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ANNUAL REPORT

Crystal Growth of Device Quality GaAs in Space

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TABLE OF CONTENTS

Preprints and reprints of publications since last annual report

I. GENERAL REMARKS

We believe that our original expectations that GaAs would emerge as critical electronic material for government and civilian applications has been proven perfectly valid. During the tenure of the program we have made a basic contribution to the art and science of GaAs growth and characterization by developing novel techniques and the necessary fundamental framework of theory and applications. A direct outcome of this work has been the joint venture between NASA and Microgravity Research Associates for the growth of GaAs in space on a commercial basis. In addition, our findings have been adopted and used in a number of industrial and non-profit organizations.

We are now in an excellent position to see clearly the realization of our goals in the near future, i.e., the growth of superior quality GaAs in space, and the analysis, assessment, and formulation of the micro- and macro- effects of near-zero gravity conditions.

II. SUMMARY

Our program on "Crystal Growth of Device Quality GaAs in Space" was initiated in 1977, and it has been carried out in two stages. The initial stage covering 1977-84, was devoted strictly to ground-based research. By 1985 the program evolved into its next logical stage whereby the ground-based research is carried out in parallel, in direct correlation with and in support of the space growth experiments.

The results of our ground-based research on fundamental aspects of crystal growth in zero-gravity environment have clearly surpassed our expectations: IT WAS ~~we~~ established that the findings on elemental semiconductors Ge and Si regarding crystal growth, segregation, chemical composition, defect interactions, and materials properties-electronic properties relationships are not necessarily applicable to GaAs (and to other semiconductor compounds). ~~In fact,~~ in many instances ~~we found~~ totally unexpected relationships to prevail. WAS FOUND IT WAS ~~We~~ further established that in compound semiconductors with a volatile constituent, control of stoichiometry is far more critical that any other crystal growth parameter. Detailed results of our ground studies and their discussions have appeared in about seventy publications which have provided a fundamental back-up for technological advancement in GaAs. IT WAS ~~We have~~ also shown that, due to suppression of nonstoichiometric fluctuations, the advantages of space for growth of semiconductor compounds extend far beyond those observed in elemental semiconductors.

Having developed the necessary characterization techniques, having identified the immense importance of stoichiometry, and having assessed the potential benefits of processing GaAs in space, we proceeded recently with the development of a suitable configuration for the growth of GaAs from the melt in space. We have discovered a novel configuration WAS DISCOVERED for "partial confinement of GaAs melt in space" which overcomes the two major problems associated with growth of semiconductors in total confinement: volume expansion during solidification and control of pressure of the

CRYSTAL GROWTH
MELTS (CRYSTAL GROWTH)
GALLIUM ARSENIDES
SEMICONDUCTOR DEVICES
SPACE PROCESSING

STOICHIOMETRY
CRYSTAL DEFECTS
REDUCED GRAVITY
SOLIDIFICATION

volatile constituent. (details discussed below). Development of this configuration for space experimentation has been approved and is realized under the sponsorship of the Office of Materials Processing in Space.

We should also point out that our experimental arguments and discussions on the potential benefits of space processing of GaAs led to an already-signed Agreement between the National Aeronautics and Space Administration and Microgravity Research Associates, Inc., for a Joint Endeavor in the Area of Materials Processing in Space. This endeavor involves the growth of GaAs and other compound semiconductors employing liquid phase electroepitaxy. For about the last two-and-a-half years the development of a breadboard configuration for space growth of GaAs with this method has been sponsored in our laboratory by Microgravity Research Associates and is distinctly separate from our work supported by NASA.

At its present stage our program combines three elements: crystal growth, device-related properties, and characterization on a micro- and macro-scale. We believe, based on our several years of experience, that the research along these lines is now critical for ensuring the successful growth of device quality GaAs in space.

During recent years continuous improvements in GaAs crystal quality have been made on earth having an immediate impact on GaAs electronic and opto-electronic devices for governmental and commercial applications. We believe that significant improvements will continue to be made one earth. However, we are convinced that the quality and findings potentially attainable in space can under no circumstances be obtained on earth, as discussed later on.

III. PROGRESS TO DATE

III.1. Introduction

In order to present last year's accomplishments and their analysis in the proper perspective, we will discuss them in the context of the program's achievements in recent years, as they are direct derivatives of those achievements. We believe that last year's results provide indispensable knowledge and tools for effectively exploiting the immense advantages of zero gravity conditions in GaAs crystal growth. For example, our earlier findings on dislocation formation in melt-grown GaAs led us to a definitive model of the origin of dislocations in GaAs which is founded on the condensation of vacancies in dislocation loops. On the basis of this model we can now optimize the parameters of crystal growth in space and minimize the concentration of dislocations, one of the most undesirable defects in GaAs.

Again, on the basis of our earlier findings we have successfully initiated development of new means of achieving semi-insulating GaAs-related compounds. Semi-insulating III-V compounds constitute the starting material for ultra-high speed integrated circuits whose performance and potential performance, if fabricated on "space-grown quality material" is at this time difficult, if not impossible, to perceive. Another important item is the development of a unique technique for growing GaAs in space from the melt, which makes possible the elimination of the two greatest problems we have been confronted with thus far in this type of growth in space, i.e., control of the partial pressure of the volatile constituent and complete confinement of the melt which introduces unacceptable concentrations of lattice defects. These and the other achievements of last year are clearly outlined in Table I and discussed in the text.

At this point it is very relevant to point out that the electronic applications of GaAs are increasing at an extremely rapid rate in recent years. It is generally agreed that "space quality GaAs" should launch revolutionary advances in GaAs applications associated with super high electronic speeds and radiation resistant performance, particularly as related to space exploration and military applications.

