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LIQUID PHASE EPITAXY OF GaAsSb
ON InP SUBSTRATES

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Solid State Device Research Group

July 31, 1977

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FINAL TECHNICAL REPORT
for period Oct. 1, 1976-Dec. 31, 1976

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FINAL TECHNICAL REPORT

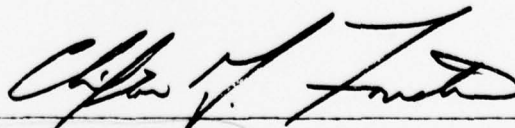
LIQUID PHASE EPITAXY OF GaAsSb
ON InP SUBSTRATES

Effective Dates: October 1, 1976 through December 31, 1976

Principle Investigator: C. G. Fonstad

ABSTRACT

The Ga-As-Sb system is shown to exhibit immiscibility-like behavior, i.e. certain solid compositions do not exist, for growth from ternary melts in spite of the fact that the pseudobinary system is fully miscible. The ternary melt miscibility gap narrows with increasing growth temperature and disappears above a certain temperature but even then the solid composition remains a very sensitive function of the growth temperature. For growth of $\text{GaAs}_x\text{Sb}_{1-x}$ layers lattice matched to InP (i.e. layers with $x \approx 0.5$) these results imply that conventional, variable temperature LPE techniques are not adequate. Instead any successful growth system must use constant temperature growth, and must include provisions to prevent decomposition of the InP substrate at the relatively high growth temperatures anticipated and to prevent dissolution of the InP substrate by the melt. Experimental observations supporting these conclusions are discussed.

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I. OVERVIEW

The work reported here was initiated under a three month contract with the Naval Air Systems Command covering the period October 1, 1976 through December 31, 1976. It was completed in the first three months of a consecutive contract with International Telephone and Telegraph Electro-Optical Products Division. The work's purpose was to experimentally and theoretically consider the epitaxy by liquid phase techniques of gallium arsenide antimonide, $\text{GaAs}_x\text{Sb}_{1-x}$ on indium phosphide and to evaluate this material for application in 1.0-1.4 μm light emitters suitable for optical fiber communications. In the short period available only a beginning could be made but it was possible to do numerous growth runs and to do complete phase calculations in the critical region, $x \approx 0.5$, which allow us to clearly describe the growth situation, state the difficulties that must be overcome, and make some intelligent, i.e. knowledgeable, statements about the importance of this system relative to alternative ternaries and quaternaries.

A. General Goal

The need for light emitters and detectors in the 1.0 to 1.4 μm wavelength region for use on glass optical fiber communication systems is by now well known. Figures 1 and 2 illustrate the fiber characteristics, absorption and dispersion, respectively, that are minimized by operating in this wavelength range. Because currently available light emitting diodes and laser diodes based on AlGaAs, GaAsP, or GaP emit at wavelengths less than 0.9 μm , there is a need to develop new narrower band-gap materials and to fabricate devices in them. GaAsSb, and the related quaternary AlGaAsSb, is one possible material choice for this wavelength region.

B. Ternaries and Quaternaries on GaAs

Binary semiconductor compounds such as GaAs have a specific, char-

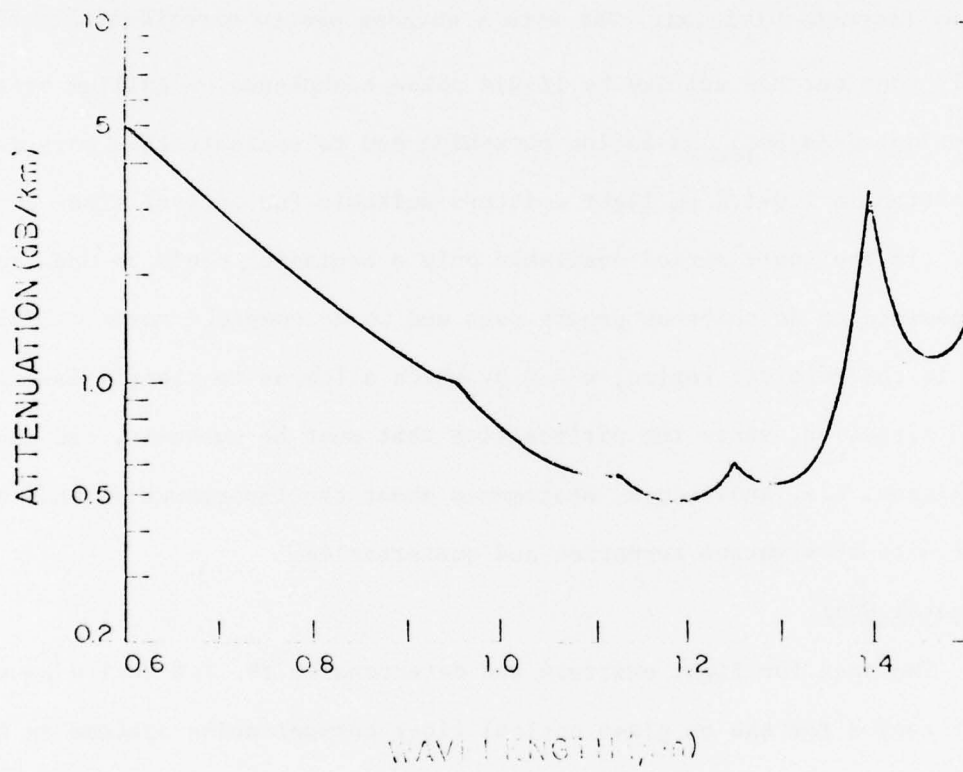


Figure 1 - Loss spectrum of a low-loss optical fiber waveguide. [Ref: M. Horiguchi, Elec. Lett. 12 (1976) 311.]

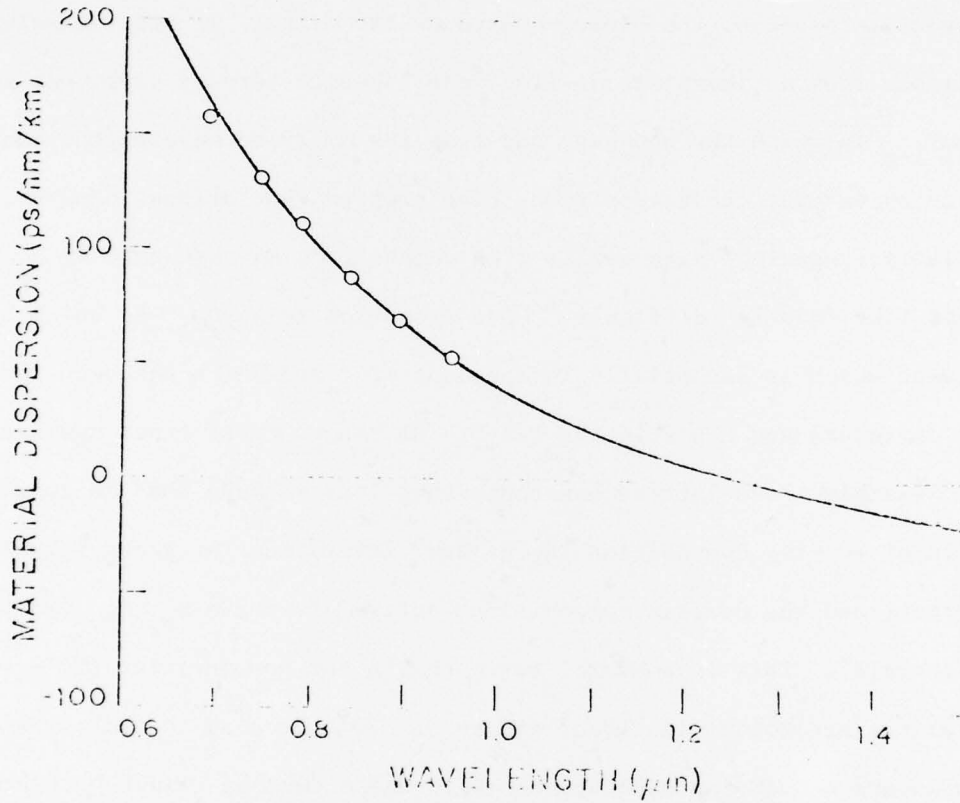


Figure 2 - Material dispersion, $d\tau/d\lambda = (-\lambda/c)d^2n/d\lambda^2$, as a function of wavelength for a typical optical fiber. [Ref: D. N. Payne and W. A. Gambling, Elec. Lett. 11 (1975) 176.]

