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III-V SEMICONDUCTOR SOLID SOLUTION SINGLE CRYSTAL GROWTH

ANNUAL REPORT #1 FOR THE PERIOD April 6, 1979 through March 15, 1980

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4800 Oak Grove Drive
Pasadena, CA 91103

E. R. Gertner
Principal Investigator

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This is the annual report of a project to develop a growth technique that would allow higher quality single crystal bulk semiconductor materials to be synthesized. The baseline approach is a float zone technique in a low gravity environment and, in addition, can potentially result in the synthesis of a class of semiconductors that can not be grown in normal gravity because of fundamental growth problems rooted in the nature of their phase diagrams.

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FOREWORD

The work reported in this document was performed at the Rockwell International Science Center, Thousand Oaks, California for the National Aeronautics and Space Administration with the support of the California Institute of Technology, Jet Propulsion Lab, Pasadena, California under Subcontract number 955352. The monitoring engineer is Dr. J. Zoutendyke.

The principal investigators are E.R. Gertner and M.D. Lind with additional technical support provided by R.A. Reidel. The program manager is W.E. Tennant.

1.0 INTRODUCTION

1.1 Motivation

The motivation for this program lies in the fact that while highest device performance is often demonstrated in epitaxial material ultimate device performance is often limited by the quality of the substrate material upon which the epitaxial material is deposited. Gravity is the main cause in limiting the quality of current substrate material. While gravity effects both epitaxial and bulk single crystal growth processes its effect is much more pronounced in the bulk growth processes since epitaxial growth processes typically are confined to thin layers and short growth times. Gravity has a range of deleterious effects in bulk growth processes. They range from periodic doping variations to compositional inhomogeneities caused by convective flow. Also, the presence of gravity excludes the use of the float zoning technique for materials whose values of surface tension and density do not allow a stable liquid zone in a normal gravity environment. This class of material includes all of the III-V and II-VI solid-solution materials where the use of float zoning is essential to achieve large, uniformly doped and compositionally homogeneous single crystals. In general, the use of a low gravity environment for crystal growth would have two benefits - first, material quality improvements for crystals presently grown in normal gravity and second, potential synthesis of crystals via growth techniques which can not be used in normal gravity.

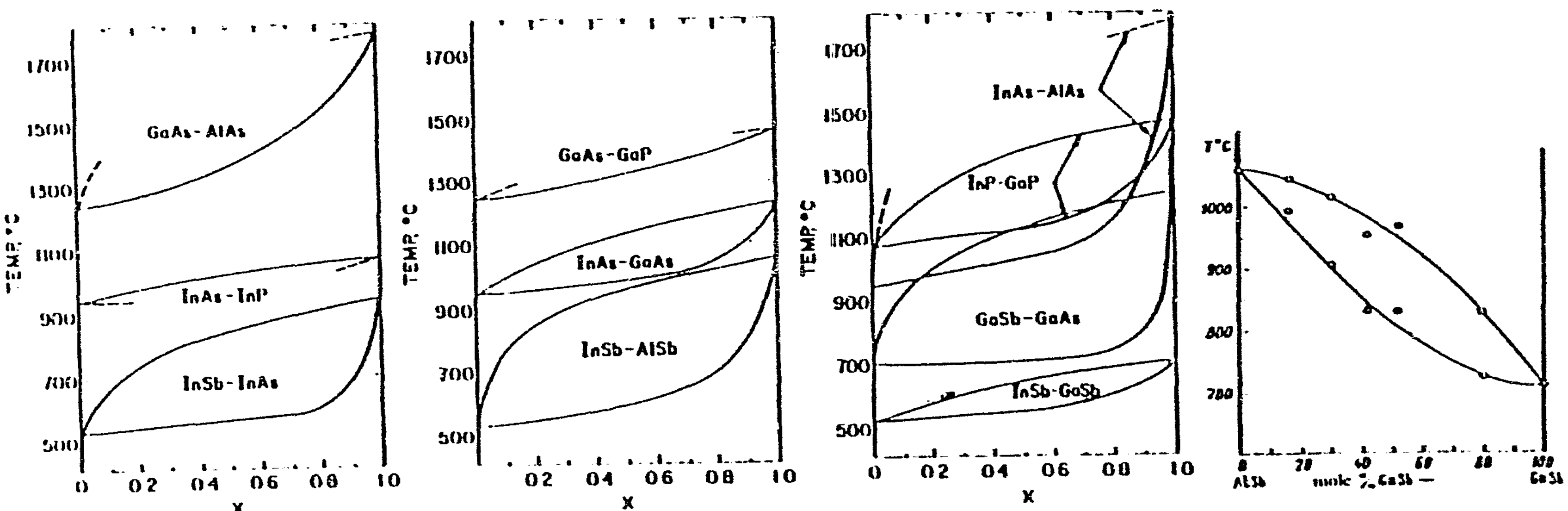
1.2 Material Selection

For this program initially two material systems were considered - the III-V and II-VI compounds and solid solutions. While the II-VI system has greater versatility in the infrared detection area the III-V system has a much broader applications base with a variety of devices, such as lasers, LEDs, microwave, avalanche photodiodes, solar cells, and infrared detectors being fabricated in various III-V compounds and solid-solutions. Because of this wide application base we chose the III-V system in which to perform the low gravity growth experiments. Other considerations which supported this initial choice were the high stoichiometry typical of most III-V compound material - qualities important for device fabrication. Furthermore, the III-V solid-stolution were selected because of the relatively high quality and availability of commercially grown III-V binary compounds.

For device technology spanning the IR-visible range, it would be desirable to have lattice matching substrate materials continuously spanning the entire range of lattice parameters and energy gaps from GaP or AlP to InSb shown in Fig. 1. At present, the only III-V materials available in the size and quality required for use as substrates are the binary compounds, and cases of substantial lattice misfit are encountered. Because of this limitation, some device concepts are presently not feasible. Thus, there is strong motivation for attempting to grow bulk crystals of III-V solid solutions to provide lattice matching for any desired epitaxial structure.

Figure 2 shows calculated pseudobinary phase diagrams for the III-V solid solutions. The relatively large separations between the liquidus and

Fig. 1 Energy gap versus lattice constant for all III-V solid solutions.



REF. - L. M. FOSTER, "THE PREPARATION OF III-V COMPOUND SEMICONDUCTOR ALLOYS" IN PREPARATION AND PROPERTIES OF SOLID STATE MATERIALS, VOL. 3, W. R. WILCOX AND R. A. LEFEVER, EDS, MARCEL DECKER, INC., NEW YORK, 1977; N. A. GORYUNOVA, "THE CHEMISTRY OF DIAMOND-LIKE SEMICONDUCTORS", MIT PRESS, CAMBRIDGE, MA, 1965.

Fig. 2 Pseudobinary phase diagram for III-V solid solutions.

solidus and the relatively small slopes of portions of the curves in each of the diagrams are the primary reasons for the difficulty in growing solid solution single crystals, and reasonably large, compositionally homogeneous, strain free crystals have not been successfully synthesized in a normal gravity environment despite a variety of attempts by numerous investigators.

To summarize, the two main risk areas in the single crystal growth of III-V solid solutions are growth problems due to the separation of liquidus and solidus and lattice mismatch. The technical problem therefore is to develop a growth technique for the single crystal growth of III-V solid-solutions.

1.3 Original Approach

The baseline approach for the crystal growth experiments is a float zone technique in a low gravity environment.

The floating zone is a derivative of the zone melting technique first proposed by Pfann.[1] A molten zone is established at one end of an ingot and is passed through the ingot by moving it or the heating element. The molten zone is maintained by the surface tension of the material. If a seed is provided at one end of the ingot, and care is taken not to melt the seed by the molten zone, the entire ingot can be grown as a single crystal. A substantial amount of the commercially available silicon is grown by this technique.

The float zone technique is ideally suited for the growth of the III-V solid-solutions because of three key aspects. First, it is capable of producing homogeneous crystals since growth occurs at constant temperature with continued replenishment of the liquid by the dissolving feed ingot. This aspect is very

important since compositionally graded III-V solid-solution material will suffer from severe strain because of lattice-mismatch. Second, zone dimensions are reasonable with respect to solute diffusion rates since the maximum growth rates are determined by the diffusion of solute through the liquid zone thus smaller zones allow higher growth rates. Third, the technique is containerless which is an important consideration in the III-V solid-solution growth since many III-V compounds and solid-solutions expand upon solidification. Use of a container often results in higher dislocation densities, strain and in severe cases polycrystallinity - all caused by varying degrees of "keying" or "wetting" of the containers by the liquid. Containerless growth also eliminates the possibility of contamination by chemical reaction between liquid and container.

There are two main reasons for the requirement of a low gravity environment for the float zone growth experiments - liquid zone stability and elimination of convection. Using Heywang's[2] criteria for the maximum zone length in normal gravity, we find for the $Ga_{.5}In_{.5}Sb$ case a length of approximately seven mm - half the length of that for silicon because of the lower surface tension and higher densities of the III-V compounds. Maintaining such short zone length with reasonable crystal diameter is difficult and to our knowledge no successful float-zoning of any III-V compounds or solid-solution has been accomplished as yet in normal gravity. Liquid zone stability therefore is the first reason for a low gravity environment and the elimination of convection the second major reason. In crystal growth from solution, there always exists a boundary layer in front of the freezing interface which is either rich or depleted in constituents other than the material being grown. The concentration of these "impurities" depends on their individual distribution coefficients.

