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IN VACUO THERMAL DECOMPOSITION OF CADMIUM SILICON DIARSENIDE, $CdSiAs_2$

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ABSTRACT

The thermal decomposition of $CdSiAs_2$ in vacuum was undertaken in order to deposit this film of potential photovoltaic and other electronics applications. A model for the evaporation process is presented which predicts a cubic time dependence of the film deposition process. The experimental deposition process approximated the cubic law. Deviations from it are attributed to the stepwise nature of the process: a film of SiAs is deposited, followed by the deposition of silicon.

INTRODUCTION

Ternary compounds of elements from the periodic groups II, IV, and V have long been of interest for their semiconductive characteristics [1]. The diamond-like chalcopyrite structure gives rise to electronic structure of use in electro-optic and semiconductor device technology [2]. In particular, $CdSiAs_2$ has been proposed for photovoltaic applications in view of its high spectral absorptivity, direct ionization energy gap, and potential for high solar energy conversion efficiency [3]. Because of its inherent *p*-type conductivity [4] and lattice match with cadmium sulfide, it is being studied as a candidate material for large area polycrystalline thin film solar cell applications [5].

Inasmuch as the cadmium and arsenic constituents are low-melting and volatile as compared to the silicon component, it is a matter of critical interest to examine the thermal stability of the compound. This information can give insight as to workable methods for obtaining thin films of the ternary compound, environmental degradation of such films, and limits on post-deposition device processing parameters.

Of particular practical interest is the question as to whether stoichiometric ternary thin films may readily be obtained by direct thermal evaporation.

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 1 is a summary of such pertinent data. As indicated, both Cd and As are volatile at low temperatures. One might expect

TABLE 1

Properties of some compositions in the Cd—Si—As ternary system

Composition	Density ($g\ cm^{-3}$)	M.p. (°C)	Vapor species	Vapor pressure (Torr)		
				200°C	600°C	1100°C
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_3As_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.

similar behavior in the combined state. Roenkov [6] has presented calculations on the vapor phase equilibria and partial pressures for these compounds, as well as a summary of experimentally determined vapor pressures. The vapor pressure trends are, as expected, found to behave as $p(\text{As}) > p(\text{Cd}) \gg p(\text{Si})$ in this sytem.

Therefore, one might expect that in a non-equilibrium situation, arsenides in general may decompose with disproportionation. In this case, direct thermal vacuum evaporation should result primarily in evolution of the heavy element species, leaving some form of siliceous matter behind. The purpose of the experimentation was to reveal the mechanisms and temperature limits for the evaporation processes.

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, as follows. Let

$$\frac{\mathrm{d}W}{\mathrm{d}t} = \frac{\rho\,\mathrm{d}V}{\mathrm{d}t} = 4\pi r 2\rho\,\frac{\mathrm{d}r}{\mathrm{d}t} \tag{1}$$

where, W = weight loss from the evaporant source; V = volume of the evaporant source; ρ = density of the evaporant source; r = radius of the evaporant source; and t = elapsed time of evaporation. Furthermore

$$\kappa = \frac{1}{A}\frac{\mathrm{d}W}{\mathrm{d}t} = \rho\,\frac{\mathrm{d}r}{\mathrm{d}t} \tag{2}$$

where, A = surface area of the evaporant source, and κ = flux from the evaporant surface. Therefore

$$\frac{\mathrm{d}W}{\mathrm{d}t} = 4\pi r^2 \rho \cdot \frac{\kappa}{\rho} = 4\pi r^2 \kappa \tag{3}$$

from which

$$W = 4\pi\kappa \int r^2\,\mathrm{d}t \tag{4}$$

but also since $\mathrm{d}r/\mathrm{d}t = \kappa/\rho$

$$r = \int \frac{\mathrm{d}r}{\mathrm{d}t} \cdot \mathrm{d}t = \frac{\kappa}{\rho} t + r_0 \tag{5}$$

