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CdSiAs₂ THIN FILMS FOR SOLAR CELL APPLICATIONS

Final Report, April 9, 1979—April 8, 1980

MASTER

By
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June 1980

Work Performed Under Contract No. AC02-79ET23007

Virginia Polytechnic Institute and State University
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CELL APPLICATIONS

FINAL REPORT: 4/9/79-4/8/80

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June, 1980

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ABSTRACT

Compounds of Cd-Si-As required for sputtering targets and evaporation charges were synthesized by direct fusion. These include CdSiAs_2 , Cd_3As_2 , CdAs_2 and SiAs . Polycrystalline ingots of CdSiAs_2 were found to be porous, with the chalcopyrite structure, and with minor amounts of other phases such as CdAs_2 , SiAs , As and Cd_3As_2 .

Sputtered films were formed in a single target RF system. A homogeneous CdSiAs_2 target was initially used, followed by composite targets consisting of $\text{CdAs}_2 + \text{Si}$. Films from the latter targets were superior to the others and were more extensively studied. As deposited films were amorphous, off stoichiometry, with resistivities over $10^8 \Omega\text{-cm}$ and band gaps of $\sim 1.4 \text{ eV}$. Subsequent reactive heat treatments in the $515^\circ - 615^\circ\text{C}$ range resulted in crystalline films, resistivities of $1-10 \Omega \text{ cm}$, CdSiAs_2 compositions within 1% of stoichiometry, energy gap of $\sim 1.55 \text{ eV}$, absorption coefficient of $2 \times 10^4 \text{ cm}^{-1}$ at $0.6 \mu\text{m}$, but with poor mechanical properties (mainly cracking). A Ta/SiO_2 substrate proved to be the best for these films.

Thermal evaporation studies of CdSiAs_2 established that effusion is preferential toward Cd between 570 and 710°C , and toward As in the $710-1010^\circ\text{C}$ range. All films resulting from CdAs_2 charges were found to be Cd deficient. For these reasons, over the last 6 months of the program, only sputtered films were studied further.

Preliminary $\text{CdSiAs}_2/\text{CdS}$ junctions were formed on bulk and sputtered CdSiAs_2 . The bulk junctions produced photoresponse up to 0.25V and several μA . The thin film junctions were rectifying, but generated insignificant photoresponse, apparently due to the poor properties of the CdSiAs_2 films.

A new multi-target sputtering unit (Perkin-Elmer Mod 2400 8-J) was installed toward the end of the program, although no Cd-Si-As films were made by 4/8/80 (conclusion of contract.)

TABLE OF CONTENTS

	<u>page</u>
ABSTRACT	1
TABLE OF CONTENTS	2
1. INTRODUCTION	3
1.1 BACKGROUND	3
1.2 PROGRAM OBJECTIVES	5
2. TECHNICAL NARRATIVE	6
2.1 BULK SYNTHESIS	6
2.2 SPUTTERED FILMS	16
2.3 EVAPORATED FILMS	50
2.4 HETEROJUNCTION FABRICATION	62
3. REFERENCES	66
4. RESEARCH CONTRIBUTORS	67
5. DISTRIBUTION LIST	68

1. INTRODUCTION

This is the Final Report for DOE Contract No. DE AC04 79ET23007, "CdSiAs₂ Thin Films for Solar Cell Applications".

1.1 Background

The major reasons for studying CdSiAs₂ as a photovoltaic absorbing material were reviewed in the First Quarterly Report.⁽¹⁾ The following facts are significant in this regard:

- a) The CdSiAs₂ band gap is direct and close to the predicted conversion efficiency maximum;
- b) The lattice mismatch with CdS is less than 0.6%, making a heterojunction with this compound feasible;
- 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;
- e) For possible long term terrestrial applications, availability of materials should not pose a problem⁽²⁾, and several less expensive technologies exist for CdS thin film formation.

Using tabulated parameters, a preliminary band diagram was constructed for the CdSiAs₂/CdS heterojunction, with assumed carrier concentrations of 10^{16} cm^{-3} and 10^{18} cm^{-3} for CdSiAs₂ and CdS respectively. This diagram is shown in Figure 1. Key points here are that an aiding electric field exists in the CdSiAs₂ absorber, and no interfacial spike exists in the conduction band.

Thus, on paper, CdSiAs₂ as a potential photovoltaic absorber, especially when combined with a CdS collector, appears attractive.

Figure 1. Theoretical CdS/CdSiAs₂ Band Diagram

1.2 Program Objectives

The major objective of the program was the formation of CdSiAs_2 thin films suitable for heterojunction solar cells. The tasks⁽³⁾ are summarized below, and research related to them is reviewed in the following section.

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 irradiation.

2. TECHNICAL NARRATIVE

The discussion below is divided into four areas: Bulk Synthesis (2.1), Sputtered Films (2.2), Evaporated Films (2.3) and Heterojunction Formation (2.4). Experimental techniques used, characterization, results and conclusions will be discussed in each case.

2.1 Bulk Synthesis

This was the initial task that was addressed, and was discussed in some detail in the First Quarterly Report⁽¹⁾.

CdSiAs_2 bulk material was required for subsequent tasks, namely for sputtering targets and evaporation charge. Polycrystalline CdSiAs_2 bulk (with crystallites up to several mm in length being obtained) were formed by direct fusion of the elements, in ampoules approximately 12 cm long. The ampoule was positioned vertically in a furnace such that the temperature at the upper end was in the range 650–850°C. Temperature decreased down the ampoule. The SiAs pieces at the top of the ampoule floated on the CdAs_x and dissolved at a rate determined by the temperature. The dissolved SiAs established a concentration gradient in the CdAs_x that drove diffusion. The temperature gradient controlled the diffusion process. Super-saturation and crystallization of CdSiAs_2 occurred at the colder end of the ampoule.

Subsequent to this formation process, different ampoules received different quenching and heat treatment operations. This was necessary due to the fact that the equilibrium melting behavior of CdSiAs_2 is incongruent, thereby introducing compositional inhomogeneity into directly solidified ingots from stoichiometric melts.

X-Ray Analysis

The x-ray diffraction data for CdSiAs_2 ingots solidified from the melt

indicated that CdSiAs_2 was the major phase present. Subsequent heat treatments were found which reduced other phases to levels beyond detection via x-ray diffraction. Water, air and furnace quenchings were investigated, followed by heat treatments in certain cases.

X-ray data for a water quenched ingot is shown in Table 1. This ingot, as quenched, had a greater amount of CdSiAs_2 in the bottom section, with SiAs as a major phase at the top. A subsequent heat treatment at 825°C for 5 hours eliminated all phase peaks from the pattern other than those of CdSiAs_2 .

Table 2 shows x-ray data for a run which was water quenched from 950°C after soaking at 1050°C . No peaks corresponding to material other than CdSiAs_2 could be found in this case.

Rapid air quenching of molten CdSiAs_2 onto a cooled metal plate was also effective in minimizing inhomogeneity. SiAs_2 x-ray peaks were still detected however.

Electron Microprobe Analysis

Electron microprobe analyses of CdSiAs_2 ingots located pockets of minor phase materials in every ingot. Some ingots that had been heat treated had substantially fewer zones of phase separation from the CdSiAs_2 . Table 3 lists samples with phases identified therein by electron microprobe. It can be seen that CdAs_2 , SiAs , As and Cd_3As_2 were the minor phase materials. The solidification of the Cd-Si-As system is discussed shortly.

Microscopy

A photograph of a CdSiAs_2 chunk is shown in Figure 2. The large crystals are CdSiAs_2 , as determined by microprobe analysis. The chunk had broken off the parent ingot and is about 1 cm. long.

