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Crystal Growth of Device Quality GaAs in Space

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TABLE OF CONTENTS

CRYSTAL GROWTH OF DEVICE QUALITY GaAs IN SPACE

I. SUMMARY

GaAs device technology has recently reached a new phase of rapid advancement, made possible by the improvement of the quality of GaAs bulk crystals. At the same time, it has become apparent that the transition to the next generation of GaAs integrated circuits and optoelectronic systems for commercial and government applications hinges on new quantum steps in three interrelated areas: crystal growth, device processing and device-related properties and phenomena. Our GaAs research program continues to be aimed at radical advances in device quality GaAs bulk crystals, and it evolves about these key thrust areas. Special emphasis is placed on the establishment of quantitative relationships among crystal growth parameters-material properties-electronic properties and device applications. The overall program combines (1) studies of crystal growth on novel approaches to engineering of semiconductor material (i.e., GaAs and related compounds); (2) investigation and correlation of materials properties and electronic characteristics on a macro- and microscale; (3) investigation of electronic properties and phenomena controlling device applications and device performance.

We believe that this extensive ground program is a necessary step for insuring successful experimentation with and eventually processing of GaAs in a space environment. We further believe that this program addresses in a unique way materials engineering aspects which bear directly on the future exploitation of the potential of GaAs and related materials in device and systems applications. We will summarize below the last two-year developments of our program. An overall summary of the major developments in the course of this investigation is given in Table I.

We consider our discovery that stoichiometry is a fundamental factor affecting structural and electronic properties of melt-grown GaAs the most

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TABLE I

PROGRESS TO DATE - SUMMARY OF MAJOR DEVELOPMENTS
(Shaded areas indicate the most important achievements in the last two years)

	Development	Comments	Reference
LPEE-Liquid Phase Electroepitaxy	1. Growth Kinetics Model 2. Dopant Segregation Model 3. Growth Model of Multicomponent Systems	Quantitative understanding of the role of electromigation & of the Peltier effect in the electroepitaxy of binary & multicomponent systems.	1-6
	4. Interface Stability Model	Theoretical model is developed which accounts for the enhancement of interface stability in LPEE. The model defines conditions which lead to the optimization of surface morphology	6,7
	5. Improvement in Defect Structure & Electronic Characteristics	Reduction of microdefect density has been achieved in electroepitaxial growth with high growth rates	8
	6. Contactless Configuration	A new electroepitaxial configuration is introduced in which the practical problems related to the substrate back-contact are elimina[illegible]	9
	7. In-situ Measurements of Growth Kinetics	Utilizing contactless configuration & computerized monitoring system we have realized for the first time in LPE in situ measurements of layer thickness & growth velocity	10
	8. Growth of Thick Crystals	Successful epitaxial growth of thick layers (1 mm) has been achieved for the first time using a modified LPEE configuration	
	9. Advanced Apparatus for the Growth of Heterostructures	Highly advanced microprocessor-controlled apparatus has been constructed for electroepitaxial growth of heterostructures	
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 & monitoring growth parameters	10,12
	2. Growth of Undoped 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	12,13

TABLE I (continued)

	Development	Comments	Reference
	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.	14,15
	4. Identification of the Roie of Oxygen in Melt Growth of GaAs	Oxygen has been identified as a constituent of growth system which indirectly affects electronic properties of GaAs	16
	5. Role of Stoichiometry	Stoichiometry was identified as a fundamental factor controlling structural & electronic properties of GaAs	12-17
CHARACTERIZATION	1. IR Scanning Absorption	Quantitative method was developed for microprofiling of carrier concentration & compensation ratio through free carrier absorption	18
	2. Derivative Surface Photo-voltage Spectroscopy	A new approach was developed for the determination of deep levels, band structure & shallow impurities	19,20
	3. Derivative Photocapacitance Spectroscopy	Wavelength modulated photocapacitance spectroscopy was developed for the determination of deep levels	21
	4. Deep Level Transient Capacitance Spectroscopy	DLTS system was set up suitable for the determination of bulk levels and interface states	22
	5. Optical Transient Capacitance Spectroscopy	Optical transient capacitance technique was adopted for determinationof minority carrier traps	
	6. Transport Techniques	New approach was developed for reliable determination of electron concentration & compensation ratio from electron mobility & free carrier absorption	23-29
	7. Characterization of Semi-Insulating GaAs	A rigorous procedure was developed for the determination of ionized impurity concentration from transport measurements in SI material	29
	8. SEM-Cathodoluminescence	Advanced variable temperature system was set up for cathodoluminesecence microprofiling of defects, impurities & carrier concentration	30
	9. SEM-Electron Beam-Induced Current	Variable temperature system was set up for instantaneous profiling of diffusion length	
	10. Laser Scanning Photovoltage	Photovoltage microprofiling was developed for studying homogeneity of semi-insulating GaAs	

TABLE I (continued)

	Development	Comments	Reference
PROPERTIES & PHENOMENA	1. Electronic Properties of Melt-Grown GaAs	It was shown that presently available melt-grown GaAs is highly inhomogeneous in microscale; it exhibits noticeable compensation & high density of deep levels	32
	2. Interaction between Epitaxial Layer & Substrate	It was demonstrated that outdiffusion of recombination centers from the substrate into LPE layers during growth process takes place. Growth conditions were formulated to minimize outdiffusion	33
	3. Growth-Property Relationships in Epitaxial Growth	It was found that growth rate variations have significant effect on the formation of recombination centers in GaAs	34,35
	4. Relationships between Electronic Properties & Melt-Growth Conditions	Microprofiles of electron & ionized impurity concentrations in melt-grown GaAs were obtained for the first time. It was shown that the electronic properties of GaAs on a microscale are governed by amphoteric doping & deviation from stoichiometry rather than impurity segregation	11,18
	5. Relationships between As Pressure & Deep Levels	A direct relationship was established between As pressure above the melt & the electron trap concentration in melt-grown GaAs	11-16
	6. Origin 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}	36-40
	7. 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	39
	8. Minority Carrier Mobility	Minority carrier mobility in p-type GaAs was computed as a function of carrier concentration & temperature	41
	9. Free Carrier Scattering in GaAs	It was shown on a theoretical basis that electron scattering by centers with a short-range potential plays a minor role in GaAs	28-29
	10. Interface States	Surface states on GaAs-anodic oxide interface were determined with modified DLTS	

TABLE I (continued)

	Development	Comments	Reference
	11. Current Oscillations in SI GaAs	New type current oscillations were observed in SI GaAs, their frequency being controlled by thermal emission of electrons from deep traps	40
	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	42-45
	13. Optoelectronic Properties of InP	Cathodoluminescence studies of InP were completed	30
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	32
	2. Literature Survey	The literature survey on GaAs was updated identifying the leading orgnaization & 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	46
	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	

significant and promising result of our most recent research. Thus, we have established that deviation from stoichiometry controls dislocation density, concentration of point defects, related deep levels, and the amphoteric behavior of impurities. This discovery has also led to identification of the causes of irreproducible growth and of the lack of precise control of the electronic properties of bulk GaAs. We have shown for the first time that these processes are linked directly to stoichiometry-induced defects and their interactions during the post-solidification cooling. We have advanced substantially the understanding of the role of oxygen in the melt growth of GaAs and the origin of the major deep donor level (EL2). Our microscopic model of this level (i.e., arsenic on gallium site plus arsenic vacancy) enabled for the first time the consistent explanation of unique electronic properties of the EL2 and a sensitivity to the growth conditions. The above results bear directly on processes leading to semi-insulating behavior of GaAs, and thus they are of fundamental importance in the pursuit of significantly improved quality GaAs for high-speed IC applications.

We have discovered that atomic hydrogen (introduced into GaAs by exposure to a hydrogen plasma) eliminates the dominant deep level (EL2). This finding offers a new means for studying and controlling electronic characteristics of GaAs and GaAs devices.

In electroepitaxial growth we have completed the development of a unified theoretical treatment which explains quantitatively the unique growth kinetics, the segregation behavior and the morphological stability. We have also introduced new growth configurations and demonstrated the feasibility of electroepitaxial growth of bulk GaAs crystals and of the in situ monitoring of growth kinetics. Utilizing the advantages of electroepitaxy in achieving abrupt acceleration (or deceleration) of growth we showed that recombination centers are formed as a result of growth acceleration. This finding underlines the importance of the dynamics of crystal growth, which has not been explicitly considered in most investigations.

Our electronic characterization facility was extensively utilized to assess the quality of bulk and epitaxial GaAs and to study the relationships of electronic properties and growth parameters. Characterization techniques based on analysis of free carrier mobility were extended to semi-insulating (SI) GaAs and also to p-type material, i.e., to cases particularly important for IC applications.

We have completed the study of electrical and photo-electrical properties of GaAs-anodic oxide interfaces. Our interface-state model involving discrete deep and shallow levels (originating from oxidation-induced defects) made it possible to consistently explain the gigantic photoionization effect and anomalous hysteresis and frequency or temperature responses of GaAs MOS structures.