acteristic band-gap, and thus tend to emit light (photons) at only specific wavelengths. If the specific wavelengths are useful, as is the case with GaAs LED's and lasers matched to Si photodetectors, or GaP red and green LED's for visible devices, the binary compounds are useful. If other wavelengths not available from a binary are desired, one looks to ternary compounds such as $\text{GaAs}_x\text{P}_{1-x}$ in which the bandgap, and thus the emission wavelength, can be varied by varying the composition. The problem that arises, however, is that the lattice spacing also varies with composition so that epitaxy on a binary substrate like GaAs is difficult.* One exception is $\text{Al}_y\text{Ga}_{1-y}\text{As}$ which has lattice constant which is essentially independent of y and which has been successfully used in lasers and LED's in the 0.7-0.9 μm range. Most other systems, $\text{GaAs}_x\text{P}_{1-x}$ is an example, have lattice constants that vary so much that in general a thick region of varying composition (a "graded" layer) must be grown between the substrate and the desired composition "active" layer ($\text{GaAs}_{0.6}\text{P}_{0.4}$ for red LED's for example). This is awkward, but workable for homojunction LED's, but it is not useful for heterojunction laser diodes or LED's because the multiplicity of thin layers of varying bandgap needed in these devices cannot be fabricated.

To solve the problem of the inflexibility of ternaries and binaries, researchers have relatively recently begun giving attention to quaternaries. These systems have two independent variables which allow separate variation, within limits, of the band-gap and lattice spacing. With the advent of fiber communications, the need for 1.0-1.4 μm laser diode sources has accented the need to study such quaternary systems and several, in particular InGaAsP and AlGaAsSb, have been considered. The lattice parameter-energy gap relationship for these two systems is illustrated in Figure 3. The area of interest for

* No one has yet developed techniques to grown bulk ternary crystals from which ternary substrates could then be cut.

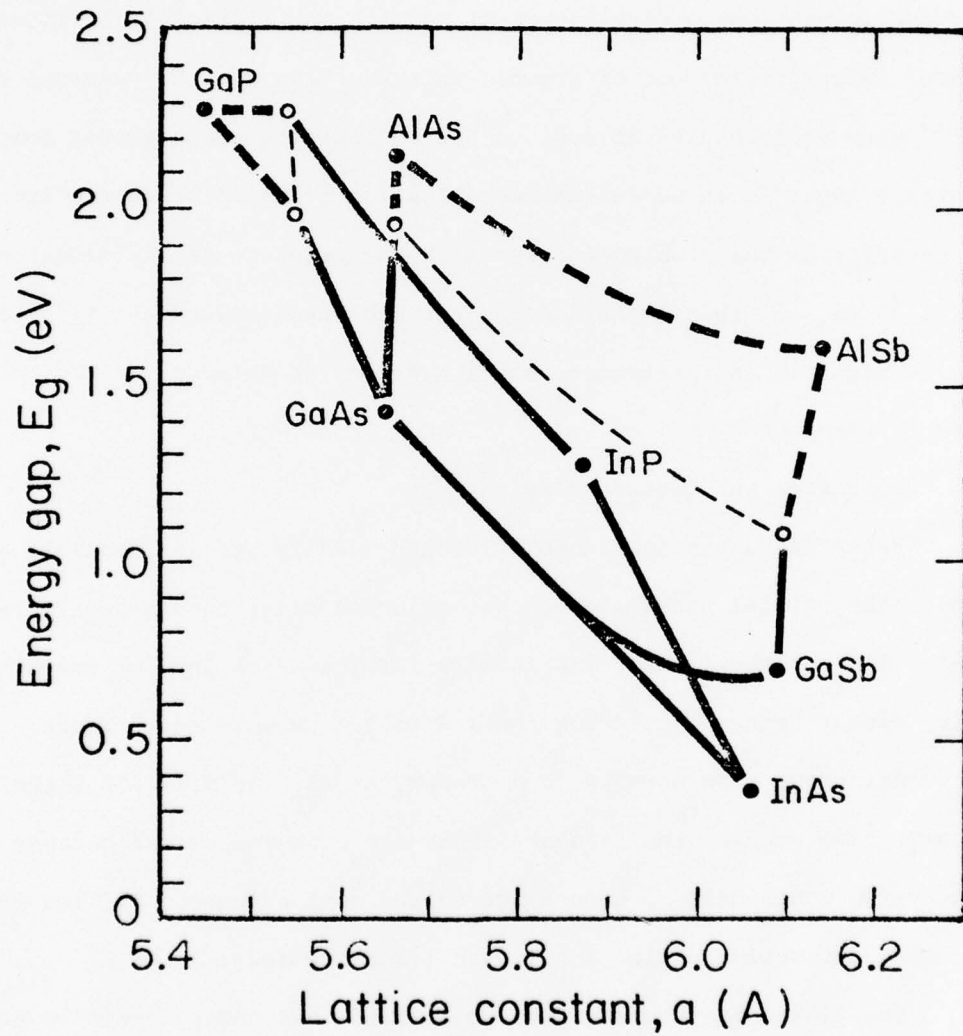


Figure 3 - A comparison of the lattice constants and energy gaps of the two quaternary systems, InGaAsP and AlGaAs Sb. In the regions enclosed by the dashed lines the bandgap is indirect.

the current discussion is in the vicinity of GaAs, and it is evident that in order to obtain emission at wavelengths longer than $1 \mu\text{m}$, a graded composition layer of InGaAs (or GaAsSb) must first be grown on GaAs, before the thin confinement and active layers of InGaAsP (or AlGaAsSb) and InGaAs (or GaAsSb) respectively, can be grown. This has been done by numerous researchers¹⁻³ with good results at $1.06 \mu\text{m}$ but the need to use a graded composition interface layer is an undesirable complication it would be attractive to avoid. The severity of the problem increases as one tries to get to longer wavelengths, i.e. $1.25 \mu\text{m}$, and this technique has not been used beyond about $1.1 \mu\text{m}$. The lattice mismatch is furthermore still a source of defects and one would like to avoid it altogether.

C. Ternaries and Quaternaries on InP

Referring again to Figure 3, we can readily see one possible solution to the problem posed above, that solution being to use a different substrate, InP. Both AlGaAsSb and InGaAsP lattice-match InP for compositions having direct bandgaps covering the 1.0 to $1.4 \mu\text{m}$ wavelength range. Various researchers, most notably J. J. Hsieh, et al.⁴ at M.I.T.'s Lincoln Laboratory, have studied the InGaAsP/InP system with impressive success and this system would have to be considered the most advanced, and for that reason, most attractive choice for 1.0 to $1.4 \mu\text{m}$ devices.

The AlGaAsSb system, on the other hand, has the potentially attractive feature that the lattice constant is essentially independent of the aluminum-to-gallium ratio, which makes growth of lattice-matching layers depend only on having the correct arsenic-to-antimony ratio. This and the possibility of other unforeseen advantages this quaternary might have over

the InGaAsP system indicate that some research into the epitaxy of AlGaAsSb on InP is warranted — the work reported here describes such a program.