TABLE 1

X-Ray Diffraction Peak Positions ($^{\circ}2\theta$) For Bulk CdSiAs_2 , Run 18

Powder	Bottom of Ingot	Top of Ingot	Top of Ingot--HT	hkl
17.1	17.1	17.1	17.1	101
		19.8		112 Cd_3As_2
		22.4		200 CdAs_2
25.8	25.8	25.8		402 SiAs
27.0	27.0	27.0	27.0	112
28.1		28.2		220,004 Cd_3As_2
28.9	28.9		28.9	103
29.2		29.3		003 SiAs
30.0	30.0	30.0		310,311 SiAs
35.1	35.1	35.1	35.1	211
		39.3		301 CdAs_2
42.6	42.5		42.5	213
43.5	43.4	43.5	43.5	220
44.4	44.4		44.4	105
45.4	45.4	45.4	45.4	204
		45.9		313 SiAs
			47.1	301
	47.7	47.8		311 $\alpha\text{Cd}_3\text{As}_2$
	49.6			
51.8	51.8		51.8	
51.9	51.9	51.9		312
		53.2		312 CdAs_2
55.3	55.3	55.3	55.3	116

TABLE 2

X-Ray Diffraction Peak Positions
($^{\circ}2\theta$) For Bulk CdSiAs₂, Run 25,
Water Quenched

$^{\circ}2\theta$	I/I_0	hkl
17.1	2	101
27.0	100	112
29.0	2	103
35.1	15	211
43.4	15	220
45.4	30	204
51.9	20	312
55.3	5	116

TABLE 3

Phase Identification in CdSiAs_2 Ingots
by Electron Microprobe Analysis

Ingot	Phases Identified
R71	CdSiAs_2 , CdAs_2 , Cd_3As_2
R73	CdSiAs_2 , CdAs_2 , Cd_3As_2
R74	CdSiAs_2 , CdAs_2 , Cd_3As_2 , As
ST-1	CdSiAs_2 , CdAs_2 , Cd_3As_2 , SiAs

Figure 2. Photograph of a CdSiAs_2 Chunk Showing Large CdSiAs_2 Crystals, Run 71

Mechanical Quality

The CdSiAs_2 ingots had non-uniform morphology, some degree (varying) of phase separation, and extensive porosity. These factors all contributed to a very low quality mechanical characteristic. The major property of the material was its brittleness. With the non-uniform properties mentioned, the brittle material easily crumbled when stressed. Some samples did not form ingots but formed flakes. This effect occurred as a result of turbulence in the melt that was "frozen in" during quenching.

Discussion

We have been able to form near-stoichiometric samples of bulk CdSiAs_2 by means of direct fusion of the elements. From these studies, the ternary system Cd-Si-As can be represented as shown in Figure 3. CdSiAs_2 is the only ternary compound known to exist in the system⁽⁴⁾. A region of glass formation determined by Houserova and Hruby is represented. The compatibility triangle drawn is between CdSiAs_2 , Cd_3As_2 and SiAs. It is based on electron microprobe data of Table 3.

This compatibility relationship is sub-solidus in nature and thereby holds for temperatures below 821°C for stoichiometric CdSiAs_2 batches (with no loss of elements to the vapor phase). The starting composition of a CdSiAs_2 batch is at the edge of the triangle. Losses of As_4 vapor from the melt change melt composition such that melt composition is located within the Cd_3As_2 - CdSiAs_2 - SiAs compatibility triangle. Losses of both Cd and As_4 vapors (often condensing as CdAs_2) also cause a compositional change moving melt composition to the interior of the triangle.

The melt composition actually loses both Cd and As_4 vapors thereby changing the effective melt composition to a point located in the Cd_3As_2 - CdSiAs_2 - SiAs compatibility triangle. The resulting melt solidifies into

Figure 3. Diagram of the Cd-Si-As System Showing One Subsolidus Compatibility Relationship and the Glass Forming Region Determined by Houserova and Hruby⁴

three phases on cooling: SiAs ($T \leq 1083^\circ\text{C}$) followed by CdSiAs_2 ($T \leq 944^\circ\text{C}$) and then by Cd_3As_2 ($T \leq 721^\circ\text{C}$) (see Table 4). The x-ray diffraction data indicate that there is indeed a melt composition change due to the loss of Cd and As_4 vapors as shown by the solidification of SiAs , CdSiAs_2 and Cd_3As_2 . The presence of small amounts of CdAs_2 can be interpreted as condensation products from the Cd and As_4 vapor phase above the melt. This condensate forms on the surface of the ingot and on the surface of the many pores distributed throughout the highly porous ingot.

The presence of free As in the ingot can be understood as also being a condensate. It was found in the presence of CdAs_2 and Cd_3As_2 indicating that condensation sites are adjacent and that condensation occurs in sequence. The free As and CdAs_2 co-condense from an arsenic rich vapor phase with free As ($T_m = 817^\circ\text{C}$, 28 atm) preceding CdAs_2 ($T_m = 621^\circ\text{C}$).

The solidification process of CdSiAs_2 melts occurs with simultaneous evolution of Cd and As_4 vapors from the hot melt in response to a condensation of these vapors on cold surfaces of the container, the external surface of the ingot, and the ingot pore surfaces. Besides the relatively indirect evidence for this behavior found in the subsolidus compatibility relationships, the obvious "constitutional" gradient found in some ingots as well as condensates on ampoule walls give further evidence of extensive vaporization and condensation.

The direct quench solidification of large ($>1\text{g}$) batches of CdSiAs_2 is especially difficult due to the turbulence mentioned above. Any further work in this area should be conducted with small batches ($< 2\text{g}$) such that very little thermal gradient would be established during quenching. Smaller batch size would also have the additional benefit of increasing the quench rate. This would bring about a minimization of peritectic dissociation

TABLE 4

Properties of Compositions in the Cd-Si-As Ternary System

Composition	Density (gm/cm ³)	Melting Point (°C)	Melting Behavior	Vapor Species	References
Cd	8.64	321	Simple	Cd	93,94
As	5.73	817 (28 atm)	Sublimes 613°C	As ₂ /As ₄	93,94
Si	2.33	1420	Simple	Si ₂	93,94
Cd ₃ As ₂	6.31	721	Congruent	Cd As ₂ /As ₄	94
CdAs ₂	5.88	621	Congruent		91-93
SiAs	3.82	1083	Congruent	As ₂ /As ₄	92,94
SiAs ₂	--	944-1040	Incongruent	As ₂ /As ₄	94
CdSiAs ₂	5.12	821-943	Incongruent Sublimes 620-800	Cd As ₂ /As ₄	68,69, 84

during the solidification of the ingot. A comparison of x-ray diffraction patterns such as those of Tables 1 and 2 shows that a qualitative decrease in ingot heterogeneity occurs with increasing quench rate (i.e., furnace quench being relatively slow, air quench being more rapid, and water quench being most rapid).

Smaller batch size would be about a lower thermal gradient across the batch thereby minimizing batch heterogeneity in both the chemical and microstructural senses. The increased microstructural homogeneity in a small batch would have the advantage of optimizing the heat treatment homogenization of the batch. Small, uniform grains with high surface to volume ratio in the ingot would provide more surface free energy to drive the interdiffusion of material as well as provide shorter paths to reaction zones.

2.2 Sputtered Films

Experimental Techniques

The initial objective was to prepare stoichiometric CdSiAs_2 films from a macrohomogeneous target of CdSiAs_2 . Subsequent efforts used composite targets of CdAs_2/Si , as described below.

The radio frequency sputtering system used to deposit Cd-Si-As thin films consisted of a commercial sputtering module (R. D. Mathis Model SP 310) mounted on a vacuum system utilizing a turbomolecular pump (Welch, Model No. 3102). The sputtering parameters used are listed in Table 5.

The film thicknesses were determined by weighing the substrates on a microbalance before and after deposition, and assuming a composition of CdSiAs_2 of near theoretical density, 5.0 gm/cm^3 . These thicknesses were in good agreement ($\pm 5\%$) with those obtained by optical interferometry.