INTRODUCTION

Since the initiation of this investigation we have succeeded in the development of unique crystal growth approaches, new effective techniques for a macro- and microscale characterization of key electronic properties and in the discovery of new phenomena and processes relevant to GaAs device applications. Growth-property relationships established for the first time have led us to defining stoichiometry as a fundamental factor controlling structural and electronic properties of GaAs and to the growth of bulk GaAs of improved quality (dislocation-free and electron trap-free material). Table I summarizes the major achievements. Detailed discussion is given in our reports and publications. This year's preprints and reprints of publications are attached. Accordingly, in this section of this report a brief outline of the most significant recent developments will be presented.

CRYSTAL GROWTH

In our crystal growth studies we have thus far concentrated on two approaches: liquid phase electroepitaxy and Bridgman-type growth from the melt. The original selection of these techniques was made on the basis of their compatibility with a space environment and also because they lend themselves to controlling the growth process and thus to studying growth-property relationships.

Electroepitaxy

Most basic developments in electroepitaxy (LPEE) were accomplished in previous stages of our research. These developments were extensively discussed in our annual reports. We will outline briefly here only some of our recent results. During the last year we have completed the development of a comprehensive theoretical model of LPEE. This model provides adequate explanation for the unique advantages of LPEE in achieving ideal surface morphology, reducing density of defects generated during the growth and/or outdiffusing from the substrate. Very high growth rates (up to 25 μm/min) render this process comparable to melt growth; thus LPEE offers a unique possibility for obtaining sizeable "bulk" crystals of epitaxial quality.

Our current research on LPEE is devoted to practical refinements of this technique as applied to growth of GaAs-related quarternary compounds and to growth of bulk crystals. These approaches require quite different experimental systems, i.e., a multiwell horizontal sliding boat and a vertical Czochralski-type configuration, respectively. These systems were constructed, tested (as discussed in our 1981 Annual Report) and are currently employed for electroepitaxial growth.

Our most recent efforts were addressed to the theoretical limitations provided by constitutional supercooling. We have theoretically predicted a significant enhancement of interface stability in liquid phase electroepitaxy (LPEE) and we have explained the experimentally attained stable growth with velocities as high as 25 μm/min (close to two orders of magnitude higher than growth rates obtained by thermal LPE). We have defined the geometry of the LPEE configuration and the growth parameters (current density and polarity, temperature and substrate characteristics) which lead to the optimization of surface morphology. These conditions are listed in Table II, and they should be considered of key importance for future extension of LPEE to the growth of high quality bulk crystals.

Melt-Growth Apparatus

A precision Bridgman-type apparatus was designed and constructed for the investigation of relationships between crystal growth parameters and the properties of GaAs crystals. Key features of the system are the use of a heat pipe for precise arsenic vapor pressure control and seeding without the presence of a viewing window. Pertinent growth parameters, such as arsenic source temperature, thermal gradients in the growing crystal and in the melt, and the macroscopic growth velocity can be independently controlled. During operation, thermal stability better than $\pm 0.02°C$ is realized; thermal gradients can be varied up to 30°C/cm in the crystal region and up to 20°C/cm in the melt region; the macroscopic growth velocity can be varied from 50 μm/hr to 6.0 cm/hr. A schematic representation of this growth apparatus is given in Fig. 1. Photographs of the system arranged to operate in a horizontal and vertical configuration are shown in Figures 2a and 2b, respectively.

TABLE II. Interface stability in liquid phase electroepitaxy.

Substrate and polarity	Comments on growth	Interface stability	Stabilizing factor
n; +	growth	enhanced over LPE; optimized with n thin substrates	solute electromigration
p; +	growth for thin p^+ substrates; dissolution for thick p^- substrates	interface always stable during growth	solute electromigration
n; —	dissolution; growth not possible	—	—
p; —	growth for thick p^- substrates; dissolution for thin p^+ substrates	interface always stable during growth	thermal gradient induced by Peltier effect

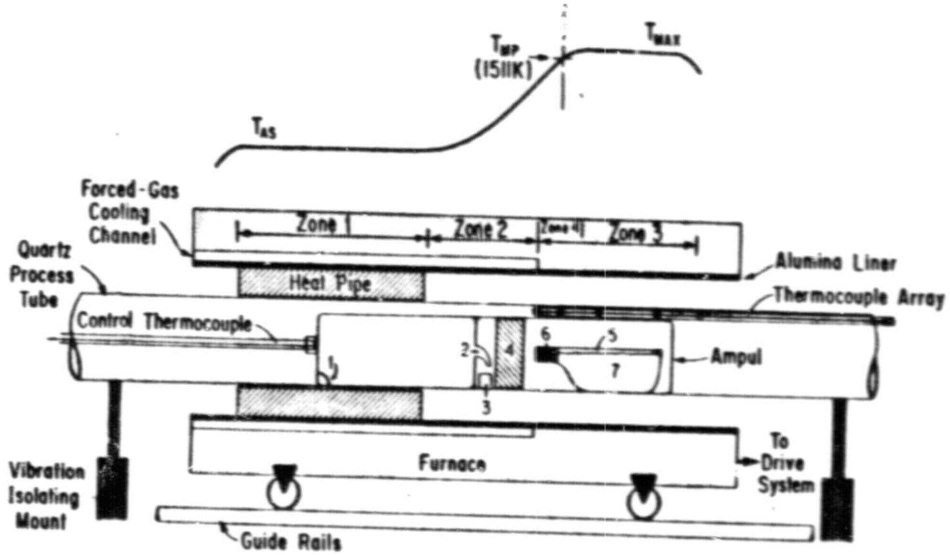
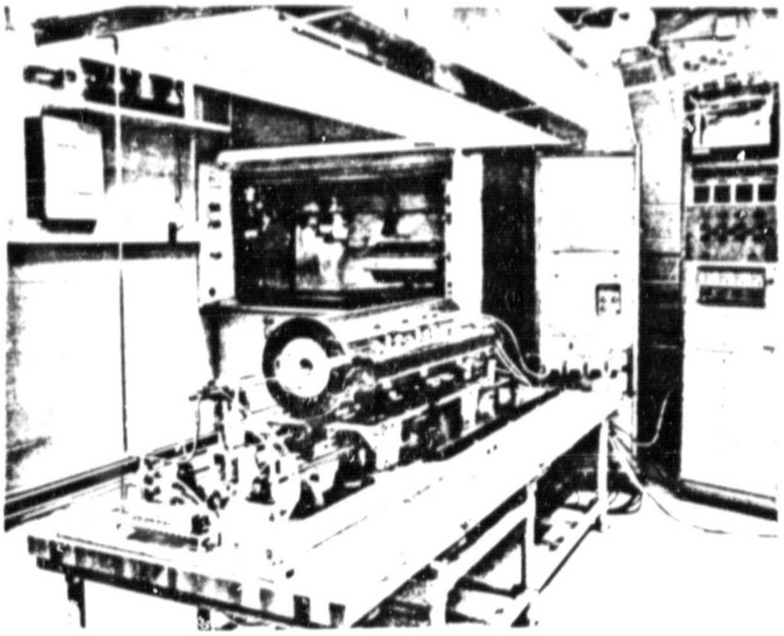
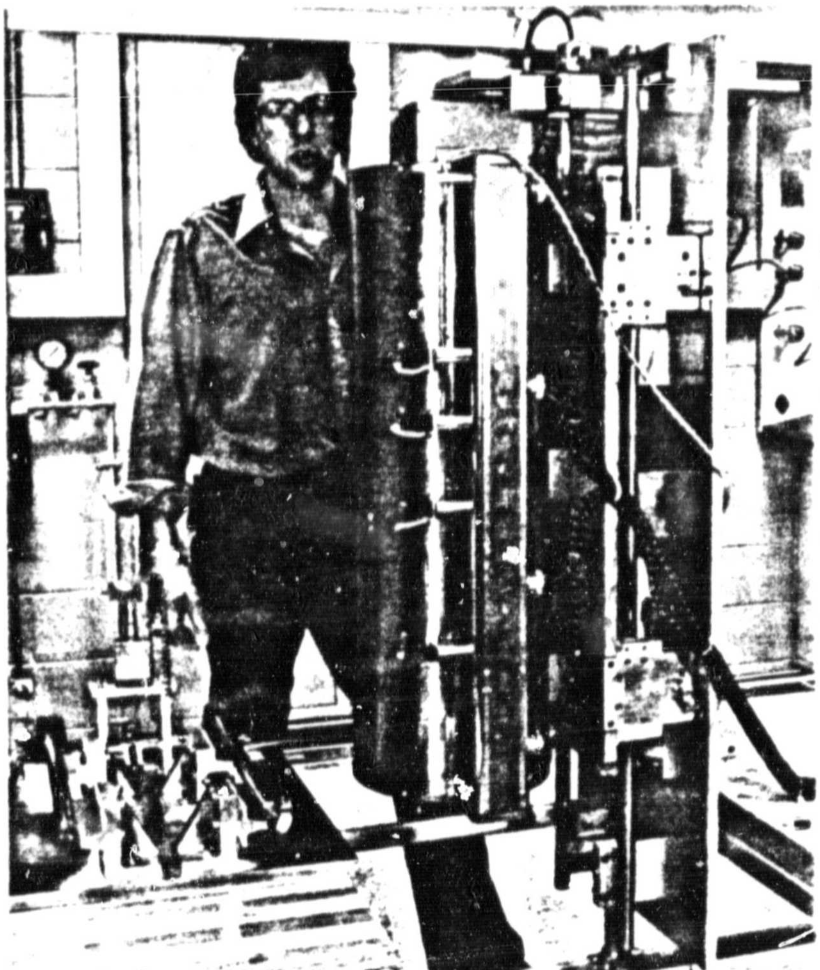


Fig. 1. Schematic representation of the growth apparatus and thermal profile (top). The quartz ampul contains the As source, 1; a breakable seal, 2; and seal breaking weight, 3; the quartz diffusion barrier, 4; a quartz boat, 5; the GaAs seed crystal, 6; and polycrystalline GaAs, 7.



