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THE EFFECT OF Ge ON THE LIQUIDUS AND SOLIDUS IN THE SYSTEM AlGaAs:Ge

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RESUME

Des mesures experimentales et les calculs du systeme Al-Ga-As-Ge dans le domaine de l'EPL sont presentes. Dans la phase liquide, la presence de Ge diminue la solubilite d'As a une concentration d'Al donnee et semble reduire quelque peu le coefficient de partage d'Al. Les calculs theoriques sont faits en respectant les donnees thermodynamiques disponibles et predisp correctement le diagramme de phase Al-Ga-As-Ge dans le domaine etudi.

ABSTRACT

Experimental and estimated phase diagram data for the Al-Ga-As-Ge system in LPE domain are presented. At a given Al concentration in the liquid phase, the As solubility decreases slightly and the distribution coefficient for Al decreases when Ge is added. Theoretical calculations are carried out using experimental thermodynamic data and they predict correctly the Al-Ga-As-Ge phase diagram in the domain of this investigation.

I. INTRODUCTION

An important problem for LPE of multicomponent systems is the perfect control of both composition and doping of the deposited layer. When considering high doping levels and using impurities with small segregation coefficient, this difficulty becomes greater. For III-V semiconductors, the amounts of doping element in the liquid phase is often larger than elemental components. In this case, the liquidus composition is far from the III-V ternary boundary. The quaternary phase diagram must then be considered but the liquid-solid equilibrium is generally modified.

This is the case for the Al-Ga-As-Ge system. A low vapor pressure, small distribution coefficient and low diffusion make Ge an ideal impurity. In this study, the displacements of the equilibrium phase boundaries in the AlGaAs system due to large amounts of Ge are determined and compared to theoretical calculations.

II. CALCULATIONS

II.1. Approach

Most of the models used for III-V phase diagram calculations are variation of the simple solution model, where the excess Gibbs energy of mixing is expressed in terms of composition independent interaction parameters. This approach has some advantages: it requires few thermodynamic data and calculations are simpler by using Vieland's equation. On the other hand this method leads to a symmetrical phase diagram. Any adjustment of the liquid phase parameter modifies the stability of the compound if the entropy of fusion is maintained constant. The enthalpy and entropy of formation referred to the pure liquid elements which are
derived from the following equations:

\[ \Delta H_f(T^F) = - \Delta S_f + \Delta H_m \]

\[ \Delta S_f(T^F) = - \Delta S_f + \Delta S_x \]

have to agree with the experimental values.

An other approach consists in optimizing the Gibbs energy of the different phases using all available experimental thermodynamic values, and phase diagram data (1). This method may lead to a more complicated formulation and then to more complex calculations. If suitable data are available, a consistent set of thermodynamic data is obtained.

For III-III and III-IV liquid solutions, data of mixing are often known. There is a lack of experimental data for these mixing parameters in the III-V systems. The only values often available are \( \Delta S, T, \Delta H, \Delta S \), vapor pressures and phase diagrams. So, mixing parameters must be estimated.

The thermodynamic data used in this study for the Ga-As, Al-Ga-As, Al-As and As-Ge systems are consistent with the phase diagrams and allow the Ga-As-Ge and the Al-Ga-As-Ge phase diagrams to be estimated.

II.2. Resolution method

At a given temperature and pressure, the minimum of the Gibbs energy of a polyphasic system defines the equilibrium state. In general:

\[ G = \sum_i P_i G_i \]

or the variation of Gibbs energy from pure liquid elements.

\[ \Delta G = \sum_i P_i \Delta G_i \]

We have chosen the simple method described by Nelder and Mead (2) which minimizes the Gibbs energy of a polyphasic system by a "hill climbing technique" and for which no differentiation of the Gibbs energy is required. The method can be described briefly as follows: for an overall composition, the Gibbs energy of a multicomponent system is calculated for a certain number of coordinates. The point which has the highest value of the Gibbs energy is replaced by another one according to a defined rule. This procedure is repeated until a minimum value is obtained.