The rate of material removal from the target was also monitored by determining the geometrical profile of the target surface with a sheet metal

TABLE 5

Sputtering Parameters Used in the Deposition
of CdSiAs₂ Thin Films

Sputtering Target	rf Power (Watts)	Argon Pressure (m Torr)	Substrate Heating (°C)	dc Voltage (KV)	Duration (Hr)
CdSiAs ₂	40-220	5-32	RT to 535	1.5-4.0	3.0-7.5
Bulls Eye (BE)	80-190	7-16	-	0.7-1.8	2.5-6.0
HEX A	100-200	9-32	-	0.4-2.3	1.5-3.5
HEX B	100-200	9-12	-	2.0-3.0	3.0-6.0
HEX C	100-200	7-15	-	2.1-3.3	3.5-4.0
Ta	140-150	7-13	-	2.0-2.6	2.5-3.5
Mo	135	13	-	3.0	3.3

micrometer.

Target Fabrication

The CdSiAs_2 was prepared by direct fusion of CdSiAs_2 that had previously been synthesized by direct fusion from the pure elements. Crushed pieces of CdSiAs_2 (containing small amounts of CdAs_2 , Cd_3As_2 and SiAs) were placed in a fused silica cylindrical container which contained a 3" graphite disk on which the CdSiAs_2 rested. The container, 3 1/4" in diameter and 2" high, was evacuated and sealed. It was then heated and quenched by sitting it on an aluminum plate. This target had an irregular shape approximately 2" in diameter and 1/4" thick. It was bonded to an aluminum backing plate with conducting epoxy.

A composite target is illustrated in Figure 4. These were prepared by core drilling 23/64" holes in a 3" diameter polycrystalline silicon plate and inserting 11/32" CdAs_2 disks into those holes. The silicon and inserts were bonded to a 3 1/4" diameter copper backing plate, with thermosetting epoxy.

The CdAs_2 inserts were synthesized by weighting stoichiometric quantities of pure cadmium (5N) and arsenic (6N) into hollow graphite cylinders, which were in turn sealed into evacuated heavy-wall silica tubing. The graphite liners kept the final ingot from fracturing on cooling.

The resulting CdAs_2 ingots were found to be single phase and crystalline by the electron microprobe and x-ray diffraction analysis. (Its relative ease of synthesis is associated with its eutectic melting and solidification behavior.) The ingots were sectioned into disks on a diamond saw. They were ultrasonically cleaned in acetone and methanol.

Four composite targets were fabricated. The first was a silicon disk with a single CdAs_2 disk bonded at its center (Bulls Eye--BE). It was used to characterize the geometry of sputtering from a single insert as a test

Figure 4. Photograph of Composite Sputter Target HEX A

of possible imaging effects between the two-phase target and the substrate plane.

The other three composite targets (HEX A, HEX B, and HEX C) consisted of a Si plate with CdAs_2 disks inserted in a hexagonal array. The number and spacing of the inserts were chosen to yield Si/ CdAs_2 area ratios of 1.00, 1.47 and 2.27 (HEX A, HEX B and HEX C).

Heat Treatment

Sputtered films were subjected to various heat treatments. The most frequently employed method was heat treatment in evacuated vycor ampoules having approximately 0.1 gram of CdAs_2 included along with the film. The CdAs_2 provided an overpressure of Cd As_4 and As_2 in order to avoid losses of Cd and As from the film and to attain stoichiometry by incorporation of Cd or As into the films. Other methods used were: heating in sealed, evacuated vycor ampoules without CdAs_2 ; heating in sealed evacuated vycor ampoule with Cd; and heating in air.

The films heat treated were on the following substrates: fused silica, Corning 7059 glass, Mo-coated fused silica, Ta-coated fused silica, Ta-coated 7059 glass, Mo shim stock (0.002"), and stainless steel shim stock (0.001" and 0.002").

Results and Discussion

Films From Ternary Target

The films formed by sputtering from the polycrystalline CdSiAs_2 target were cadmium deficient and amorphous. Attempts to induce crystallinity by heating the substrates were not successful. The effect of substrate heating on film composition as determined by electron microprobe is seen in Figure 5. The first substrate temperature shown is that obtained without applying power to the substrate heater. When the substrate heater was heated to only 270°C, the cadmium content had dropped to less than 2%, and became even

Figure 5. Effect of Substrate Temperature on Sputtered Film Composition Determined by Electron Microprobe Analysis: Films Deposited Using $CdSiAs_2$ Target

lower as higher substrate temperatures were used. At very high heater temperatures (above 400°C), the As content also dropped from 53% to 30%.

The cadmium content was also found to be a function of the previous service of the polycrystalline CdSiAs₂ target. It was found that the Cd content dropped from 21% to 10% over three 200 watt runs. It was evident that the target surface was becoming Cd deficient with continued use and this depletion was hastened, if not caused, by chamber heating during runs in which the substrate heater was turned on.

Composite Targets

Sputtering from the first composite target (BE), consisting of a single CdAs₂ disk at the center of a silicon plate, established that atom transport was diffusion controlled from target to substrate. The Cd and As atoms were evenly distributed over the entire substrate holder area, even though they originated from a small spot. This was shown by the microprobe elemental analyses of Cd, As and Si as a function of substrate location. This experiment confirmed that there would be no imaging effects between the two-phase targets and the substrates.

For the hexagonal composite targets, film composition was controlled by varying the Si/CdAs₂ area ratio of the target, by heat treatment, and by varying the power level used during sputtering.

The effect of the target Si/CdAs₂ area ratio on film composition is shown in Table 6.

Deposition rates: The deposition rates of amorphous Cd-Si-As films at the center of the substrate plane are shown in Table 7. The Si results for the bulls eye target indicate that the sputtered material condenses on an area 9 to 10 times larger than the target. The planar area of the substrate stage is approximately 50 square inches or 8.4 times the exposed area of

TABLE 6

Film Composition Determined by Electron Microprobe Analysis for Films Deposited on
Substrates Located At the Center of the Substrate Stage: rf Power
Fixed at 100 Watts; Comparison of Different Targets

Target	Si/CdAs ₂ Ratio	Composition (%)			Elemental Ratios		
		Cd	Si	As	As/Si	Cd/Si	As/Cd
	Stoichiometric CdSiAs ₂	25.0	25.0	50.0	2.00	1.00	2.00
HEX A	1.00	25.4	14.8	59.9	4.05	1.72	2.35
HEX B	1.47	25.7	17.6	56.7	3.22	1.46	2.21
HEX C	2.27	17.2	28.7	54.1	1.89	0.60	3.15
HEX C (Heat Treat at 600°C in Cd, As ₄ ambient)	2.27	24.2	26.3	49.5	1.88	0.92	2.04

TABLE 7

Deposition Rates For Films Deposited From the Composite
Targets at the Center of the Substrate Stage

Target/Run	Substrate	Power (Watts)	dc V (KV)	Rates			
				Thickness (Å/m)	Mass ($\mu\text{g}/\text{cm}^2\text{-m}$)	<u>Sputter Rate</u> Deposition Rate	
BE	1	7059	80	1.8	128	3.0	9.9
	2	7059	190	1.0	139	3.3	8.7
	3	7059	100	1.2	84	1.9	8.6
	4	7059	95	1.2	82	1.9	14.6
	5	7059	80	0.7	118	2.8	--
	6	7059	80	0.9	149	3.5	2.3
	7	7059	100	1.3	195	4.6	4.2
HEX A	1	7059	200	1.6	91	4.5	--
	2	7059	100	0.5	224	11.2	20.9
	3	7059	100	0.4	188	9.4	13.1
	4	7059	150	0.7	186	9.3	18.2
	5	7059	130	0.8	215	10.8	22.0
	6	7059	100	0.7	228	11.4	16.8
	7	7059	180	2.3	160	8.0	166.6
	8	7059	160	1.8	240	12.0	74.2
HEX B	1	7059	100	2.2	244	12.2	15.7
	2	7059	150	2.5	239	11.9	24.9
	3	7059	200	2.9	199	10.0	36.8
	4	Mo	150	2.5	66	3.3	--
	5	Mo	100	2.2	46	2.3	--
HEX C	1	7059	110	2.1	167	8.4	30.8
	2	7059	150	2.7	117	5.8	44.2
	3	7059	200	2.9	224	9.0	32.9
	4	Mo	200	2.8	112	4.5	59.7
	5	7059	100	2.1	147	7.4	35.3
	6	Mo	150	2.4	43	2.2	143.2
	7	SS	125	2.2	56	2.8	85.8
	8	Mo	90	1.9	39	1.9	143.3
	9	SiO ₂	90	2.1	156	7.8	28.8
	10	Mo/SiO ₂	100	2.0	119	6.0	78.5
	11	Ta/SiO ₂	90	1.9	112	5.6	36.2
	12	7059	90	1.9	153	7.7	26.3
	13	Ta/7059	100	3.0	104	5.2	40.7