In the melt, however, there exist thermal gradients because the thermal conductivity of the liquid is not infinite. These thermal gradients give rise to density variation and the action of gravity on these density variations results in convection. Convection in turn, disturbs the boundary layer at the liquid-solid interface which causes non-uniform incorporation of impurities. Using appropriate chemical etches on cross-sections of grown crystals, these variations in impurity incorporation show up as growth "striations" or "bands" and are well documented in the open literature.[3,4] Examples for $InAs_{1-x}Sb_x$ and $Ga_{1-x}In_xSb$ grown by liquid phase epitaxy at the Science Center, are shown in Fig. 3. In a multi-component system, such as a III-V solid-solution, where liquid and solid are of very different composition, convection not only results in impurity striations, but also in compositional variations. If the end members of the solid-solution are lattice mismatched, compositional variations cause severe strain in the grown crystal. Because of the above considerations of zone stability without containers and elimination of convection, the absence of gravity is a requirement for the successful growth of single crystal III-V solid-solution.

For the initial growth experiments the $Ga_{1-x}In_xSb$ system was chosen because it has the lowest melting point and lowest vapor pressure of all the III-V systems. An outline of the initial floating zone experiments for $Ga_{1-x}In_xSb$ is shown in Fig. 4, together with the pseudobinary phase diagram. Two source rods of composition B, the solidus composition, are precast as homogeneously as possible. The floating zone, composition A, is also precast, since it is solid at room temperature, and sandwiched between the two source rods. A seed of composition B is placed at the end of one source rod. The

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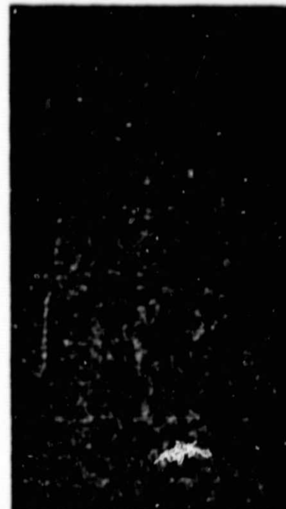

Fig. 3 Growth striations in $Ga_{1-x}In_xSb$ and $InAs_{1-x}Sb_x$.

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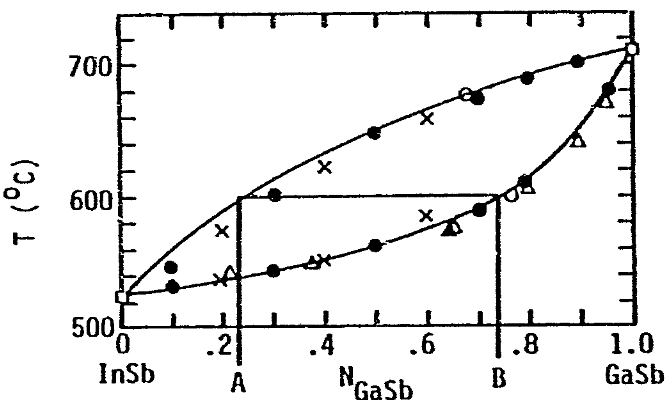

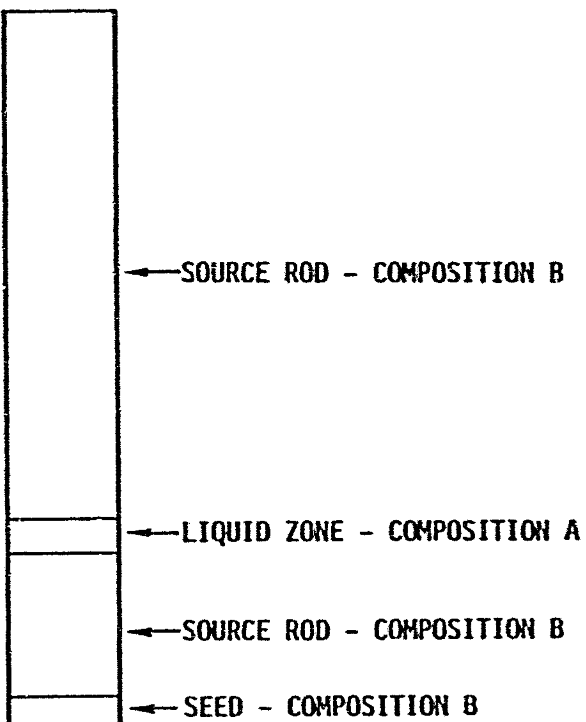

Fig. 4 Float zone experiment for $Ga_{1-x}In_xSb$.

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growth cycle is initiated by melting the zone and moving it through the source rod toward the seed in order to ensure equilibrium between liquid zone and solid. Once the seed is reached by the liquid zone and properly wetted, the direction of zone movement is reversed and single crystal growth initiated. Use of a seed is essential to achieve single crystal growth since III-V compounds rarely self-nucleate without grains and recrystallization is virtually nil because of low interdiffusion coefficients in the solid phase. This brings us to the original objective of this program - the generation of $Ga_{1-x}In_xSb$ seed crystals for future low gravity growth experiments.

1.4 Original Objective

Following are the original objectives as taken from the work statement.

- Task I - Perform initial seed growth and floating zone growth of gallium indium antimonide ($Ga_{1-x}In_xSb$) solid-solutions, using existing equipment.
- Task II - Prepare a preliminary design for a second generation floating zone apparatus, using data from Task I.
- Task III - Perform ground-based (normal gravity) experiments in support of low-gravity (space) floating zone growth of $Ga_{1-x}In_xSb$ solid-solutions.

To generate the seeds we proposed the liquid phase epitaxy (LPE) technique followed by a solute transport technique to increase the thickness of the epitaxial deposit since typical epitaxial layers are too thin to be useful as seeds for the floating zone technique since the molten zone has to "wet," that is, dissolve part of the seed in order to ensure good nucleation.

2.0 TECHNICAL APPROACH AND RESULTS

2.1 Epitaxial Growth of $Ga_{1-x}In_xSb$

The $Ga_{1-x}In_xSb$ is lattice mismatched which dictates the use of special epitaxial growth processes to obtain high quality material. These techniques are illustrated in Fig. 5. To relieve the lattice mismatch the material must either be compositionally step graded or linearly graded. In linear graded material the misfit dislocation density is proportional to the compositional grading requiring thick layers to achieve low dislocation densities. In step grading an initial set of misfit dislocation is generated which then "thread" in and out at subsequent abrupt compositional steps relieving the strain of lattice mismatch. Ideally, no other misfit dislocation needs to be generated at subsequent interfaces. There are two substrates suitable for $Ga_{1-x}In_xSb$ epitaxy - GaSb and InSb. We chose the $Ga_{1-x}In_xSb$/GaSb approach because this allows both epitaxial step and linear grading to be used while in the $Ga_{1-x}In_xSb$/InsB system only linear grading can be used since the lattice constant of the epitaxial deposit is smaller than that of the substrate.

The (111)B direction was chosen as the primary growth direction for the seeds since their intended future use is for a bulk growth techique and historically best bulk growth of III-V compounds has been accomplished using that direction.

Initially LPE growth attempts were made using the linear compositional grading technique because it is experimentally simpler than the step grading technique. Two techniques were attempted, first the gradual lowering of the

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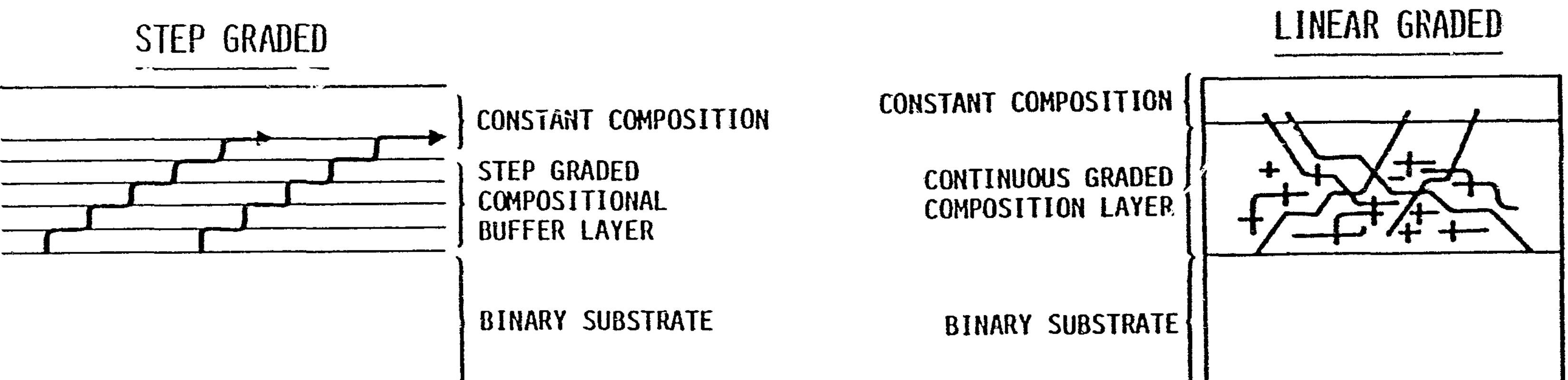

- LATTICE MISMATCH BETWEEN EPITAXIAL LAYER AND SUBSTRATE GENERATES INITIAL MISFIT DISLOCATIONS.
- IDEALLY MISFIT DISLOCATIONS "THREAD IN AND OUT" AT COMPOSITIONAL INTERFACES.
- NO OTHER MISFIT DISLOCATIONS NEEDED AT SUBSEQUENT ABRUPT COMPOSITIONAL STEPS.