II.3. Thermodynamic description of the solution phases in the AlGaAsGe system

We consider only the domain where the liquid solution is in equilibrium with the solid solution \( A_{1-x}A_{1-x}A_{1-x} \). For the liquid phase L, the Gibbs energy of mixing is equal to:

\[ \Delta G_L = RT \sum_{i=1}^{4} x_i \ln x_i + \Delta G_{x} \]

\[ \Delta G_{x} = \frac{1}{2} \sum_{i=1}^{4} \sum_{j=i+1}^{4} x_i x_j \alpha_{ij} \]

with \( \alpha_{ij} = (a_o+b_o T) + (x_i-x_j)(a_1+b_1 T) + (x_i-x_j)^2(a_2+b_2 T) \)

The solid solution is assumed to behave ideally. Its Gibbs energy is equal to:

\[ \Delta G_{s, id} = 2x_{A1} \Delta G_{A1A3} + 2x_{A1} \Delta G_{A1A3} + RT (x_{Ga} \ln x_{Ga} + x_{Al} \ln x_{Al} + \ln 2) \]

where \( \Delta G_{ij} \) is the Gibbs energy of formation of the compound \( ij \) from pure liquid elements.
II.4. Thermodynamic parameters

All units are in Joule per gram-atom (mole of atoms), T in Kelvin.

L : liquid
S : stable solid

Al : \[ G^L - G^S = 10711 - 11.506T \] (3)(4)
Ga : \[ G^L - G^S = 5390 - 18.45T \] (3)
As : \[ G^L - G^S = 24874 - 23.01T \] (4)
Ge : \[ G^L - G^S = 36945 - 30.54T \] (3)

GaAs:
\[ \Delta H_{298}^f = -43396 \text{ from pure stable elements (5) (6)} \]
\[ \Delta S_{298}^f = -6.037 \] " " " (7)
\[ \Delta C_p = -2.98 + 3.07 \times 10^{-3}T \] (8)
\[ \alpha = -25632 - 4.156T + (x_{As} - x_{Ga})(-18318 + 11.86T) \]
(adjusted by the phase diagram optimization with the data given above)

AlAs:
\[ \Delta H_{298}^f = -58565 \text{ from pure stable elements (5)} \]
\[ \Delta S_{298}^f = -3.89 \] " " " (7)
\[ \alpha = -15693 - 34.163T \]
(adjusted to the liquid of the Al-Ga-As phase diagram)

GeAs:
\[ \alpha = -8786 \text{ (obtained with the quasi regular solution model, } T^F \text{ from (9) and } \Delta S^F \text{ from (10))} \]

GeAs:
\[ \alpha = -8786 \text{ (obtained with the quasi regular solution model, } L_{Ge} \text{ from (3), and phase diagram from (11)).} \]

GaAl:
\[ \alpha = (2648.5 - 1.347T) + (-604.5 + 0.635T)(x_{Ga} - x_{Al}) + (175 - 0.21T)(x_{Ga} - x_{Al})^2 \] (12)

GaGe:
\[ \alpha = (-2593 + 0.8878T) + (125.5 + 0.0828T)(x_{Ga} - x_{Ge}) - 117.15(x_{Ga} - x_{Ge})^2 \] (13)

AlGe:
\[ \alpha = -13000 - 3.954T + (-418.4 - 0.3347T)(x_{Al} - x_{Ge}) + (4552 - 2.335T)(x_{Al} - x_{Ge})^2 \] (13)

Using these data, we have estimated the Ga-As-Ge and Al-Ga-As-Ge phase diagrams.