the target. A certain smaller amount of material also deposited on the wall of the chamber. Therefore, relatively little resputtering of Si occurred as compared to Cd and As. In the case of target HEX A, the sputtering rates were from 13 to 167 times larger than the deposition rates. The great range indicates the sensitivity of Cd net deposition rate (and As to a lesser degree) to the sputter conditions. The larger discrepancies between CdAs₂ sputter rates and film deposition rates are most likely due to resputtering/backscattering phenomena. The last two runs of HEX A with relatively high dc voltages had large differences in sputtering and deposition indicating that dc voltage/rf power influenced both sputtering and resputtering rates.

This finding is consistent with all of the hexagonal targets for films on glass substrates. Films on metal shim stock and metal coated glass experience considerably more resputtering except for the case of Ta coated glass. In that instance the resputtering increase was slight. The increased resputtering losses of Cd and As could be seen more clearly in the light of poor metal-substrate contact. The poor contact was responsible for increased substrate heating that enhanced resputtering.

The ratios of sputtering rates to deposition rates for the BE target did not respond to changes in dc voltage. This is understandable in the light of the resistance of Si to sublimation/resputtering. They did respond, however, to the decrease from 3 to 2 inches in target-substrate separation. The effective deposition area was decreased by a factor of approximately 2 yielding films of twice the thickness. This effect is anticipated from a consideration of the system geometry.

It can also be seen that higher dc voltages were generally maintained

on targets HEX B and HEX C than on targets HEX A and BE. A corresponding increase in sputter yields resulted.

Film composition: The composition of deposited films did not closely resemble the material ratios sputtered from the targets, as already mentioned in the case of Cd deficient films deposited from target HEX C. The rf power levels used and the associated localized plasma heating of substrates were seen to influence the resulting film composition. As an example, the effect of rf power on film composition is shown in Figure 6 for target HEX A.

The dependence of film composition on substrate location is illustrated in Figure 7, for target HEX C. The other targets yielded similar results. The cadmium content was consistently less in the center of the substrate holder, and this effect was more pronounced at the higher power levels. The Si content nearly mirrors the Cd content. The Cd contents of the films varied about 1% over a central two centimeters where power levels of 100 and 150 watts were used. At 200 watts, the variation was 9.5%.

These Cd deficiencies at the center of the stage are associated with elevated temperatures at the film surface. Substrate temperature (as measured by a thin film sensor) versus sputtering power is shown in Figure 8. A center temperature of 480°C was measured when the power level was 200 watts, 410°C when the power level was 150 w, and only 270°C when it was 100 w. In the latter case, the temperature was 270°C at 2 cm from the center, and 150°C at 4 cm. These strong temperature profiles are due to the greater plasma densities near the center, and they cause more pronounced Cd resputtering there. The substrate temperature follows a T^4 relationship with rf power as was seen by other investigators⁽⁵⁾.

Compositions for several runs of films sputtered onto glass and metal

Figure 6. Effect of rf Power on Film Composition, Target HEX A

Figure 7. Effect of Power and Position in Cd Content in Sputtered Thin Films of CdSiAs₂, Target HEX C

Figure 8. Effect of rf Power on Substrate Temperature, Target HEX C

coated glass are shown in Table 8. The range of values for each component along with average value $\pm$ standard deviation are listed along with ratios As/Si, Cd/Si and As/Cd for each run. The general range of compositions was similar in each case, since the sputtering conditions were very similar with power levels of 90 to 100 watts.

On the average, the Cd content of the amorphous films was 3 to 3.5% below the "stoichiometric" value of 25% in all but the Ta coated glass specimens. Films on the Ta coated substrates had average Cd content at or near (-1.6%) the "stoichiometric" value. This effect when coupled with lower As content on Ta coated glass gave As/Cd ratios of 2.09 and 1.89-- much lower than for films on other substrates.

The average Si content was 27.2, 27.2 and 27.8% or 2.2 to 2.8% above the "stoichiometric" value in the case of films on metal coated glass substrates (either Mo or Ta). Films formed directly on glass had higher Si contents of 28.5 and 29.6%.

The average As values were either very close to the "stoichiometric" value of 50% or within 2% of it (i.e., a 4% deviation). The % deviation of As from the "stoichiometric" value (-4%) was much less than the deviation for either Cd, having a deviation of -14%, or Si which had a deviation of +12%. This indicated that variations in the film content were due in large measure to variations in Cd and Si content.

Heat Treatment

Of Films on Glass

Thin film $a\text{-CdSiAs}_2$ on glass was transformed from amorphous to crystalline CdSiAs_2 by heat treatment at 550°C to 615°C. Lower temperature did not provide enough thermal energy to effect the crystallization, and

TABLE 8

Low rf Power Sputter Deposition of Thin Films From Target HEX C Onto Glass and Metal Coated Glass Substrates--
Electron Microprobe Analysis of Film Composition

Run	Power (Watts)	Substrate	EMPA Range (%)			EMPA Average (%) ± S			Ratios		
			Cd	Si	As	Cd	Si	As	As/Si	Cd/Si	As/Cd
9	90	SiO ₂ Glass	15.5 - 28.0	24.3 - 31.4	46.9 - 53.4	21.5 ± 3.3	28.5 ± 1.8	50.0 ± 1.8	1.75	0.75	2.33
10	100	Mo/SiO ₂	17.2 - 25.4	24.5 - 29.4	48.9 - 54.3	21.5 ± 2.4	27.2 ± 1.5	51.3 ± 1.6	1.89	0.79	2.39
11	90	Ta/SiO ₂	18.3 - 27.7	25.8 - 31.5	46.0 - 50.8	23.4 ± 3.0	27.8 ± 1.7	48.8 ± 1.5	1.75	0.84	2.09
12	90	7059	18.2 - 26.3	26.2 - 32.1	46.6 - 50.0	21.9 ± 2.4	29.6 ± 1.9	48.4 ± 1.1	1.64	0.74	2.21
13	100	Ta/7059	20.5 - 28.7	25.3 - 29.7	45.4 - 50.3	25.2 ± 2.6	27.2 ± 1.2	47.6 ± 1.6	1.75	0.93	1.89
14	100	Ta	23.4 - 27.2	26.3 - 29.2	46.1 - 48.6	24.9 ± 1.2	28.0 ± 0.9	47.1 ± 0.7	1.68	0.89	1.89

higher temperature caused diffusion of film and substrate leaving the glass substrate tinted in appearance. As little as 3 hours effected the change.

The resulting crystal structure was the chalcopyrite structure of CdSiAs_2 . The crystals were extremely small as evidenced by broad peaks on the x-ray diffraction patterns and by low peak heights. Increasing the heat treatment duration from one day to one week was found to alter the film structure. The x-ray patterns of the longer heat treated films had narrower peaks, increased peak heights, and increased crystal texture as seen by the presence of more CdSiAs_2 peaks (Table 9).

The increased heat treatment time of one week brought about the noticeable effect of diffusion/reaction as evidenced by the presence of a non- CdSiAs_2 x-ray peak corresponding to As_2O_3 at $32.2^\circ 2\theta$.

The type of glass substrate was found to be of little significance in obtaining crystalline CdSiAs_2 films. The large thermal expansion mismatch of CdSiAs_2 films and fused SiO_2 resulted in film cracking and in a few cases of peel off. Films on Corning 7059 glass tended to be pitted. They may have been due to insufficient cleaning and/or to thermal expansion mismatch.