State-of-the Art apparatus for GaAs crystal growth from the melt designed and constructed by John Parsey (graduate student) and Dr. Y. Nanishi.



Above apparatus in the vertical configuration (John Parsey).

Figure 2.

During the last two years we have grown about 70 GaAs crystals utilizing this unique Bridgman-type apparatus. The results of these studies have surpassed our expectation, as they led for the first time to the establishment of growth-property relationships of fundamental importance for obtaining undoped dislocation-free GaAs and electron trap-free shallow donor doped GaAs. These relationships made it possible to resolve the origin of the dominating deep levels and elucidate the role of oxygen in obtaining undoped semi-insulating GaAs.

Growth-Property Relationships--Critical Role of Stoichiometry

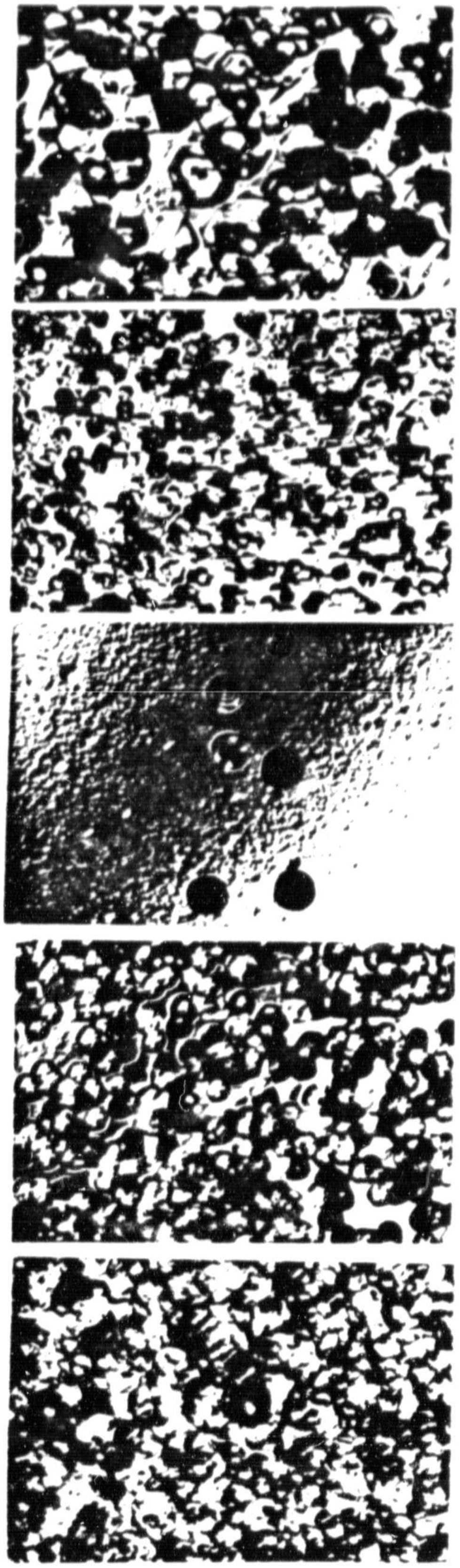
In our growth experiments the stoichiometry was varied by varying the arsenic source temperature, T_{As}, which in turn controls the arsenic pressure over the melt and thus the melt composition. A typical range of T_{As}, 610-628°C, corresponded to melt composition (determined by arsenic to gallium ratio) changes from 0.52 to 0.485.

We have found that the dislocation density is a very sensitive function of T_{As}. Typical results are shown in Fig. 3a. They demonstrate that dislocation etch pit density (revealed by etching in a molten KOH) exhibits minimum concentration for $T_{As} \approx 617$°C. In a number of crystal growth experiments we have confirmed the importance of these optimum stoichiometry conditions. Thus, undoped crystals routinely grown under these optimum conditions exhibited dislocation density below 500. Doping at the level of 10^{17} cm^{-3} with shallow donors suppressed dislocation density to values below 100 cm^{-2}, i.e., to values referred to as corresponding to "dislocation free" material.

Dislocations are commonly known to play a detrimental role in GaAs integrated circuits. Accordingly, the establishment of growth conditions yielding minimum dislocation density can be considered as a significant step toward the growth of improved device quality GaAs bulk crystals. We also believe that this finding will become of critical importance in future stages of crystal growth developments as other factors contributing to dislocation formation during post-solidification (e.g., thermal stress during cooling) are addressed in conjunction with large diameter crystals.

The optimum arsenic source temperature 617°C was also found to yield the lowest compensation ratio and the highest electron mobility value of n-type GaAs crystals. Thus, these results showed that deviation from stoichiometry is a contributing factor to the amphoteric behavior of shallow impurities in melt-grown GaAs crystals. In earlier studies we have observed unique spacial variations which could not be explained on the basis of classic segregation kinetics controlled by the microscopic growth rate. Representative results are shown in Fig. 3b where the carrier concentration undergoes significant variations, whereas the concentration of the dopant impurity (N_D+N_A) remains essentially constant. As seen in Fig. 3c, similar behavior is caused by changes in arsenic pressure.

The arsenic pressure was also found to control the concentration of a major deep level EL2. Typical dependence of the EL2 concentration on T_{As} obtained for unintentionally doped GaAs is presented in Fig. 4. It is seen that the concentration of the EL2 decreases in going from arsenic-rich to gallium-rich growth conditions. This finding proves that the arsenic-rich conditions are most desired for the growth of undoped semi-insulating GaAs which requires a high concentration of EL2. Such behavior has been indeed confirmed by a recent study of Liquid-Encapsulated Czochralski growth of semi-insulating GaAs.



626°C

620°C

617°C

614°C

610°C

(x 60)

Fig. 3a Dislocations in segments of GaAs crystal grown under different As source temperatures.

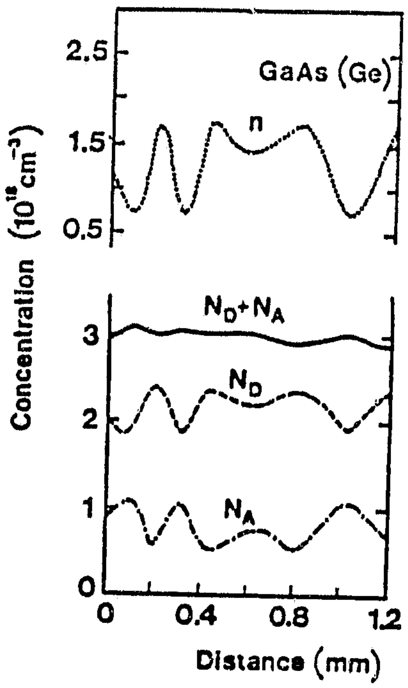


Figure 3b. Electron concentration and ionized impurity microprofiles of Ge-doped melt-grown GaAs obtained with scanning IR absorption spectroscopy. Note different behavior of N_D and N_A.

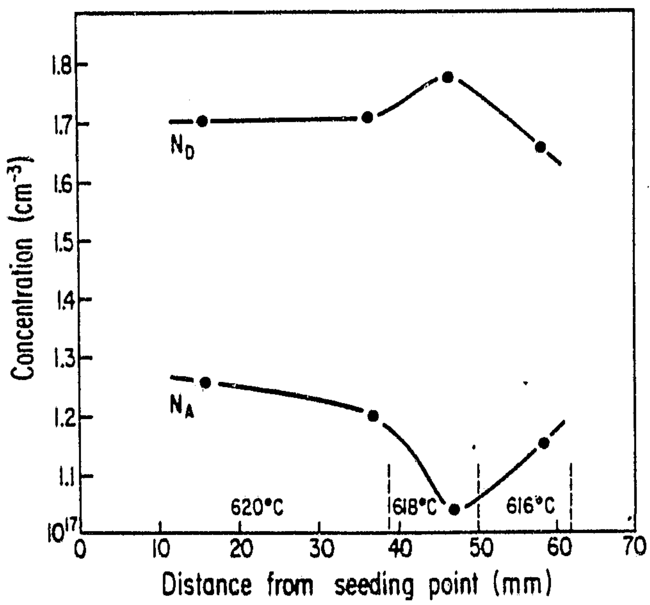


Figure 3c. Stoichiometry-induced changes in incorporation of donors and acceptors. Note similarity to Fig. 2a.