- INCLINED DISLOCATIONS PROPAGATE TO ACTIVE MATERIAL.
- DISLOCATION DENSITY PROPORTIONAL TO COMPOSITION GRADIENT.

Fig. 5 Epitaxial growth techniques for lattice mismatched systems.

Ga-In-Sb liquid temperature which should, because of the phase diagram, increase the X value in the epitaxial deposit. Second, the periodic addition of small amounts of In to the Ga-In-Sb melt which should have the same effect. However, neither technique produced X values beyond the X value known to be in equilibrium with the initial liquid. This is due to an effect called lattice "latching" or "pulling" once a certain lattice constant, or X value, is established, the epitaxial deposit continues to grow at that lattice constant despite the fact that the composition of the liquid is changed such that the lattice constant should increase. We have also observed this effect in the $InAs_{1-x}Sb_x$ system. Unable to increase the In fraction with the linear grading technique we redirected the growth attempts to the compositional step grading technique. Using growth parameters established for relatively smooth $Ga_{1-x}In_xSb$ epitaxial growth for the (100) orientation established in other programs, resulted in epitaxial deposits with excessive "hillock" formation for (111) orientation. This is shown for a single $Ga_{.90}In_{.10}Sb$ layer on (111)B GaSb in Fig. 6. Shown is the entire wafer, general surface morphology and the top of a hillock under higher magnification. The "slash" at he top of the hillock appears to be a facet formation and is always parallel to a <110> direction. The general "roughness" of the epitaxial layer is due to the lattice mismatch. Height differences, taken from cleaned and stained cross-sections between valleys and tops of hillocks are typical 10 - 20 μm which is undesirable since it would lead to a nonplanar growth front in following bulk growth experiments. This is shown in Fig. 7. The origin of these "hillocks" is unknown, but have benn observed in other III-V solid solution growth.

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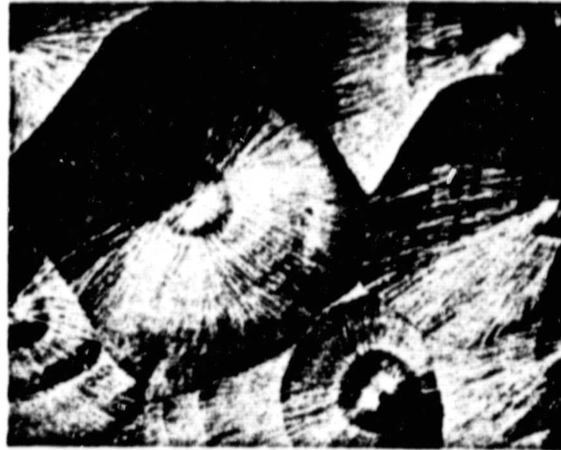

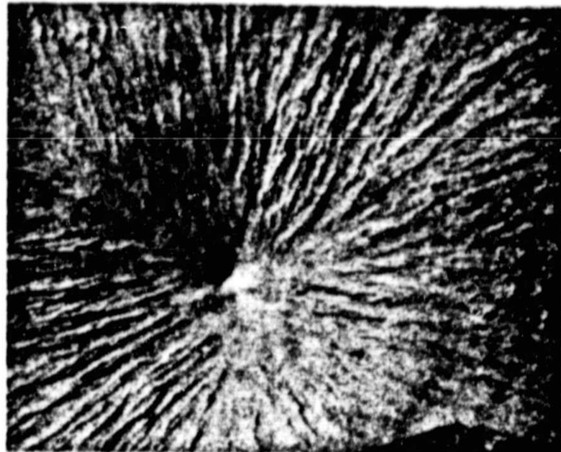

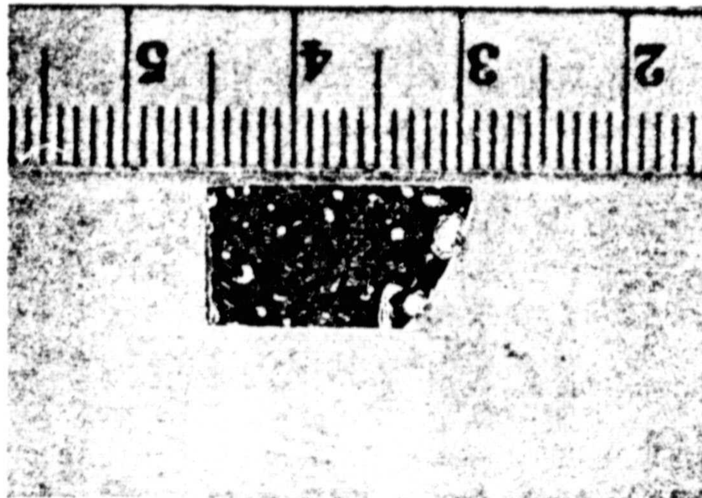

Fig. 6 Wafer, surface morphology showing "Hillock" formation on (111)B LPE grown $Ga_{.90}In_{.10}Sb$.

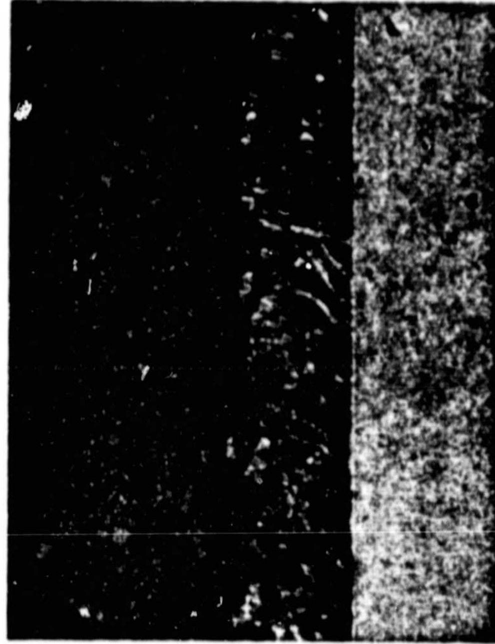

Fig. 7 Cross-section of LPE grown $Ga_{.90}In_{.10}Sb$ layer with Hillocks.

Raising the temperature above 500°C eliminated the hillock formation. The surface morphology of a typical single $Ga_{.90}In_{.10}Sb$ layer grown on GaSb is shown in Fig. 8a. While there is no "hillock" formation, the rough surface morphology is partially a result of the lattice mismatch between the $Ga_{.90}In_{.10}Sb$ epitaxial layer and the GaSb substrate.

In Fig. 8b, the etch pit density (E.P.D.), as revealed by chemical dislocation etching, is shown for a $Ga_{.90}In_{.10}Sb$ layer grown directly on GaSb. The E.P.D. is approximately 10^6 cm^{-2} which is reasonable for the lattice mismatch involved. The dislocation distribution, however, is not uniform but tends to "cluster." The majority of the dislocations are found along lines parallel to <110> directions. This is seen clearly in the center of Fig. 8b. The reason for this "clustering" is not known at present.

Another reason for the surface roughness of the $Ga_{.90}In_{.10}Sb$/GaSb structure may be compositional variations in the epitaxial layer caused by convection in the liquid during growth. X-ray topography studies of the $Ga_{.90}In_{.10}Sb$ material are shown in Fig. 9a and b.

Figure 9a is a topograph of the as-grown material. To ensure that surface morphology of the $Ga_{.90}In_{.10}Sb$ material did not contribute to the structure seen in Fig. 9a, the material was polished and again analyzed by x-ray topography. The result is shown in Fig. 9b. There is virtually no difference between the features of Fig. 9a and 9b. The conclusion that can be drawn from the x-ray topographs is that the $Ga_{.90}In_{.10}Sb$ material is not single, but polycrystalline.

To eliminate the GaSb substrate quality as a potential source of this polycrystallinity in the epitaxial layer, a x-ray topograph was taken of a

Fig. 8 Morphology and etch pit density of LPE grown (111)B $Ga_{.90}In_{.10}Sb$.