III.2. Nonstoichiometric Defects in GaAs

Defects in as-grown GaAs crystals and their evolution during subsequent device processing depends critically on the stoichiometry of the growth melt. Beginning in 1981 our MIT group has been playing a leading role in establishing the crucial role of melt stoichiometry in controlling the concentration of midgap levels EL2, the density of dislocations, and the microscopic inhomogeneities. According to our study the formation and nature of native defects in GaAs is intimately related to two stages of crystal growth: (a) solidification phenomena, which take place at the solid-liquid interface during crystal growth; and (b) post-solidification phenomena which take place in the solidified material during subsequent cooling. The evolution of EL2 during GaAs growth involves both solidification and post-solidification phenomena. As summarized in Table II, the various midgap levels in GaAs grown by different methods originate from differences in the characteristics of solidification and/or post-solidification processes.

TABLE I

PROGRESS TO DATE - SUMMARY OF MAJOR DEVELOPMENTS

	Development	Comments	Representative References
LPEE-Liquid Phase Electroepitaxy	1. Growth Kinetics Model 2. Dopant Segregation Model 3. Model of Multicomponent Systems 4. Interface Stability Model	Theoretical model was developed which explains experimental LPEE characteristics. The model is based on a mass transport process with two driving forces: solute electromigration and the Peltier Effect.	1-3 14,15,21,33
	5. In-situ Monitoring of Growth	Successful in-situ monitoring of the growth velocity was realized for the first time in LPE using the contactless LPEE configuration.	
	6. Growth of Bulk Crystals	LPEE process was successfully extended to a growth of bulk crystals of the thickness of the order of 1 mm.	
	7. Growth in Space Environment	LPEE process was selected in 1983 in order to realize the growth of GaAs in Space. Further R&D effort in this area is realized under a sponsorship of Microgravity Research Associates.	
MELT GROWTH	1. Construction of Advanced GaAs Melt-Growth System	Advanced system has been designed & constructed for horizontal and/or vertical growth of GaAs. The system provides unique feasibility for controlling and monitoring growth parameters.	34,35
	2. Growth of n-type Dislocation-Free GaAs	Utilizing precise control of As pressure above the melt we have achieved reproducible growth of dislocation-free GaAs in a horizontal Bridgman configuration.	43,56,67
	3. Growth of Electron Trap-Free GaAs	Growth conditions were discovered which lead to melt-grown GaAs of superior structural & electronic properties. For the first time electron trap-free bulk GaAs was achieved.	38
	4. Identification of the Role of Oxygen in Melt Growth of GaAs	Oxygen has been identified as a constituent of growth system which affects electronic and stuctual properties of GaAs.	23,57

TABLE I

PROGRESS TO DATE - SUMMARY OF MAJOR DEVELOPMENTS

	Development	Comments	Representative References
MELT GROWTH (cont.)	5. Role of Stoichiometry	Stoichiometry was identified as a fundamental factor controlling structural & electronic properties of GaAs.	56,34,43,62
PROPERTIES AND PHENOMENA	1. Relationships between Electronic Properties & Melt-Growth Conditions on Micro-Scale	Microprofiles of electron & ionized impurity concentrations in melt-grown GaAs were obtained for the first time.	17
	2. Stoichiometry controlled segregation;	It was shown that impurity segregation in melt-grown GaAs is governed by amphoteric doping and deviation from stoichiometry.	17,43
	3. Interaction between Epitaxial Layer & Substrate	It was demonstrated that outdiffusion of recombination centers from the substrate into LEP layers during growth process takes place. Growth conditions were formulated to minimize outdiffusion	6
	4. Growth-Property Relationships in Epitaxial Growth	It was found that growth rate variations have significant effect on the formation of recombination centers in GaAs.	7,25
	5. Stoichiometry controlled deep levels	A direct relationship was established between As atom fraction in the melt and the concentration of electron traps in GaAs.	36, 56
	6. Stoichiometry controlled dislocation density	It was found that an optimum stoichiometry defined by arsenic source temperature 617-618°C corresponds to a minimum dislocation density	56
	7. Oxygen related midgap level	We have unambiguously identified the oxygen related deep level ELO at 0.825 eV below the conduction band.	52,55,57
	8. Origin and properties of Major Electron Trap in GaAs	0.82 eV electron trap in GaAs has been identified as native defect complex involving the antisite As_{Ga}	36, 56

TABLE I

PROGRESS TO DATE - SUMMARY OF MAJOR DEVELOPMENTS

	Development	Comments	Representative References
PROPERTIES AND PHENOMENA (cont.)	9. Passivation of Deep Levels by Hydrogen	It was found that a concentration of the major deep level in GaAs can be effectively controlled by atomic hydrogen introduced by a standard plasma treatment.	38
	10. Optoelectronic Properties of InP	Cathodoluminescence studies of InP were completed	26
	11. Interface States	Surface states on GaAs-anodic oxide interface were determined with modified DLTS	18
	12. GaAs-Anodic Oxide Interface	A gigantic photoionization effect on GaAs-oxide interfaces was discovered. Utilizing this phenomenon it was shown, for the first time, that both deep & shallow interface states originate from Ga and As vacancies.	28
	13. Fermi Energy Control of Point Defect Formation	Electron Traps in GaAs can be controlled by changing the Fermi Energy during postsolidification cooling of crystals.	56
	14. Fermi Energy Control of Dislocations	Dislocation density in GaAs was found to vary over 5 orders of magnitude when the Fermi Energy was shifted by about 0.3 eV. This discovery was explained in terms of vancancy coalescence which is controlled by the charge state of vacancies.	57
	15. Fundamental Limitations of High Mobility Transistors	A theoretical model was formulated for electron scattering in a two-dimensional electron gas. Absolute and inherent mobility limits were calibrated for GaAlAs-GaAs heterostructures.	51 54
FUNDAMENTAL ASPECTS OF SPACE PROCESSING	1. Advantages of Space for the Growth of GaAs	We have identified for the first time potential advantages of zero-gravity for the growth of GaAs which stem from recently discovered nonstoichiometric defects affected by thermal and solutal convection.	58