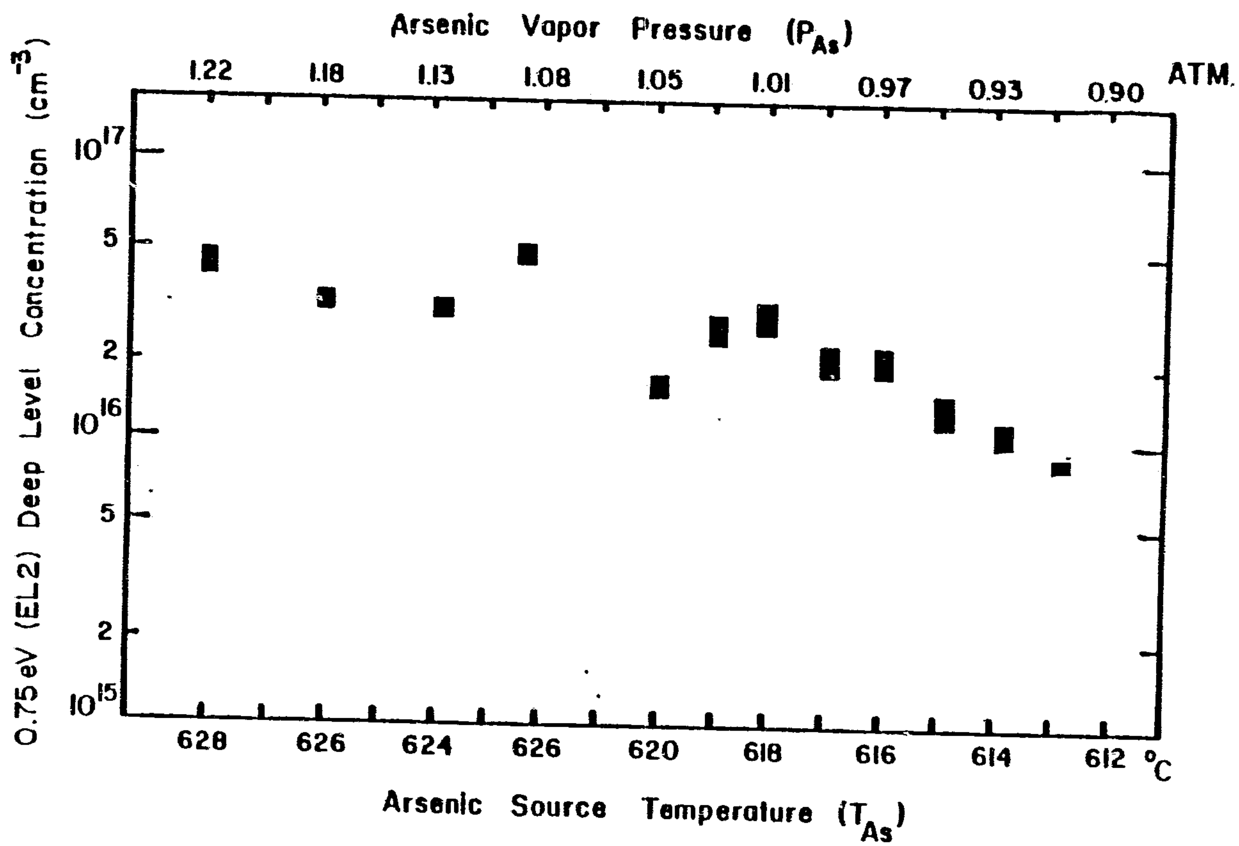


Fig. 4. Concentration of the 0.75 eV deep level (EL2) vs. the arsenic source temperature (T_{As})

Post-Solidification Processes; Role of Impurities

The stoichiometry effects discussed above are caused by native defects generated during the solidification process. Upon post-solidification cooling of the crystal these defects interact and form other defects and defect complexes which determine the final properties of the as-grown crystal and also its behavior during subsequent heat treatment involved in device processing. In our study we have employed intentional doping in order to distinguish between solidification effects and the post-solidification phenomena (during cooling of the crystal). It is a general feature of the post-solidification defect interactions in GaAs that they are affected by shallow donors or acceptors, irrespective of the lattice-site the dopant occupied. Furthermore, the threshhold dopant concentration determines the critical temperature range at which the post-solidification interactions take place.

The annihilation of the EL2 level by shallow donors shown in Fig. 5 and the basically similar suppression of the dislocation density by shallow donors shown in Fig. 6 provide unique evidence of the above behavior. The post-solidification defect interactions leading to the suppression of dislocation density are currently under study. The effects of doping on the EL2 level were adequately explained by our recently formulated microscopic model of this center identifying the EL2 with a complex consisting of an antisite defect (arsenic on a gallium site) and an arsenic vacancy, $As_{Ga}V_{As}$. This complex (shown in Fig. 7) is formed during the migration of a gallium vacancy V_{Ga} to a neighboring arsenic site. The pertinent reaction of charge defects is $V_{Ga}^{-}+As_{As}\rightleftarrows As_{Ga}^{++}+V_{As}^{+}+4e$; thus the concentration of the EL2 center $[As_{Ga}V_{As}]$ is proportional to n^{-4} where n is the electron concentration at elevated temperature. By increasing n above the intrinsic concentration, the

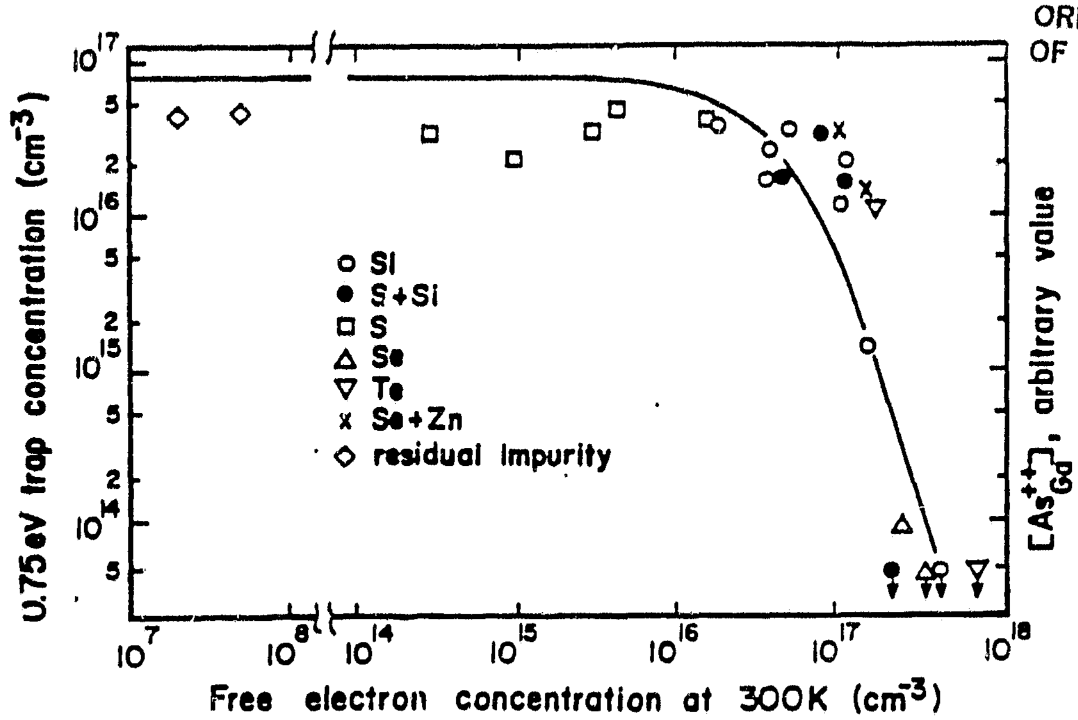


Figure 5. Experimental and theoretical dependence of the concentration of the E_c-0.75eV deep level (EL2). The solid line is the theoretical dependence of $[As_{Ga}^{++}]$ determined from Eq. 19.