The AlGaAsSb/InP system has two major potential problems which have to be addressed immediately. The first is that there is a purported miscibility gap in the GaAsSb ternary system, which if it exists would imply that the necessary lattice-matching compositions, $x \approx 0.5$, could not be grown. The existence of this miscibility gap has been a subject of dispute but until the present need to grow compositions within it, it has remained simply a curiosity with no practical consequence. The present work requires that we look specifically at its existence, or non-existence. The other potential difficulty with the AlGaAsSb/InP system is that the growth melt would contain no indium or phosphorous and thus the substrate will most certainly be soluble to some extent in the melt. Techniques may therefore have to be developed to prevent dissolution, or melt-back, of the substrate.

D. Scope of the Program

There were both an experimental and a theoretical component to the work described and summarized in this report. Experimentally, the first (to our knowledge) attempts to grow $\text{GaAs}_x\text{Sb}_{1-x}$, $x \approx 0.5$ on InP were made and the resultant deposits were analyzed by optical and electron microprobe techniques. Simultaneously phase equilibria calculations were performed to model the growth system and permit comparison of the experimental results with theoretical predictions.

Lattice matched layers of GaAsSb were not successfully grown, but sufficient information was obtained to demonstrate the problems in applying conventional LPE techniques to do this, and to understand requirements for successful growth. The concept of a miscibility gap in the context of solution epitaxy (LPE) has also been examined and its implications quant-

ified. These results indicate that a fixed temperature growth technique is desired and that growth must be done at relatively high temperatures, $> 650^{\circ}\text{C}$. It is concluded that the difficulties inherent in growing GaAsSb heteroepitaxially on InP are such that unless other requirements make this system far more attractive than any of the alternative systems, such as GaInAsP on InP, there is no practical incentive to investigate it further. On a purely theoretical basis, it would be of interest to determine if adding aluminum to the system, i.e. going to the quaternary, decreased the degree of "immiscibility" and to determine if, in this delicately balanced system, pulling effects such as lattice pulling, might be used to advantage. This might be an interesting system in which to apply Peltier-cooled growth techniques, for example. Unquestionably such a program would contribute significantly to our understanding of how phase equilibria can be biased by externally imposed forces.

II. RESEARCH REPORT*

A. Introduction

Nahory, et al.⁵ have recently published an extensive summary of their work studying GaAsSb and AlGaAsSb layers hetero epitaxially grown by liquid phase epitaxy on GaAs substrates. In the course of their presentation they discuss the question of a miscibility gap in the GaAsSb system and present a comprehensive review of the literature concerning this issue. They conclude from their own data that the GaAsSb system is miscible but also that it is a borderline case between miscible and immiscible solid solutions, conclusions consistent with our results, also.

The concept of a "miscibility gap" is presented by Nahory et al.⁵ in terms of the GaAs-GaSb pseudobinary solidus curve which is reproduced in Figure 4. Various curves are presented, each one calculated for a different value of the solidus interaction parameter, β . This is the main "unknown" in these type of calculations (values in the literature vary between 2700 and 4500) and is the parameter varied in order to fit the theoretical curves to experimental data. Nahory et al.⁵ conclude that a value of 4000 fits their data best but the important thing to note at this point is that all of the curves shown in Figure 4 indicate that a pseudobinary melt is cooled, the solid composition jumps very quickly - in fact, discontinuously if there is a miscibility gap - from one having a high Sb fraction to one having a high As fraction. Compositions between $\text{GaAs}_{0.4}\text{Sb}_{0.6}$ and $\text{GaAs}_{0.6}\text{Sb}_{0.4}$ either exist over only a very narrow temperature range or not at all. This is significant because a solid with equal fractions of Sb and As, i.e. $\text{GaAs}_{0.5}\text{Sb}_{0.5}$, would lattice match InP and producing it would open the way

* The material in this chapter is to be submitted for publication.

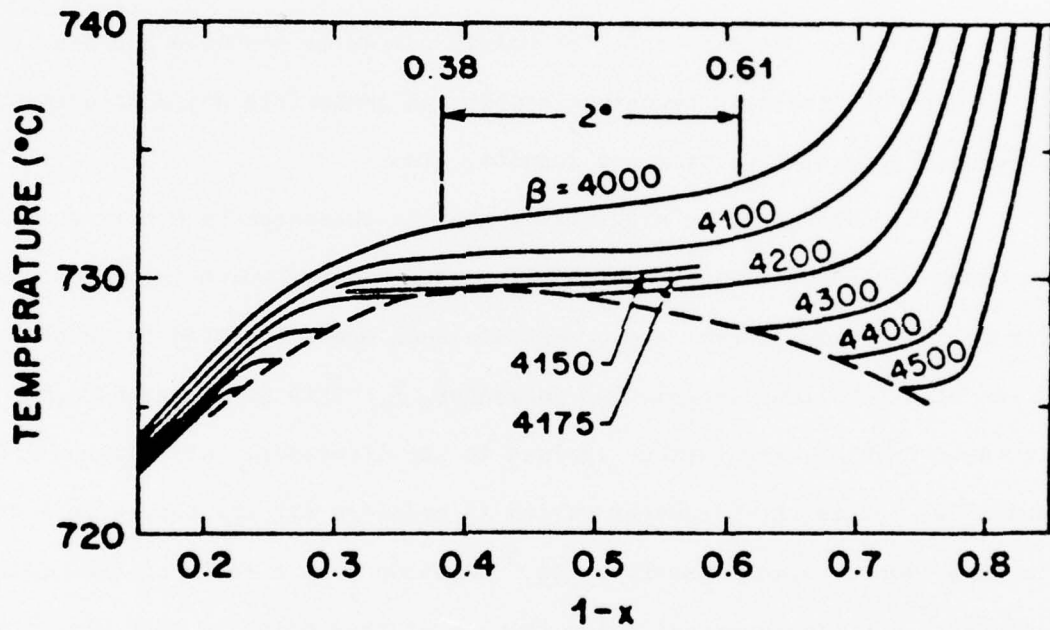


Figure 4 - The GaAs-GaSb pseudobinary solidus curve for various values of the solidus interaction parameter, β . When $\beta \geq 4185$ there is a miscibility gap in the pseudobinary solidus. [This is Figure 4 from Nahory *et al.*, Reference 5.]

to production of InP/AlGaAsSb/InP DH laser diodes for the 1.0 to 1.4 μm wavelength range.

Double heterojunction devices such as this one would not typically be grown from a pseudobinary melt, however, but would be grown by liquid phase epitaxy from a Ga-rich melt. It is consequently necessary to ask what the implications of the miscibility gap behavior are for liquid phase epitaxy. We will consider these implications here and will show that even if the pseudobinary does not indicate immiscibility, the tendency towards immiscibility leads to "miscibility gap" like behavior in liquid phase epitaxy (LPE) and to an extreme sensitivity of composition to temperature. Both effects all but preclude successful LPE of GaAsSb on InP, at least by conventional techniques.

B. Substrate Considerations

Because growth of $\text{GaAs}_{1-x}\text{Sb}_x$ with $x \approx 0.5$ is of interest particularly when InP is used as the substrate, we must first consider what restrictions use of this material places on our discussion. There are two: 1) the composition of the epi-layer must be so as to lattice match InP, and 2) the growth temperature must be sufficiently low that the substrate does not decompose.

The first item can be considered by assuming that $\text{GaAs}_{1-x}\text{Sb}_x$ follows Vegard's law and has a lattice parameter, a_0 which varies linearly with x . We thus have $a_0(\text{GaAs}_{1-x}\text{Sb}_x) = 5.6534 + 0.4421 x$ (in \AA). Setting this equal to $a_0(\text{InP}) = 5.8688 \text{ \AA}$ yields $x = 0.487$ for the lattice matching tern-

ary at room temperature. For simplicity in our subsequent discussions we will speak of a value of $x = 0.5$ as being the one of interest.