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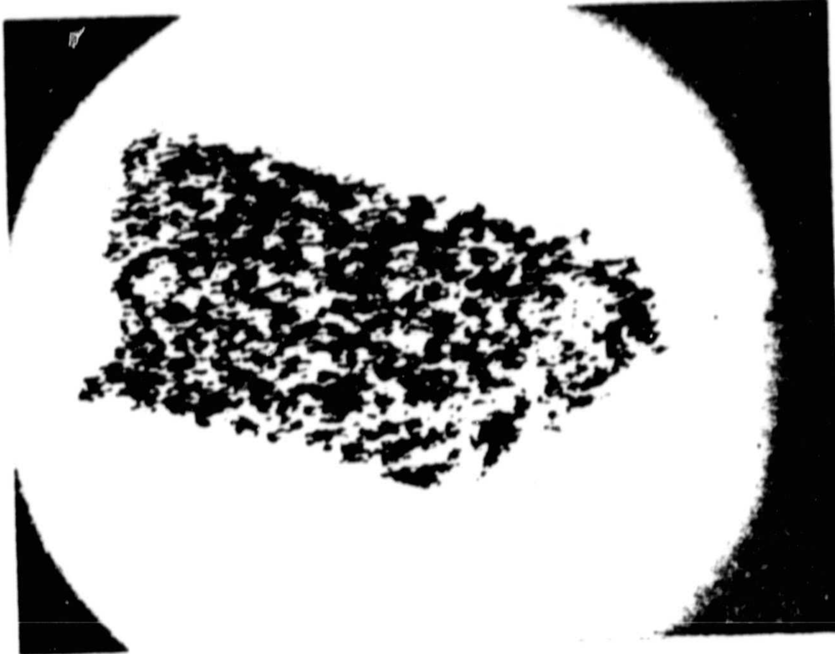

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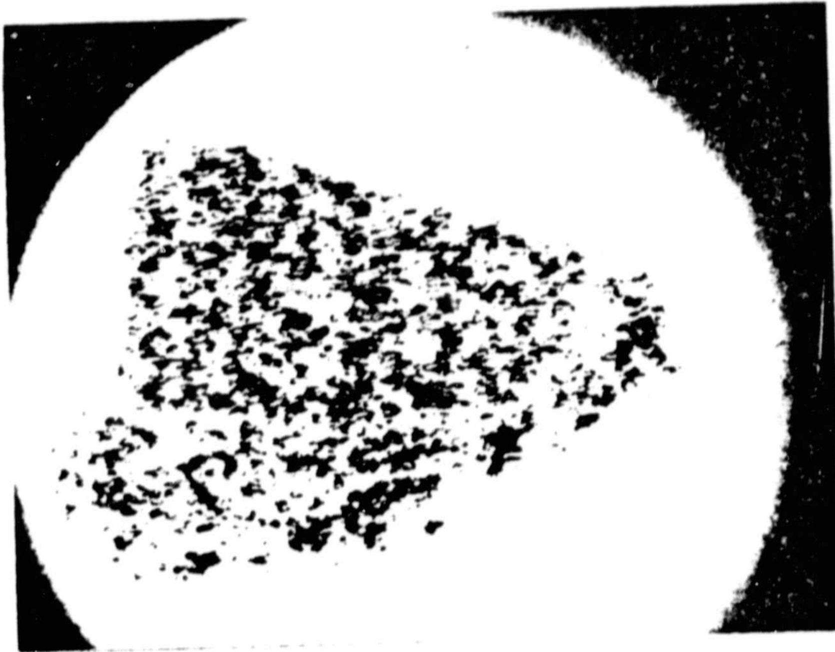

AS GROWN

Fig. 9 X-ray topograph of (111)B $Ga_{.90}In_{.10}Sb$ epitaxial layer.

polished (III)B GaSb substrate. The result is shown in Fig. 10. The topograph is basically featureless, indicating single crystal material. The variation in intensity across the slice is due to slight bowing of the wafer due to polishing. The fine dark lines visible in some parts are scratches on the photographic film from which the print was taken and not features of the GaSb substrate material. The dark line running across the center of the wafer is probably due to overexposure because of mechanical hangup of the translation at that position during exposure.

From the above results it became obvious that in order to achieve higher quality epitaxial $Ga_{1-x}In_xSb$ material smaller compositonal steps than 10% were needed. However, numerous attempts to use a large number of compositional steps met with very little success. Tyically, using multiple layers resulted in higher quality material, that is lower etch pit density but rather poor morphology. This is shown in Fig. 11 where the cross-section and morphology for a two and four layer structure are compared. This is for (100) structures grown under a separately funded program. While the four layer structure has a much lower EPD than the two layer structure its morphology is much rougher. The same effects occurred for (111) growth except for even rougher morphology with very little useful material due to numerous melt spots. These results are remarkably different from those found for the $InAs_{1-x}Sb_x$ system where the use of multilayers not only reduced the EPD but also improved the surface morphology.[5] Possible explanation of this effect in the $Ga_{1-x}In_xSb$ system is that the solid and liquid are of comparable density and that during the repeated mechanical sliding of the melts on and off the substrate excess solid is "rolled" into the growth

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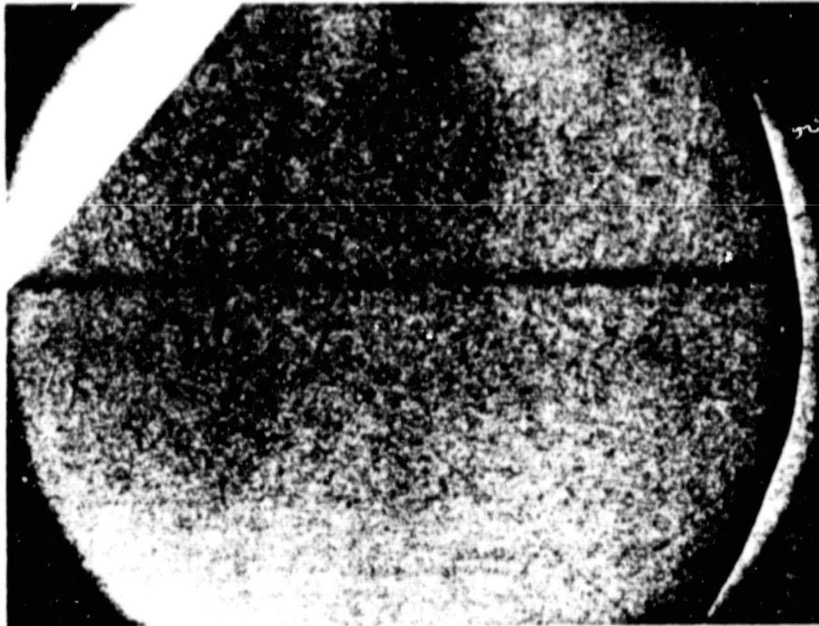

Fig. 10 X-ray topograph of (111)B GaSb substrate.

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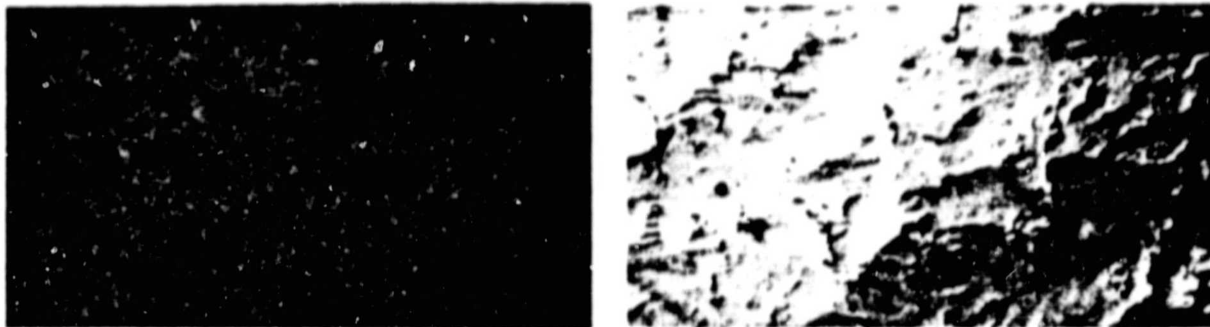

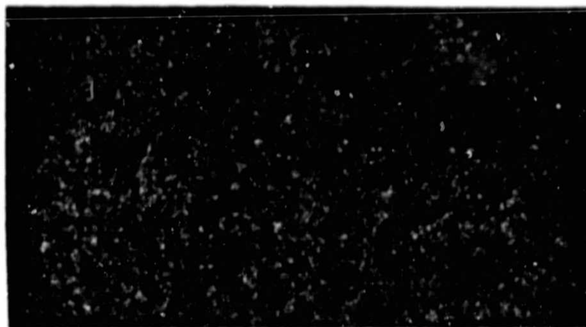

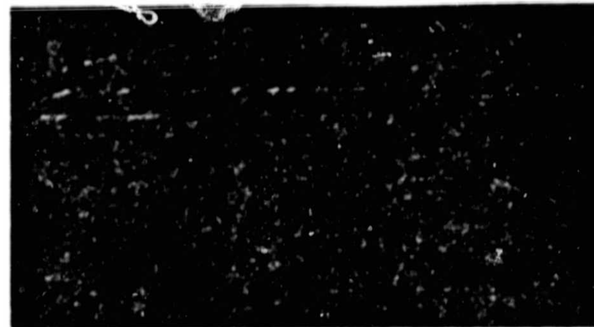

Fig. 11 Cross-section and morphology of a two and four multilayer (100) LPE grown $Ga_{1-x}In_xSb$ structure.

interface. Poor epitaxial growth occurs at and around these particles, typically resulting in metallic inclusions and melt spots.

