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DETERMINATION OF THE WIDTH OF THE GaAs + ZnAs$_2$ TWO PHASE REGION IN THE Ga–As–Zn SYSTEM BY OPTICAL ABSORPTION SPECTROSCOPY*

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ABSTRACT

The width of the GaAs + ZnAs two-phase region in the Ga–As–Zn system was studied by optical absorption spectroscopy. The vapor pressure of zinc and arsenic were measured as a function of temperature in a closed optical cell containing GaAs and ZnAs$_2$. The width of the two-phase region was then determined from the measured discontinuity in the partial pressure of arsenic produced by dissociative evaporation of arsenic from ZnAs$_2$ to form Zn$_3$As$_2$. The importance of the results with regard to the vapor phase diffusion of Zn in GaAs using the solid source ZnAs$_2$ is discussed.

Introduction

Vapor pressure measurements of a vapor in equilibrium with a condensed phase are useful in determining the activities of volatile elements in the condensed phase (1). In a closed system, the selective volatilization of high-vapor pressure elements from condensed phases by dissociative evaporation can produce a shift in the composition of the condensed phase by loss of the volatile components. This occurrence makes possible a simple method for the determination of the positions of phase boundaries in multi-component systems. By monitoring the vapor pressure of volatile components in a closed system as the temperature is raised, the composition of a condensed phase mixture can be shifted until one condensed phase is depleted by vaporization, or a new phase is formed by dissociative reactions. The resulting discontinuity in the activities of volatile components can be directly sensed by vapor pressure measurements.

In this study, the phase width of the pseudo-binary, GaAs + ZnAs$_2$ region in the Ga–As–Zn ternary system was measured by above method using uv-visible, optical absorption spectroscopy to determine the partial pressures of vapor species (2,3). This system is important industrially because ZnAs$_2$ is

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utilized as a solid diffusion source for zinc in high-temperature doping processes involving the formation of p-n junctions in GaAs electro-optical devices. The extent of dissociative evaporation of ZnAs₂ during the diffusion process determines the zinc surface concentration in the GaAs.

Theory

Optical absorption spectroscopy has been applied previously to the measurement of optical density at different temperatures for zinc vapor over zinc alloys by Herbenar (4), and by Scatchard and Westlund (5). K. K. Shih measured the partial pressures to zinc and arsenic over Ga-As-Zn mixtures in the temperature range of 900-1050°C by using a similar optical method (3).

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, Zn₃As₂, ZnAs₂ 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 for into GaAs is possible. Thus, regions II through VII represent regions of multi-phase equilibria with GaAs. Areas in the diagram designated by Arabic numbers represent phase regions in the Zn-As system. The GaAs-ZnAs pseudo-binary region is denoted by VI.

FIG. 1
The 700°C isothermal section in the Ga-As-Zn system.
If an experimental optical cell is partially filled with condensed phases, evacuated and sealed at room temperature, essentially all of the molar components within the cell are present in condensed phases. Vaporization losses at high temperatures produce a significant vapor pressure of volatile components due to dissociative decomposition of the condensed phases. The formation of the vapor phase produces a change in the condensed phase composition.

Consider a closed cell containing only condensed phases in the Ga-As-Zn system, such that the condensed phases lie in the GaAs-ZnAs two-phase region, as shown in Fig. 1. The total moles of Ga, As and Zn are initially equal to \( n_{Ga}^o, n_{As}^o + n_{Zn}^o \) and \( n_{Ga}^o \), respectively, where the superscript \( o \) denotes the initial molar amounts. After the cell is heated to a sufficiently high temperature, zinc and arsenic are dissociatively evaporated so that the condensed phase composition shifts to the phase boundary of the two-phase region, and \( Zn_3As \) is formed by the reaction,

\[
4 \text{ZnAs} \rightarrow \text{Zn}_3\text{As}_2 + \text{Zn}(v) + \frac{3}{2} \text{As}_4(v) .
\]

The total numbers of component moles of Ga, As and Zn are then equal to \( n_{Ga}^0, n_{Ga}^o + 2n_{Zn}\text{As}_2 + 3n_{Zn}\text{As}_2 + n_{Zn}^o \) and \( n_{Ga}^o + 3n_{Zn}\text{As}_2 + n_{Zn}^o \), respectively, where \( n_{Zn}^o \) and \( n_{As}^o \) represent the total molar concentrations of arsenic and zinc in the vapor phase. The mass balance on Ga then shows that no GaAs decomposes. The mass balances of arsenic and zinc, respectively, are therefore

\[
\begin{align*}
2n_{ZnAs}^o &= 2n_{ZnAs}^0 + 2n_{Zn_3As_2} + n_{As}^v , \\
n_{ZnAs}^o &= n_{ZnAs}^0 + 3n_{Zn_3As_2} + n_{Zn}^v .
\end{align*}
\]