Of Films on Metal Coated Glass

Molybdenum coated silica was found to be an unsatisfactory substrate material due to loss of adhesion of Mo during heat treatment.

Tantalum coated silica served well as a conductive substrate material in that the Glass-Metal and Metal- CdSiAs_2 bond strengths were sufficient to maintain a good degree of mechanical integrity in spite of high thermal expansion stresses. Cracks were observed extending from the glass-metal interface through the Ta into the CdSiAs_2 . This is seen in Figure 9. No cracks were observed in the Ta that had not been covered by CdSiAs_2 . No appreciable loss of film occurred as a result of the cracking. This

TABLE 9

X-Ray Diffraction Pattern of Heat Treated Films on Glass: One
Day Duration Compared to One Week Duration

1 Day			1 Week			hkl
d(Å)	2θ	I/I ₀	d (Å)	2θ	I/I ₀	
5.185	17.1	2	5.185	17.1	7	101
3.314	26.9	100 (250 cps)	3.314	26.9	100 (700 cps)	112
			3.084	28.95	10	103
			2.780	32.2		As ₂ O ₃
2.557	35.1	10	2.557	35.1	15	211
			2.132	42.4	5	213
2.080	43.5	15	2.083	43.45	20	220
			2.036	44.5	3	105
2.000	45.45	25	1.998	45.4	30	204
			1.945	46.7	2	222
			1.929	47.1	5	301
			1.870	48.7	5	
1.762	51.9	5	1.762	51.9	20	312
			1.658	55.4	10	116

Figure 9. Photomicrograph of $\text{CdSiAs}_2/\text{Ta}/\text{SiO}_2$ Thin Film on Glass Layer Structure Showing Cracks Initiating at Ta/SiO_2 Interface (260 x)

indicated that cracking relieved the residual thermal stresses while high interfacial bond strengths maintained the CdSiAs_2 -Ta-Glass layers intact. Extended heat treatment for periods of one week or more did not produce the same effect in films on Ta coated glass as in their counterparts on glass alone. The crystallites did not increase in texture or grain size. Totally unrelated XRD peaks were observed. The new peaks were found to be Ta peaks, indicating that diffusion of Ta into the CdSiAs_2 or loss of CdSiAs_2 into ambient had taken place. The introduction of Ta into the CdSiAs_2 lattice would have a deleterious effect on attainment of CdSiAs_2 crystal perfection. It is this factor that causes the difference between CdSiAs_2 on Ta coated glass (poorly crystalline) and CdSiAs_2 on glass (improved crystallinity) when both were heat treated for one week.

Of Films on Metal

Heat treated films on steel and moly shim stock exhibited diffusion/chemical reaction effects at temperature lower than the crystallization temperature ($\sim 500^\circ\text{C}$). This showed the unsuitability of these substrates for CdSiAs_2 films where post deposition heat treatments above 500°C are necessary.

Effect on Film Composition and Structure

The results of microprobe analysis of heat treated films are plotted in Figure 10. In this figure, Cd content ranges from 18% to 26%. The Si content ranged from 26.5% to 31.5% while the As content ranged from 47.5% to 50.3%.

The effect of heat treatment seen in Figure 10 was to narrow the compositional differences between the films and to generate films deficient in both Cd and As. For example, the Cd content of heat treated films ranged from 22% to 24%, the Si content ranged from 29% to 31%, and the As content ranged from 46.8% to 48.5%. The average Cd and As deficiencies were found

Figure 10. Compositional Changes Occurring in Heat Treated Films, HEX C--11

to be 2.3% and 2.5% respectively.

Properties of Films

The quality of films was not especially conducive to property measurements (primarily due to cracking) except in a few cases. It was found that films underwent a great change in their optical and electrical behavior due to crystallization.

Indium was found to form an ohmic contact to heat treated films, as evidenced by I-V linearity. Typical values for a heat treated film (No. 17, 615°C, 17 hours) are as follows: sheet resistance $12\Omega/\square$, resistivity $2.1\Omega\text{ cm}$ (across a range of $\pm 10\text{v}$).

The resistivity of amorphous CdSiAs_2 films was generally too high to measure with methods employed in the laboratory. The resistivity would therefore be greater than 10^8 ohm-cm . Comparison of the crystallized and amorphous films shows a greater than 10^7 decrease in resistivity due to crystallization. Resistivities of single crystal CdSiAs_2 reported in the literature range from 0.3 to 5.0 ohm-cm, which is very close to the resistivity measured for our heat treated films.

In like manner, optical properties of films also changed markedly with heat treatment. Amorphous films has absorption edge at about 1.39eV, similar to the band gap of 1.4eV reported for bulk a- CdSiAs_2 ^(6,7). On one of the better (i.e. less cracks) samples, the absorption coefficient at $0.6\mu\text{m}$ was measured to be $2 \times 10^4\text{ cm}^{-1}$, with an optical cutoff at 1.55eV.

Discussion of Heat Treatment of a- CdSiAs_2 Thin Films

Crystallization

The crystallization of CdSiAs_2 films occurs at temperatures greater than about 500°C. This compares with the crystallization of bulk a- CdSiAs_2

at temperatures of $480^{\circ}\text{C}^{(4)}$ and $520^{\circ}\text{C}^{(8,9)}$. The slightly higher recrystallization temperature may be due to the Cd and As deficiency of the films. This deficiency would have the effects of increasing the disorder of the film "structure" as well as increasing the relative Si content both of which would increase the amorphous film's resistance to atomic rearrangement and thereby recrystallization.

The amorphous film compositions are deficient in As in all cases and also deficient in Cd in all but two cases. The glass forming region in the Cd-Si-As system does not cover the compositions of the amorphous films. The region is located in a Si deficient region of the diagram. The maximum glass forming tendency composition is $\text{Cd}_2\text{SiAs}_7^{(4)}$. This discrepancy indicates that the films are highly metastable in the amorphous state and are substantially increased in stability on going through the glass to crystalline transition.

Film-Substrate Effects

Film-substrate effects arise from either of two interactions:

1. Thermal expansion coefficient difference related stresses and strains.
2. Interdiffusion of film and substrate constituents.

The thermal expansion of CdSiAs_2 is very likely to be similar to that of CdGeAs_2 for which thermal expansion data are available. The expansion of the latter compound is highly anisotropic with linear expansion in the a direction of $8.3 \times 10^{-6}/\text{K}$ and $0.4 \times 10^{-6}/\text{K}$ in the c direction ($T = 120^{\circ}\text{C}$) yielding a ratio of almost 21 to 1⁽¹⁰⁾. The linear expansion of CdSiAs_2 in the a direction is probably compatible with the linear expansions of 7059 glass, Ta metal, Mo metal and stainless steel. The linear expansion of CdSiAs_2 in the c direction is probably compatible with the linear expansion of fused silica ($0.5 \times 10^{-6}/\text{K}$).

Due to the large differences in thermal expansion coefficient between CdSiAs_2 and the substrate materials of this study, varying degrees of cracking were observed. The most notable case of cracking without extensive peel off occurs in films deposited on Ta coated 7059 glass (Figure 9).

Films deposited on fused silica exhibit less cracking than films on higher expansion materials. The inhibition of film contraction in the a direction is apparently less deleterious to film integrity than the imposition of contraction in the c direction.

The interdiffusion of film and substrate is a function of heat treatment duration and temperature as well as substrate composition. In the case of a- CdSiAs_2 on glass substrates the migration of atoms during heat treatment occurs principally within the films allowing time for film crystallization before an appreciable degree of interdiffusion with substrate occurs. The type of substrate has a strong bearing on the rates of diffusion of film and substrate constituents. Oxide glass substrates being more stable than base metal substrates do not interdiffuse with the films as rapidly. This is shown in that a- CdSiAs_2 films on stainless steel and Mo shim stock are found to diffuse into and react with the substrates at 500°C . The same type of films on glass do not diffuse and react to a similar extent until heated to temperatures in excess of 620°C (800°C).

