resulting compositions were poor, and the mechanical integrity of the arrangement was proven. It was not anticipated that CdSiAs₂ would result from this target, but it was hoped that an initial calibration, and verification of mechanical integrity, could be obtained.

The films as grown from this target were uniform in composition across 2" of the substrate plane, and were amorphous. The composition, as determined

Figure 14. Composite Si + CdAs₂ sputtering targets

by microprobe analysis, was Cd ~ 0.4%, Si ~ 91.6% and As ~ 8.0%. The high Si content was expected, but the large difference between Cd and As was not.

With the multi-disc target, films were deposited initially onto water cooled substrates, and were amorphous. Films were seen by microprobe analysis to be uniform in composition across 2" of the substrate plane.

Film composition is a strong function of sputtering power. This dependence is shown in Figure 15. As the sputtering power is increased, the Cd and Si contents of the films apparently approach equality at about 165 watts. It is planned to concentrate on this power region (160-170 watts) for the next set of samples.

2.3 EVAPORATED FILMS

We have found no reports of CdSiAs_2 thin films in the literature. Over this reporting period, only single source evaporation of CdSiAs_2 has been studied. It was anticipated that the Si vapor pressure over the molten compound would be significantly less than for Cd or As⁽²³⁾, and that evaporated films would be rich in the latter two elements. This was found to be the case.

The bulk CdSiAs_2 charges were synthesized as described earlier in section 2.1.2. Evaporations were carried out in a Denton Mod 503 system from a graphite source bottle contained in a cylindrical Ta heater. On each run, four substrates were utilized: one of polished Al (for microprobe measurements); one soda-lime microscope slide, and two Corning No. 7059 borosilicate slides. The source temperature was monitored throughout the run by means of a Pt-Pt/10% Rh thermocouple and a strip chart recorder.

Figure 15. Dependence of film composition on sputtering power.

Runs were conducted at peak source temperatures of 570°, 618°, 713°, 812° and 1010°C. Substantial vapor effusion was seen starting at about 620°C, becoming negligible below the peak temperature (if above 620°), indicating depletion of volatile species from the charge.

The evaporated films were analyzed by x-ray diffraction, electron microprobe and SEM/EDAX. Source bottle residue was analyzed by means of x-ray powder diffraction.

Film compositions deduced from microprobe data are shown in Table 5. (For this series, substrates were maintained at room temperature, and all films are amorphous.)

TABLE 5: Electron Microprobe Analysis of Evaporated Films

<u>Run No.</u>	<u>Source Peak Temp (°C)</u>	<u>Film Composition (at. %)</u>			
		<u>Cd</u>	<u>As</u>	<u>Si</u>	<u>Cd/As</u>
CSA-7	570	37.4	62.5	0.2	0.60
CSA-4	618	41.3	58.5	0.2	0.71
CSA-5a	713	27.1	72.8	0.1	0.38
CSA-5b	713	26.0	72.8	0.2	0.36
CSA-6	812	4.0	95.2	0.8	0.04
CSA-9	1010	2.1	95.5	2.4	0.02

The data in Table 5 do not represent average compositions since the films are not uniform in a vertical direction, due to the preferential evaporation. The data does, however, indicate that Cd and As are initially preferentially evaporated in that order to exhaustion, followed by Si. This trend is verified by x-ray analysis of the charge residues. Crystalline phases identified here are indicated in Table 6. The SiAs component of the

residue becomes weaker as source temperature is increased, with elemental Si being predominant at higher temperatures. It should also be noted that several films were examined by means of SEM/EDAX, the results agreeing with those of the microprobe.

TABLE 6: X-ray Diffraction Analysis of CdSiAs_2 Source Residue

<u>Run No.</u>	<u>Source Peak Temp (°C)</u>	<u>Phases Identified</u>	
		<u>SiAs</u>	<u>Si</u>
CSA-7	570	weak	-
CSA-4	618	strong	-
CSA-5	713	strong	-
CSA-6	812	weak	strong
CSA-9	1010	-	strong

The above results related to the thermal decomposition of CdSiAs_2 in vacuum can be summarized in the following equation:

This stepwise decomposition is compatible with the high As compositions at temperatures above 800°C , and with the residue analyses. Nearly all the Cd is contained in an initial layer formed between 570 and 710°C . Then a layer of nearly pure As is deposited on this in the 710 - 1010°C range. To see this trend more distinctly, composition profiles would have to be obtained.

The major conclusion from these tests is that formation of CdSiAs_2 films by means of thermal decomposition of CdSiAs_2 bulk material in vacuum does not appear feasible. An alternate technique that will be tried in the near future is discussed in the next section.

3. NEXT QUARTER PLANS

1. Sputtered Films - Runs will continue with the multi-disc composite target. The power region of 160-170 watts will be investigated more extensively in an effort to improve film composition. The dependence of crystallinity and composition on substrate temperature will also be studied.

2. Evaporated Films - The dual source technique will be set up. Silicon deposition by means of e-gun will first be studied, and a modified thermal source will be installed for CdAs_2 . The objective is to determine the feasibility of this method for producing CdSiAs_2 films.

3. Film Characterization - More extensive measurements of film properties will be made this period. Microprobe, x-ray and SEM/EDAX measurements will continue for routine characterization. Additional studies will include optical absorption and carrier concentration, and effects of processing on those parameters. Heat treatments of films will continue in an effort to improve stoichiometry and crystallinity.

4. Solar Cells - It is planned to form heterojunctions with CdS on improved bulk CdSiAs_2 . The objectives are to test recent bulk material for photovoltaic response and to define a preliminary standard for thin film cells to be fabricated later in the program.

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