In view of these difficulties with the LPE multilayer step grading and linear grading appraoch, on both this and other programs, we began to consider vapor epitaxial approaches.

2.2 Vapor Phase Epitaxy of $Ga_{1-x}In_xSb$

The advantages of vapor phase epitaxy (VPE) over liquid phase epitaxy lie in several areas. First, there is better control over compositional grading both step or linear since changes in vapor composition are readily accomplished allowing both a larger number of multilayers to be used or very smooth linear grading to be achieved since the effect of lattice pulling is not as prominant in vapor epitaxy. Second, thickness control in VPE is superior to LPE which is important for lattice mismatched system where a large number of thin compositional graded layers is desirable to reduce the EPD. Third, in VPE no thermodynamic limitations exist between liquid and substrate allowing eptiaxy in system were no equilibrium exist between liquid and substrate. This consideration does not apply to this program but was important for other programs.

With IR&D funds a prototype VPE system was assembled. The organometallic approach was used because of the low vapor pressure of elemental antimony makes the chloride transport technique unattractive. The flow diagram of the system is shown in Fig. 12. High purity hydrogen controlled by mass flow controllers are bubbled through the metal alkyls of trimethylgallium (TMGa),

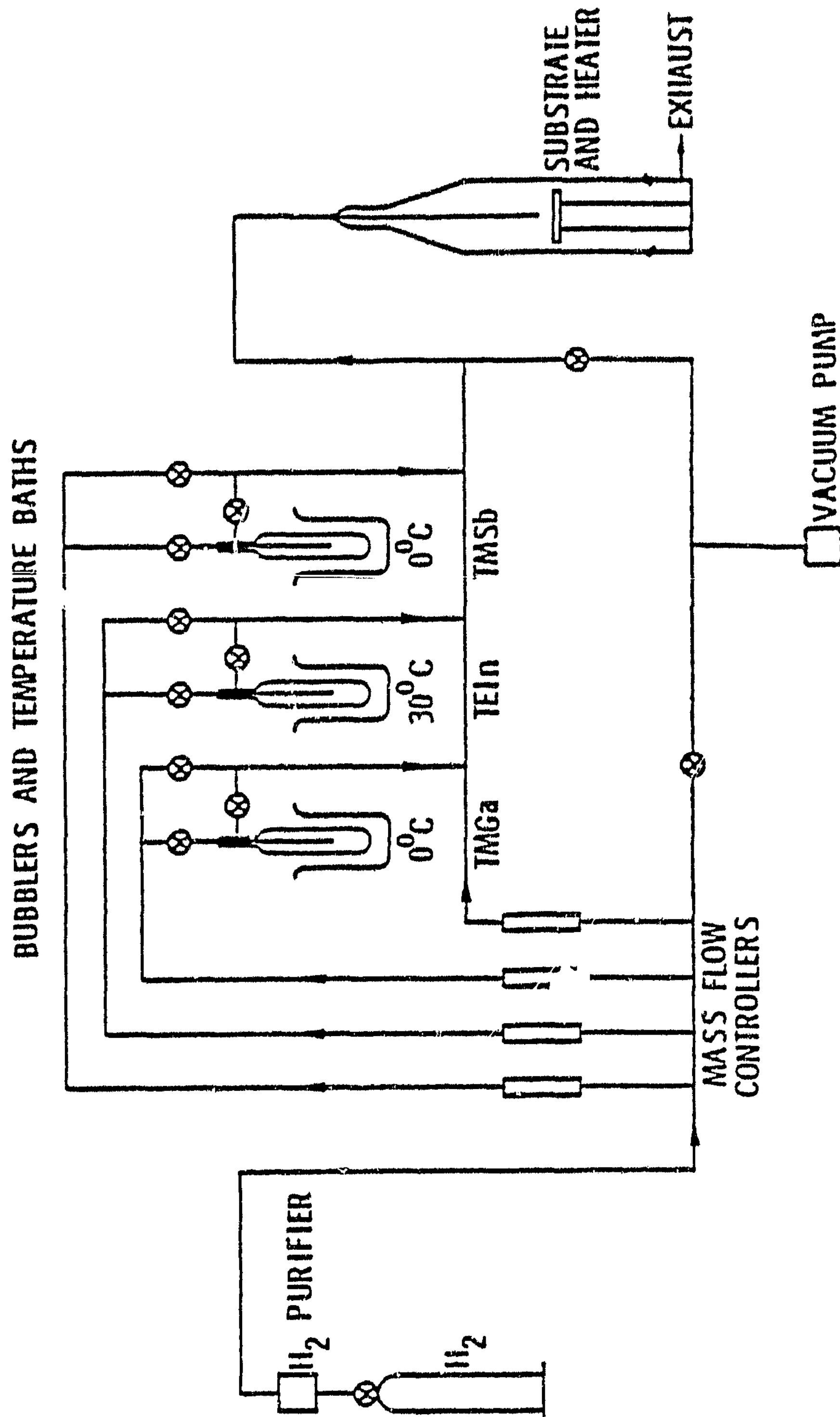

Fig. 12 Simplified VPE flow diagram.

triethylindium (TEIn), and trimethylantimony (TMSb). This gas mixture is further diluted by hydrogen carrier gas, fed into a bell jar where the organo metallics are thermally decomposed forming $Ga_{1-x}In_xSb$.

Initial (100) growth results, funded by IR&D and other programs, were promising. First we achieved X values of up to .6 in relatively smooth layers. The highest X value achieved for a reasonably smooth layer by LPE techniques (111) or (100), has been x .3. Furthermore, for the first time we observed "cross-hatch" in epitaxial $Ga_{1-x}In_xSb$ a phenomena never observed in LPE grown material. Cross-hatch is usually a sign of higher quality material because it is the result of an "ordered" set of misfit dislocation generated by lattice-mismatch. Results are shown in Fig. 13. The linear graded (100) material, accomplished manually, shows a smooth morphology even at high X values. On the basis of these results a second generator OM-VPE reactor was built where all gas flows are under computer control. Figure 14 is an X-ray topograph of an $Ga_{.92}In_{.08}Sb$ step graded layer grown on (100) GaSb. The seven compositional steps consist of 1% In fraction increments, each layer is .5 μm thick; the final constant composition layer is 3.6 μm thick. To note is the regular cross-hatch pattern indicating that most of the misfit dislocations are confined to the compositional buffer layer interfaces resulting in a final constant composition layer with a low dislocation density - a result confirmed by chemical dislocation etching. However, using growth parameters developed for (100) growth for (111) growth for this program resulted in basically polycrystalline material. Figure 15 is a comparison between a concurrent (100) and (111)B $Ga_{.90}In_{.10}Sb$ growth. While the (100) growth is relatively smooth, the (111) growth is

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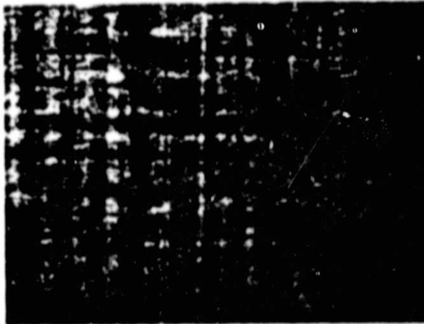
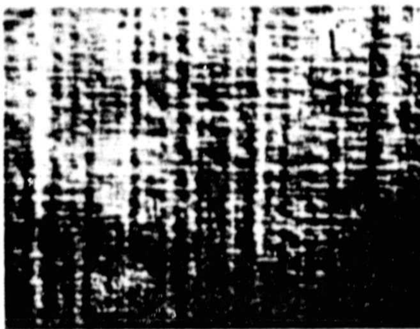


X = .20

X = .20



X = .40

X = .53

100 μm

Fig. 13 Comparison of surface morphologies of graded and nongraded OM-VPE (100) $Ga_{1-x}In_xSb/GaSb$.

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Fig. 14 X-ray topograph of an OM-VPE grown, step graded (100) $Ga_{.92}In_{.08}Sb/GaSb$ structure.

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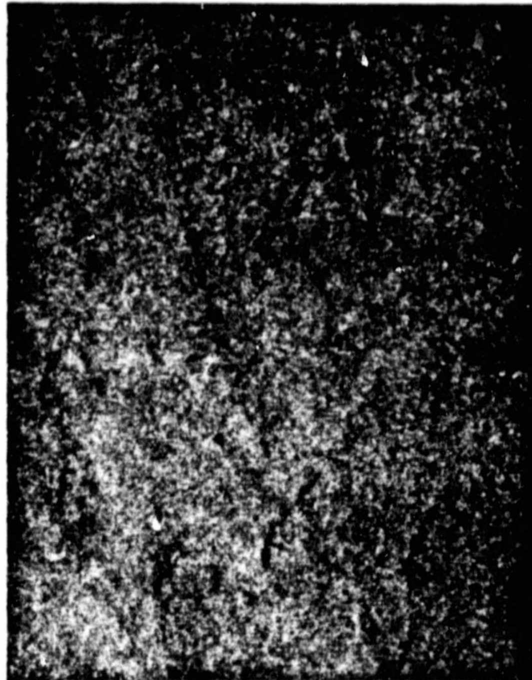

Fig. 15 Comparison of (100) and (111)B OM-VPE grown $Ga_{.90}In_{.10}Sb$.

polycrystalline. Changing growth conditions from optimum (100) parameters resulted in no improvement for (111) growth. These results, plus other developments led to reassessment of the proposed approach which is discussed in the next section.