TABLE I

PROFRESS TO DATE - SUMMARY OF MAJOR DEVELOPMENTS

	Development	Comments	Representative References
FUNDAMENTAL ASPECTS OF SPACE PROPERTIES (cont.)	2. Novel configurations for semiconductor growth in space	We have proposed a new configuration which is based on a partial confinement of the growth melt by a prism of the triangular cross section. This configuration permits a control of the melt composition during the growth and accomodates volume expression of GaAs upon solidification.	58,59
CHARACTERIZATION	1. Characterization methods based on electron mobility and free carrier absorption	Quantitative methods were developed for determination of compensation ratio in GaAs and InP	12,17,19
	2. IR Scanning Absorption	Quantitative method was developed for microprofiling of carrier concentration & compensation ratio through free carrier absorption	17
	3. Derivative Surface Photovoltage and Photocapacitance Spectroscopies	New Approach was developed for determination of deep levels, band structure and shallow impurites	19,20
	4. Characterization of Semi-Insulating GaAs	A rigorous procedure was developed for the determination of ionized impurity concentration from transport measurements in SI material	
	5. SEM-Cathodoluminescence	Advanced variable temperature system was set up for cathodoluminescence microprofiling of defects, impurities & carrier concentration	41

TABLE I

PROGRESS TO DATE - SUMMARY OF MAJOR DEVELOPMENTS

	Development	Comments	Representative References
CHARACTERIZATION (cont.)	6. SEM-Electron Beam-Induced Current	Variable temperature system was set up for instantaneous profiling of diffusion length	
	7. Laser Scanning Photovoltage	Photovoltage microprofiling was developed for studying homogeneity of semi-insulating GaAs	
INTERACTION WITH INDUSTRIAL ORGANIZATIONS	1. Workshops, 1977 1981	Workshops were held with representatives of leading industrial & educational institutions devoted to the assessment of present status, major problems & future prospects for GaAs growth & applications	5
	2. Literature Survey, 1977 1982	The literature survey on GaAs was updated identifying the leading organization & most important trends in GaAs research and development	
	3. Exposure of the Program to Scientific Community	The present program and its major developments were exposed to the scientific community through a series of seminars given in industrial organizations (RCA, Texas Instruments, Hewlett-Packard, Hughes Int'l., Xerox, Eastman Kodak, Fujitsu Laboratories, NTT, etc.), presentations at scientific meetings and/or direct contacts with individual scientists	
	4. Working Contacts	Contacts were established with industrial organizations in the area of GaAs characterization, growth & device applications. Material supplied by industrial organizations has been characterized on many occasions Interaction with Microgravity Research Associates was established and aimed at the growth of GaAs in a space environment.	

TABLE I ANNEX

PROGRESS TO DATE - MAJOR DEVELOPMENTS OF 1985

Development	Comments	Representative References
MELT GROWTH		
Oxygen in Melt-Grown GaAs	Using oxygen isotope ^{18}O we have reliably determined for the first time the concentration of oxygen in GaAs by the SIMS technique to be about 10^{14} cm^{-3}	In preparation for publication
Growth in Magnetic Field	Employing an axial magnetic field we suppressed convection in LEC & we showed the beneficial effects on microscopic homogeneity of GaAs crystals	59
FUNDAMENTAL ASPECTS OF SPACE PROCESSING		
Partially Confined Growth Configuration	We have developed a new configuration for growth of semiconductor crystals from the melt in zero-gravity environment	60-61
PROPERTIES & PHENOMENA		
Heterogeneous Generation of Dislocations	We have completed development of a model for dislocation generation during GaAs growth from the melt based on condensation of vacancies into dislocation loops	62
Properties of EL2	We have discovered a hole trap associated with the double-charge state of the arsenic antisite defect in GaAs & we have completed assessment of optical properties of this technologically important defect	61-69
New Semi-Insulating III-V Compounds	We have discovered that a new semi-insulating behavior can be achieved in a wide range of III-V compounds employing doping with titanium	70

Table II. MIDGAP LEVELS IN GaAs GROWN BY DIFFERENT METHODS

Growth Method	Concentration cm^{-3}	Dominant Level	Additional Levels	Major Factor	
				Upon Solidification	Post-Solidification
HB	1 to 5 x 10^{16}	EL2 EL2	-- ELO(1)	arsenic pressure above the melt	slow cooling low thermal gradients
CZ LEC	0.3 to 2 x 10^{16}	EL2 EL2 and/or others(3)	ELO(2)	[As]/[Ga] in the melt	fast cooling, thermal gradients
VPE & MOVPE	0.1 to 5 x 10^{14}	EL2		[As]/[Ga] ratio in gas phase	low temperature
LPE	undetectable			Ga-rich conditions	low temperature
MBE	undetectable			very low growth temp.	very low temp.

(1) heavily O-doped crystals
(2) small diameter crystals
(3) other midgap levels in large diameter crystals

III.3. Heterogeneous Generation of Dislocations

Dislocations can have a detrimental effect on GaAs integrated circuits (IC) and they can degrade the performance and yield of active devices. A reduction of dislocation densities in bulk GaAs crystals has thus received a great deal of attention as a critical material issue in further advancement of GaAs IC technology.

In GaAs crystals grown by the Horizontal Bridgman (HB) method a change in the melt stoichiometry toward Ga-rich or As-rich conditions increases the density of dislocations up to $10^5 cm^{-2}$. We have found that this increase can be significantly reduced by doping with In at a concentration exceeding $10^{18} cm^{-3}$ (see Fig. 1). These results provide evidence of a decrease in point defect concentration induced by isoelectronic doping and its profound consequences for dislocation generation. They also provided a missing link in the development of a heterogeneous dislocation generation model in which vacancy clusters play the role of generation sites for a dislocation network, including the dislocations induced by low thermal stresses. The model is outlined in Fig. 2. It should be emphasized that our preliminary electron microscopy study of HB-GaAs has indeed identified the presence of vacancy type dislocation loops postulated by our theoretical model.