The second issue, that of the growth temperature, is harder to quantify but it is true that growth should be done at as low a temperature as possible in order to minimize decomposition of the InP substrate. Growth at 620°C or below is desirable (the lower the better). One can possibly go as high as $\sim 650^\circ\text{C}$, although decomposition becomes a severe problem at this temperature, particularly when no flux is used and no over pressure of P is provided. We will consider temperatures as high as 725°C in some of our subsequent discussions but it should be kept in mind that growth at such temperatures would not be possible on InP substrates using most conventional, unsealed, horizontal sliding boat LPE systems, and that this is at least 100°C higher than what is normally considered the safe operating range using InP substrates.

C. Phase Equilibria Calculations

The procedure used to calculate the ternary phase diagrams* used in subsequent discussions was essentially identical to that of Nahory et al.^{5,7} who followed closely the work of Panish and Illegems.⁸ Except for the solidus interaction parameter, β , which we treat as an unknown quantity, the values of all of the other parameters were taken to be the same as those used by Nahory, et al.⁵ (see Table III of Ref. 5). This is done to permit more ready comparison to their results and because they are reasonable values. We have no reason to choose any different ones.

*See Appendix A for a print out of the program used.

Nahory, et al⁵ present the solidus isotherms for the Ga-As-Sb ternary phase diagram for $x \leq 0.3$ and $700^\circ < T < 900^\circ\text{C}$ in their Figure 2. In Figure 5, we extend these calculations to cover the whole range of x , $0 \leq x \leq 1$, and do them over a lower range of temperatures, 575 to 750 C. We do this in order to cover the ranges that are of interest when using InP substrates. Figure 5 presents a family of curves between 575 and 750 C in 25 °C steps. In Figure 6 the range from 700 to 750 C is expanded. Curves are presented for 5 °C steps over this whole range, and for 1 °C steps between 725 and 735 C. $\beta = 4000$ was used in these calculations.

We see two important features of the curves in Figs. 5a and 6. We see that the curves become multivalued in the solid composition in equilibrium with a given melt composition at temperatures below, 725 C. Although it is not shown in Figs. 5a or 6, the curves are actually s-shaped in the shaded region with three solutions, i.e. values of x , for each x_{sb}^{l} . As T increases the size of the multivalued region decreases and above 725 C the curves are single valued. However, x still changes very rapidly with x_{sb}^{l} here, and the curves are almost vertical in the range $x \approx 0.5$.

Secondly, we see that the curves are extremely temperature sensitive, particularly at higher temperatures where the steepness of the curves is reduced. Because LPE growth occurs from nearly constant x_{sb}^{l} melts, this implies that it would be very difficult to control the depositing solid composition using typical temperature lowering LPE methods. This is illustrated in Figure 7 where x is plotted versus T assuming a constant $x_{\text{sb}}^{\text{l}} = 0.43$. If we say that the condition for obtaining lattice matching layers is $x = 0.50 \pm 0.01$, we find that the growth temperature is 729.5 ± 0.01 C. This temperature specification is meaningless in the sense that the nominal growth temperature determined

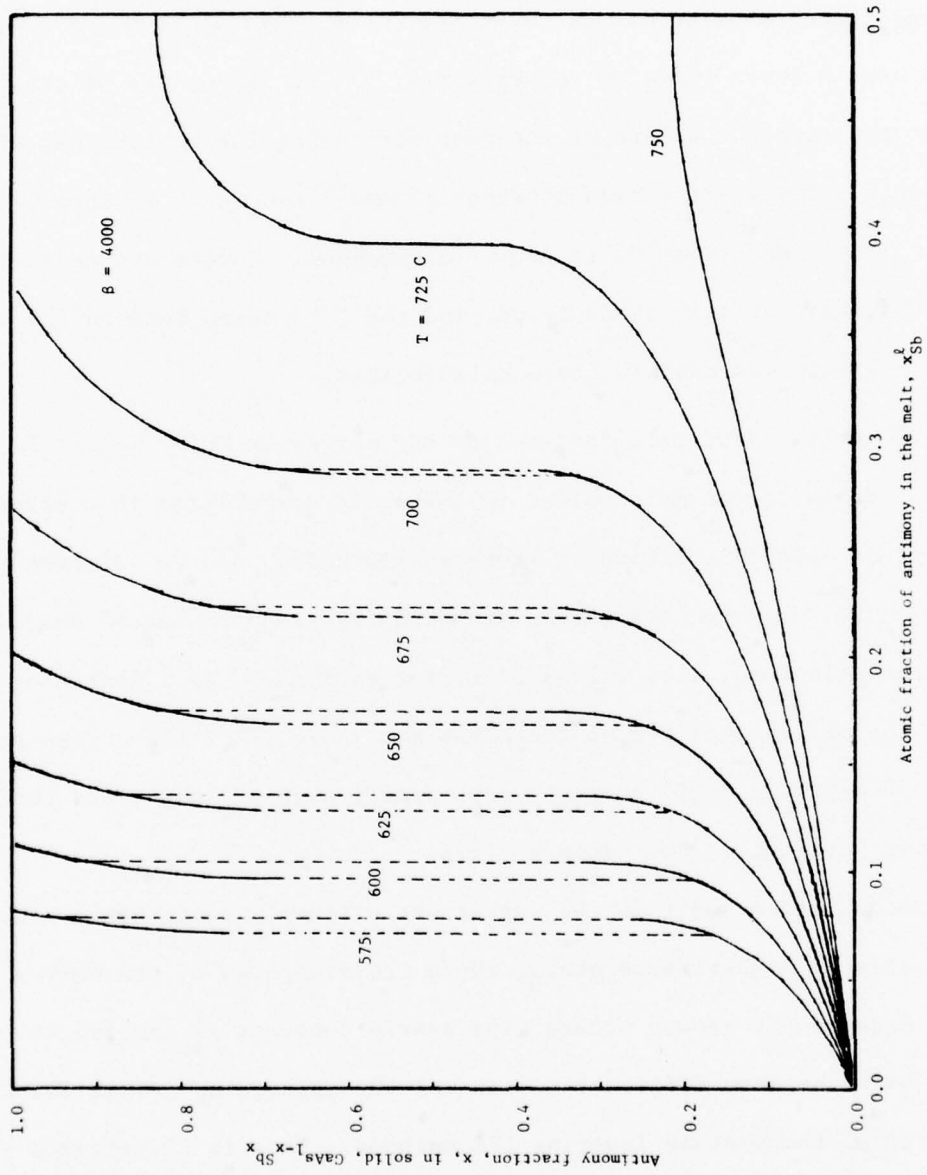


Figure 5a - The composition of the solid $\text{GaAs}_{1-x}\text{Sb}_x$ in equilibrium with a ternary melt of antimony fraction x_{Sb}^l calculated at various temperatures between 575 and 750°C when $\beta = 4000$. The corresponding atomic fraction of arsenic is given in Figure 5b and the remainder of the melt is gallium.