In order for heat treatment to effect crystallization of films, the substrate needs to be very stable with respect to temperature and the film constituents. Steel and Ta shim stock do not fulfill this requirement. Glass fulfills the requirements very well while Ta coated glass meets the requirement moderately well.

The extension of heat treatment times from 6 hours to one week or more reveals that the Ta coating diffuses into the CdSiAs_2 film and that

a relatively small amount of interdiffusion followed by oxidation of As occurs for CdSiAs_2 on glass. The glass constituents do not diffuse into the CdSiAs_2 as much as do the Ta, but the x-ray diffraction evidence of diffusion/reaction products indicates that they were also mobile at 500°C . Larger grain size is found in films on glass. This was due to the fact that diffusion of Ta inhibits grain growth.

Effect of Heat Treatment on Film Composition

The clustering of heat treated film compositions in a region of Cd and As deficiency (with respect to stoichiometric CdSiAs_2) is shown in Figure 11. The projection of these points onto the Cd_3As_2 - CdSiAs_2 and the CdSiAs_2 - SiAs pseudobinary lines is shown in Figure 12.

The points are shown to exist in a region lying between Cd_3As_2 , CdSiAs_2 and SiAs . The films all have the CdSiAs_2 crystal structure as determined by x-ray diffraction. This indicates that the films are solid solutions of either Cd_3As_2 or SiAs in CdSiAs_2 . This is not surprising in view of the fact that complete solid solution has been found in the system CdSiAs_2 - ZnSiAs_2 ⁽¹¹⁾. Similar findings in related II-IV-V₂ compounds and systems have been made^(12,13). A large solid solubility of Ge in ZnGeAs_2 has been found⁽¹⁴⁾. Both CdGeP_2 and CdGeAs_2 are reported to have large homogeneity regions⁽¹⁴⁾. Up to 20% solid solubility of InAs in ZnGeAs_2 (chalcopyrite structure) has been determined⁽¹⁵⁾. ZnGeAs_2 also dissolves in InAs (zincblende structure) to a great extent (approximately 80%)⁽¹⁵⁾. ZnSnAs_2 and InAs form solid solutions in all proportions⁽¹⁶⁾. CdSnAs_2 and InAs also form solid solutions for all compositions⁽¹⁴⁾. About 50 mol% InAs was found to bring about transition from chalcopyrite to zincblende structure⁽¹⁷⁾. These findings show the similarity of CdSiAs_2 to other chalcopyrite semiconductors in this regard.

Figure 11. Diagram of the Cd-Si-As System (Limited in Composition to the Compositions Near to CdSiAs_2 With Either Cd and As Deficiencies or Both) Showing Compositions of Crystalline, Non-Stoichiometric CdSiAs_2 Thin Films

Figure 12. Pseudobinary Phase Diagram of the Cd_3As_2 - CdSiAs_2 and CdSiAs_2 - SiAs Joins Showing Observed CdSiAs_2 Solid Solution

The heat treated films had the chalcopyrite structure of CdSiAs_2 and were deficient in Cd and As due to the fact that the equilibrium vapor pressures of Cd and As_4 over the compound were not sufficiently reduced by the presence of CdAs_2 in the heat treatment ampoule.

This preparation method can be used successfully for the fabrication of homogeneous, crystalline CdSiAs_2 thin films that are nearly stoichiometric.

Models Describing Film Growth

The events occurring during sputter deposition of a- CdSiAs_2 films determine film composition, structure, and properties. Film composition can vary over an unrestricted range in the case of amorphous sputtered films. There is no stoichiometric selection process in effect during film deposition.

Amorphous film composition is determined by the impingement ratios of Cd, Si and As as well as by short range ordering of atoms into a random network of tetrahedra lacking long range periodicity (Figure 13). The different bond strengths of Cd to As and Si to As lead to different sticking/re-emission probabilities. The Si-As bond is stronger than the Cd-As bond as reflected in the melting points of SiAs_2 and CdAs_2 which are 944°C and 621°C respectively.

The stoichiometric composition is to be expected for films grown during sputtering of target HEX C at 100 watts rf power, as the impingement ratio of CdAs_2 to Si is close to the stoichiometric ratio. The observed film compositions are generally deficient in Cd and As. The discrepancy indicates that not all of the Cd and As remain in the film after arriving from the target. The loss of these film constituents is either occurring by backscattering or by re-emission processes. The end result is the same.

(a)

(b)

● Cd
□ As
○ Si

Figure 13. Schematic Drawing of the (112) Plane of CdSiAs_2 and $a\text{-CdSiAs}_2$

Two models are formulated to further describe the loss of Cd and As and to relate losses to film composition. The first model assumes that only Cd is lost from the growing film after arriving at the substrate. The As loss is assumed to be negligible. The second model assumes that both Cd and As are lost from the growing film after arriving at the substrate and that the re-emitted Cd is replaced by Si and Cd in equal quantities.

Comparison of the calculated results for each model with actual film compositions shows which set of deposition events is more likely to occur. In the following discussion, models are described, assumptions are stated, relationships of material losses to film compositions are derived, and film compositions are calculated for comparison purposes.

Model A

To begin modeling the sputter deposition process, the most simple set of conditions are assumed to hold. Since Cd content was found very low with respect to that of stoichiometric CdSiAs_2 , it is assumed that deviations in film composition from the "stoichiometric" composition are due to Cd losses alone. Relative increases in Si and As result. Normalization to 100% is used as a basis for comparison to observed results. The assumption is also made that Cd, Si and As are sputtered from the target in the ratio 1:1:2.

The objective of the model is description of the relative increase in Si and As and decrease in Cd resulting from the loss of a quantity of Cd designated as "x".

The assumptions made are:

1. Cd, Si and As are sputtered from the target in the ratio 1:1:2 and arrive at the substrate surface in that ratio.
2. The sticking coefficient of both Si and As is 1.

3. There is no re-emission of either Si or As.
4. Cd is re-emitted/backscattered in quantity x.

The calculation of normalized film compositions is discussed in detail elsewhere⁽¹⁸⁾.

The conclusions made from this model are:

1. The decrease in Cd is equal to the sum of the increases in Si and As.
2. The increase in As is twice that of Si.

Some possible events unaccounted for in the simple model are:

1. A loss of As on or after arrival at the substrate.
2. Substitution of Si for Cd on a vacated Cd site.

The second event makes mention of a Cd site. This refers to the concept already mentioned of short range ordering of two Cd atoms and two Si atoms (the "cations") around an As atom (the "anion") in a network of tetrahedra (Figure 13). The network is not very ordered as is crystalline CdSiAs_2 such that a Si atom substituting for Cd would not need to overcome large energy barriers. Short range order would inhibit As from substituting for Cd in that As would then be bonded adjacent to another As atom.

The amount of Si substituting for Cd can be approximated by assuming that one half of the x vacated Cd sites are filled with Si and the other half with Cd, due to equivalent influxes. If the Cd re-emission occurs a second time with $\frac{1}{2}x$ Cd loss, $\frac{1}{2}(\frac{1}{2}x)$ sites are replaced with Si and the remaining $\frac{1}{4}x$ with Cd. With sufficient time for many iterations to occur, the x Cd sites would be filled with Si. The time available for the iteration of the process is limited.

One can consider Figure 13 as a top view of the 112 plane of a growing film in an ideal crystal. Soon after a Cd atom is re-emitted from the film surface it is replaced by a Si or Cd atom. Arsenic atoms are condensing as

the nearest neighbors to the row of cations in which the Cd is located. The time available for the Cd site to be vacated and refilled is limited to the time in which a newly condensed As "covers" it. Since the arrival rate of As is nearly equal to twice that of Cd and Si, the re-emission/replacement process would be limited to one event per site.

