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Vapor Pressures of Zn and As during Closed-System
Zn Diffusion into GaAs from a ZnAs_2 Source

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Abstract

The vapor pressures of Zn and As during closed-system diffusion of Zn into GaAs from a ZnAs_2 diffusion source were measured by optical absorption spectroscopy over the temperature range from 800 to 1025°K. The preparation of arsenic-saturated ZnAs_2 is described. The fractional dissociative decomposition Δy_3 of $\text{ZnAs}_{2(1+y)}$ required to produce the three-phase GaAs- ZnAs_2 - Zn_3As_2 equilibrium is measured to be 0.0024 at 910°K. The activities of arsenic and zinc in the three-phase mixture were found to be 0.28 ± 1 and ~ 0.04 , respectively.

Introduction

The compound ZnAs_2 is industrially important as a zinc source for P-type impurity diffusion into III-V compounds. The design of diffusion processes requires that the vapor pressures of vapor phase species be accurately known. Lyons (1) studied the dissociation pressure of ZnAs_2 , and Jordan (2) has utilized this data for theoretical analysis of zinc diffusion into GaAs. Arsenic vapor pressures in equilibrium with GaAs and a ZnAs_2 diffusion source has not been previously reported. Also, the more important data on the vapor pressure of zinc in diffusion processes utilizing ZnAs_2 has not been previously studied. In this paper, the preparation of arsenic-saturated ZnAs_2 is described, and the results of vapor pressure measurements on zinc and arsenic are given. In particular, the extent of and the effects of dissociative decomposition of ZnAs_2 on the component partial pressures within the diffusion system are explored in detail.

The Ga-As-Zn System

A schematic form of the Ga-As-Zn ternary isothermal diagram at 700°C is shown in Figure 1. The regions of solid solubility for GaAs, Zn_3As_2 , ZnAs_2 and As are greatly exaggerated for clarity. Regions in the diagram where GaAs and phases containing zinc are designed by Roman numerals. These are regions of phase equilibrium where diffusion of zinc into GaAs is possible. Thus, regions II through VII represent regions of multi-phase equilibria with GaAs. Areas

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FIG. 1
The 700°C isothermal
section in the
Ga-As-Zn system.

in the diagram designated by Arabic numbers represent phase regions in the Zn-As system. The GaAs-ZnAs₂ pseudo-binary region is denoted by VI, and the phase boundary lines are not necessarily parallel.

In a closed diffusion system containing GaAs and arsenic-rich ZnAs_{2(1+y)}, the dissociative decomposition of zinc arsenide proceeds by the reaction,

At the limit of the solid solution range, corresponding to $x = x_1$, continued dissociative decomposition proceeds further by the reaction,

where the partial pressures of Zn₃As_{2(v)} and As_{2(v)} are negligible in the temperature range below 1025°K. Also, zinc vapor is formed by the decomposition reaction,

If the closed system initially contains n_{GaAs}^0 moles of GaAs and $n_{\text{ZnAs}_{2(1+y)}}^0$ moles of ZnAs_{2(1+y)}, then the total moles of Ga, As and Zn following partial vaporization are related to the initial molar quantities by

$$\begin{aligned}
 n_{\text{GaAs}}^{\circ} &= n_{\text{GaAs}} \\
 n_{\text{GaAs}}^{\circ} + n_{\text{ZnAs}_2(1+y)}^{\circ} &= \begin{cases} n_{\text{GaAs}} + 2(1-x)n_{\text{ZnAs}_2(1-x)} + n_{\text{As}}^{\text{v}}, & x < x_1 \\ n_{\text{GaAs}} + 2(1-x_1)n_{\text{ZnAs}_2(1-x_1)} + 2n_{\text{Zn}_3\text{As}_2} + n_{\text{As}}^{\text{v}}, & x = x_1 \end{cases} \\
 n_{\text{ZnAs}_2(1+y)}^{\circ} &= \begin{cases} n_{\text{ZnAs}_2(1+x)} + n_{\text{As}}^{\text{v}}, & x < x_1 \\ n_{\text{ZnAs}_2(1-x_1)} + 3n_{\text{Zn}_3\text{As}_2} + n_{\text{As}}^{\text{v}}, & x = x_1 \end{cases} \quad (4)
 \end{aligned}$$

where n_{As}^{v} and n_{Zn}^{v} represent the moles of arsenic and zinc, respectively, in the vapor phase.