then squaring

$$r^2 = \frac{\kappa^2 t^2}{\rho^2} + \frac{2\kappa t r_0}{\rho} + r_0^2 \tag{6}$$

and finally

$$W = 4\pi\kappa \int \left\{ \frac{\kappa^2 t^2}{\rho^2} + \frac{2\kappa t r_0}{\rho} + r_0^2 \right\} \mathrm{d}t \tag{7a}$$

$$W = 4\pi\kappa \left[\frac{\kappa^2}{3\rho^2} t^3 + \frac{r_0 \kappa t^2}{\rho} + r_0^2 t + C \right] \tag{7b}$$

where C is a constant of integration. Thus, it is seen that the model predicts an equation of the first order and third degree for the time dependence of evaporant weight.

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

$$D = at^3 + bt^2 + ct + d \tag{8}$$

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 in eqn. (8) above should be directly proportional to the evaporation flux. A plot of $\log c$ vs. reciprocal temperature should indicate whether the evaporation is simple or complex.

EXPERIMENTAL

The $CdSiAs_2$ material used in this investigation was prepared by weighing appropriate amounts of 99.99% or better purity elements into a high purity graphite crucible 1 cm diameter × 7 cm length; and sealing this crucible, capped with a graphite cover, into a fused quartz ampoule 1 cm i.d. × 3 mm wall. Also included within the ampoule was excess cadmium and arsenic to provide a source, external to the primary reactant container, for generation of vapor to fill the free space in the capsule. This was intended to prevent non-stoichiometry of the ternary which might result from selective evaporation of the reactants.

After heating at 1100° C for 5 days, the ampoule was furnace-quenched by air convection to 815° C, where the temperature was equilibrated and held just above 815° C but below 821° C for 1 week to homogenize the contents below the $CdSiAs_2$ solidus. After this period, the reaction vessel was cooled to room temperature at $50°C\ h^{-1}$ or less. The resulting ingot was crushed with a mortar and pestle. X-Ray powder diffraction analysis did not reveal any other crystalline phase present than cadmium silicon diarsenide.

The experimental apparatus consisted of a Denton Model DV-503 vacuum evaporator equipped with a perforated cylindrical tantalum element heating a 2.5 cm o.d. × 5 cm long high purity graphite source bottle. The source bottle was fitted with a threaded cap to effect a vapor seal, and with a carbon felt filter to prevent efflux of particulate material under conditions of rapid vapor effusion. The vapor was emitted through a 3 mm hole in this cap. A Pt—10Rh thermocouple, inserted into a 6 mm well bored in the bottom of the source bottle to within 3 mm of the evaporant, served to support and center the vessel within the heating element. The thermocouple output was continuously monitored throughout the evaporation run using a Leeds and Northrup Azar millivolt recorder. The substrate holder was located 23 cm vertically from the point of emission, and supported four substrates each of 2.5 cm × 4.5 cm rectangular dimension.

The evaporator assembly also incorporated a movable shutter between the source bottle and the substrate holder. The source bottle with contents and the substrates were carefully weighed before and after evaporation. The amount of $CdSiAs_2$ source material was about 1 g in each case.

Film deposition was monitored by means of a quartz transducer coupled to a Kronos® QM-300 series thickness monitor. The thickness monitor was available only toward the end of the experimentation, so deposition progress data for some of the earlier runs are not available. The critical use of the sensitivity of the monitor was in determining lower bounds for initial evaporation and in determining the cessation of decomposition at the chosen reaction temperature.

RESULTS AND DISCUSSION

To determine the lowest measureable temperature of thermal degradation, 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 μTorr in the one case, and again at 220°C and 15 μTorr 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 these data that oxidation reactions might proceed at rather low temperatures in normal atmospheric ambient.