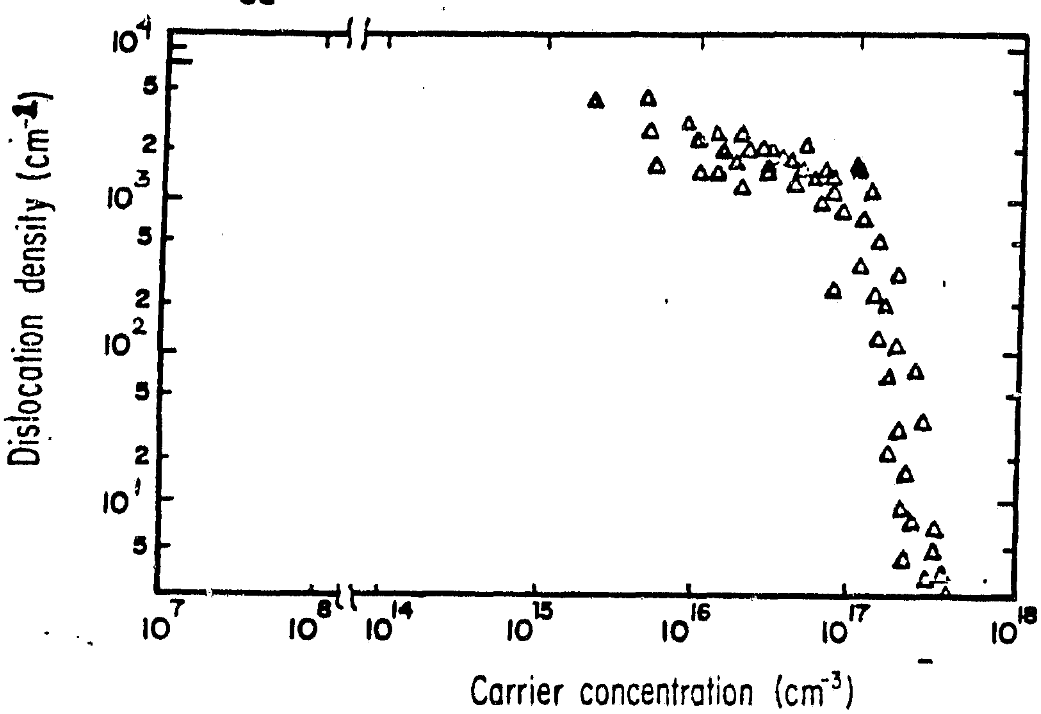


Figure 6. Dislocation density vs. free electron concentration in GaAs grown under optimum arsenic pressure.

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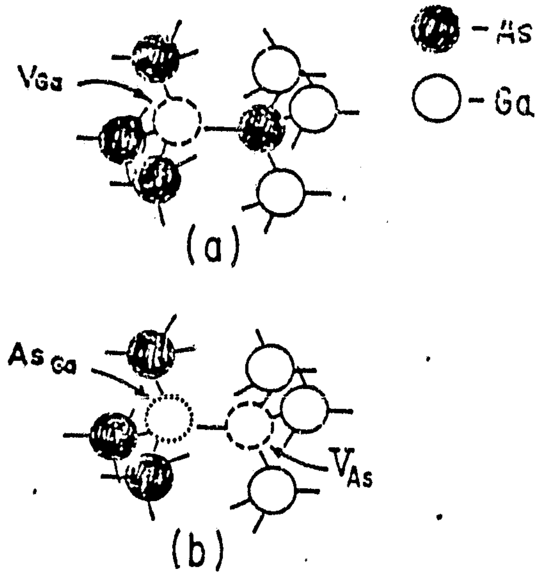

Figure 7. Formation of the EL2 complex; (a) gallium vacancy, (b) $As_{Ga}V_{As}$ complex formed as a result of V_{Ga} migration to As site.

EL2 level is effectively suppressed and annihilated as demonstrated by the results of Fig. 5. From the threshold value of electron concentration, it is concluded that the formation of the 0.82 eV deep level takes place at temperatures below about 1050 K, i.e., during the post-growth cooling in the case of melt-grown GaAs.

PROPERTIES AND PHENOMENA

Electronic Properties of Bulk GaAs

Since 1980 we have been actively involved in detailed analysis of the electronic properties of commercially available melt-grown GaAs. Representative results of our study were given in the previous Annual Report. We have recently extended our study to microscale characterization of semi-insulating GaAs. Commonly present electrical inhomogeneities of SI GaAs are considered highly undesirable and limit the transition into the next generation of GaAs integrated circuits.

Free Carrier Mobility

Free carrier mobility values are commonly taken as an overall measure of perfection and purity. We have completed a rigorous theoretical and experimental study of carrier mobilities in GaAs which led to the development of a practical means for fast quantitative characterization of GaAs using computed values of mobility conveniently tabulated as a function of free carrier concentration and compensation ratio. More recently we have succeeded in developing a straightforward (but rigorous) procedure for the characterization of Semi-Insulating GaAs from Hall mobility values measured at slightly elevated temperatures. Thus, the mobility curves presented in figures 8a and 8b permit the determination of the total concentration of ionized impurities ($N_D^+ + N_A^-$) in semi-insulating GaAs.

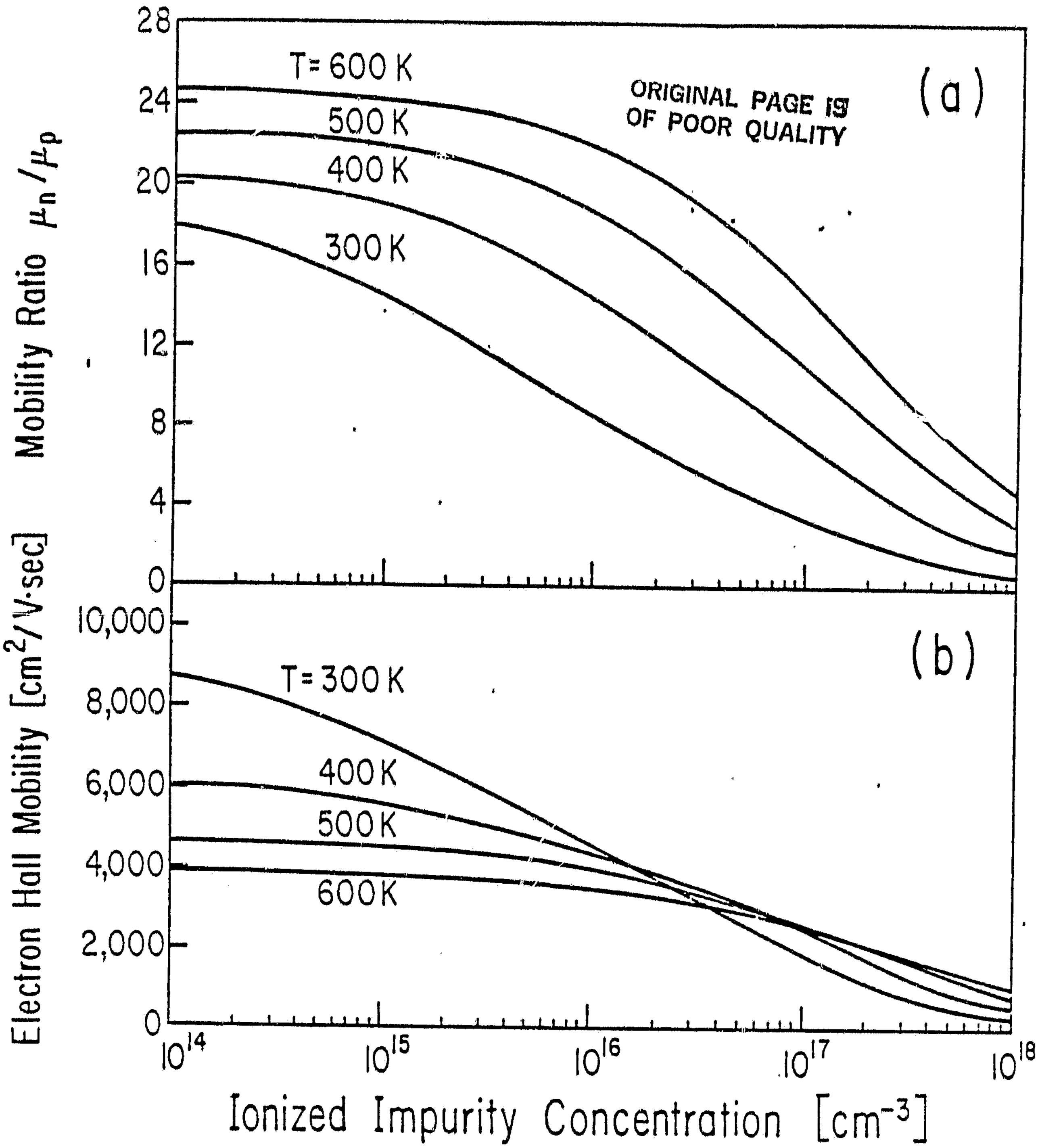

Figure 8. (a) Electron-to-hole mobility ratio for SI-GaAs vs. ionized impurity concentration for various temperatures.
(b) Electron Hall mobility for SI-GaAs vs. ionized impurity concentration for various temperatures.

Passivation of the EL2 by Hydrogen

We have discovered that atomic hydrogen passivates the EL2 level in GaAs. We consider this finding extremely promising for device-related studies. According to our results plasma hydrogenation of GaAs (i.e., 2-hour exposure of GaAs to hydrogen plasma at 300°C) constitutes an effective low temperature process for controlling (or completely passivating) the EL2 level and its effects on the electronic characteristics of GaAs and, possibly, GaAs devices.