We have also applied this model to quantitative analysis of the dependence of dislocation density on the free carrier concentration. We have found (see Fig. 3) that the suppression of dislocations in n-type crystals and the enhancement of dislocation density in p-type crystals is very well accounted for in terms of the Fermi energy effects controlling the charge state of vacancies and thus their migration and coalescence into dislocation loops.

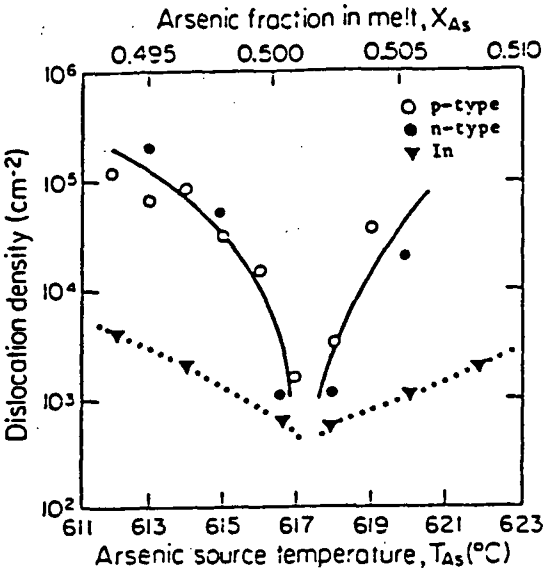

Fig. 1. Dislocation density vs. melt stoichiometry for lightly doped (n, p-type) and for In-doped GaAs. Note reduction of dislocation density induced by In doping.

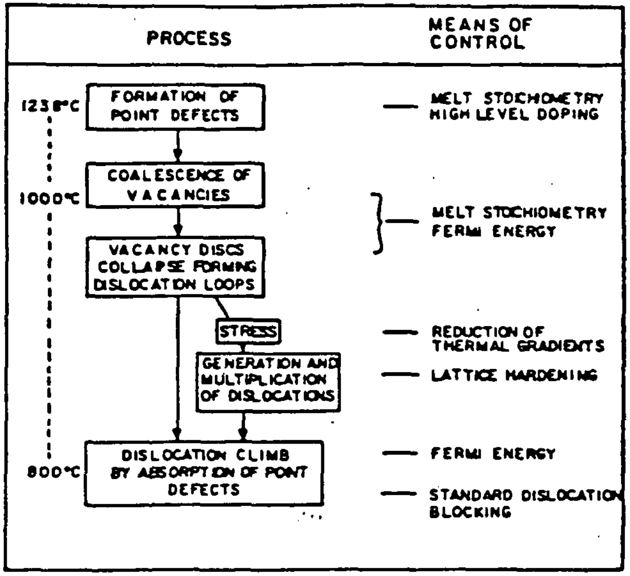

Fig. 2. Mechanism for heterogeneous generation of dislocations in melt-grown GaAs.

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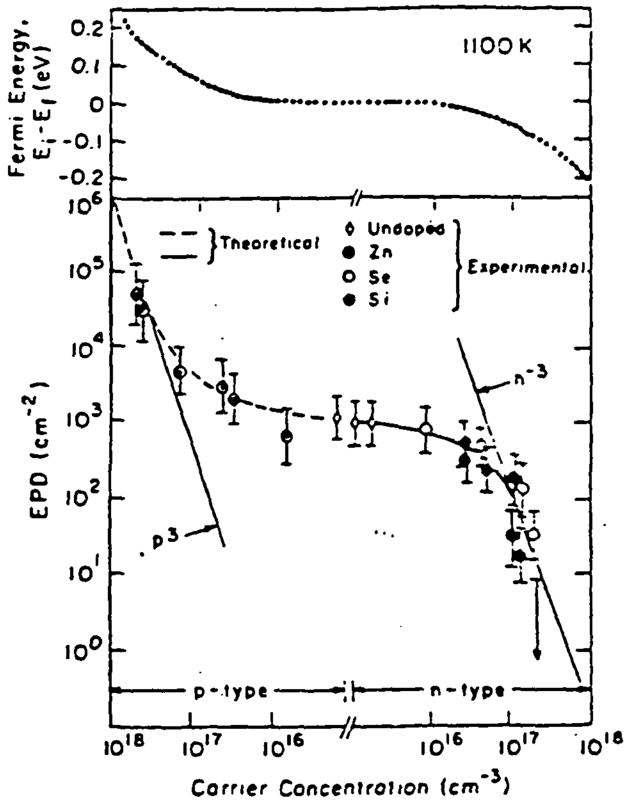

Fig. 3. Dislocation density vs. 300K free carrier concentration. Points-experimental, line-theoretical. Upper portion shows the corresponding Fermi energy at 1100K.

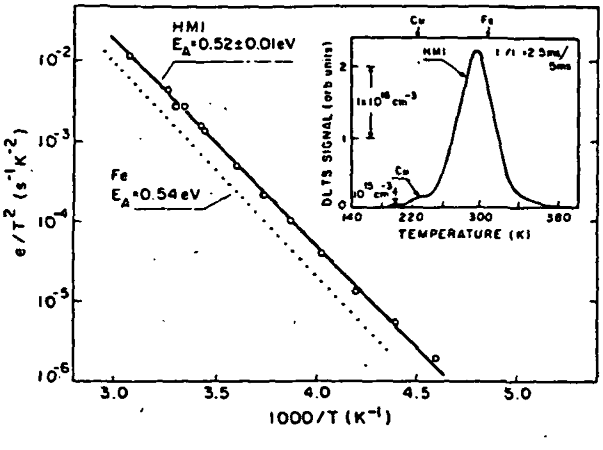

Fig. 4. DLTS spectrum (insert) and thermal activation plot of the hole emission rate of the HM1 trap. Emission rate for the Fe level is also shown.

