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Effect of Iso-Electronic Dopants on the Dislocation Density of GaAs

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The addition of 1% In to LEC GaAs has been reported to reduce the dislocation density in this material; similar data exists for Sb doping. Several effects have been inferred to explain these phenomena, the most prevailing one stating that the solid stoichiometry is affected by an as yet unknown mechanism. Similar postulations have been made to explain the growth of semi-insulating GaAs. A thermodynamic model is described, based on earlier work, that shows a broadening of the existence region of GaAs when In or Sb are added to GaAs. Comparing the solidus phase diagrams of In- or Sb-doped GaAs to undoped GaAs shows that addition of either one of these two iso-electronic dopants has a similar effect on the solid stoichiometry as adding more As to the melt. However, the increased pressure problems in LEC growth of GaAs, normally associated with adding As, are circumvented if instead In or Sb are added to the melt. From our calculations it is also shown that the addition of the iso-electronic dopants Al or P to GaAs would not result in the same effect on the solid stoichiometry. Published experimental evidence supports this and shows that no dislocation reduction and semi-insulating GaAs is obtained with the use of these dopants. The model described in this paper explains the postulation that iso-electronic doping is of critical significance in controlling the solid stoichiometry and thereby obtaining zero dislocation density LEC GaAs and semi-insulating GaAs.

Key words: Dislocations, GaAs, iso-electronic, doping

INTRODUCTION

Two significant developments have occurred in the last few years in Liquid Encapsulation Czochralski (LEC) growth of GaAs. The first development pertains to the growth of (nearly) dislocation free material. The second major development was the growth of semi-insulating GaAs. Similar developments have occurred in GaAs grown by the horizontal or vertical gradient freeze methods and by horizontal Bridgman.

The first advantages of In doping of GaAs were long recognized[1] and were discovered in Bridgman-grown material. Today most GaAs is grown with the LEC method. It was shown that the dislocation density in 2 and 3 inch diameter LEC GaAs crystals was reduced from 10^5 cm^{-2} to nearly zero in major parts of the boule. This was achieved first by reducing the radial and axial temperature gradients, which resulted in GaAs crystals with dislocation densities in the 10^3 cm^{-2} range. Subsequent dislocation density reductions were obtained by iso-electronic doping with about 1% In in the solid, resulting in the ternary $Ga_{0.99}In_{0.01}As$. Ehrenreich and Hirth[2] suggested that the mechanism for this dislocation density reduction in GaAs, by indium addition, was the result of solid solution hardening in a similar fashion as observed in metals. It is known that InAs is less hard than GaAs.[3] Moreover, if solid solution hardening would explain the observed dislocation density reduction in GaAs, then many other dopants with atomic radii larger or smaller than Ga, if substituted on the Ga sub-lattice, would show this dislocation density reduction as well. This is not generally observed. On the other hand In is larger than Ga and the lattice will be stressed.

It has also been suggested that the addition of indium to GaAs increases the critical resolved shear stress.[4-11] This in turn suggests that the slip mechanism which produces the dislocations is inhibited. From recent measurements[12,13] of the critical resolved shear stress of undoped, indium-doped, and silicon-doped GaAs it was concluded that this mechanism for dislocation density reduction must be dis-

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counted. It was determined that the increase in the critical resolved shear stress, due to In doping, was insufficient.

The current explanation for the dislocation density reduction in GaAs from 10^5 to 10^3 cm^{-2} is that this reduction is obtained by minimizing the temperature gradients, which reduce thermal stresses. The addition of 1% In causes dislocation density reductions below 10^3 cm^{-2} towards zero and are believed to be governed by native defects and thereby influence the stoichiometry in the solid.[4–11] Until now, however, no basis, evidence, or model has been put forward suggesting that In affects the solid stoichiometry.

In this paper it will be shown that the addition of 1% indium has a pronounced effect on the stoichiometry of the GaAs solid. The native defect concentration and the solid stoichiometry will be calculated using the model used earlier.[14] The results are shown to corroborate the earlier suggestions that the solid stoichiometry can indeed be altered significantly by the addition of 1% indium to GaAs. This is not proof of the mechanism by which the addition of In reduces the dislocation density, but provides strong support for this empirical fact. The effects of other iso-electronic dopants such as Sb, Al, and P are examined as well.