The results obtained with hydrogenated samples, employing deep level transient spectroscopy (DLTS) and analysis of Schottky barrier capacitance transients are shown in Table III together with results obtained with as-grown samples and with samples heat-treated at 300°C for two hours in an H_2 ambient. It is seen that in the as-grown samples the concentration of the 0.82 eV trap exceeds that of the other commonly observed traps (EL4, EL5, and EL6) by about one order of magnitude. Exposure of GaAs to hydrogen plasma leads to a signifant decrease of the concentration of the dominant EL2 level, i.e., by a factor of 10 in sample 1, and by a favor of 5 and 4 in samples 2 and 3, respectively. The hydrogen-induced changes in the concentration of EL4, EL5, and EL6 are much less pronounced than those in that of EL2; these changes are within the range of the observed variations of the concentration of these levels caused by inhomogeneities in GaAs. It is also seen that the 300°C heat treatment had no effect on the concentration of the deep levels. We attribute the EL2 passivation process to the interaction of hydrogen with the unshared electrons of the antisite As_{Ga} defect leading to the formation of stable As-H bonds.

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TABLE III. Effect of hydrogen on deep level concentration in GaAs

		EL2 0.82 eV	EL4 0.54 eV	EL5 0.40 eV	EL6 0.32 eV	Deep Level Probing Depth
Crystal Segment	a)	1.7×10^{16} d)	2×10^{15}	2×10^{15}	1×10^{15}	∿ 0.7 μm
Si-doped	b)	1.7×10^{16}	2×10^{15}	2×10^{15}	2×10^{15}	>>
$n_{300K} \approx 8 \times 10^{16} cm^{-3}$	c)	1.6×10^{15}	2×10^{15}	1.5×10^{15}	4×10^{14}	>>
	c)	undetectable	2×10^{15}	1.5×10^{15}	3×10^{14}	< 0.2 μm
Crystal Segment	a)	1.9×10^{16}	9×10^{14}	2×10^{15}	3×10^{15}	∿ 0.5 μm
Si-doped	b)	1.9×10^{16}	9×10^{14}	1.5×10^{15}	2×10^{15}	>>
$n_{300K} \approx 6 \times 10^{16} cm^{-3}$	c)	3.6×10^{15}	7×10^{14}	1×10^{15}	1×10^{15}	>>
Undoped	a)	9×10^{15}	$<10^{15}$	8×10^{14}	5×10^{14}	∿ 0.5 μm
$n_{300K} \approx 1 \times 10^{16} cm^{-3}$	c)	2.6×10^{15}	2.5×10^{15}	1×10^{15}	8×10^{14}	>>

a) "As grown" samples

b) Heat treated control samples

c) Hydrogenated samples

d) Concentration in cm^{-3}

Current Oscillations in SI GaAs

We have discovered a new type of current oscillations which are controlled by the thermal release of electrons from deep levels. Such oscillations associated with electron traps at E_c-0.34 eV and E_c-0.40 eV are shown in Fig. 9. Oscillations due to the dominant deep level EL2 are presented in Fig. 10. Both types of oscillations require that a sufficiently high electric field is applied to the sample. We believe that they are due to electric field-enhanced capture of electrons by the EL2 which leads to a negative resistance. The effect of an electric field on the capture rate of the EL2 is caused by a configurational barrier characteristic for this level. This barrier (about 70 meV) becomes readily penetrable to hot electrons accelerated by the electric field.

We believe that thermally stimulated current oscillations constitute an effective means for studying the dynamic properties of deep levels. It should also be noted that in view of the nearly three orders of magnitude change of the frequency for a temperature change of about 80 K (see Fig. 10) these oscillations might provide a means for high precision temperature measurements.

Microscopic Model of the EL2 Center

We have found that the defect responsible for the dominant deep donor E_c-0.76 eV (EL2) in melt-grown GaAs also introduces a shallow donor level at E_c-0.025 eV. This finding makes possible the refinement of our antisite defect As_{Ga} model of the EL2 formation in melt growth to a microscopic model which accounts for the, thus far, observed electronic behavior of EL2 (including its metastable state). In addition to the antisite defect As_{Ga}, the proposed defect center involves an arsenic vacancy, V_{As}, on a neighboring site. This complex (shown in Fig. 7) is similar to a DX center exhibiting a large lattice relaxation energy and thus a configurational barrier required to account for electric

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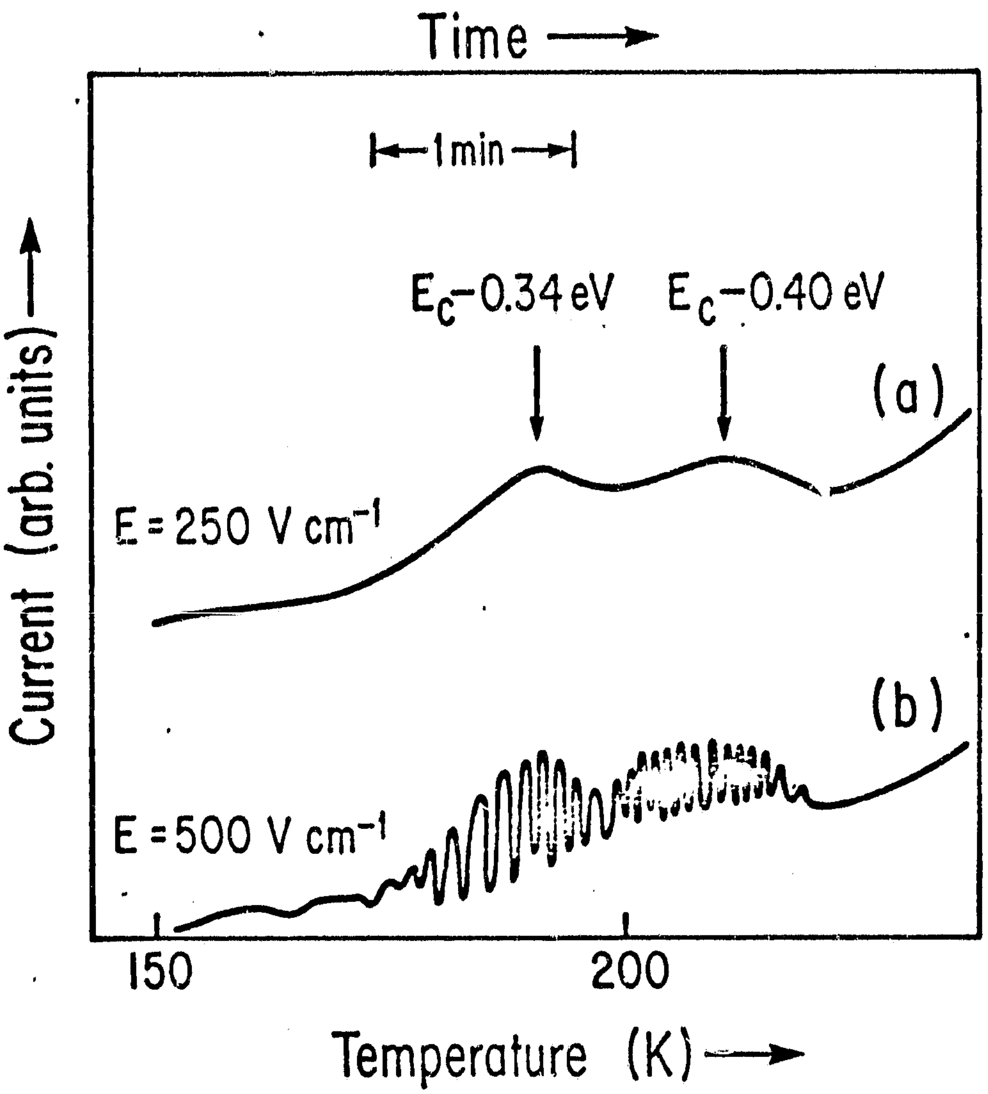

Figure 9. Thermally stimulated current in SI GaAs under different electric fields. TSC_1 oscillations were observed under high field, 500 V cm^{-1} (b).