III.4. Properties of EL2; Relationship with the Arsenic Antisite Defect As_{Ga}

Hole Trap HMI - Associated with As_{Ga} Defect

We have identified a dominant hole trap in p-type bulk GaAs employing deep level transient and photocapacitance spectroscopies. The trap is present at a concentration up to about $4 \times 10^{16} cm^{-3}$, and it has two charge states with energies 0.54 ± 0.02 and 0.77 ± 0.02 eV above the top of the valence band (at 77 K). From the upper level the trap can be photoexcited to a persistent metastable state just as the dominant midgap level, EL2. Impurity analysis and the photoionization characteristics rule out association of the trap with impurities Fe, Cu, or Mn. Taking into consideration theoretical results, it appears most likely that the two charge states of the trap are single and double donor levels of the arsenic antisite As_{Ga} defect.

A deep level transient capacitance spectrum of the trap is shown in Fig. 4 together with the corresponding emission rate thermal activation plot. The photocapacitance spectrum shown in Fig. 5 illustrates transitions involving two charge states of the trap.

It should be emphasized that the identification of a native hole trap in GaAs associated with a double charge donor provides the missing experimental link for establishing a working model of the As_{Ga} defect and understanding its role in the presence and in the characteristics of the dominant deep levels in GaAs.

Metastability of EL2; Relationship with the As_{Ga} Antisite Defect

We have made two discoveries which imply a relationship between metastability of EL2 and intracenter transitions of the As_{Ga} defect. Thus, as shown in Fig. 6, the rate of the photoinduced transition of the

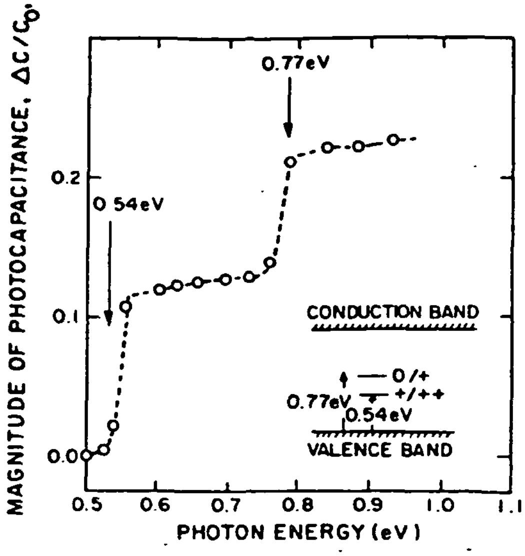

Fig. 5. Low-temperature (77K) spectrum of steady-state photocapacitance showing transitions to two charge states of EL2.

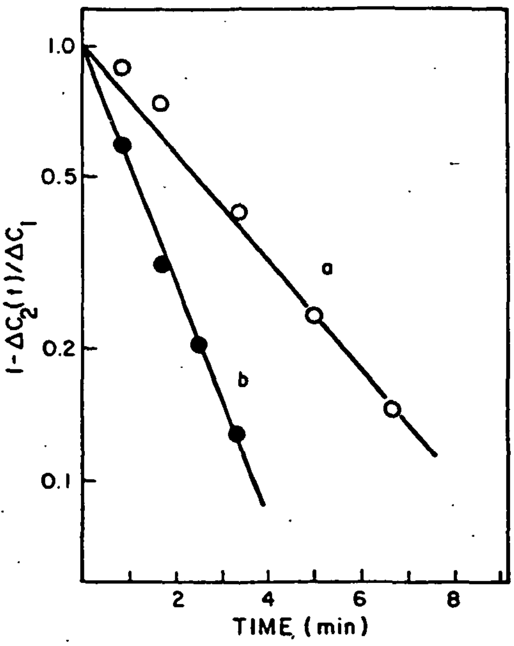

Fig. 6. Dependence of $N_t^*/N_t \approx 1 - \Delta C_2(t)/\Delta C_1$ on illumination time for curve a diode under reverse bias during illumination, and curve b diode under forward bias. Measurement done at 8 K; photon energy $h\nu$ = 1.18 eV. Fast transient b corresponds to EL2 completely occupied by electrons.

GaAs midgap level EL2 to its metastable state increases as its occupation increases. High-resolution optical spectra of this transition exhibit a sharp peak very similar to the no-phonon line of the intracenter absorption of the As antisite defect (see Fig. 7). These findings show that the transition to the metastable state is initiated from the ground state $^1A_1$, and it is finalized via the excited state $^1T_2$ of the neutral As antisite defect. They provide a new basis for the critical assessment of the EL2 metastability models and further confirmation of the association of EL2 with the isolated As antisite defect.

III.5. New Semi-insulating Behavior of III-V Compounds Based on Titanium Doping

We have found that titanium introduces new levels in InP and in GaAs-related compounds with midgap energy positions suitable for creating semi-insulating (SI) materials. The thermal stability of this new class of SI materials should be superior to that of Fe- or Cr-doped compounds due to the low thermal diffusivity of Ti. The Ti-doped SI InP-related compounds should also have a large safety margin to processing-induced acceptor type defects and contaminants since the compensation mechanism in InP involves a midgap donor level.