III. EXPERIMENTAL

III.1. Liquidus determination

The determination of the quaternary liquid in equilibrium with the solid solution AlGaAs is made in a LPE apparatus using a transparent furnace. With this equipment, the "seed dissolution" and the "direct observation" techniques are possible. GaAs is not the solid in equilibrium for such a quaternary liquid solution, some problems can exist when large amounts
of dopant are used in liquid phase (14); these two points make that we prefer to use the second method which is more rigorous. The experimental apparatus consists of a horizontal furnace, a fused silica tube through which a flow of purified \( \text{H}_2 \) is maintained, and a graphite boat. Temperatures were measured with a calibrated thermocouple inside the boat body, the accuracy being of 3 degrees.

With Ga, GaAs, Al, Ge, the principal problems are the loss of As and the oxidation of Al. As the solution is rich in Ga, and the temperature below 1200 K the loss of As is negligible and this has been checked experimentally. The use of Al involves a careful preparation of the components, a good purity of the atmosphere and a very adapted method. In fact, the oxidation of even a small quantity of aluminium would have caused substantial error in the liquidus determination because of a loss of Al and because this oxide forms a surface haze on the liquid. For this reason, the Ga and the boat are baked. GaAs and Ge are loaded in the melt and Al in the tube at room temperature under Hydrogen flux in a glove box. The \((\text{Ga+GaAs+Ge})\) melt is baked at 823 K and the water content is controlled in the \( \text{H}_2 \) outflow (usually this content varies between 0.15 and 0.05 VPM). Al is then loaded in the melt without silica tube opening. In this way, the melt surface is free from any scum and haze. The temperature is measured by the classical "visualisation technique" which is described for example in ref. (14).

### III.2. Solidus determination

To determine the composition of the solid solution in equilibrium with a given liquid, epitaxial layers of Ge doped Al-Ga-As were grown and analysed.

The growth is made onto \(<100>\) oriented semi-insulating GaAs substrates. The apparatus is the same as the one described above. Using our liquidus data, the precise amounts of components are weighed; this way, the growth is at "one phase". The step-cooling method is used with an undercooling of four degrees for 15 minutes. Glossy layers are obtained with thicknesses of 2 to 5 \( \mu \text{m} \) depending upon the Al concentration. The choice of the undercooling was made for no \( \Delta T_c \) excess, the melt impoverishment problem is thus avoided. The small thickness and the step cooling technique lead to layers with uniform composition. We have also verified that concentration is the same all along the surface.

There are many methods to obtain the composition of the AlGaAs but all of them show problems for absolute analysis. We have systematically used X-Ray diffraction and compared the results with those obtained by electron microanalysis and by the wavelength modulation technique. X-ray diffractometer rocking curves of 711 and 711 \( \text{Cu} \) \( \text{K} \alpha_1 \) reflections are made on the AlGaAs layer and GaAs substrate. The peak shift of the Bragg angle gives the Aluminium ratio taking into account the elastic strain and the resulting tetragonal distorsion. Conventional electron microanalysis, employing wavelength dispersive X Ray detection, was used to determine the intensities of \( \text{Ga}_L \alpha \), \( \text{Al}_K \alpha \) and \( \text{As}_L \alpha \) lines from the samples and from GaAs and Al standards. The sum of Ga and Al weight fraction was 1 % to 4 % too small. We have assumed that this error was only due to Al which was very corrected.

In the wavelength modulation technique, the first accident of the \( \text{dR/R} = f(\lambda) \) line is taken and we suppose it is the direct gap. Using the \( E_\Gamma = f(X_{\text{AlAs}}) \) curve of (15), \( X_{\text{AlAs}} \) of the epitaxial layer is obtained.