2.3 Assessment and Conclusion (Original Approach)

The difficulties encountered both with the LPE and OM-VPE techniques in the growth of (111) $Ga_{1-x}In_xSb$ will make the seed synthesis for the space experiments a major task, but it is a task that can be solved especially in view of the recent advances in MBE and OM-VPE technology. Ironically, success in growing high quality lattice-mismatched III-V structures by those techniques would reduce the need for III-V solid-solution bulk cyrstals for the realization of lattice matched device structures. Furthermore, we believe that quaternary III-V growth on existing binary compound substrates will solve most of the III-V device structure requirements. Quaternary growth allows a decoupling of the lattice constant and energy gap allowing lattice matched heterostructures with varying bandgap to be grown. At the time the proposal for this project was written many of the problems that hindered development of several quaternaries because of thermodynamic instability (AlGaAsSb on InP for example) between substrate and liquid in LPE no longer apply since MBE and OM-VPE techniques have matured. Neither of these techniques has the thermodynamic limitations of the LPE approach. The only region in which quarternaries can not be grown is in the IR region since no intermediate substrate exist between the end points of InAs, GaSb and InSb. (see Fig. 1). But even in this range, for IR applications, the superior performance of $Hg_{1-x}Cd_xTe$ IR devices will relegate III-V IR detectors to a secondary backup status.

The significance of the above observations is that growth of bulk III-V solid solutions single crystals in a low gravity environment will not have a major technological impact and in view of this we have redirected our effort in a direction where low gravity growth will have a potential major technological impact - the bulk growth of CdTe.

3.0 ALTERNATE APPROACH

3.1 Material Selection

CdTe was selected as a candidated for low gravity growth because of critical needs for large, high quality single crystals in several areas. First and foremost is the need for larger area, high quality CdTe single crystal substrates for $Hg_{1-x}Cd_xTe$ backside illuminated IR focal planes. Currently, $Hg_{1-x}Cd_xTe$ epitaxy is limited by the grain size of commercially available Bridgeman grown multigrain ingots. Other fields which would benefit from the availability of large single crystals of CdTe are the optical modulators and X-ray detector areas.

Other considerations which led to the selection of CdTe is that it is a binary hence there is no separation of liquidus and solidus thereby easing the necessity for a large temperature gradient across the liquid-solid interface to maintain interface stability in a ternary, such as $Ga_{1-x}In_xSb$ growth. Also, with the CdTe approach there is no delay due to seed generation - commercial multigrain ingots typically contain grains large enough to serve as seeds for immediate start or normal gravity float zone experiments.

A further advantage of the current material approach is that it addresses NASA needs in the IR detection area. $Hg_{1-x}Cd_xTe$ will dominate the IR field due to ease of wavelength tunability. HgTe-CdTe are nearly lattice matched and high performance IR detectors have been fabricated in LPE grown $Hg_{1-x}Cd_xTe$/CdTe structures with X values varying from x = .40 to x = .20. This corresponds to the 1 - 12 μm IR region. In contrast, a previous longer term effort to achieve a

similar tunability in the $InAs_{1-x}Sb_x$ system failed because of the problems associated with lattice mismatch.

Last, the new approach will benefit from "spillover" support from other major DoD funded CdTe and HgCdTe programs.

Currently pursued growth techniques at the Science Center are the Bridgman technique and closed tube vapor transport. The Bridgman technique will be developed to a process where high crystallinity multi grain ingots are routinely grown to supply near term substrate needs for $Hg_{1-x}Cd_xTe$ epitaxial processes. For larger, single crystals of CdTe we are developing a closed tube vapor transport technique whose feasibility was recently demonstrated by growing or small eight cm^3 single crystal.

3.2 Rationale

Why use the float zone technique in a low gravity environment for CdTe? Because that technique has inherently the best thermal symmetry of all the major growth techniques which can result in the synthesis of very large crystals. In other bulk growth techniques such as Bridgman and Czochralski the thermal environment changes as the liquid fraction decreases and the solid fraction increases, especially if the thermal conductivities of the liquid and solid differ widely. This limits the size of the crystal that can be grown since compromises need to be made between the optimum thermal environment for the start and end of the growth. No such compromises need to be made for the float zone technique because it has a high degree of thermal symmetry because of its physical configuration which keeps the mass ratio of the liquid to solid

constant during growth. Furthermore, float zoning utilizes all of the advantages that low gravity offers - attributes that other growth techniques such as Czochralski and Bridgman do not.

The need for low gravity arises because density and surface tension consideration for CdTe will probably limit any float zoning to very small diameter crystals in a normal gravity environment. An estimate of zone size is made in Section 3.3.

3.3 Technical Problem and Approach

The synthesis of completely single crystal CdTe has not yet been achieved despite the usage of a variety of techniques. A typical multigrain, vertical, Bridgman grown CdTe crystal is shown in Fig. 16. The grain boundaries are enhanced by a felt tipped pen. Our in-house CdTe material shows similar grain size. The use of other techniques such as traveling zone,[6] traveling solvent,[7] Czochralski,[8] solution growth[9] and solvent evaporation[10] have had similar results. While no investigator has been able to identify the underlying cause or causes that result in this multigrain growth behavior several areas which are important in the growth of CdTe have been identified. But before covering these areas the physical properties involved in the preparation and crystal growth of CdTe are discussed.

The CdTe temperature vs composition project of the phase diagram[11] is shown in Fig. 17a. The maximum melting point is 1092°C and lies slightly on the Te-rich side. The homogeneity region of CdTe, represented by a solid line in Fig. 17a, extends both into Te- and Cd-rich sides from the stoichiometric

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Fig. 16 Commercial Bridgeman grown CdTe boule.

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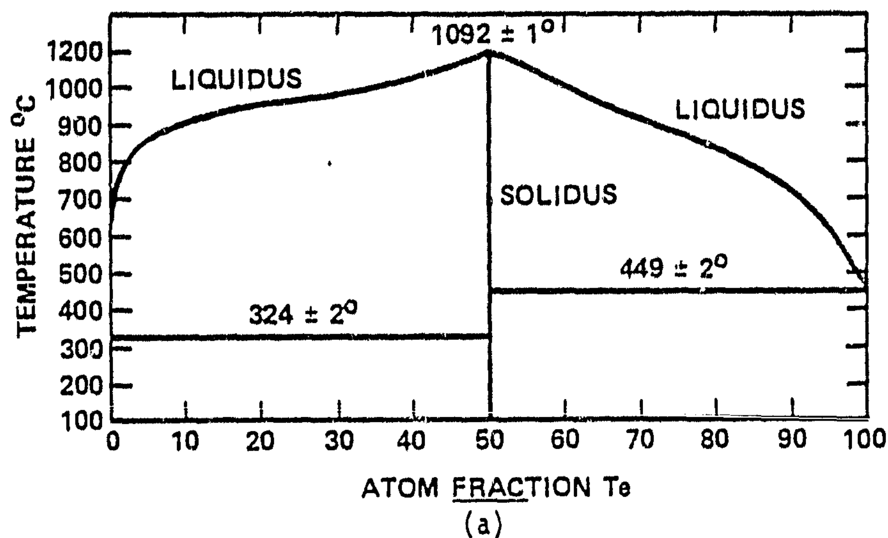
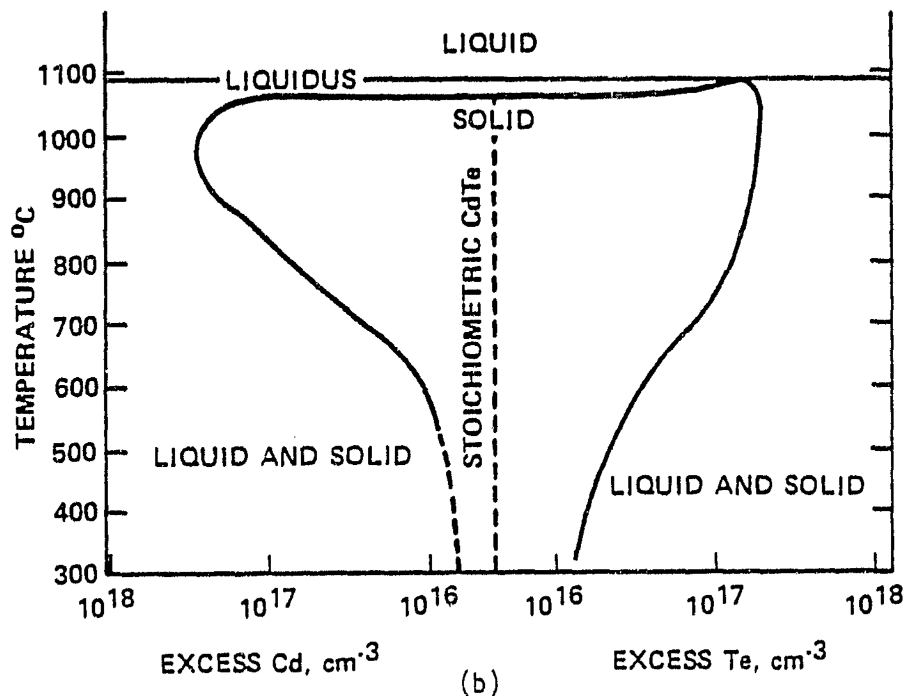