Our study of Ti-related deep levels was carried out employing Ti-doped GaAs and InP grown by the liquid encapsulated (LEC) technique and also thick epitaxial crystals of related binary and ternary compounds. Characteristic optical absorption spectra involving intracenter transitions of the $Ti^{2+}(3d^2)$ and $Ti^{3+}(3d^1)$ charge states were used to identify the presence of Ti and to estimate the concentration of Ti in a given charge state. Deep levels wee studied using deep level transient spectroscopy (DLTS) and capacitance transient measurements. In

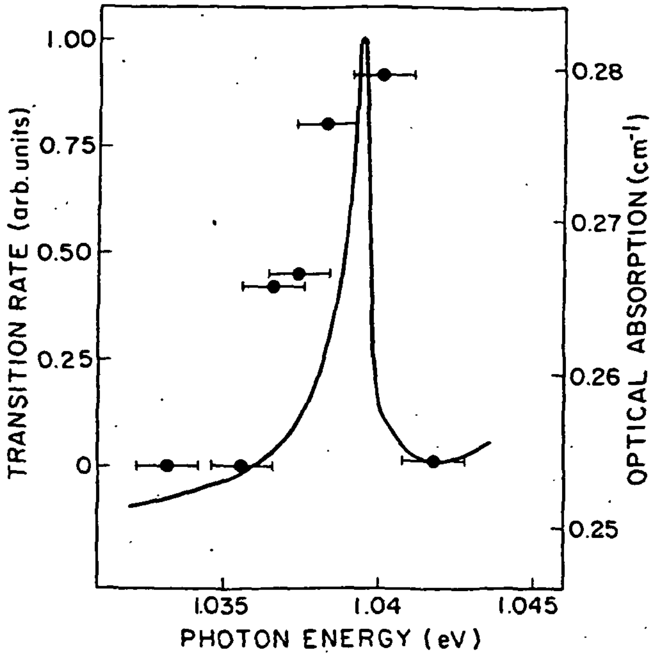

Fig. 7. High-resolution spectrum of the transition rate to the metastable state of EL2 (points) and corresponding no-phonon absorption line of EL2 intracenter transition (solid line).

GaAs, the Ti^{3+}/Ti^{2+} acceptor level and Ti^{4+}/Ti^{3+} donor levels are located at E_c-0.23±0.01 eV and E_c-0.90±0.02 eV (see Fig. 8), respectively. In the ternary compound $Ga_{1-x}Al_xAs$, the separation of these Ti levels from the conduction band increases with Al concentration. For x>0.3 eV the Ti^{3+}/Ti^{2+} acceptor level becomes sufficiently deep to yield SI $Ga_{1-x}Al_xAs$. The technologically most significant compensation is encountered in InP, in which the Ti^{4+}/Ti^{3+} donor level is located near the midgap at E_c-0.60 eV, while the Ti^{3+}/Ti^{2+} acceptor level is within the conduction band (see Fig. 8). In view of the position of this midgap level, Ti doping was successfully employed for the growth of semi-insulating InP with a resistivity of about 5×10^6 ohm-cm. To the best of our knowledge, this is the first SI III-V compound having a compensation mechanism based on a deep donor impurity rather than a deep acceptor impurity. The Ti level energies in InP, GaAs and GaAlAs were found to be in very good agreement with the vacuum-referred binding energy method (VRBE). Thus, we used this method to predict Ti energy levels in other III-V compounds, and we defined the compositional range for SI GaAs-related and InP-related ternary and quarternary compounds based on TI doping.

III.6. Advantages of GaAs Growth in Space

The advantages of zero-gravity conditions in solidification in general, and semiconductor crystal growth in particular, stem primarily from the suppression (or virtual elimination) of thermal and solutal convection in the melt. Furthermore, growth in space is a promising means for overcoming constitutional supercooling, which on the ground limits the yield of crystal growth of alloys and heavily doped semiconductors. As demonstrated in early experiments, elimination of