In fact, for the related compound SiAs, Wadsten [7] has shown a slow reactivity with atmospheric oxygen at room temperature to form arsenic trioxide as a surface product. It was also shown that this arsenic oxide could be sublimated at about 190°C. Perhaps similar reactions can occur with the crushed ternary material. If so, it is difficult to distinguish whether this low temperature volatilization is due to the oxide sublimation or to very low temperature dissociation and evaporation of the heavy elements from the $CdSiAs_2$.

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 Fig. 1, which shows a characteristic curvilinear deposition, as suggested by eqn. (8). 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 2, and the temperature dependence of the coefficient c, a deposition flux-related quantity, is shown in Fig. 2.

A point-by-point check of the expressions gave very good correspondence with the observed data, usually better than 1%. From Fig. 2, it is seen that the deposition flux first increases more rapidly than predicted from the log c

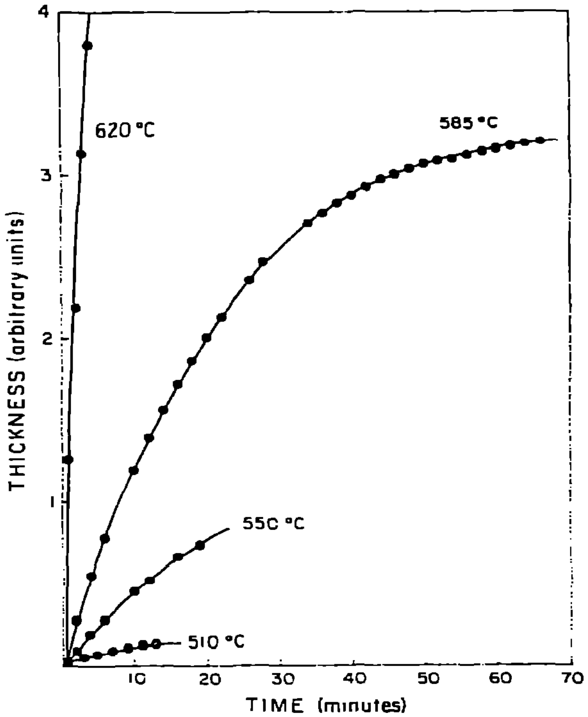

Fig. 1. Deposition progress of films derived from thermal decomposition of $CdSiAs_2$.

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

Evaporations from the ternary compound were conducted according to the stepwise heating schedules and final peak holding temperatures as depicted in Fig. 3. The resulting evaporated films, as well as the evaporation bottle residues, were analyzed by X-ray powder diffraction, electron micro-

TABLE 2

Coefficients for best least-squares fit of deposition data to cubic equation

Temp. (°C)	$a \times 10^5$	$b \times 10^3$	$c \times 10^2$	$d \times 10^2$
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

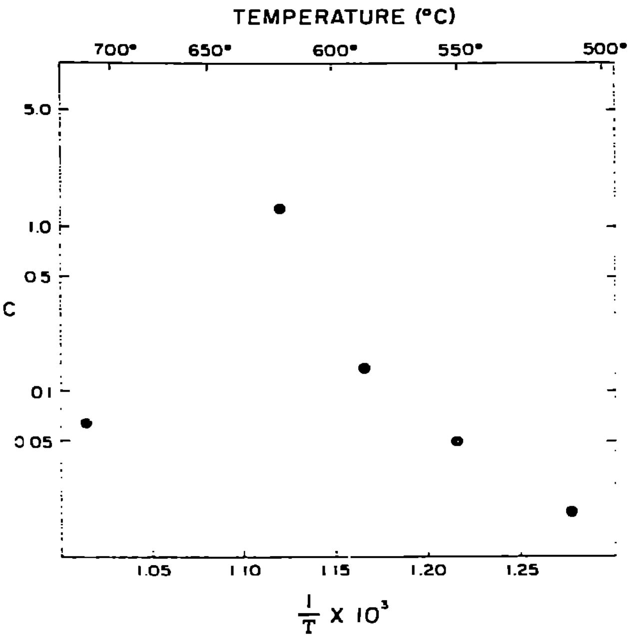

Fig. 2. Temperature dependence of flux-related deposition parameter coefficient *c*.