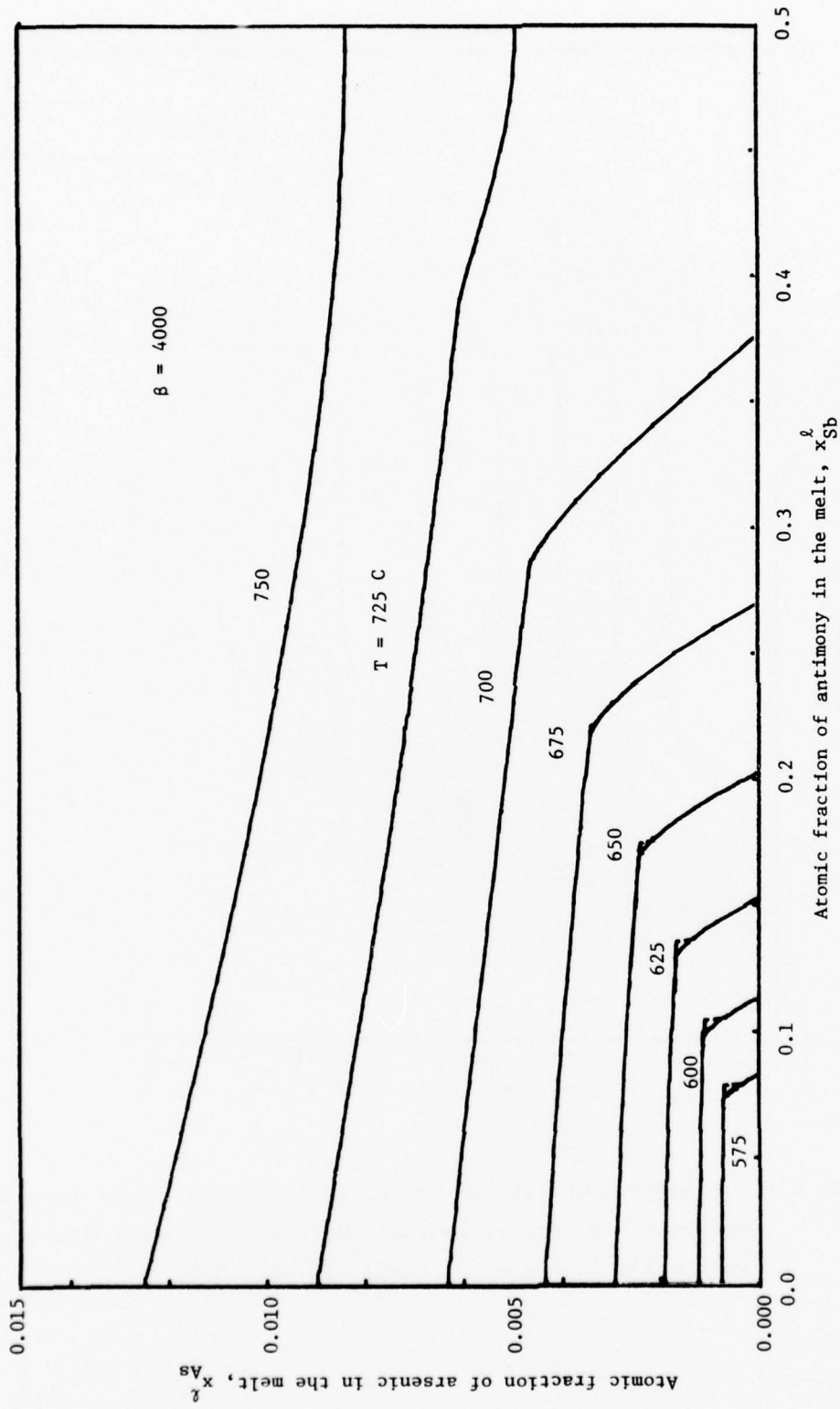


Figure 5b - Arsenic solubility in gallium-antimony solutions as a function of the atomic fraction of antimony and for various temperatures between 575 and 750°C with $\beta = 4000$. (See also Figure 5a)

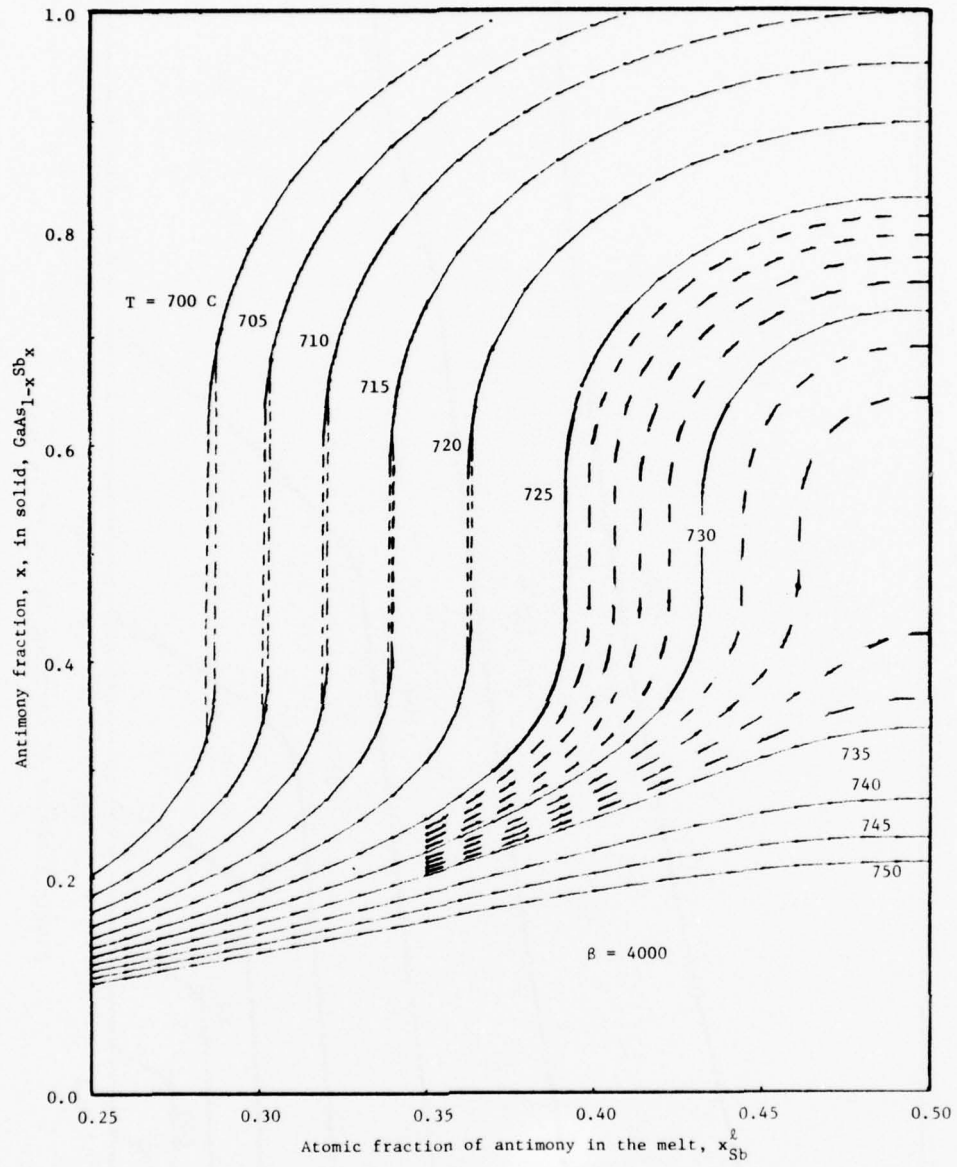


Figure 6 - The same quantities as presented in Figure 5a but over a narrower temperature range, 700 to 750°C, in 5°C increments, and in 1°C increments between 725 and 735°C.