The mass balance on Ga shows that there is no change in the number of moles of GaAs, if the diffusion of zinc is neglected. Solving the remaining equations simultaneously in the limit of small $n_{\text{Zn}}^{\text{v}}/n_{\text{ZnAs}_2}^{\circ}$ one finds that the non-stoichiometry parameter x is related to measurable partial pressure by

$$x = \frac{n_{\text{As}}^{\text{v}} - 4n_{\text{Zn}}^{\text{v}}}{2n_{\text{ZnAs}_2(1+y)}^{\circ}}, \quad x \leq x_1 \quad (5)$$

where the parameter is assumed to be known. After the initial dissociative decomposition parameter reaches x_1 , Zn_3As_2 is formed, with the amount given by

$$n_{\text{Zn}_3\text{As}_2} = \frac{\frac{1}{2} n_{\text{As}}^{\text{v}} - (1-x_1)n_{\text{Zn}}^{\text{v}} - (x_1+y)n_{\text{ZnAs}_2(1+y)}^{\circ}}{2 - 3x_1} \quad (6)$$

For sufficient volatilization of Zn and As from an initially condensed-phase mixture of GaAs and ZnAs_2 , Zn_3As_2 will be caused to form at the phase boundary of the GaAs-ZnAs pseudo-binary region. This reaction will cause a discontinuity in the activities of arsenic and zinc in the condensed phases and a similar discontinuity in the vapor phase. Therefore, from measurements of the vapor phase concentrations, n_{As}^{v} and n_{Zn}^{v} and from a mass balance on volatile components, one can calculate the stoichiometry and molar amounts of condensed-phases.

Preparation of ZnAs_2

ZnAs_2 was synthesized by a vapor transport process in an evacuated and sealed, quartz tube containing 99.9999% pure zinc metal (United Mineral and Chemical Corp.) and 99.999% pure arsenic metal (Ventron Corp.) in individual open quartz crucibles. The quartz tube was placed in a two-zone furnace so that the temperatures of the two crucibles could be independently controlled. The zinc crucible was raised to 1025°K and maintained while the temperature of the arsenic crucible was raised slowly to 980°K, where ZnAs_2 formed by arsenic vapor transport to the zinc crucible. The excess arsenic was sufficient to maintain an arsenic partial pressure of 8 atm. Approximately one day was allowed for the reaction forming ZnAs_2 to go to completion. Then the zinc crucible was slowly cooled in a temperature gradient to below 875°K while the excess arsenic pressure was maintained,

whereupon both temperature zones were lowered to room temperature.

Large grained polycrystals were produced by the synthesis process. Material interior from the crucible surfaces was removed for use in the study.

X-ray powder diffraction analysis with a Picker X-ray diffractometer was performed to determine whether additional phases were present. The results are shown in Table 1, and compared to the diffraction data of Senko et al., obtained with ZnAs_2 grown by the Czochralski growth process (3). The interplanar d spacings are in good agreement with the data of Senko, with the line intensities in fair agreement. The width of diffraction lines indicated minimal residual strain in the synthesized ZnAs_2 .

Because of the high arsenic pressure during synthesis, it is anticipated that the ZnAs_2 would be arsenic-saturated at the synthesis temperature. The X-ray diffraction data showed minute diffraction lines for arsenic, indicating an arsenic concentration of $\ll 0.1\%$. It is suspected that arsenic precipitated from solution during cooling of the ZnAs_2 , since crystals with arsenic-free surfaces were used in the analysis.

Vapor Partial Pressure Measurements

Vapor partial pressures in high temperature diffusion cells containing GaAs and ZnAs_2 were measured by optical absorption spectroscopy (4). Quartz optical cells constructed from uv-transparent quartz were rinsed in dilute HF, rinsed