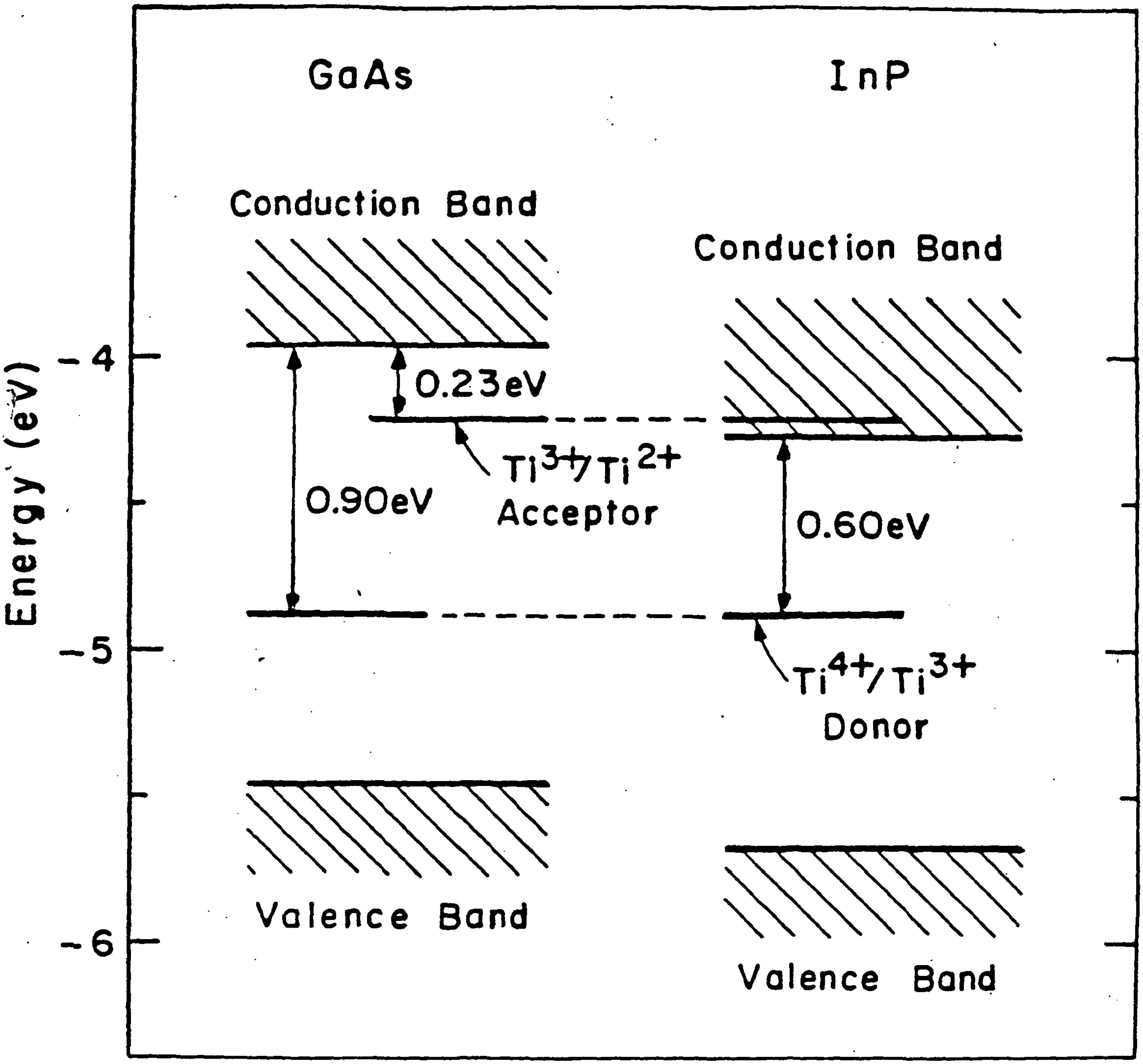

Fig. 8. Newly discovered energy levels of titanium impurity in GaAs and InP.

thermal convection causes impurity segregation to proceed under ideal diffusion-controlled conditions and leads to a uniform dopant distribution and enhanced homogeniety of the crystals.

Regarding the growth of compound semiconductors, and especially GaAs, the potential advantages of space extend far beyond the effects of impurity segregation and constitutional supercooling. They relate to the profound role of the melt stoichiometry and stoichiometry fluctuations discussed above. The effects of stoichiometry were discovered only recently, and thus are not yet fully appreciated by many researchers.

The potential advantages of space for growth of GaAs crystals predicted from our ground-based research are summarized below in Table III. Stoichiometry and its control are the overwhelmingly important factors involved, as clearly indicated by our ground-based studies. For comparison, the advantages of space for the growth of elemental semiconductors, as deduced from previous space experiments, are included.

III.7. Direct Impact on Space Growth Programs

Our ground-based research has had a direct impact on crystal growth in space. Our developments in liquid phase electroepitaxy and in melt growth have evolved into two unique programs on GaAs growth in space which are currently being carried out under the sponsorship of Microgravity Research Associates and NASA, respectively. These two programs are briefly outlined below.

Electroepitaxial Growth of Bulk GaAs in Space. Liquid phase electroepitaxy (LPEE) is the only known growth process which has yielded thick GaAs crystals of ultra-high structural and electronic perfection. We have been developing this method and have established that implementation of this technique on the ground is impeded by the

TABLE III

SUMMARY OF ADVANTAGES OF SPACE FOR GROWTH OF SEMICONDUCTOR CRYSTALS FROM THE MELT

	Elemental Semiconductors (Ge;Si)	Semiconductor Compounds (GaAs & Related)
Effects of Micro-gravity on Crystal Growth Parameters	o Elimination of growth velocity fluctuations caused by thermal convection	o Elimination of growth velocity fluctuations caused by thermal convection in the melt o Elimination of growth velocity fluctuations caused by solutal convection o Elimination of stoichiometry variations caused by solutal convection o Elimination of stoichiometry variations caused by thermal convection in the melt o Elimination of stoichiometry variations caused by thermal convection in the vapor phase
	o Reduced effects of constitutional supercooling	o Reduced effects of constitutional supercooling
Effects of Micro-gravity on Crystal Properties		
Impurity	o Homogeneous distribution (due to diffusion-controlled growth	o Elimination of variations in amphoteric behavior (due to constant stoichiometry)
Native Point Defects		o Elimination of variations in deep compensating centers (resulting from stoichiometry variations) o Elimination of variations in recombination centers (resulting from stoichiometry variations) o Elimination of resistivity variations (resulting from stoichiometry variations)
Dislocations		o Suppression of dislocations due to enhanced control of stoichiometry

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detrimental effects of thermal convection and of solutal convection in the liquid phase.

In 1983 under the sponsorship of Microgravity Research Associates, we initiated an extensive study on the fundamental and practical problems related to the adaptation of the LPEE process to the microgravity space environment. The long-term goals of this work include: conceptual development of electroepitaxy apparatus compatible with space environment (recently developed model of space growth cell is shown in Fig. 9); analysis of processes and phenomena limiting the quality of material grown in space by the LPEE process; optimization of hardware design and related interaction with the hardware manufacturer. Electroepitaxy growth experiments carried out under MRA sponsorship have shown that this technique indeed makes it possible to achieve thick GaAs crystals of outstanding electronic and structural characteristics. Thus, we have grown GaAs up to 3 mm thick with free electron concentration of about $2 \times 10^{14} \mathrm{cm}^{-3}$ and electron mobility $\mu_{300} = 7000\ \mathrm{cm}^2/\mathrm{Vs}$. Furthermore, we have discovered that dislocation density decreases during prolonged LPEE growth, which opens the possibility of achieving virtually defect-free GaAs.

These developments we consider striking. It is now evident that the successful realization of the LPEE process in space carries the promise of a major breakthrough in GaAs and related compounds.