(a)



(b)

Fig. 17 CdTe phase diagram.
(a) temperature vs. composition projection
(b) homogeneity region of solid CdTe.

composition. Deviation from the stoichiometric composition determines the conduction type and carrier concentration of the material. Cd and Te saturated CdTe have n- and p-type conduction, respectively, with the carrier concentration proportional to the deviation from stoichiometry. Compositions near stoichiometry are high resistivity to semi-insulating. Shown in Fig. 17b is a greatly expanded schematic of the homogeneity range of CdTe.[12] The border of this homogeneity range, however, is not only influenced by the liquid composition, but also by the vapor composition over liquid and solid. The temperature vs pressure projection of the Cd-Te phase diagram is shown in Fig. 18.[13] At points along the loops marked p_{Cd} and p_{Te_2} solid, liquid and vapor co-exist. Inside the loop, only solid and vapor exist; and only liquid and vapor in the region outside the loops. The dashed line for each loop is the vapor pressure of p_{Cd} and p_{Te_2}, at the homogeneity limit, over Te saturated CdTe, while the solid line for each loop is the vapor pressure of p_{Cd} and p_{Te_2} over Cd saturated CdTe. The maximum melting point of CdTe lies where the dashed and solid lines meet. p^o_{Cd} and $p^o_{Te_2}$ are the vapor pressures of pure Cd and Te_2, respectively. At any temperature, the lowest total pressure exists for congruently subliming CdTe satisfying the condition

$$p_{Cd} = 2p_{Te_2}$$

Experimentally Cd (atoms) and Te_2 (molecules) are the only constituents found in the vapor phase over CdTe.[14,15] At the maximum melting point of CdTe, the vapor pressure for p_{Cd} and p_{Te_2} are 0.65 tm and 5.5×10^{-3} atm for Cd and Te_2 saturated CdTe, respectively. For congruently subliming CdTe, the total

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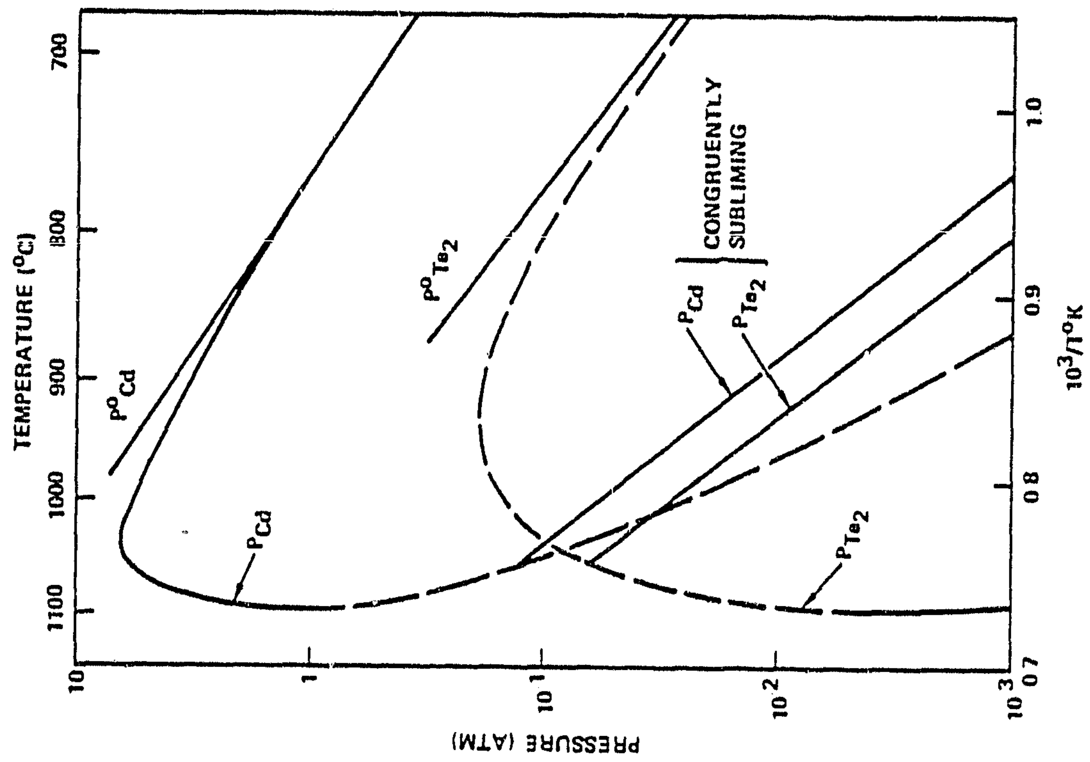

Fig. 18 CdTe phase diagram, pressure vs. temperature projection.

vapor pressure is approximately 0.18 atm at the melting point. This brings up the first area that must be addressed during the crystal growth of CdTe - the loss of Cd. Stoichiometric growth conditions must be maintained via control of the gas phase over the liquid. This is relatively simple with a closed ampule configuration such as Bridgman or traveling zone but more difficult with float zoning because Cd will condense on any cold surface. This can be prevented by having a hot wall system where all surfaces are at such temperature that the Cd pressure equals that of Cd over liquid CdTe. Additionally, from Fig. 18 we can see that a Cd reservoir at ≈ 720°C will establish a Cd pressure equal to that of Cd over liquid CdTe thus establishing equilibrium conditions. Care must be taken to accurately control the temperature and the pressure because a too low Cd pressure in the container will lead to a loss of Cd from the molten zone while too high a Cd pressure will cause the zone to become Cd-rich - i.e., both conditions will lead to nonstoichiometric growth conditions.

Fast growth rates can not be expected for CdTe because of its rather poor thermal conductivity which prevents large temperature gradients to be established at the liquid-solid interface. To reduce twinning or grain formation it will be essential to establish crystal diameter control since abrupt changes in crystal shape usually result in grain formation. This task will be difficult due to the limits on the stablizing temperature gradients that can be established at the liquid-solid interface of CdTe.

An outline of the programs activities is shown in Table 1 and the near term objectives are as follows:

Task I - Perform initial floating zone growth of CdTe using existing equipment.

Task II - Prepare a preliminary design for a second generation floating zone apparatus, using data from Task I.

Task III - Perform ground-based (normal gravity) experiments in support of low-gravity (space) floating zone growth of CdTe.

The initial experiments will be traveling zone growth where the liquid zone is supported by an ampule wall. These experiments are designed to optimize growth and equipment parameters for the float zone experiments.

To achieve the smallest possible molten zone, RF heating will be used. To ensure zone stability either temperature or power control modifications will need to be made. The existing Lepel RF generator can accept a 0 - 5 ma PC signal to control and vary the power output. Commercial temperature controllers, using thermocouple inputs, have 0 - 5 ma outputs and could readily be adapted to the RF generator for temperature control. However, the use of a thermocouple in the float zone growth has two major drawbacks. First, the physical separation between molten zone and thermocouple, caused by the necessity of using an ampule, will result in large discrepancies between molten zone temperature and thermocouple reading. Second, and more important, spurious temperature fluctuation may be introduced due to convective air currents around the ampule to which the thermocouple and controller will respond. These problems can be avoided by using the RF generator in an essentially manual mode through manual

control of the 0 - 5 ma input signal. We have installed this mode of control on the RF generator.

The float zone apparatus is shown in Fig. 19. The major dimensions are indicated. The unit will be mounted vertically. The two short furnaces mounted next to the RF coil are necessary to keep the entire ampule at 720°C, to prevent constant loss of Cd from the molten zone to cooler parts of the ampule. At ≈ 720°C the vapor pressure of elemental Cd, .7 atmosphere, equals that of Cd over molten CdTe. Thus, by keeping the entire ampule at that temperature, Cd loss from the molten zone is prevented. Purchase orders for materials needed in the construction of the float zone apparatus have been placed, with actual construction to begin in approximately four weeks.

The growth attempts will be carried out in closed ampules to prevent the loss of Cd and Te from the molten zone. The traveling zone growth will be carried out in conventional quartz ampules, slightly carbonized to reduce disolution of the quartz by the molten CdTe, of six to twelve mm diameter. For the floating zone growth experiments an ampule as shown in Fig. 20, will be used initially. The key feature of the ampule are the two quartz sleeves which will center and support the precast, polycrystalline CdTe rod in the outer ampule. The top sleeve will also serve as the seal-off point.