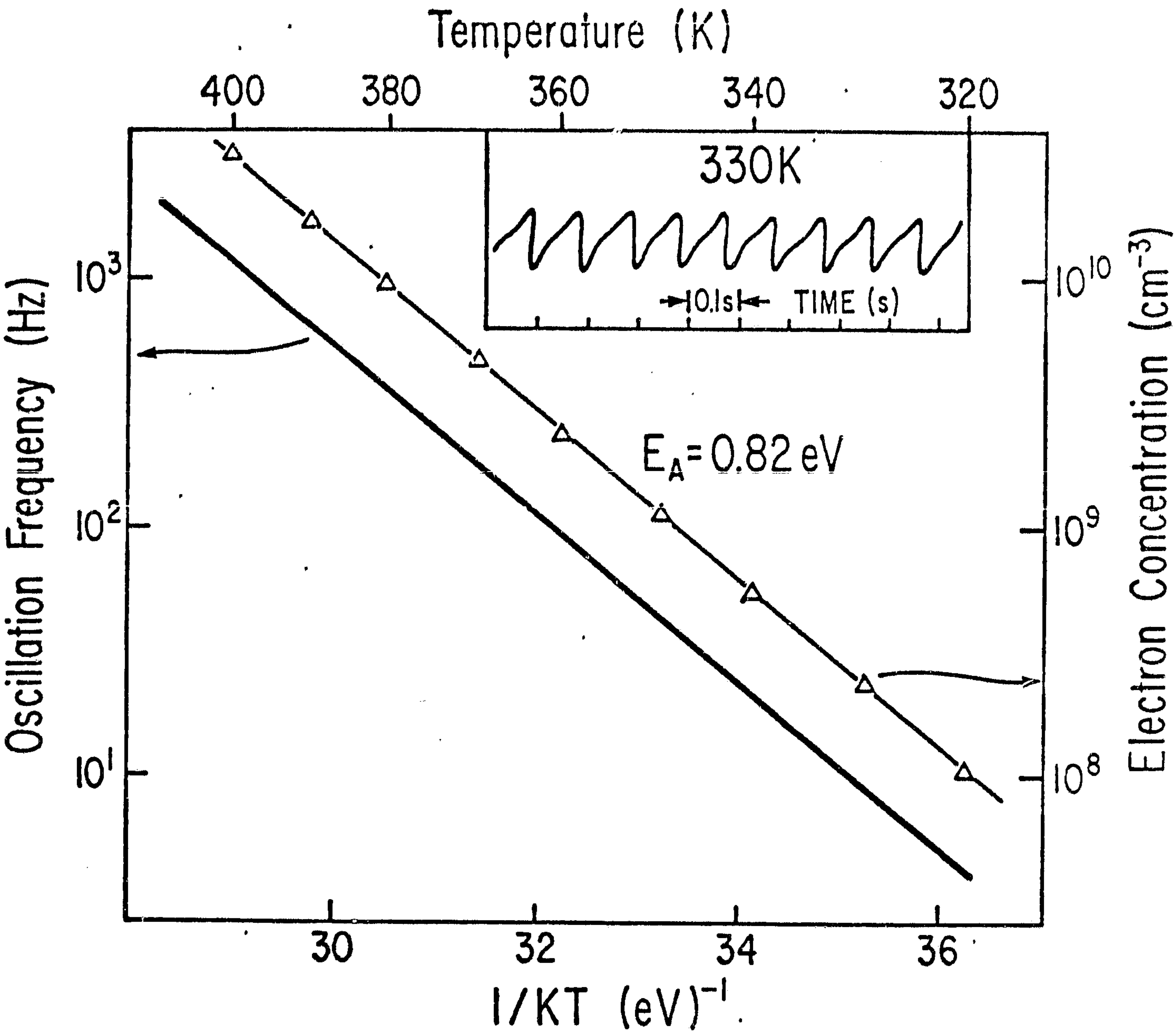

Figure 10. Temperature dependence of the thermal equilibrium current oscillation frequency and of the electron concentration. Insert: TEC oscillations at T = 330 K, electric field = 500 V cm^{-1}.

field-enhanced capture rate discussed above. The proposed configurational representation of the EL2 is given in Fig. 11.

GaAs-Oxide Interface

We have completed the study of the electrical properties of GaAs-native oxide interface. In this study we utilized the photoionization discharge of GaAs-oxide interfaces in order to identify the energy position and the dynamic parameters of interface states. We have found two discrete states with energies 0.7 and 0.85 eV below the conduction band. Furthermore, a new gigantic photionization process was discovered which leads to photodischarge of the interface surface states (at $E_c - E_t \approx 0.7$ eV) with rates up to three orders of magnitude greater than those of standard photoionization transitions to the conduction band. It exhibits a sharp peak at 45 meV below the energy gap with a shape similar to acceptor-donor transitions and is attributed to an Auger-like process. This process involves the ejection of electrons from deep surface states following an energy transfer from photo-excited donor-acceptor pairs associated with a high density of states (about $10^{14} cm^{-2}$) in the interface region. Utilizing the new process it was possible to confirm the energetics and dynamic parameters of the deep levels and also, for the first time, those of donor and acceptor interface levels, consistent with theoretical predictions.

Our interface photodischarge study of p-type GaAs MOS structures revealed the presence of deep interface states and shallow donors and acceptors which were also observed in n-type GaAs MOS through subbandgap photoionization transitions. For higher photon energies internal photoemission was observed, i.e., injection of electrons to the conduction band of the oxide from either the metal (Au) or from the GaAs valence band; the threshold energies were found to be 3.25 ± 0.1 eV and 3.7 ± 0.1 eV, respectively. The measured photoemission current exhibites a thermal activation energy of about 0.06 eV

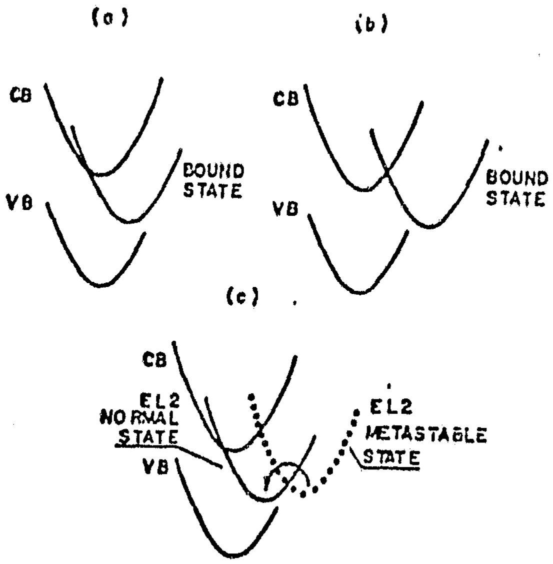

Figure 11. Configuration coordinate (cc) diagrams for: (a) low lattice relaxation energy; (b) large lattice relaxation energy; (c) EL2 center involving both cases.

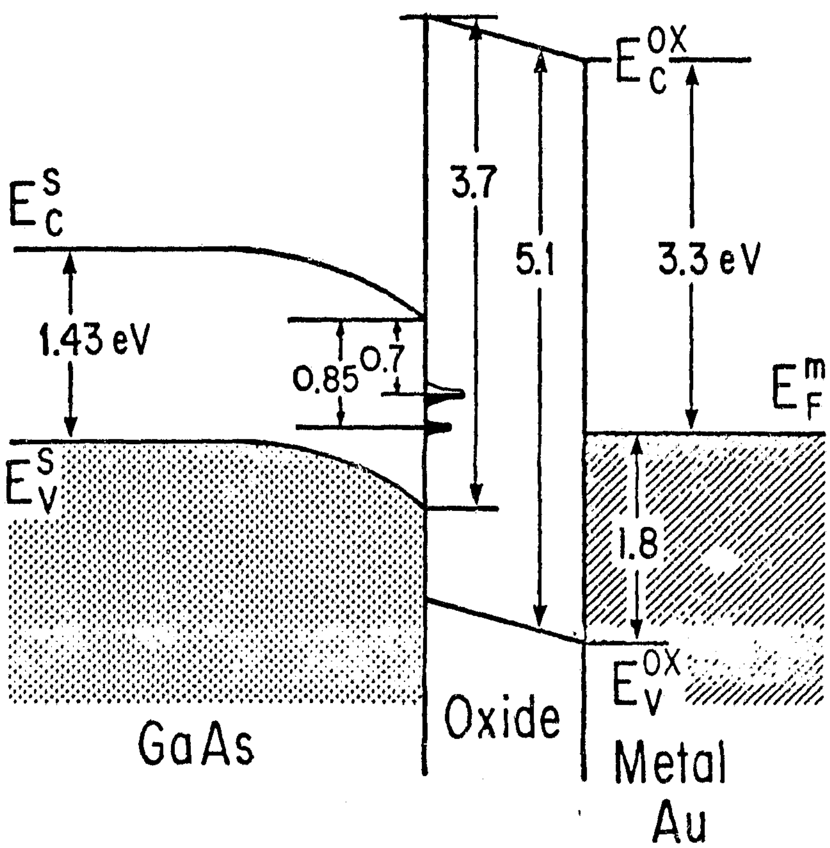

Figure 12. Energy band configuration of the GaAs-native oxide MOS structure.

which is consistent with a hopping mechanism of electron transport in the oxide.

The energy band diagram of the GaAs-native oxide MOS structure determined from our internal photoemission study is shown in Fig. 12.

We have also utilized the photoionization discharge of GaAs-oxide interface in conjunction with capacitance measurements and thermal emission to establish the origin of C-V hysteresis and anomalous frequency dispersion inherent to GaAs-MOS structures. It was shown that, for n-type GaAs, discrete states at $E_c-E_t \approx 0.7$ eV present at concentrations of the order of $10^{13}cm^{-2}$ play a major role. Due to the low rate of thermal emission the occupation of these states does not obey equilibrium characteristics (determined by Fermi level position at the surface) which leads at low temperatures to very large C-V hysteresis.