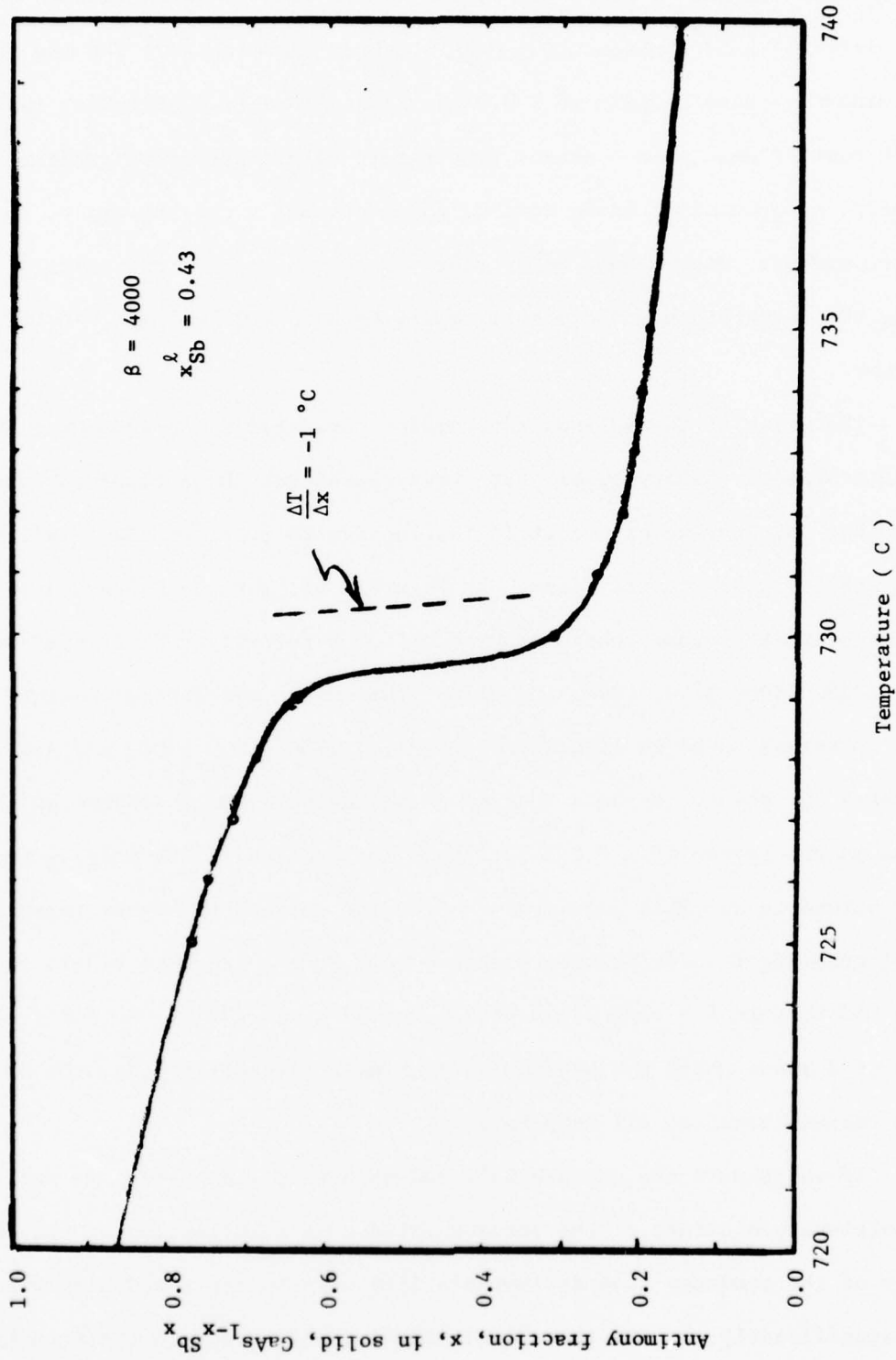


Figure 7 - The antimony fraction, x , of the solid $\text{GaAs}_{1-x}\text{Sb}_x$ in equilibrium with a melt containing 43 atomic % Sb as a function of temperature. The dashed line has a slope $\Delta T/\Delta x = -1(^\circ\text{C})$.

by the phase diagram is uncertain to $\pm 1^\circ\text{C}$, and we are asking that it be controlled and held constant to $\pm 0.01^\circ\text{C}$. Even assuming that one was able to determine the phase diagram to $\pm 0.01^\circ\text{C}$, this allowable uncertainty implies growth must be done at a constant temperature with temperature gradients in the melt, as opposed to being done by going through a cooling cycle, and that the temperature control must be extremely good. As a practical matter, determining the temperature and controlling it, both to $\pm 0.01^\circ\text{C}$ are formidable problems.

The value of the solidus interaction parameter β , of 4000 used above was determined by Nahory *et al.*⁵, but other researchers have found various values for this parameter and it is instructive to consider the sensitivity of our observations to its value. In Figure 8 we plot the solidus isotherms for the Ga-As-Sb ternary phase diagram at 650 C for values of β equal to 2750, 3000, 3250, 3500, 3750, 4000, and 4250. This range corresponds roughly to the range of values found in literature^{9,10}, i.e. $2700 \leq \beta \leq 4500$, and amply illustrates our point. We note that as β is increased the steepness of the curves in the region of $x \approx 0.5$ increases and eventually the solidus becomes multi-valued in x . This multi-valued behavior extends to higher temperature with increasing β . For example when $\beta = 3000$, the solidus is single valued above 460 C; when $\beta = 3500$ it is single valued above 590 C. When $\beta = 4185$, the value of β above which the pseudobinary shows a miscibility gap, the multi-value region exists at all temperatures.

If we compare the pseudobinary and ternary solidus lines we see that the multi-valued nature of the ternary solidus is a reflection of the immiscibility or the tendency towards immiscibility seen in the pseudobinary solidus. Most significantly, we see that "immiscibility" can occur on the ternary solidus even though the system is, strictly speaking, miscible, i.e. even if $\beta < 4185$.

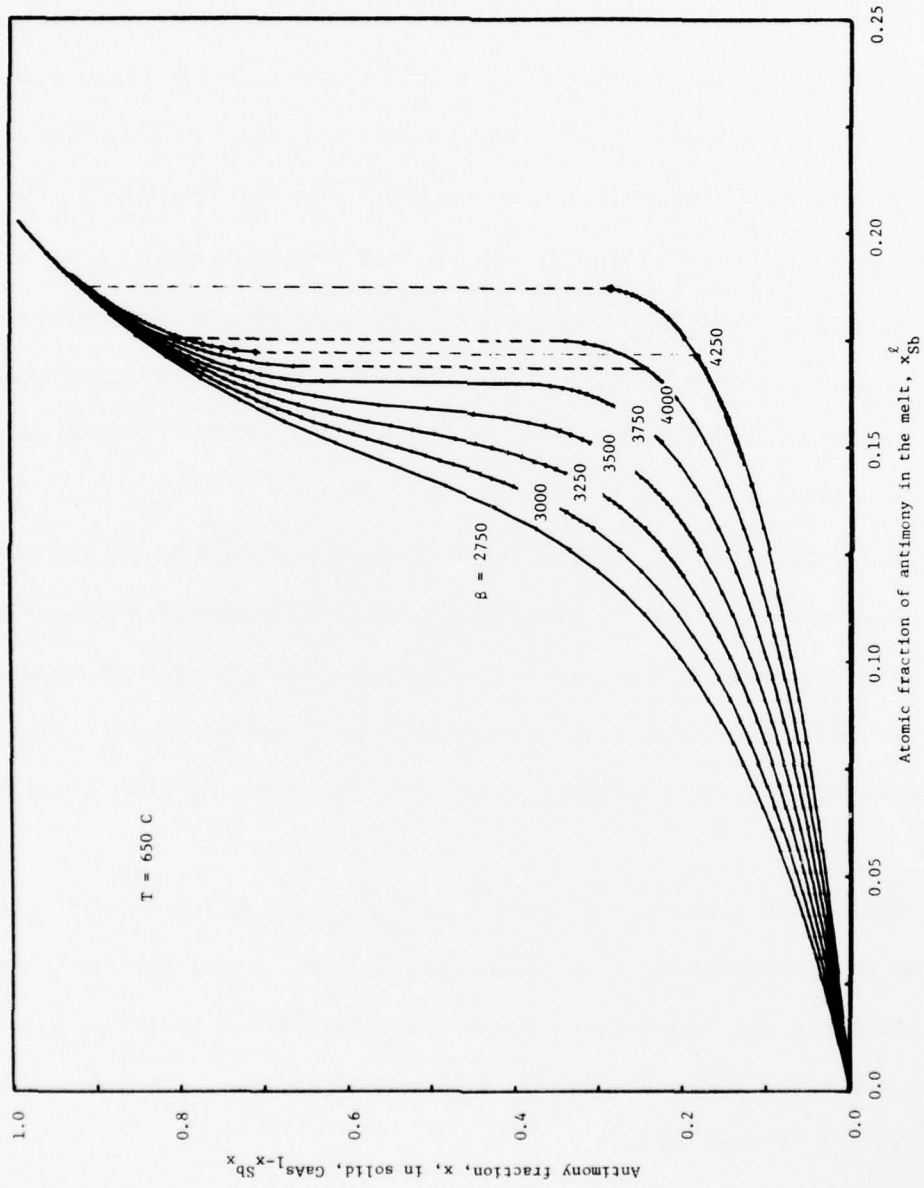


Figure 8 - The ternary solidus at 750°C - calculated for values of β between 2750 and 4250 to illustrate the onset of the multi-valued behavior with increasing β .