It was first observed by Holmes *et al.*[15] that semi-insulating LEC GaAs could be obtained when growing from a melt which contained more than the usual fraction of arsenic. Again it was speculated that the solid stoichiometry and the native defect concentration were affected, which could cause this semi-insulating behavior.[15–18] It will be shown from our model that the addition of indium to GaAs has a similar effect on the solid stoichiometry as growing from an arsenic-rich melt. Hence, the addition of indium to GaAs potentially has a two fold effect: (i) the dislocation density is reduced, and (ii) semi-insulating material might be obtained.

The effects of changes in equilibrium native defect concentrations on EL2 are beyond the scope of this paper.

MODEL

The thermodynamic model which is used to describe the native defect concentration and solid stoichiometry for iso-electronic doping of GaAs is the same as used earlier[14] for the successful description of the GaAlAs ternary. The model and the definition of parameters were described in detail in that reference and will not be treated similarly at this time. That model is based on the presence of charged and neutral vacancies and anti-site defects. The enthalpies and entropies of the various defect reactions are derived identically as described earlier. Some of these parameters are obtained from Van Vechten.[19,20] The defect reactions and the associated enthalpies (ΔH) and entropies (ΔS) are presented in Table I for GaAs, in Table II for InAs, in Table III for GaSb, in Table IV for AlAs, and in Table V for GaP. Also listed in these Tables are the values for the enthalpy (ΔH_{cv}) and entropy (ΔS_{cv}) of the bandgap, the entropy (ΔS^f) and enthalpy (ΔH^f) of fusion, and the interaction parameters (α) for the liquid and solid. (In our model we assume the liquid to be a regular solution). For the bandgap (E_g) of GaAs doped with 1% In or other group III or group V constituent, the value and temperature (T) dependence of the GaAs bandgap were computed from:

$$E_g = 1.522 - 5.8 \times 10^{-4} \frac{T^2}{T + 320} \tag{1}$$

It was found that the minor change in the bandgap from the 1% doping was insignificant in determining the native defect concentration and solid stoichiometry.

To respective equilibrium constants (K) for the defect reactions can be calculated from the enthalpy and entropy values as follows:

$$K = \exp\left(-\frac{\Delta H}{kT}\right) \exp\left(\frac{\Delta S}{k}\right) \tag{2}$$

The electroneutrality condition can be solved after the equilibrium constants are determined. For instance, for $\mathrm{Ga}_{1-x}\mathrm{In}_x\mathrm{As}$ the electroneutrality condition is:

$$\begin{aligned} n + [\mathrm{V}^{-}_{\mathrm{Ga+In}}] + 2[\mathrm{Ga}^{2-}_{\mathrm{As}}] + 2[\mathrm{In}^{2-}_{\mathrm{as}}] \\ = p + [V^{+}_{\mathrm{As}}] + 2[As^{2+}_{\mathrm{Ga+In}}] \end{aligned} \tag{3}$$

Upon solving Eq. 3 the values for the carrier concentration, the concentration of vacancies (charged and neutral) and anti-sites are obtained as a function of temperature. Subsequently, the solid stoichiometry is calculated, again as a function of temperature, as described earlier.[14] The solid stoichiometry, which is typically taken as the amount of arsenic in In doped GaAs, is:

$$x^s_{\mathrm{As}} = 1 - (x^s_{\mathrm{Ga}} + x^s_{\mathrm{In}}) \tag{4}$$

Hence, for each temperature we know the defect concentration, the composition of the solid, the deviation from stoichiometry, and the liquid composition which is in equilibrium with the solid.