Table 1

X-ray Powder Diffraction Pattern of ZnAs₂

<u>This Study</u>			<u>Senko,et al.</u>		<u>This Study</u>			<u>Senko,et al.</u>	
<u>hkl</u>	<u>d(Å)</u>	<u>I/I₁</u>	<u>d(Å)</u>	<u>I/I₁</u>	<u>hkl</u>	<u>d(Å)</u>	<u>I/I₁</u>	<u>d(Å)</u>	<u>I/I₁</u>
100	9.027	10	9.02	20	231	2.086	10	2.086	10
110	5.866	20	5.85	55	132,232	2.028	8	2.032	10
200	4.541	10	4.53	20	104	2.001	20	2.007	20
210	3.902	30	3.903	40	330,420	1.954	40	1.952	25
020	3.852	40	3.840	10	040	1.919	2	1.920	16
120	3.536	100	3.537	70	422	1.893	95	1.892	40
202	3.348	10	3.340	75	140	1.877	17	1.879	16
112,212	3.063	12	3.060	16	232,332	1.853	7	1.854	20
300	3.021	7	3.021	25	500	1.812	8	1.812	10
220	2.958	100	2.928	100	502	1.800	40	1.799	16
310	2.810	13	2.812	20	124	1.781	2	1.780	8
202,302	2.682	5	2.689	10	133	1.740	5	1.742	10
212,312	2.533	3	2.535	16	042,142	1.723	10	1.724	16
222	2.519	3	2.518	8	430,241	1.698	4	1.697	8
130	2.465	10	2.463	16	142,242	1.662	16	1.665	16
400	2.262	1	2.266	8	124	1.657	16	1.658	16
230	2.226	20	2.230	16	324	1.653	23	1.654	12
322	2.202	35	2.202	65	520	1.640	25	1.640	30
302,321	2.174	5	2.176	20	234,341	1.553	3	1.554	8
412	2.090	10	2.091	10	413,243	1.524	2	1.524	10

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in de-ionized water, ultrasonically cleaned in methanol, rinsed in de-ionized water and vacuum dried at 875°K before use. Measured amounts of semiconductor grade GaAs (Monsanto Corp.) and ZnAs₂ whose synthesis is described above were placed in the cells which were evacuated to 10⁻⁵ torr at 200°C for several hours before the cells were sealed. The cells were placed in a two-zone furnace which maintained the optical path at a constant temperature of 940°C, while the condensed phases were held at a lower variable temperature.

Zinc diffusion processes were studied in which the GaAs to ZnAs₂ order ratio was approximately 2:1. In each experiment the 2 cm optical path of the cell was raised to 1210°K and the condensed phases to a selected diffusion temperature for a period of between 12 and 24 h. The length of the diffusion period was sufficient to assure phase equilibrium and to simulate actual semiconductor production conditions yet was insufficient to homogenize the zinc concentration in the GaAs. However, the total moles of zinc in the diffused GaAs was small compared to that in the cell.

The optical absorption data was analyzed by a linear analysis assuming independent optical absorption coefficients for the vapor species (4). Vapor pressure data for the pure elements was taken from Hultgren et al. (5).

FIG. 2

Partial pressure of arsenic in a diffusion cell containing 1.0509×10^{-3} g moles of GaAs and 5.4765×10^{-4} g moles of ZnAs_2 .

Results

The results of the arsenic vapor pressure measurement in a cell containing a GaAs to ZnAs_2 molar ratio of 1.919 is shown in Figure 2. The arsenic partial pressure above 910°K is given by

$$\log P_{\text{As}_4} = 7.716 - 8,250T^{-1} \quad (7)$$

The discontinuity at 910°K indicates the onset of the reaction forming Zn_3As_2 given in Eq. 3.

The zinc partial pressure could not be accurately determined at low temperature because of interference effects in the optical adsorption spectra. The zinc partial pressure was estimated to be 4×10^{-3} atm at 1000°K and 1×10^{-3} at 910°K.

The range of nonstoichiometry of ZnAs_2 was deduced at 910°K from the discontinuity observed in the temperature dependence of the arsenic partial pressure, and with the aid of Eq. 5:

$$x_1 + Y = 0.0024. \quad (8)$$

The nonstoichiometry parameter, y , could not be independently determined by the optical method. The high arsenic partial pressure compared to the zinc partial pressure suggests that the criterion for the appearance of Zn_3As_2 as a reaction product is

$$n_{\text{As}}^{\text{V}} > 0.005 n_{\text{ZnAs}_2}^{\circ} (1+y) \quad (9)$$

Following simulated, closed-system diffusion at 1025°K for 15 h. the condensed solid phases were removed, ground and analyzed by X-ray powder diffraction. Examination of the diffusion source showed that the ZnAs_2 had partly decomposed into Zn_3As_2 , by dissociative decomposition of ZnAs_2 . The amount of Zn_3As_2 formed is in agreement with the arsenic partial pressure measured at the equilibration temperature. The fact that no additional diffraction lines appeared in the diffraction pattern indicates that there are no additional intermetallic phases in the $\text{GaAs-ZnAs}_2\text{-Zn}_3\text{As}_2$ ternary system.