Model B

A second model can be constructed to describe the relative changes in Cd, Si and As contents resulting from As and Cd loss with partial replacement of Cd by Si. The model is based on the following assumptions:

1. Cd, Si and As arrive at the substrate in the ratio 1:1:2.
2. Si sticking coefficient = 1.
3. Short range ordering occurs in which Cd and Si bond only to As, and As bonds only to Cd and Si.
4. Cd is re-emitted/backscattered in quantity x .
5. As is re-emitted/backscattered in quantity y ; $y < x$.
6. Si is not re-emitted.
7. Si replaces $\frac{1}{2}$ of re-emitted Cd.
8. Cd replaces $\frac{1}{2}$ of re-emitted Cd.
9. Interaction of Cd and As losses is negligible.

The results of this model can be summarized as:⁽¹⁸⁾

1. The increase of Si is slightly greater than the decrease of Cd.
2. The decrease in Cd is greater than that of As by a factor less than x/y .

Comparison With Actual Observation

The observed % deviations from the stoichiometric quantities of Cd, Si and As in CdSiAs_2 are listed in Table 10 for runs HEX C-9 through HEX C-13 along with the calculated % deviations for Model A and for Model B. The observed deviations show that Model A does not describe the actual

TABLE 10

Average Deviations From Stoichiometric CdSiAs_2 of rf Sputter
 Deposited $\alpha\text{-CdSiAs}_2$ Films Deposited From HEX C
 Target at rf Power = 90 to 100 Watts

	$\Delta\%$				
	Cd	Si	As	$\Delta\text{Si}/\text{Cd}$	$\Delta\text{As}/\Delta\text{Cd}$
<u>Run</u>					
9	-3.5	3.5	0	-1.0	0
10	-3.5	2.2	1.3	-0.6	-0.4
11	-1.6	2.8	-1.2	-1.8	0.8
12	-3.1	4.6	-1.6	-1.5	0.5
13	0.2	2.2	-2.4	11.0	-12.0
<u>Model</u>					
A					
x = 2.7	-2.1	0.7	1.4	-0.3	-0.7
B					
y = 2.8					
x = 2.8 · (2.7)	-3.1	4.6	-1.4	-1.5	0.5

sputter deposition process. The deviations in As content are most frequently negative. In the one case where the deviation in As content was positive, its magnitude was less than that of Si. The Si deviations were often found to be greater in magnitude than the Cd deviations.

Table 10 lists two calculated results of Model B assuming $x = 2.7 y$ and $y = 2\%$. The assumption of $x = 2.7 y$ is based on the fact that the heat of sublimation of As is 2.7 times that of Cd. The tendency for Cd to be re-emitted would therefore be higher than As, and a first approximation to the ratio of their re-emission rates would be the inverse ratio of their heats of sublimation.

Comparison of the observed results with calculated results of Model B accurately describes runs 9, 11 and 12. Run 9 could be described by setting y equal to zero.

2.3 Evaporated Films

The contract began with studies of both sputtered and evaporated films in parallel. Of particular interest was the question of whether stoichiometric CdSiAs_2 films could be obtained by direct thermal evaporation. This work concentrated on evaporation of the ternary compound (CdSiAs_2), followed by studies of a binary (CdAs_2). At this point, since feasibility of forming CdSiAs_2 by means of evaporation was not established, only sputtered films were studied further. The CdSiAs_2 and CdAs_2 thermal evaporation studies are summarized below.

CdSiAs_2 Evaporation

The major fraction of the CdSiAs_2 evaporation studies were made over the first four months of the contract, and are described in the First Quarterly Report⁽¹⁾.

Although no reports of CdSiAs_2 thin films have been found in the literature, some degree of prediction of the ternary thermal behavior may be afforded by a review of the characteristics of the elements and binary compounds in this system. Table 11 is a summary of such data. As indicated, both Cd and As are volatile at low temperatures. One might expect similar behavior in the combined state. The vapor pressure trends are, as expected, found to behave as $p(\text{As}) > p(\text{Cd}) \gg p(\text{Si})$ in this system.

Therefore, one might expect that in a non-equilibrium situation, arsenides in general may decompose with disproportionation. In this case,

TABLE 11.

PROPERTIES OF SOME COMPOSITIONS IN THE Cd-Si-As TERNARY SYSTEM

<u>Composition</u>	<u>Density (gm/cm³)</u>	<u>Melting Point (°C)</u>	<u>Vapor Species</u>	<u>Vapor Pressure (Torr)</u>		
				<u>200°C</u>	<u>600°C</u>	<u>1100°C</u>
Cd	8.64	321	Cd	5×10^{-3}	1×10^2	2×10^4
As	5.73	817 (28 Atm.)	As ₂ /As ₄	10^{-4}	8×10^2	8×10^4
Si	2.33	1420	Si ₂	-	-	$\sim 2 \times 10^{-6}$
Cd ₃ As ₂	6.31	721	Cd	$\sim 7 \times 10^{-4}$	17	1.1×10^3
			As ₂ /As ₄	$\sim 3 \times 10^{-3}$	17	7×10^2
CdAs ₂	5.88	621	Cd, As ₂ /As ₄	-	~ 20	$\sim 10^3$
SiAs	3.82	955-1083	As ₂ /As ₄	-	$* < 10^{-5}$	-
CdSiAs ₂	5.12	821-943	Cd	$* \sim 10^{-6}$	-	$\sim 10^3$
			As ₂ /As ₄		-	$\sim 8 \times 10^2$

* Suggested by this work

direct thermal vacuum evaporation should result primarily in evolution of the heavy element species, leaving some form of silicon compound behind.

A simple model for the evaporation and/or deposition behavior can be developed on the basis of the vapor flux from a simple sphere of the material⁽¹⁹⁾. Evaporations were performed in a Denton DV 503 18" bell jar system, utilizing a graphite source bottle heated by a Ta element. Source temperature was monitored during the runs using a Pt-Pt/10% Rh thermocouple imbedded in the source. Four 2.5 cm x 4.5 cm substrates (glass) were deposited per run. Film deposition was monitored by a Kronos QM-300 thickness monitor.

To determine the lowest measureable temperature of decomposition, the initial vapor effusion as registered by the thickness monitor was noted. In two different trials, initial deposition was noted at about 90°C and 0.6 microTorr in the one case, and again at 220°C and 15 microTorr in the second instance. The indication is that the lower temperature bound for decomposition is strongly dependent on the level of evacuation. One might also surmise from this data that oxidation reactions might proceed at rather low temperatures in normal atmospheric ambient. If the deposition is directly proportional to the evaporation, and if the evaporation follows this simple model, not being chemically rate-limited, the deposition also ought to follow a trend cubic in the time parameter at any given temperature. The form of the equation for deposition weight gain D as a function of time should then be:

$$D = at^3 + bt^2 + ct + d$$

and in this case the coefficient d may be given the value zero.

In simple evaporation one would expect the evaporation flux to be directly proportional to the vapor pressure, which in turn should follow the

well-known Clausius-Clapeyron relationship. If the evaporation is not simple, but rather requires a preceding disproportionation, the temperature dependence of evaporation flux should be more complex. Since the deposition flux should be related to the evaporation flux by a constant of proportionality, the coefficient c above should be directly proportional to the evaporation flux. A plot of $\log c$ against reciprocal temperature should indicate whether the evaporation is simple or complex.

The CdSiAs_2 material used was prepared as described earlier in this report.

As the evaporation source temperature was increased, the rate of deposition greatly increased. The condensation progress was recorded at various steady state source temperature levels in order to estimate the dependence of evaporation and deposition on time and temperature. Some typical results are given in Figure 14, which shows as characteristic curvilinear deposition, as suggested by the previous equation. The data were submitted for computer assisted least squares analysis to find a set of coefficients giving a good fit to the cubic polynomial expression. These coefficients are listed in Table 12, and the temperature dependence of the coefficient c , a deposition flux-related quantity, is shown in Figure 15.

A point-by-point check of the expressions gave very good correspondence with the observed data. From Figure 15, it is seen that the deposition flux first increases more rapidly than predicted from the $\log c$ against reciprocal temperature relationship, then falls off sharply. The indication is, of course, that the mechanism for evaporation is not a simple, direct one.