RESULTS AND DISCUSSION

The solidus phase diagrams for GaAs, $\mathrm{Ga}_{0.99}\mathrm{In}_{0.01}\mathrm{As}$, and $\mathrm{GaAs}_{0.99}\mathrm{Sb}_{0.01}$ are plotted in Fig. 1. It shows that the deviations from stoichiometry are typically in the 10^{-5} range and that the greatest deviations from solid stoichiometry occur on the gallium-rich side of the phase diagram, resulting in a broader range of arsenic-deficient solids. Upon iso-electronic doping a significant increase in the deviation from solid stoichiometry on the arsenic-rich side is observed as well. Anti-site defects are the main cause for the broadening of the phase diagram

Table I. GaAs

Defect reaction	ΔH (eV)	ΔS (k)
$Ga(l) = Ga_{Ga} + V^{*}_{As}$	1.81	−6.64
$As(l) = V^{*}_{Ga} + As_{As}$	2.47	−0.06
$V^{*}_{Ga} = V^{-}_{Ga} + e^{+}$	0.33	6.35
$V^{*}_{As} = V^{+}_{As} + e^{-}$	0.33	6.35
$Ga(l) = V^{*}_{Ga} + Ga^{2-}_{As} + 2e^{+}$	5.43	6.06
$As(l) = As^{2+}_{Ga} + V^{*}_{As} + 2e^{-}$	6.09	12.64
bandgap:	$\Delta H_{cv} = 1.635$ eV	$\Delta S_{cv} = 6.35$ k
melting point:	$T^{f} = 1511$ K	$\Delta S^{f} = 16.6$ eu
	interaction parameter	
Ga-As: $\alpha = a - bT$	$a = 5160$ cal	$b = 9.16$ cal/K

Table II. InAs

Defect reaction	ΔH (eV)	ΔS (k)
$In(l) = In_{In} + V^{*}_{As}$	1.79	−2.90
$As(l) = V^{*}_{In} + As_{As}$	2.33	−2.90
$V^{*}_{In} = V^{-}_{In} + e^{+}$	0.09	3.58
$V^{*}_{As} = V^{+}_{As} + e^{+}$	0.09	3.58
$In(l) = V^{*}_{In} + In^{2-}_{As} + 2e^{+}$	3.79	4.26
$As(l) = As^{2+}_{In} + V^{*}_{As} + 2e^{-}$	3.01	4.26
bandgap:	$\Delta H_{cv} = 0.446$ eV	$\Delta S_{cv} = 3.58$ k
melting point	$T^{f} = 1216$ K	$\Delta S^{f} = 14.52$ eu
	interaction parameters	
In-As: $\alpha = a - bT$	$a = 3860$ cal	$b = 10.8$ cal/K
GaAs-InAs	2815 cal	
Ga-In	1060 cal	

as a whole and on the arsenic side in particular. It is also evident from Fig. 1 that the highest temperature, corresponding to a liquid composition of 50% arsenic, does not correspond to the smallest deviation from stoichiometry. Strictly, this implies that the maximum melting point is unequal to the congruent melting point. Figure 2 illustrates this more clearly for GaAs and $Ga_{0.99}In_{0.01}As$, where the arsenic fraction in the liquid is plotted against the arsenic fraction in the solid in equilibrium with that liquid. It indicates that a zero deviation from stoichiometry for undoped and In-doped GaAs is obtained at an arsenic fraction in the liquidus exceeding 0.6. Hence, the crystal is As deficient at its maximum melting point.

Further examination of Fig. 1 shows that the existence region is noticeably increased when only 1% In is added to GaAs. A careful comparison indicates that a greater temperature dependence on the deviation from stoichiometry is achieved for $Ga_{0.99}In_{0.01}As$ than for GaAs. This greater change in stoichiometry is the result of the increased equilibrium native defect concentrations.

An increased sensitivity to changes is apparent in both temperature and melt composition variations. A small change in melt stoichiometry near As(l) =

Table III. GaSb

Defect reaction	ΔH (eV)	ΔS (k)
$Ga(l) = Ga_{Ga} + V^{*}_{Sb}$	2.33	−0.25
$Sb(l) = V^{*}_{Ga} + Sb_{Sb}$	1.80	−0.25
$V^{*}_{Ga} = V^{-}_{Ga} + e^{+}$	0.16	6.35
$V^{*}_{Sb} = V^{+}_{Sb} + e^{-}$	0.16	6.35
$Ga(l) = V^{*}_{Ga} + Ga^{2-}_{Sb} + 2e^{+}$	3.72	12.45
$Sb(l) = Sb^{2+}_{Ga} + V^{*}_{Sb} + 2e^{-}$	4.01	12.45
bandgap:	$\Delta H_{cv} = 0.80$ eV	$\Delta S_{cv} = 6.35$ k
melting point:	$T^{f} = 985$ K	$\Delta S^{f} = 15.8$ eu
	interaction parameters	
Ga-Sb: $\alpha = a - bT$	$a = 4700$ cal	$b = 6$ cal/K
GaAs-GaSb	3300 cal	
As-Sb	750 cal	