What zone length can be expected for CdTe? Using Heywang's[2] criteria for the maximum zone length possible in a normal gravity environment

$$\ell_m \sim 2.8 \sqrt{\frac{\gamma}{\rho g}}$$

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AMPULE CARRIAGE
LINEAR BEARING ROD
SPINDLE
RF COIL
TRANSPARENT FURNACE TYP.
LINEAR BEARING TYP.
MAIN FRAME
BALL BEARING DRIVE
ADAPTOR TO D.C. MOTOR FOR LINEAR MOTION

NOTE: DIMENSIONS ARE IN INCHES

Fig. 19 Linear motion apparatus for CdTe float zone experiments.

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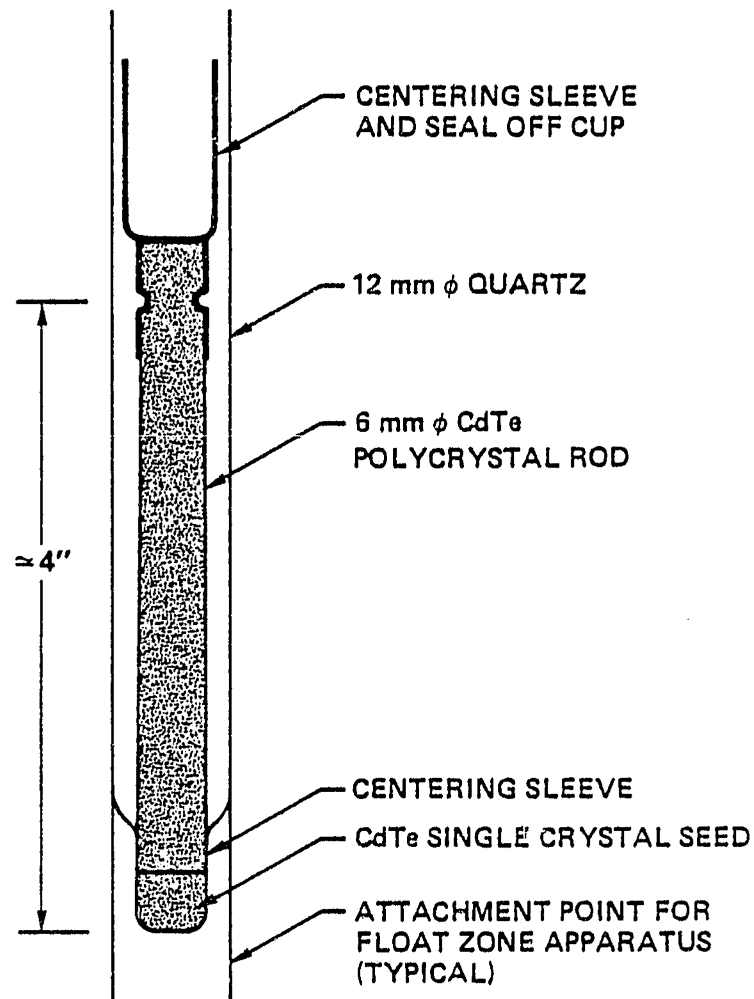

Fig. 20 Ampule design for CdTe floating zone experiments.

where

γ = surface tension

ρ = density

g = gravitational constant

for the CdTe case we had to assume a value for the surface tension since no data could be found

CdTe

γ = 200 dynes/cm

ρ = 5.86 gram/cm^3

$\ell_m \sim 0.5$ cm

and for comparison Si

Si

γ = 700 dynes/cm

ρ = 2.53 gram/cm^3

$\ell_m \sim 1.5$ cm.

Thus for CdTe, because of lower surface tension and higher density, the zone length is three times shorter than for Si which can be float zoned in normal

gravity. This will allow float zoning of only very small diameter CdTe because of its low thermal conductivity. Of course, the maximum zone length would be even less if the value for the surface tension is less than the assumed value.

3.4 Normal Gravity Experiments and Characterization

The schedule for the normal gravity experiments, Task 2, and material characterization, Task 3, are outlined in Table 1.

Parameters which need to be known in the design of a second generation float zone apparatus for CdTe are its surface tension and thermal conductivity. If data for these parameters can not be found we will determine them experimentally.

Characterization of the material grown will follow closely the program outlined in the original proposal and consist of optical microscopy, dislocation etching, x-ray diffraction and topography, infrared spectroscopy and electrical measurements such as Hall effect.

4.0 SUMMARY

The base line approach for the crystal growth experiments is the float zone technique in a low gravity environment. This technique was selected because it uniquely utilizes all of the advantages low gravity offers.

This technique has the potential to improve the material quality of presently grown crystals plus the additional advantage of producing homogeneous

Table 1

ACTIVITY	JAN	FEB	MAR	APR	MAY	JUNE	JULY	AUG	SEP	OCT
1. TASK 1 TRAVELING AND FLOATING ZONE GROWTH										
1.1 DESIGN AND ASSEMBLY OF EQUIPMENT										
1.2 6 mm DIA GROWTH										
1.3 12 mm DIA GROWTH										
1.4 6 mm DIA GROWTH, SEEDED										
1.5 12 mm DIA GROWTH, SEEDED										
1.6 ESTABLISH ZONE STABILITY										
1.7 DETERMINE Cd LOSS FROM ZONE										
1.8 USE OF BORIC OXIDE ALTERNATIVE TO STABILIZE ZONE AND TO REDUCE Cd LOSS										
2. TASK 2 PRELIMINARY DESIGN FOR FLOAT ZONE APPARATUS										
2.1 DETERMINATION OF THERMAL CONDUCTIVITY OF SOLID AND LIQUID CdTe										
2.2 DETERMINATION OF SURFACE TENSION OF LIQUID CdTe										
2.3 TEMPERATURE CONTROL AND GRADIENT REQUIREMENTS										
3. TASK 3 CHARACTERIZATION										
3.1 OPTICAL MICROSCOPY										
3.2 X-RAY DIFFRACTION AND TOPOGRAPHY										
3.3 INFRARED SPECTROSCOPY										
3.4 ELECTRICAL MEASUREMENTS										
4. PROGRESS AND COST REPORTS	▲	▲	▲	▲	▲	▲	▲	▲	▲	▲
5. ANNUAL REPORT					▲					
6. FINAL REPORT										▲

ingots in materials where liquidus and solidus differ in composition. The III-V solid solution belong to this class of materials and under normal gravity conditions homogeneous, large single crystals have not yet been synthesized. $Ga_{1-x}In_xSb$ was chosen as the initial candidate for the growth experiments because it has the lowest melting point and vapor pressure of the III-V solid solution. Technical difficulties in the synthesis of the $Ga_{1-x}In_xSb$ seed material needed for the float zone experiments, plus development in other fields such as MBE and OM-VPE, led to a reassessment of the original approach with a conclusion that the future synthesis of III-V solid solution would not have a technological impact. The program was then redirected and CdTe chosen as a suitable candidate for the low gravity experiments. Large, twin-face, single crystal boules of CdTe have not been grown despite the use of various technique during the last twenty years. Synthesis of such boules would have a significant impact on the IR electron and optical modulator field. Low gravity - elimination of convective flow disturbing the liquid-solid interface plus a containerless environment - may be necessary to routinely synthesize large single crystals of CdTe. The current approach is to attempt float zoning of CdTe of small diameter in normal gravity and to determine physical parameters necessary to design successful flight experiments.

5.0 NEW TECHNOLOGY

No new technology has been developed on this contract at this time.

6.0 REFERENCES

1. W. G. Pfann, Trans. AIME 194, 747 (1952).

2. W. Heywang, Z. Naturforsch. 11A, 238 (1956).

3. A.F. Witt and H.C. Gatos, J. Electrochem. Soc. 113, 808 (1966).

4. A.F. Witt, H.C. Gatos, M. Lichtensteiger, M.C. Lavine and C.J. Herman, Proc. of the 3rd Space Symp. of Skylab, NASA TMX-70252 (1974).

5. A.M. Andrews, D.T. Cheung, E.R. Gertner, and J.T. Longo, J. Vac. Sci. Technol. 13, 961 (1976).

6. R. Triboulet, Y. Marfaing, A. Cornet and P. Siffert, J. Apply Phy., 45, 2759, (1974).

7. R.O. Bell, N. Hemmat, and F. Wald, Phys. Stat. Sol. (a) 1, 375 (1970).

8. J.B. Mullin and B.W. Straughan Rev. Phys. Appliquee, 12, 105 (1977).

9. K. Zanio, J. Elect. Mat. 3, 327 (1974).

10. B. Lunn and J. Bettridge, Rev. Phys. Appliquee, 12, 151 (1977).

11. K. Zanio, Semiconductors and Semimetals, Vol. 13, Academic Press, 1978, (eds., R.K. Willardson and A.C. Beer).

12. ibid, p. 6.

13. A.J. Strauss, Proc. of Int. Sym. on Cadmium Telluride, Strasbourg, 1971, Eds., P. Siffert and A. Cornet, Centre de Recherches Nucleaires (publishers).

14. J. Drowart and P.J. Goldfinger, J. Chem. Phys. 55, 721 (1958).

15. P.J. Goldfinger and M. Jeunehomme Trans. Faraday Soc. 59, 2851 (1963).