<u>Growth of GaAs Crystals from the Melt in a Partially Confined Configuration</u>. As pointed out earlier, our ground-based research has demonstrated that stoichiometry is the single most important factor in the melt growth of GaAs (see Table III). It is, thus, imperative that in order to benefit fully from the space environment a new growth

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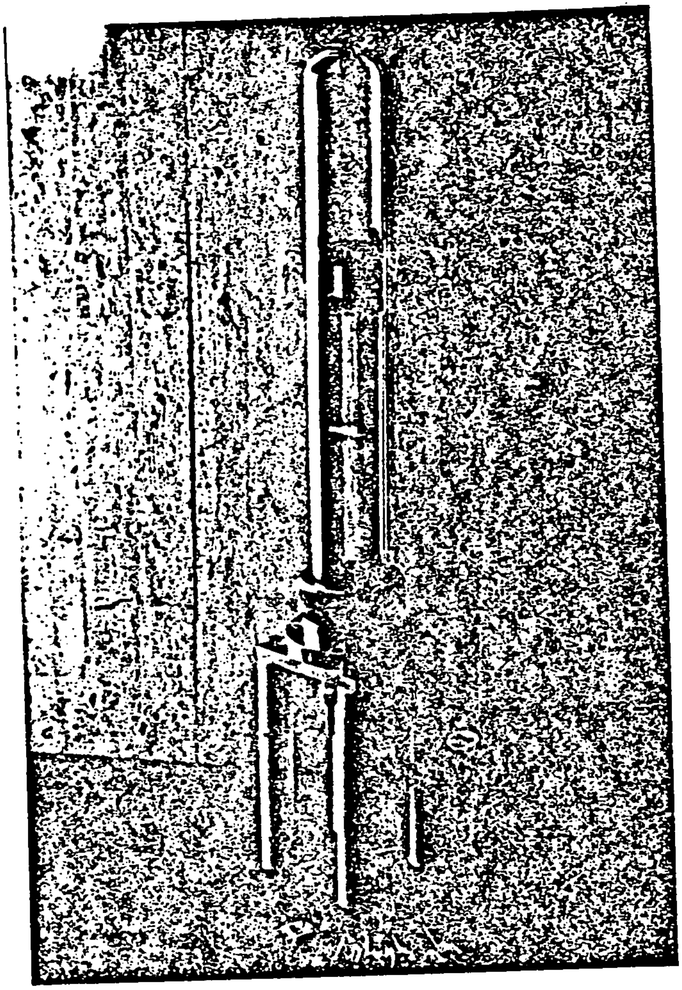

Fig. 9. Growth cell model for LPEE growth in space.

configuration must be developed which permits the control of melt stoichiometry during the growth process and accommodates volume expansion during solidification.

Under zero gravity, melts acquire a shape corresponding to the minimum surface energy. Unconfined melts, generally preferred to avoid contamination, would acquire a spherical shape which is not suitable for directional single crystal growth. In previous space growth experiments cylindrical containers were employed. This confinement cannot accommodate the volume expansion upon solidification, and furthermore, it leads to major problems in controlling the melt stoichiometry during growth.

Under the sponsorship of NASA's Office of Materials Processing in Space we undertook in 1985 the development of GaAs growth from the melt in a novel "partially confined configuration"[58,59] which we believe offers a unique solution to the problems outlined above. In this novel growth configuration a triangular prism is employed to contain the growth melt as shown in Fig. 10. The melt in a triangular prism acquires a shape (Fig. 11) which leaves the empty spaces between the cylindrical melt and the edges of the prism the necessary room to accommodate expansion during solidification. Furthermore, these spaces constitute three channels through which a vapor phase of controlled pressure can be in contact with the melt during the growth process. In Figs. 10 and 11 GaAs crystal growth is considered in a Bridgman-type configuration. An arsenic source is used to provide the arsenic vapor pressure desired to control the melt composition during growth by means of an arsenic source temperature. This aspect is of fundamental importance for the reasons pointed out above.

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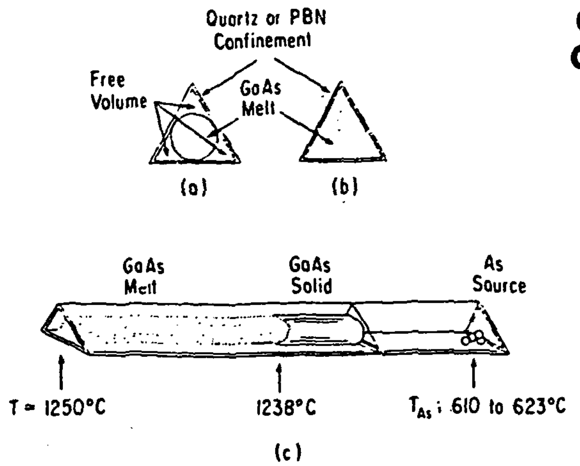

Fig. 10. Schematic representation of a partially-confined configuration for the growth of GaAs crystals from the melt in space.

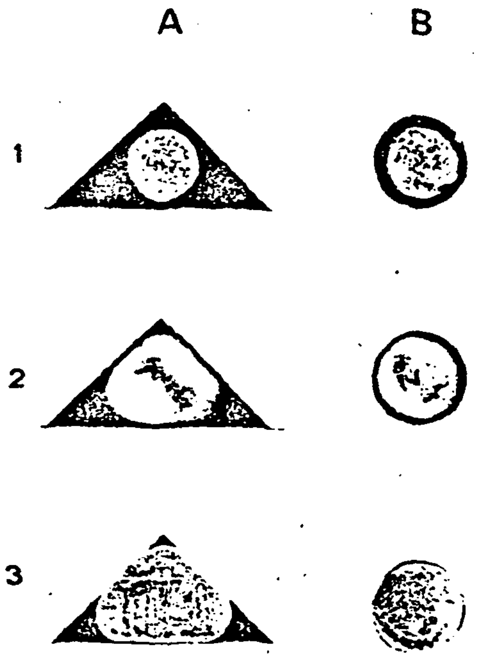

Fig. 11. Solidification in a triangular prism (A) and cylindrical container (B): (1) metal wires in containers; (2) end view after melting; (3) cross section after melting.

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APPENDIX

Reprints and preprints of papers which appeared in the literature or were submitted for publication since our last annual report are attached. They provide a more detailed account of some of the work discussed in the text of the present report.