In table I the comparative results of these 3 methods are presented. This comparison gives a objective idea of accuracies.
Experimental liquidus points and the calculated liquidus curves at 1073 K and 1173 K for the Ga rich part of the Al-Ga-As system are shown in figure 1. We have redetermined these liquidus because the previous works (16, 17, 18, 19, 20 and 21) show a too large discrepancy to observe the effect of Ge in this system. Temperature measurements in this study have an absolute precision of about 3 to 4 degrees, but they are reproducible to better than one degree. For the same reason, we have also re-determined some points of the solidus isotherm (figure 2). The growth of the layers was made at 1073 ± 4 K. The precision of the AlAs composition measurements has previously been discussed. The experimental liquidus agree with previous determination and they follow a smooth curve. We have compared the composition of the liquidus obtained by the visualisation technique and by dissolution for AlAs compositions up to

<table>
<thead>
<tr>
<th>$x_{Al}$</th>
<th>$X_{AlAs}$ Microprobe</th>
<th>$X_{AlAs}$ X Ray</th>
<th>$X_{AlAs}$ Wavelength modulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002</td>
<td>0.332</td>
<td>0.337</td>
<td>0.32</td>
</tr>
<tr>
<td>0.004</td>
<td>0.527</td>
<td>0.521</td>
<td>0.51</td>
</tr>
<tr>
<td>0.01</td>
<td>0.76</td>
<td>0.79</td>
<td>0.73</td>
</tr>
<tr>
<td>0.016</td>
<td>0.823</td>
<td>0.83</td>
<td></td>
</tr>
</tbody>
</table>

Table I: Comparative results of the composition of the solid phase.

IV. RESULTS AND DISCUSSION

0.55 and they agree very well. This is in accordance with study of Small (22). Apparently, the seed is protected by a thin layer of AlGaAs at equilibrium.

For the AlGaAs phase diagram, we have used the data of the GaAs and AlGa systems and we have adjusted slightly the stability parameters of AlAs which remain within interval of the estimations of the enthalpy and entropy of formation. The calculated liquidus agree well with the experimental values.

Experimental liquidus data and the estimated liquidus curves at 1073 K for the Ga-rich part of the Al-Ga-As-Ge system are given in fig.3. The quaternary isotherms are given for several concentrations of Al in the liquid. We observe that large amounts of Ge (40 %) have a small effect on the solubility of As at a given Al concentration. For example, at small Al concentrations, the solubility of As decreases of about 10 % when the molar fraction of Ge varies from 0 to 30 % (the accuracy of these measurements is about 1 or 2 %). Experimental solidus points and estimated solidus curves at 1073 K are given in fig.4 for several Al liquid concentrations. The presence of large amount of Ge in the liquid phase for a given Al concentration seems to decrease slightly the AlAs fraction of the solid in equilibrium. This behaviour appears for the different percentages of AlAs.

These results can be compared to Minden's results (23) who made a similar work at 1123 K and for a fraction of AlAs of about 0.3. He concluded to a more effective decrease of the Al distribution coefficient. A similar work on Al-Ga-As-Sn has been made by Panish (14). Sn and Ge are both amphoteric electrically active impurities in AlGaAs, but Sn has a clear opposite effect on the solidus and a more intensive effect on the liquidus.

If we compare the experimental points with the estimated curves, we must consider the greatly expanded scales of figures 3 and 4. These scales exaggerate the discrepancy between experimental and calculated values. We must also recall that the Ge-As system is not precisely known, and thus its liquid interaction parameter has not a precise value. Considering these remarks, the theoretical calculations predict correctly the Al-Ga-As-Ge phases diagram in the range of this investigation.
Figure 3 - AlGaAsGe system. Calculated and experimental liquidus isotherms at several constant values of $x_{Al}$ at 1073 K. • $x_{Al} = 0.00$; ■ $x_{Al} = 0.002$; ▼ $x_{Al} = 0.004$; △ $x_{Al} = 0.01$; ▲ $x_{Al} = 0.02$; solid lines: calculated curves.

Figure 4 - AlGaAsGe system. Calculated and experimental solidus isotherms at 1073 K. ▲, composition from X Ray diffraction. •, composition from electron beam microprobe. Solid lines: calculated curves.
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