The two unknown quantities in Eqs. 2 and 3 are \( n_{ZnAs}^0 \) and \( n_{Zn_3As_2}^0 \), since \( n_{As}^o \) and \( n_{Zn}^o \) are experimentally measurable by uv-visible, optical absorption spectroscopy. Solving those two equations for the unknown quantities, one obtains

\[
n_{ZnAs}^0 = n_{ZnAs}^0 + (1/2)n_{Zn}^v - (3/4)n_{As}^v
\]

and

\[
n_{Zn_3As_2}^0 = (1/4)n_{As}^v - (1/2)n_{Zn}^v .
\]

The vapor species present in arsenic vapor in the temperature range of interest for vapor phase diffusion of zinc into GaAs, 600-900°C, consists of \( \text{As}_4 \) and \( \text{As}_2 \), with \( \text{As}_4 \) the principal species (4). The vapor species present in zinc vapor in the temperature range from 600 to 900°C consists almost entirely of monatomic zinc (4). The vapor pressure of gallium is negligible at these temperatures. Shih reports negligible absorption due to gallium vapor for temperatures up to 1000°C (3). The presence of gallium vapor was therefore not considered in this study.

The gaseous mixture of groups IIB and VB elements are not expected to interact in the vapor phase because the valence electrons in the group VB tetramer are fully paired and not available for bonding. From considerations
of the magnitude of London forces between atoms of these groups, it is anticipated that less than 1% of the gaseous components in a mixture of zinc and arsenic are associated at 1000°K. Therefore, the spectral dependence of the optical absorption in such a gaseous mixture can be decoupled, using optical absorption data for the pure species to determine vapor phase compositions of zinc and arsenic.

At sufficiently low pressures, the ideal gas law can thus be used to calculate the magnitude of the change in condensed phase composition produced by dissociative evaporation. For an optical cell of 5 cm³ containing a vapor pressure of 0.5 atm at 1000°K, the number of moles of a monatomic gas would be 3.047×10⁻⁵ g-moles. If this vapor represents pure Cd(v), Zn(v) or As(v) with molecular weights of 112.40, 65.37 and 299.69, respectively, then the above number of moles of vapor represents 3.42 mg Cd, 1.99 mg Zn or 9.13 mg As in the vapor phase. Thus, the molar concentrations of the solid phase can be changed by these amounts on heating the cell through a temperature interval which produces a change in vapor pressure of 0.5 atm.

The selective volatilization of Zn and As from an initially condensed-phase mixture of GaAs and ZnAs₂ will cause the formation of Zn₃As₂ at the phase boundary of the GaAs-ZnAs pseudo-binary region. This section will cause a discontinuity in the activities of arsenic and zinc in the condensed phases and a similar discontinuity in the vapor phase. From measurements of the vapor phase concentrations \( n_A \) and \( n_Z \) and from a mass balance on volatile components applied at the temperature of the observed discontinuity, one can calculate the composition of the phase boundary in the ternary diagram.

Experimental Method

Semiconductor-grade GaAs wafers were obtained from Monsanto Corp. Stoichiometric ZnAs was synthesized from 99.999% pure arsenic metal (Ventron), and zinc metal of 99.999% purity (United Mineral and Chemical Corp.) in a closed quartz ampoule by slow heating to the melting point and slow cooling to solidify large grain crystals. Quartz optical cells in the shape of a T were constructed from UV-transparent quartz. The cross bar of the T served as the optical path 2 cm in length. The cells were rinsed in dilute HF, rinsed in de-ionized water, ultrasonic cleaned in methanol, rinsed in de-ionized water, then vacuum dried at 600°C before use. The component phases were placed in each cell and heated in a 10⁻⁵ torr vacuum at 200°C for several hours before the cell was sealed.

A specially constructed two-zone furnace was used to maintain the optical path at a fixed temperature, 940°C, while the condensed phases were held at a lower temperature. Temperatures were maintained within 1°C by temperature controllers and nickel leaves around each zone of the furnace. This experimental arrangement is similar to that employed by Brebrick for the study of II-VI compounds (7,8).

For each run, the optical-path furnace was heated to 940°C and the optical density measured with the sidearm temperatures equilibrated at a series of temperature values. The spectral range from 2000-5000 Å was scanned at a speed of 5 Å/sec with a slit width of 100 μm. The logarithm of the optical intensity was recorded as a function of spectral wavelength at 50 Å/inch. The
specific optical density was obtained by dividing the optical density by the optical path length (2).

Results

The specific optical density of pure arsenic vapor plotted for various wavelengths as a function of inverse absolute temperature showed nearly linear dependence for the spectral range between 2800°C and 3800 Å. This data indicate that wavelengths between 2800 Å and 3800 Å are best suited for use in arsenic partial pressure analysis. The specific optical density of pure zinc vapor showed linear dependence of log d versus inverse absolute temperature for optical wavelengths between 2200 Å and 2600 Å. Therefore, this wavelength was preferred for use in zinc partial pressure analysis. The dependence of the vapor pressure of pure zinc and arsenic were obtained from Hultgren (4) for calibration.