Table IV. AlAs

Defect reaction	ΔH (eV)	ΔS (k)
$Al(l) = Al_{Al} + V^{*}_{As}$	1.91	−2.08
$As(l) = V^{*}_{Al} + As_{As}$	1.92	−2.08
$V^{*}_{Al} = V^{-}_{Al} + e^{+}$	0.48	6.45
$V^{*}_{As} = V^{+}_{As} + e^{-}$	0.48	6.45
$Al(l) = V^{*}_{Al} + Al^{2-}_{As} + 2e^{+}$	6.98	10.82
$As(l) = As^{2+}_{Al} + V^{*}_{As} + 2e^{-}$	7.12	10.82
bandgap:	$\Delta H_{cv} = 2.38$ eV	$\Delta S_{cv} = 6.45$ k
melting point:	$T^{f} = 2043$ K	$\Delta S^{f} = 15.6$ eu
interaction parameters		
Al-As: $\alpha = a - bT$	$a = 600$ cal	$b = 12$ cal/K
GaAs-AlAs	0 cal	
Ga-Al	104 cal	

0.5, for instance making the melt more As-rich, has a more pronounced effect on the equilibrium native defect concentration in $Ga_{0.99}In_{0.01}As$ than on GaAs. Also, the addition of In to GaAs is, a far as solid stoichiometry is concerned, equivalent to increasing the arsenic fraction in the liquid and solid. This is significant, because the arsenic fraction in the liquid can not be increased at will; the arsenic pressure increases to values which are difficult to control experimentally. However, the addition of In has a similar effect on the solid stoichiometry, thereby suggesting that GaAs with 1% In is equivalent to growing GaAs from a more arsenic-rich melt. The calculations indicate that a 1% In addition results in a doubling of the antisite concentration and a small change in the vacancy concentration. Such a factor of two change in equilibrium antisite concentration is also achieved in an undoped GaAs melt with a 10% change in As concentration.

It has been demonstrated that dislocation-free GaAs can be obtained by adding 1% In. Various suggestions have been made as to the cause of this reduced dislocation density. As discussed earlier most of these postulations have been rebutted. Currently, the prevailing explanation is that the solid stoichiometry could be responsible, although a firm basis for this explanation was missing. The results in this paper form this basis and imply that the solid stoichiometry has changed via the native defect concentrations when GaAs is In-doped. The detailed mechanism governing the dramatic reduction in dislocation density, through changes in the solidus via In doping, is unclear at this time. One may speculate that the increased antisite concentration prevents dislocation formation, although the increase in critical resolved shear stress in insufficient.

As mentioned earlier, it has been well established[15–18] that growing LEC GaAs from arsenic rich melts results in semi-insulating material. The reason for this behavior was believed also to be related to native defects, which in turn impact the solid stoichiometry of the material. Based on the work described above, it is our contention that semi-insulating GaAs can also be obtained by growing from a slightly indium doped melt.[10,11] This is based on the observation that adding arsenic is equivalent to adding In as far as the changes in solid stoichiometry are concerned.