The behavior might be explained by a process limited by decomposition

Fig.14 - Deposition Progress of Films Derived from Thermal Decomposition of CdSiAs_2 .

TABLE 12
COEFFICIENTS FOR BEST LEAST-SQUARES
FIT OF DEPOSITION DATA TO CUBIC EQUATION

<u>Temperature</u> <u>(°C)</u>	<u>$ax10^5$</u>	<u>$bx10^3$</u>	<u>$cx10^2$</u>	<u>$dx10^2$</u>
510	3.37	-1.13	1.94	0.01
550	0.677	-0.626	5.01	-0.41
585	1.112	-2.072	13.68	1.67
620	385.8	-108.1	131.6	-0.70
714	22.34	-5.24	6.29	-0.12
810	48.26	-12.28	12.42	-0.65
913	9.14	1.68	2.41	-0.03

Fig. 15 - Temperature Dependence of Flux-related Deposition Parameter Coefficient c.

rate at low temperatures and exhaustion of decomposition products at high temperature, with evaporation rate controlling in the mid temperatures circa 600-650°C.

Evaporations of the ternary over several heating schedules indicated that the vaporizing species are products of the following stepwise decomposition reactions:

Films as well as source residue were analyzed by x-ray diffraction, electron microprobe and SEM methods. The major results are shown in Tables 13 and 14. The indications are that Cd and As are initially preferentially evaporated to exhaustion of the Cd, followed by emission of the remaining As. Thus the evidence from the films and residues correlate well and lead to the same conclusions. It should be noted that in no case were any of the resulting films found to have any crystalline structure. The only structure found in x-ray diffraction of the films was the broad, diffuse weak scattering at low angles characteristic of amorphous material.

The x-ray diffraction analysis of the bottle residues distinguished intensity peaks not attributable to any of the elements or known binaries in the Cd-Si-As ternary system. These peaks were further differentiated in that intensities designated as pattern A, and corresponding to lattice spacings of 4.02 and 4.99 Å appeared consistently in all the residues.

Wadsten⁽²⁰⁾ has studied the thermal decomposition of silicon arsenides and claims to have observed the compound Si_6As as resulting from heating of SiAs to 930°C. While this investigation does not support his findings, it was felt that pattern B of Table 13 might arise as such an intermediate phase. However, no correlation was found between the reported pattern for

TABLE 13
X-RAY DIFFRACTION ANALYSIS OF RESIDUE
FROM CdSiAs_2 EVAPORATION

Evaporation Source Temperature ($^{\circ}\text{C}$)	Diffraction Patterns Identified				
	CdSiAs_2	SiAs	Si	A	B
570	Very weak	Strong	-	Trace	Very weak
619	Trace	Strong	Very weak	Trace	Weak
712	-	Strong	Weak	Very weak	Weak
812	-	Weak	Strong	Weak	-
912	-	-	Strong	Weak	-
1010	-	-	Strong	Weak	-

TABLE 14
ELECTRON MICROPROBE ANALYSIS OF EVAPORATED FILMS

<u>Source Peak Temp (°C)</u>	<u>Film Composition (At. %)</u>			
	<u>Cd</u>	<u>As</u>	<u>Si</u>	<u>Cd/As</u>
570	37.4	62.5	0.2	0.60
618	41.3	58.5	0.2	0.71
713	27.1	72.8	0.1	0.38
812	4.0	95.2	0.8	0.04
1010	2.1	95.5	2.4	0.02

Si₆As and pattern B.

It is clear that the decomposition in vacuum of the ternary compound CdSiAs₂ proceeds in a stepwise fashion to produce first silicon arsenide, then silicon at a higher temperature. This behavior precludes the formation of homogeneous thin ternary CdSiAs₂ films by direct evaporation, since such films would inevitably be sharply graded in composition, and perhaps non-stoichiometric in the averaged composition due to other deposition-related effects.

The evaporation/deposition seems to follow the predicted cubic law, but is not simple. From the low temperature volatility, one might expect either that oxidation may occur readily under ambient atmospheric conditions, or that such oxidation had already occurred with the powders used.

CdAs₂ Evaporation

Following the CdSiAs₂ evaporation study, a study of CdAs₂ evaporation was initiated. The objective was to determine if a dual effusion setup, composed of CdAs₂ + Si sources would be feasible. Due to the preferential effusion of Cd and As species from the CdAs₂ charge, the above technique is not feasible. The situation could possibly be rectified by modifying the Cd-As charge composition - however due to time constraints this was not attempted.

The CdAs₂ study was described in some detail in the Second Quarterly Report, including a model for the decomposition and evaporation process.

For runs performed at several source temperatures, all films were Cd deficient⁽²¹⁾. This is seen in Figure 16.

One possible gross remedy for the non-stoichiometry problem would be to use a physical mixture of CdAs₂ and Cd₃As₂ powders as evaporation sources,

Figure 16. Cd-As film composition as a function of evaporation source temperature.

with enough Cd_3As_2 admixture to enrich the cadmium content of the film to achieve an apparent overall Cd/As ratio of 1:2. However, this would probably not satisfy the chemistry requirements on a microscale without post-evaporation treatment. In any case, x-ray data indicate the necessity of post deposition heat treatment to develop crystallinity.

The evaporation of CdAs_2 seems to follow a polynomial time dependence and a semilogarithmic temperature dependence. During evaporation, the CdAs_2 partially decomposed to a CdAs_3 α " phase and a third phase, as well as probably free arsenic.

From these general results, it was concluded that the direct formation of crystalline CdSiAs_2 thin films by co-evaporation of Cd/As material and Si from separate sources was not practical with the time and equipment restraints at hand.

2.4 Heterojunction Fabrication

Two types of preliminary junctions were fabricated. The first was with evaporated CdS on cut and polished bulk polycrystalline CdSiAs_2 (plus other minor phases), and the second was with evaporated CdS on heat treated CdSiAs_2 films.

For the first type, bulk CdSiAs_2 sections were cut from ingots with a diamond saw, mounted onto a 2"x1"x $\frac{1}{4}$ " copper plate with conducting epoxy, ground via SiC and polished successively with 1.0, 0.1 and 0.05 μm Al_2O_3 powder/slurry.

CdS was then sublimed onto this surface, which was maintained at 300°C.

Only a few of these were formed. Contact was made to the CdS by means of an In dot (0.5 mm) pressed onto the surface.

An open circuit voltage of over 200 mv was measured for one of the

devices, at a current of about $3.4 \mu\text{A}$. This device was series resistance limited, as indicated in the I-V curves of Figure 17. This is attributed mainly to the dot contact, but also to the thin CdS layer ($< \mu\text{m}$). The device degraded with subsequent heat treatments, but the feasibility of a rectifying, photogenerating junction was established.

Some CdSiAs_2 heat treated films were used to form CdS/ CdSiAs_2 junctions. These junctions should be viewed as very preliminary ones, due mainly to the non-optimized film properties (as described earlier). CdS was sublimed onto the CdSiAs_2 film, which was on a Ta/glass substrate. Rectifying behavior was observed, although with no measurable photoresponse. An I-V characteristic is shown in Figure 18.

Even though the photoresponses measured for the very few bulk and thin film cells that were fabricated were not large, the results are encouraging in that rectifying behavior is obtained with CdS and a measurable photoresponse was obtained. This is encouraging in that the bulk CdSiAs_2 was porous, brittle and not perfectly homogeneous in composition (i.e. the polished "surface" was still quite rough due to pores). The thin film CdSiAs_2 used for junction fabrication was cracked, non-stoichiometric and had very small grains. Thus, drastic increases in photoresponse are expected as the CdSiAs_2 is improved.

Figure 17. Current-Voltage Characteristic of an Illuminated Heterojunction Made From Thin Film CdS and Bulk, Polycrystalline CdSiAs₂, Run 52, Showing Photoresponse

Figure 18. Current-Voltage Characteristic of a CdS/CdSiAs₂ Thin Film Heterojunction

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