LITERATURE SURVEY

Our updated literature survey covering the period 1971-1981 shows a definite ascending trend in research and device development of GaAs. The number of sicentific publications (which can be considered as a rough measure of the over-all activities in a given area) on GaAs applications (see Fig. 13) such as lasers, high speed devices, solar cells and integrated optic devices increased roughly by an order of magnitude between 1971 and 1981, and still exhibits a definite ascending trend.

In GaAs crystal growth (Fig. 14) a drastic shift of emphasis took place from liquid phase epitaxy, dominant in the early seventies, to molcular beam epitaxy and vapor phase growth. This shift is primarily due to the development and widespread use of metalo-organic CVD techniques. Advancements in the melt growth were discernible in 1981, and we believe they mark the beginning of a new stage of extensive research and development on crystal growth in numerous industrial organizations all over the world. This rapid increase in research

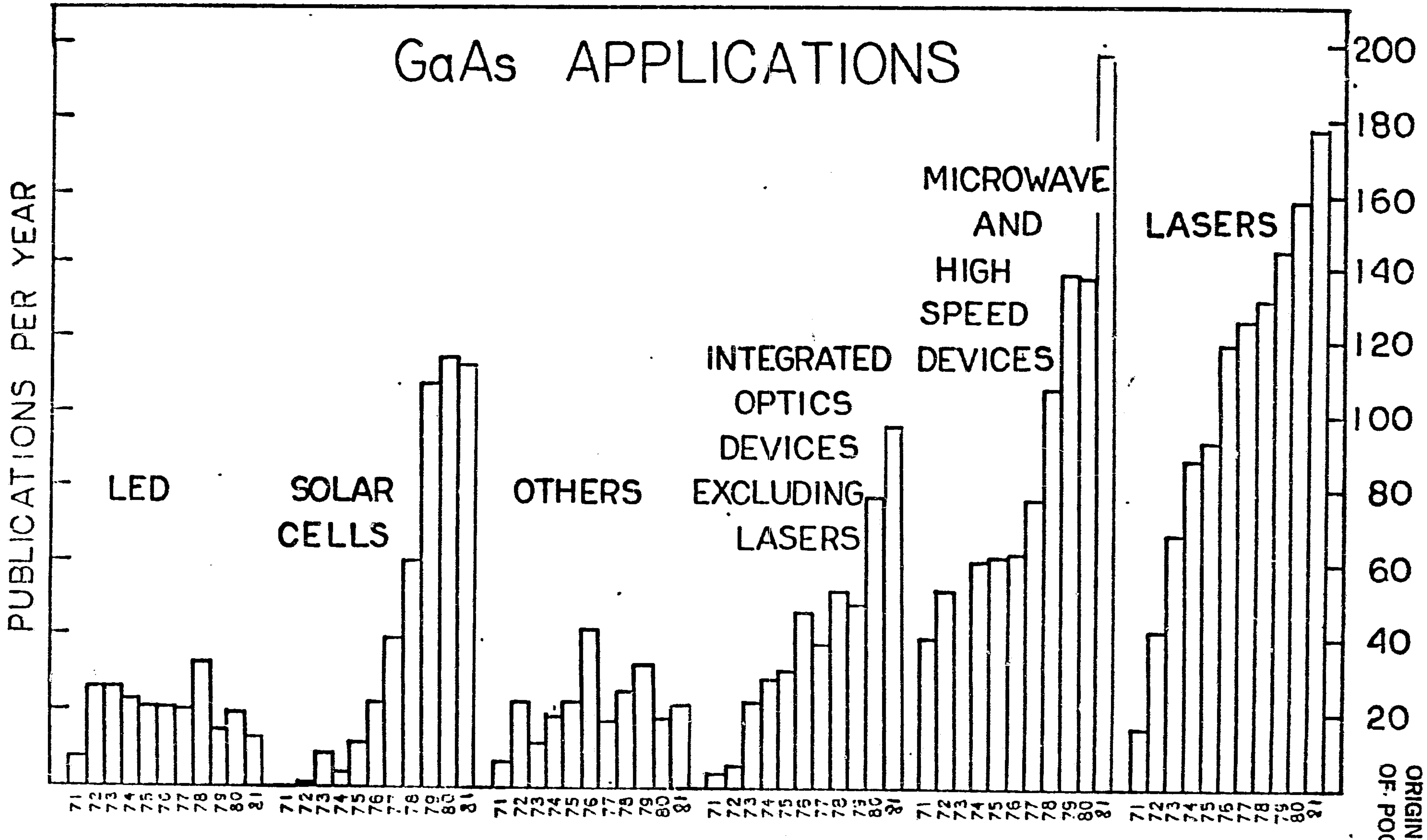

Figure 13. Trends in GaAs device applications as illustrated by the number of publications per year in open literature.

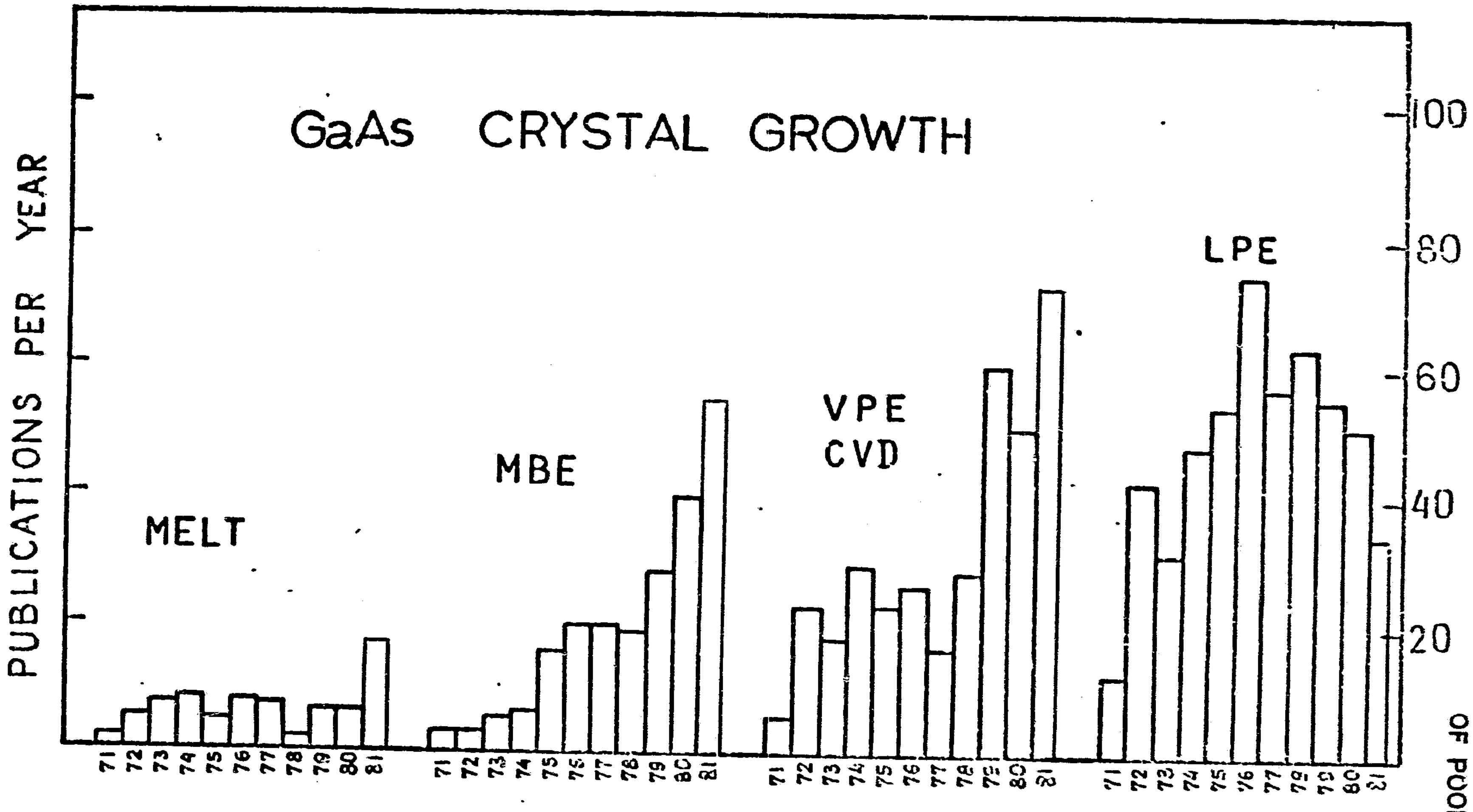

Figure 14. Trends in GaAs growth as illustrated by the number of publications per year in open literature.

and development is motivated by the growing need for bulk GaAs with improved electrical homogeneity and structural perfection.

Most recent progress in the purity of liquid encapsulated Czochralski GaAs achieved through utilization of BN crucibles and advances in Bridgman growth achieved through ultra- precise control and optimization of growth conditions have clearly demonstrated the feasibility of dramatic improvements in the quality of bulk GaAs.

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