Figure 2 shows the specific optical density of mixture cell No. 1 containing GaAs + ZnAs₂ in a volume of 4.76 cm³. A comparison with calibration curves for the pure components indicates that the principal vapor species present in this cell is arsenic. The calculated arsenic pressure present in the cell is shown in Fig. 3, together with the arsenic pressure over pure arsenic (solid). The pure arsenic vapor pressure is approximately one hundred times greater than that for the GaAs + ZnAs₂ and the GaAs + ZnAs₂ + Zn₃As₂ mixtures.

![Graph of specific optical density vs. inverse absolute temperature for cell No. 1.](image-url)
Discussion

The rapid pressure change in mixture cell No. 1 between $1.10 < 10^3/T < 1.15$ can be interpreted as follows. Referring to Fig. 1 which shows the 700°C ternary isotherm for the Ga-As-Zn system, one finds that the condensed phase has an initial composition in the narrow Region VI. As the temperature of the cell is increased, more arsenic enters the vapor phase than zinc, since arsenic is more volatile than zinc. The composition of the condensed phase then moves away from the arsenic corner of the ternary isothermal phase diagrams into Region V. Once in this three-phase region, the arsenic activity becomes fixed by the four-phase equilibrium at a constant value of $0.28 \pm 0.01$.

The boundary of the two-phase region of GaAs + ZnAs$_2$ was deduced from the temperature of the discontinuity of arsenic partial pressure in each experimental cell. The discontinuity in arsenic partial pressure for the cell shown in Fig. 3 occurred at $909^\circ K$. The optical density data indicated that arsenic was the predominant vapor species at this temperature. With a cell volume of 4.75 cm$^3$, the total moles of arsenic in the vapor phase was found to be $1.10 \times 10^{-5}$ g-moles.

The pressure of zinc was smaller than could be measured with arsenic vapor present because of interference effects. An examination of the zinc calibration
curves indicated that at 909°K, $P_{Zn}$ is on the order of $10^{-3}$ atm. The corresponding number of moles of zinc vapor present is then $6.37 \times 10^3$ g-moles.

Table 1 summarizes the calculated changes in mole fractions of the condensed components for cell No. 1 where $n_i^0$ and $x_i^0$ denote the total moles and mole fractions, respectively, of condensed phases at the GaAs-ZnAs$_2$-Zn$_3$As$_2$ phase boundary.

<table>
<thead>
<tr>
<th>Component</th>
<th>$n_1^0 \times 10^3$ (g-moles)</th>
<th>$n_1^* \times 10^3$ (g-moles)</th>
<th>$x_1^0$</th>
<th>$x_1^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>1.0509</td>
<td>1.0509</td>
<td>0.6571</td>
<td>0.6594</td>
</tr>
<tr>
<td>ZnAs$_2$</td>
<td>0.5483</td>
<td>0.5401</td>
<td>0.3428</td>
<td>0.3389</td>
</tr>
<tr>
<td>Zn$_3$As$_2$</td>
<td>0.0000</td>
<td>0.0027</td>
<td>0.0000</td>
<td>0.00171</td>
</tr>
</tbody>
</table>

Thus, the width of the phase field between solid GaAs and solid ZnAs$_2$ at 909°K is seen to be 0.17 mole percent in the direction away from the arsenic-rich corner of the ternary phase diagram. This value should represent approximately half of the width of the solid solution at 909°K. The total width of the phase region is therefore about 0.34 mole percent.

For the analysis of the vapor pressures by optical absorption methods, there were two primary requirements: 1) that there is no interaction between different vapor species, and 2) that the partial optical density values can be related to the pure species values at the same conditions by a Raoult's Law type of behavior. These two conditions were found to hold in the present study.

It is possible to extend the present method to measure the entire width of narrow two-phase regions such as the GaAs-ZnAs$_2$ region in the Ga-As-Zn system by adding a small excess (~0.1%) of the most volatile element, e.g., arsenic. This addition will produce a three-phase equilibrium at low temperature, with a shift of the condensed phase across the two-phase region as the temperature is increased. The measured partial pressures will then undergo two discontinuities, one at each boundary of one-fold saturation, thereby allowing a measure of the full width of the two-phase region. The limitations of the method are that the temperature at which the phase boundary is measured cannot be independently controlled, and that the accuracy of the optical absorption method is generally greater than several percent.

**Application to Zinc Diffusion Processes**

The results reported above show that the arsenic and zinc partial pressures are composition-dependent when ZnAs$_2$ is used as a zinc diffusion source in closed-system diffusion processes, and that these partial pressures can be stabilized by dissociative evaporation of ZnAs$_2$ to form Zn$_3$As$_2$. The importance of the three-phase region for zinc diffusion has been recognized (9,10). To produce this three-phase region with a ZnAs$_2$ source, it is sufficient to choose a volume sufficiently large to cause dissociative vaporization of sufficient ZnAs$_2$ to change the condensed-phase mole fraction of ZnAs$_2$ by >0.17%. At 909°K this change is achieved by setting the ZnAs$_2$ source concentration at less than 0.0248 gm/cm$^3$ of diffusion-system volume. This interior should be useful for applying ZnAs$_2$ in closed-system diffusion processes involving III-V compounds.
References


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