Since the dislocation density and the semi-insulating behavior of GaAs are both affected by iso-electronic doping with indium, the question arises if the role of indium is unique. Would other iso-electronic dopants show a similar behavior to the GaAs solidus phase diagram and if so which ones? The effect of the addition of 1% antimony to GaAs, re-

Table V. GaP

Defect reaction	ΔH (eV)	ΔS (k)
$Ga(l) = Ga_{Ga} + V^{*}_{P}$	1.86	−6.64
$P(l) = V^{*}_{Ga} + P_{P}$	1.86	−3.28
$V^{*}_{Ga} = V^{-}_{Ga} + e^{+}$	0.50	6.45
$V^{*}_{P} = V^{+}_{P} + e^{-}$	0.50	6.45
$Ga(l) = V^{*}_{Ga} + Ga^{2-}_{P} + 2e^{+}$	7.22	9.62
$P(l) = P^{2+}_{Ga} + V^{*}_{P} + 2e^{-}$	7.52	11.19
bandgap:	$\Delta H_{cv} = 2.49$ eV	$\Delta S_{cv} = 6.45$ k
melting point:	$T^{f} = 1748$ K	$\Delta S^{f} = 16.8$ eu
interaction parameters		
Ga-P: $\alpha = a - bT$	$a = 2800$ cal	$b = 4.8$ cal/K
GaAs-GaP	900 cal	
As-P	1500 cal	

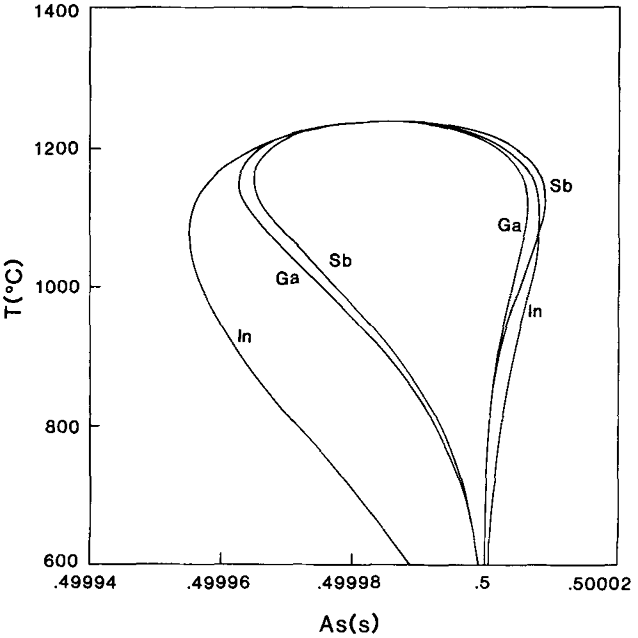

Fig. 1 — Calculated solidus phase diagrams for GaAs, Ga$_{0.99}$In$_{0.01}$As, and GaAs$_{0.99}$Sb$_{0.01}$.

sulting in GaAs$_{0.99}$Sb$_{0.01}$ is shown also in Fig. 1. It shows that the effects of In and Sb are similar with respect to the GaAs phase diagram. Hence, also in the Sb case the native defect concentrations are changed resulting in an increase in the existence region for GaAs. Similarly, the addition of 1% Sb has a much greater effect on the solid stoichiometry than adding a small additional amount of arsenic to the melt. One moves to the right in the GaAs phase diagram, as illustrated in Fig. 1 when adding this small amount of antimony. Experimentally it has been demonstrated that the addition of 1% Sb indeed can result in a decrease in the dislocation density in GaAs.[4] Similarly, one might expect that semi-insulating GaAs can be obtained as a result of iso-electronic doping with antimony.