probe, and scanning electron microscope methods. The major results are reported in Tables 3 and 4. It is clear from the examination of the source bottle residues that the vaporizing species must be products of the stepwise decomposition reactions

$$\mathrm{CdSiAs_2(s)} \xrightarrow{570-710^{\circ}\mathrm{C}} \mathrm{SiAs(s)} + \mathrm{Cd(g)} + \tfrac{1}{4}\mathrm{As_4}\ \mathrm{(g)} \tag{9a}$$

$$\mathrm{SiAs(s)} \xrightarrow{>710^{\circ}\mathrm{C}} \mathrm{Si(s)} + \tfrac{1}{4}\ \mathrm{As_4}\ \mathrm{(g)} \tag{9b}$$

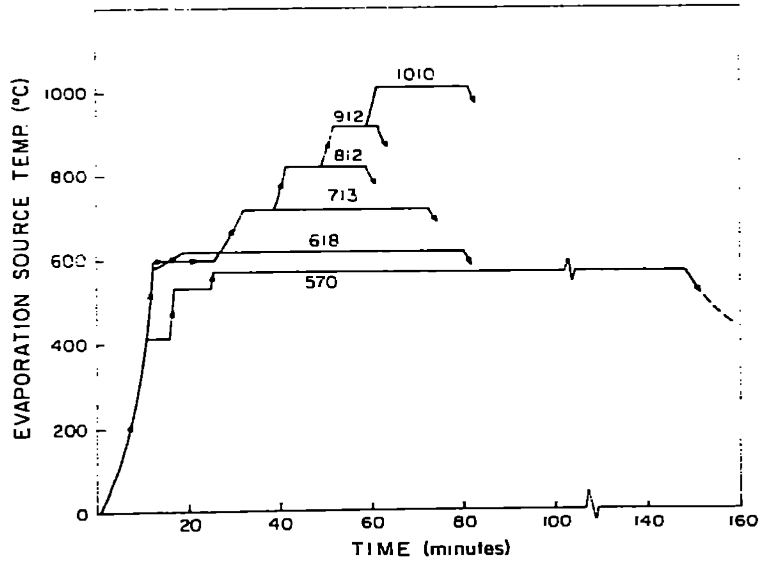

Fig. 3. Evaporation source heating schedules.

TABLE 3

X-Ray diffraction analysis of residue from $CdSiAs_2$ evaporation

Evaporation source temp. (°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	

The data in Table 4 do not represent average film compositions since, due to the stepwise evaporation, the films are not uniform through the thickness dimension. 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 a.u., appeared consistently in all the residues. The pattern designated as B (Table 5) appeared only in the residues from lower temperature heating, and was absent altogether from the patterns for both unheated and high temperature treated powders. Particle-by-particle compositional

TABLE 4

Electron microprobe analysis of evaporated films

Source peak temp. (°C)	Film composition (at. %)			
	Cd	As	Si	Cd/As
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

TABLE 5

X-Ray diffraction pattern B

d (a.u.)	Intensity	*d* (a.u.)	Intensity
3.904	Weak	1.903	Medium
3.212	Medium	1.822	Strong
2.689	Weak	(1.742—1.757)	Medium (broad)
2.580	Very weak	1.685	Medium
1.975	Strong	1.615	Weak
		(1.179—1.186) shifts	Weak (shifts)

analysis by electron microprobe failed to reveal any unusual phase composition other than a very minor amount of silicon dioxide.

Wadsten [8] 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 might arise as such an intermediate phase. However, no correlation was found between the reported pattern for Si_6As and pattern B. At this point, the origin of the pattern is obscure.

CONCLUSIONS

It is clear that the decomposition in vacuum of the ternary compound $CdSiAs_2$ 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 $CdSiAs_2$ 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.

A previously reported Si_6As phase as a decomposition product of SiAs was not confirmed, but the possibility of its existence was not excluded.

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