D. Experimental Observations

We have grown many layers of GaAsSb and AlGaAsSb on GaAs substrates and have made numerous attempts to grow GaAsSb on InP substrates. We will discuss here observations made on such growths which relate to the present discussion. The growth technique used is a standard horizontal, slider technique using a graphite boat, a quartz walled furnace, and a hydrogen atmosphere. A GaAs substrate was used to saturate the melt with As at the growth temperature in the case of the growths on InP substrates, while in the case of the growths on GaAs the components of the melt were individually weighed and the liquidus temperature, and therefore the growth initiation temperature, was determined by direct observation of the melt. Cooling rates were typically either 0.1 or 0.25 °C/min.

The growths on GaAs substrates¹¹ were restricted to layers with $x \leq 0.1$ and to 665 to 740 C. Thus they, like the growths of Nahory et al⁵ occurred in a region of the phase diagram far from the area of interest for growth on InP. The value of β we deduced from these growths is 3850 ± 100 ; this is similar to, but slightly lower than the value of 4000 found by Nahory et al.⁵

While high quality layers of $\text{GaAs}_{1-x}\text{Sb}_x$, $x \leq 0.1$, could be grown on GaAs, no successful growths were achieved on InP. These growth attempts were limited to the temperature range $600 < T < 660$ C with the majority being done in the range $650 < T < 660$ C.* Growth ranges, i.e. total cooling ranges, as narrow as 1 °C were used.†

Two major observations were made: (1) there was consistently severe dissolution of the InP substrate by the melt, and (2) no phase with similar

* A typical melt might contain 17 atomic % Sb, 0.1 atomic % As, and 83 atomic % Ga, and have a liquidus temperature of 650°C.

† See Appendix B for a summary of the GaAsSb/InP growth runs.

As and Sb fractions was observed but frequently two phases, one of large Sb fraction, the other of high As fraction, were found mixed together and adjacent to each other.

The first observation that some of the InP substrate was consistently dissolved by the melt is not directly relevant to the issue of immiscibility along the ternary solidus but it does bring to evidence another problem of using LPE to grow GaAsSb on InP. There is neither In or P in the melt and thus with respect to these elements, the melt is always undersaturated, and will tend to dissolve some of the substrate. This occurred in our experience even when the melt was step-cooled by as much as 5°C prior to bringing it in contact with the InP substrate. It is interesting to contrast this behavior to that of a melt which has one element, but only one, in common with the substrate: A saturated In-Ga-As melt, for example, will not dissolve an InP substrate even though there is no P in the melt because to do so would require adding more In to the melt at the same time.

Electron beam microprobe of deposits left on InP substrates often showed the presence of two regions one rich in As, the other rich in Sb. For example, in one typical growth run^{*}, the analysis of the two regions was (1) 36% As, 6.5% P, 7.5% Sb, 50% Ga and (2) 11% As, 1% P, 38% Sb, 50% Ga (all atomic percent). In this case growth was done over a 1°C cooling range although because of the severe attack of the substrate it is impossible to say that the melt was completely wiped off the substrate after growth and to be certain that some of this deposition did not occur at lower temperatures from remnant melt. However, the existence of these two phases in direct contact with each other and the absence of any intermediate compositions is felt

^{*} See Appendix B for a summary of the growth analyses.

to be experimental evidence that the solidus line is very steep if not discontinuous in the region of $x \approx 0.5$ as our phase calculations using $\beta \approx 4000$ predict.

III DISCUSSION AND SUMMARY

Although the extension of the concept of a miscibility gap in the pseudo-binary solidus into the ternary melt solidus, and the observation that a miscibility gap can exist for LPE growth even if the binary system is fully miscible, are both important results of this study, the practical message is largely negative in the sense that the results also indicate that growth of GaAsSb on InP using liquid phase epitaxy is extremely difficult if not impossible. Experimentally the two major problems which would have to be addressed are (1) maintaining the integrity of the InP substrate in the presence of the Ga-As-Sb melt and at relatively high temperatures, and (2) controlling the solidifying composition in spite of the vertical nature of the solidus on the ternary phase diagram (one would, of course, be forced to work above the temperature region where the solidus was multi-valued). The latter is the more fundamental problem as it is the one dictated by the phase diagram and is the one inherent to the Ga-As-Sb materials system. It clearly points to use of a fixed temperature growth technique if LPE is to be used.

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APPENDIX A - PHASE EQUILIBRA PROGRAM

A program was written to generate ternary phase equilibra data for the Ga-As-Sb system on an HP-9820A desk-top calculator and to plot the data on an HP 9862A calculator plotter. A listing of this program is given below.

The program begins by asking the operator if he wishes to change step 42. Step 42 is to plot Y, the atomic fraction of antimony in the melt, and C, the atomic fraction of arsenic in the melt. By replacing the "C" by "X", the value of x in the solid $\text{GaAs}_{1-x}\text{Sb}_x$, will be plotted.

The operator then types in the plot limits, "XMIN," "XMAX," "YMIN," and "YMAX," where "X" and "Y" correspond to the horizontal and vertical axes, respectively. Then the first value of the atomic fraction of antimony in the melt, now labeled "XSB," and next the increment in XSB are inserted. Next the value of the solidus interaction parameter, called β in the text but called "ALPH. GAAS-GASB" in the program, is inserted. Finally the temperature is requested by the statement "TEMPERATURE CEL." When the temperature is inserted the calculation begins.

In the multivalued ranges, see Figure 5, the hysteresis in the curves is seen by plotting with both positive and negative increments of XSB.

Listing:

```
0:
PRT "CHANGE 42?"
;ENT "XMIN?";R50
,"XMAX?";R51,"YM
IN?";R52,"YMAX?"
;R53+
1:
SCL R50,R51,R52,
R53;AXE 0,0,(R51
-R50)/10,(R53-R5
2)/10;SFG 14+
```

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2:
 ENT "FIRST VALUE
 XSB",R54,"STEP
 XSB",R55F
 3:
 ENT "ALPH. GAAS-G
 ASB",R1F
 4:
 F
 5:
 F
 6:
 F
 7:
 F
 8:
 F
 9:
 F
 10:
 16.64+R8F
 11:
 15.8+R9F
 12:
 1238+R10;710+R11
 F
 13:
 ENT "TEMPERATURE
 CEL.",A;0+C;.5+
 XF
 14:
 F
 15:
 5160-9.16*(A+273
)+R12;4700-6*(A+
 273)+R13;R54+YF
 16:
 IF Y>R51F
 17:
 -1800+3300*Y+R14
 F
 18:
 R12+R14-R13+R15F
 19:
 R12+R13-R14+R16F
 20:
 8.314/4.18+R17F
 21:
 -R12/2+R8*R10+R1
 7*(A+273)*LN 4+R
 18F
 22:
 -R8+R19F