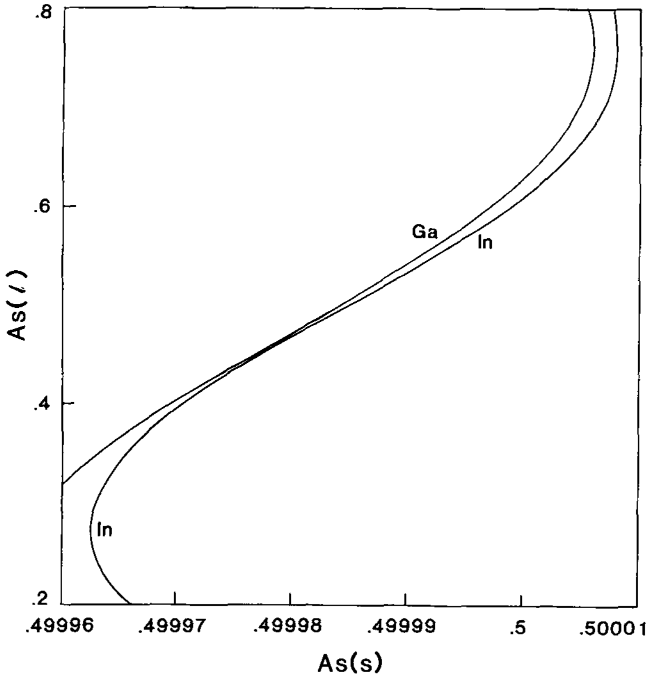

Fig. 2 — Arsenic fraction in the liquid vs arsenic fraction in the solid for GaAs and Ga$_{0.99}$In$_{0.01}$As.

Since the calculations shown here for In and Sb indicate the same effects on dislocation density reduction and possibly on the semi-insulating behavior of GaAs as well, the influence of the iso-electronic dopants aluminum and phosphorus was investigated. Figure 3 shows the phase diagrams for GaAs, Ga$_{0.99}$Al$_{0.01}$As, and GaAs$_{0.99}$P$_{0.01}$. It indicates that the existence region narrows, and that adding Al or P have not the described desirable effects on GaAs. To the best of our knowledge, no decrease in dislocation density or semi-insulating behavior has been reported upon iso-electronic doping of GaAs with either Al or P. The calculation presented here suggests that such effects would not be expected.

A common factor between the various iso-electronic dopants is that In and Sb both have larger covalent radii than the atoms for which they substitute, while the opposite is true for Al and P. The two larger atoms cause an increase in the width of the solidus phase diagram of GaAs and their incorporation in the GaAs lattice results in a shift to the right compared to the binary phase diagram. The opposite can be said for incorporation of Al and P into the GaAs lattice.

CONCLUSION

It was demonstrated that adding 1% indium of 1% antimony broadens the existence range of GaAs, principally on the Ga-rich side but, importantly also in the direction of higher arsenic concentrations. These results support the suggestions made in the literature that, through the influence of native defects when adding these two dopants, the disloca-

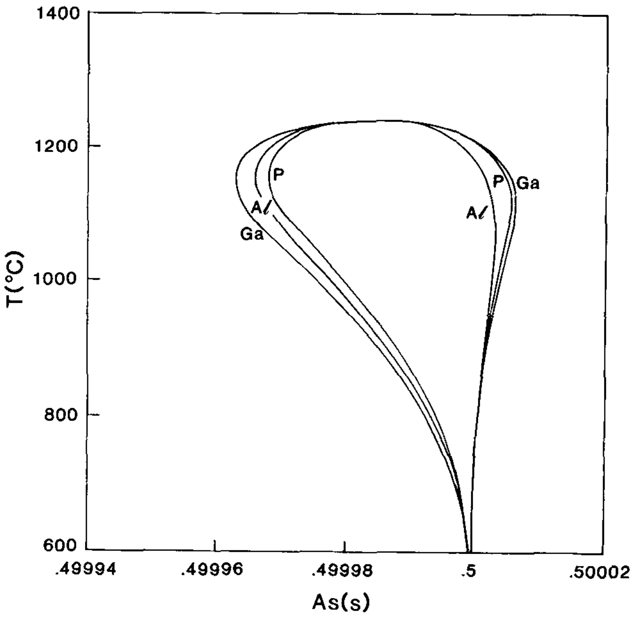

Fig. 3. — Solidus phase diagram for GaAs, Ga$_{0.99}$Al$_{0.01}$As, and GaAs$_{0.99}$Sb$_{0.01}$.

tion density can be reduced to zero in LEC material and that semi-insulating GaAs can be obtained. We predict that anti-sites are the predominant native defect in iso-electronic doped GaAs.

The calculations described here also suggest that the role of indium and antimony is unique among iso-electronic dopants, because they have larger atomic radii than gallium and arsenic, respectively. Iso-electronic substitutions such as aluminum and phosphorus, which have both smaller covalent radii than gallium and arsenic, restrict the existence range of GaAs on the Ga and As side of the phase diagram. At the same time these latter substitutions do not give rise to a reduction in dislocation density or semi-insulating behavior.

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