Discussion

The measured arsenic pressure in the diffusion cell, (Fig. 2), is in agreement with the ZnAs_2 dissociation pressure measured by Lyons (1) over the temperature range from 635 to 680°C. Above 680°C, the ZnAs_2 dissociation pressures measured by Lyons are higher than those over the $\text{GaAs} + \text{AsAs}_2 + \text{Zn}_2\text{As}_3$ mixture. Lyons found a noticeable increase in $\text{Zn}_3\text{As}_2(\text{v})$ above 750°C which raises the decomposition pressure of ZnAs_2 in this range, whereas in this study the arsenic pressure was selectively measured. The present results show that the arsenic activity in the $\text{GaAs} + \text{ZnAs}_2 + \text{Zn}_3\text{As}_2$ mixture is lower than in the $\text{ZnAs}_2 + \text{Zn}_3\text{As}_2$ mixture at temperatures above 910°K.

The arsenic activity in the three-phase equilibrium $\text{GaAs} - \text{ZnAs}_2 - \text{Zn}_3\text{As}_2$ was found to be 0.28 ± 0.01 for the temperature range from 910 to 1000°K. At 910°K this value is in excellent agreement with the value calculated by Jordan (2) for the $\text{ZnAs}_2 - \text{Zn}_3\text{As}_2$ equilibrium, using an estimated dissociation constant for Zn_3As_2 and the experimental

data of Lyons (1). At higher temperatures, the measured arsenic activity lies below that predicted by Jordan, indicating that the solid solubility of Ga in Zn_3As_2 and ZnAs_2 , or of Zn in GaAs are not negligible.

The zinc activity in the three-phase equilibrium could not be determined with high accuracy because of interference effects in the optical absorption spectra. These data given an approximate zinc activity of 0.04 in the temperature range from 910 to 1000°K. Above 1023°K the zinc activity increases consistent with the formation of $\text{ZnAs}_2(\text{v})$ in the vapor phase.

The importance of the GaAs - ZnAs_2 - Zn_3As_2 three-phase equilibrium for maintaining invariant zinc and arsenic activities during the diffusion has already been recognized by Jordan (2) in theoretical work and by Casey and Parrish (6) in experimental studies. In the present study it is shown that the three-phase equilibrium can be produced with the ZnAs_2 diffusion source only if the fractional dissociative decomposition of ZnAs_2 exceeds a critical value. The critical system volume required to produce the three-phase equilibrium from the ZnAs_2 source whose synthesis is described above, can be estimated from Eqs. 7 and 9. The critical system volume is then

$$V_{\text{crit}} = 81.0 w_{\text{ZnAs}_2}^{\circ} T 10^{-7.716 + 8,250T^{-1}} (\text{cm}^3) \quad (10)$$

where $w_{\text{ZnAs}_2}^{\circ}$ is the initial weight of the ZnAs_2 source.

For 10 mg of source compound, the system volume required to produce the three-phase equilibrium must exceed $2,520 \text{ cm}^3$ at 1000°K . Owing to the narrowness of the $\text{GaAs} + \text{ZnAs}_2$ two-phase region, this critical system volume should be relatively independent of the ratio of ZnAs_2 to GaAs . The calculated critical system-volume should be useful in the design of closed-system diffusion processes utilizing ZnAs_2 as a zinc diffusion source for the P-type doping of III-V compounds.

Conclusions

The vapor pressures of arsenic and zinc in closed diffusion system containing GaAs and ZnAs_2 are dependent upon the extent of dissociative decomposition of the ZnAs_2 source. The fractional dissociation required to produce the $\text{GaAs} - \text{ZnAs}_2 - \text{Zn}_2\text{As}_3$ three-phase equilibrium is 0.0024 at 910°K . In the temperature range above 910°K the arsenic activity was found to be 0.28 ± 0.01 and the zinc activity was approximately 0.04 for the $\text{GaAs} - \text{ZnAs}_2 - \text{Zn}_3\text{As}_2$ three-phase region. The absence of other intermetallic compounds produced during zinc diffusion in GaAs from ZnAs_2 was confirmed by X-ray powder diffraction. For closed-system diffusion processes using ZnAs_2 as the zinc source, a minimum system volume is required to produce the three-phase equilibrium.

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