23:
 R13+R14-R12+R20F
 24:
 -R13/2+R9*R11+R1
 7*(A+273)*LN 4+R
 21F
 25:
 -R9+R22F
 26:
 R13*(1-Y-C)+2+R1
 4+C+2+R20+C*(1-Y
 -C)+R23F
 27:
 R12+C+2+R13+Y+2+
 R16+C*Y+R21+R23*
 A+R24F
 28:
 R23+R24+R17*(A+2
 73)*(LN Y+LN (1-
 Y-C))+R25F
 29:
 F
 30:
 R25-R1*(1-X)+2+R
 26F
 31:
 R26/R17/(A+273)+
 R27F
 32:
 EXP R27+R28F
 33:
 IF ABS (R28-X)/X
 <.0001;GTO 35F
 34:
 R28+X;GTO 30F
 35:
 R1*X+2+R17*(A+27
 3)+LN ABS (1-X)+
 R29F
 36:
 R12*(1-Y-C)+2+R1
 4*Y+2+R15*(1-Y-C
)*Y+R30F
 37:
 R12+C+2+R13+Y+2+
 R16+C*Y+R18+R19*
 A+R31F
 38:
 (R29-R30-R31)/R1
 7/(A+273)-LN (1-
 Y-C)+R32F
 39:
 EXP R32+R33F

40:
IF ABS (R33-C)/R
334.0001;GTO 42F
41:
R33+C;GTO 26F
42:
PLT Y,CF
43:
Y+R55+Y;GTO 16F
44:
PEN F
45:
END F
R290

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APPENDIX B - SUMMARY OF GaAsSb/InP GROWTHS

Seventeen liquid phase epitaxy runs were made in an attempt to grow GaAsSb epitaxially on InP. Because in many of these runs two separate growth depositions were done, one on each half of a substrate, over two dozen growth attempts were actually made. These growths will first be discussed as a group, and then a table will be presented in which details of individual runs can be found.

Numerous growth procedures and temperature cycles were investigated. It is particularly significant to note that step-cooling the melt prior to moving it over the substrate did not appear to reduce the amount of substrate etch-back. In later growths when the extreme sensitivity of the ternary melt solidus to temperature was better understood, growth was performed with cooling ranges of only one degree. In these growths the melt was brought into contact with only one half of the substrate and cooled one degree. It was then moved to cover only the second half of the substrate and cooling was continued for another degree. Then the melt was moved off the InP substrate and the run was terminated.

The majority of runs was done in the temperature range of 650 to 660 C. Growth attempts at higher temperatures, 700 C for example, showed very severe degradation of the InP substrate surfaces and even at 650 C the substrates showed clear evidence of surface attack and decomposition.

In the earlier growth runs which were done before the size of β was more firmly established it was anticipated that $\text{GaAs}_{0.5}\text{Sb}_{0.5}$ might be grown on InP at 650 C, but when it became clear that β might be closer to 4000 than 3500, the goal was more to simply determine experimental points on the phase

diagram, and to confirm the calculations and especially the value of β . The severe attack of the substrate by the melt made achieving even this goal difficult, however, because the melt became not a ternary melt but rather a quinary melt containing In and P as well as Ga, As, and Sb.

The most that can be stated with some confidence is that experimentally, for certain melts and temperatures, the composition of the deposited solid appears to change very rapidly over a narrow temperature from one containing a large As fraction to one containing a large Sb fraction.

Given the large number of growths and analyses (see below) the above conclusion may seem rather restricted and conservative, but there are definite reasons why drawing additional, more specific and quantitative conclusions is unjustified. These reasons center upon: 1) the uncertainty as to the true melt composition in light of the presence in it of In and P, 2) the uncertainty as to the true temperature of deposition in light of the occurrence of incomplete melt removal after the nominal growth cycle, and 3) the imprecision in the electron beam microprobe analysis. The ternary melt solidus is most sensitive to the value of β in the region corresponding to $x \approx 0.5$ in the solid. In the region of high Sb fraction solids the curves all converge (see Figure 8) and there is little sensitivity to β . The variation is less than the uncertainty in the microprobe analysis. Of the data that was obtained in this region, there is an indication that the actual curves are shifted more to the left, i.e. to lower x_{Sb}^l , than the calculated curves, or equivalently, that the deposition temperature was 5 to 10°C lower than that assumed, i.e. given in the table below.

In the region of high As fraction the curves are more sensitive to β (again see Figure 8) but no high As fraction solids were found that did not also contain large amounts of P. In fact the deposits had roughly the same P

fraction as Sb fraction. If one assumes that the atomic fraction of Sb in the solid was unaffected by the presence of P in the solid then the low Sb fractions are consistent with a large value of β , i.e. 4000 rather than 3500, or less.

The most dramatic observation was the intermixing of the high As and high Sb fraction solids, and the absence of any intermediate composition solids, and the absence of any intermediate composition solids between them. The two compositions can be observed visually as differently colored regions, one being grayish, the other having a tanner hue. The boundary between the two regions is sharp and any transition region that exists must be only a small fraction of a micron wide.

Table B-1 below summarizes the growths giving pertinent information on each. The compositions were determined by electron beam microprobe analysis. The typical variation observed in a given sample was ± 0.04 or $\pm 25\%$ whichever is the smaller.

Run	Ga	Sb	As	Ti(C)	T(°C)	Analysis of deposition(s)	Comments
1	82.8	17.0	0.2	652	4	---	As weighed. No equilibrating substrate.
2	82.8	17.0	0.2	655	(4)4 ⁺	GaAs _{0.82} Sb _{0.18}	4° step cooling to T _i followed by
3	76.5	23.5	*	656	(5)1	GaAs _{0.27} Sb _{0.73}	4° cooling over substrate
4	84.0	16.0	*	605	(4)0	GaSb	Result as predicted by calculations
5	80.0	20.0	*	657	(4)0	GaSb (some GaP) Ga _{0.96} In _{0.04} Sb	"
6	81.0	19.0	*	656	(4)0	GaAs _{0.09} Sb _{0.91}	"
7	82.9	18.0	*	653	(4)2	GaAs _{0.05} Sb _{0.95}	-
8	82.9	17.1	*	657	(1)1	-	Excellent rewipe
				655	2	-	No consistent analysis obtained. Both high and low As fraction solids present in both areas
9	82.9	17.1	*	658	1-8	GaAs _{0.21} Sb _{0.78} P _{0.01}	Melt moved onto substrate in 1 mm steps at 1°C intervals. No consistent pattern noted in analysis.
10	64.0	36.0	*	720	1	GaAs _{0.72} Sb _{0.15} P _{0.13}	-
11	64.0	36.0	*	720	1-9	GaAs _{0.21} Sb _{0.76} P _{0.03}	Melt moved onto substrate in 1 mm steps at 1°C intervals. Most of substrate dissolved by melt.
12	82.9	17.1	*	657	1	GaAs _{0.1} Sb _{0.9}	Melt prereacted and equilibrated on GaAs substrate; cooled and InP substrate put in place
				656	1	(Some GaInP)	Procedure as in 12.
13	82.9	17.1	*	655	1	GaAs _{0.08} Sb _{0.92}	No prereaction. Return to original procedure.
				654	1	(GaP _{0.92} Sb _{0.06} As _{0.02})	Lots of In in deposits
14	82.9	17.1	*	657	1.5	GaAs _{0.70} Sb _{0.15} P _{0.15}	
				655.5	1	GaAs _{0.15} Sb _{0.85} (In _{0.4} Ga _{0.6} P _{0.9} Sb _{0.1})	

15	82.9	17.1	*	659	1	No growth detected	Very clean wipe-off		
				658	1				
16	84.0	16.0	*	658	1.5	GaAs _{0.68} Sb _{0.17} P _{0.15}			
				656.5	1	GaAs _{0.08} Sb _{0.91} P _{0.01}			
						GaAs _{0.17} Sb _{0.80} P _{0.03}			
17	85.0	15.0	*	658	1				
				657	1	GaAs _{0.70} Sb _{0.15} P _{0.15}			Highest temperature growth only on edge of substrate due to boat misalignment
						GaAs _{0.13} Sb _{0.87}			

* As supplied from GaAs equilibrating substrate

† The step cooling from the equilibrating temperature T_e to the initiation temperature T_i is given in parenthesis.

TABLE B-1: Summary of Growths

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