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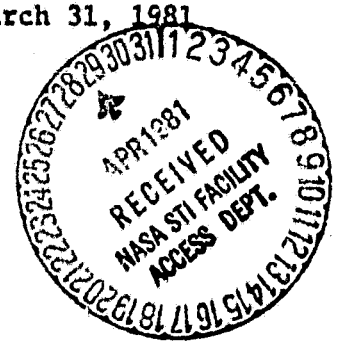
To: NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D. C. 20546

ANNUAL REPORT

Crystal Growth of Device Quality GaAs in Space

(NSG-7331)

Period April 1, 1980 to March 31, 1981



Submitted by:

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April 1981

TABLE OF CONTENTS

SUMMARY

Our research effort continues to be focused on GaAs and aimed at the establishment of quantitative relationships underlying crystal growth parameters - materials properties - electronic properties and device applications. The overall program evolves about the following thrust areas: (1) crystal growth - novel approaches to engineering of semiconductor material (i.e., GaAs and related compounds); (2) investigation 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 covers in a unique way materials engineering aspects which bear directly on exploitation of the potential of GaAs and related materials in device applications.

Our most recent literature survey covering the period 1977-1980 showed a definite ascending trend in GaAs research and device development. The position of GaAs as a material which extends semiconductor technology to areas of optoelectronic and high-speed devices has been firmly established. At the same time, most recent developments clearly identify significant problems related to the poor quality of available bulk GaAs and GaAs surfaces and interfaces. In many areas the need for better melt-grown GaAs has been recognized as critical and urgent, whereas MOS technology development hinges on suitable surface oxides or other dielectrics.

A significant aspect of our last year's program was the transition from the search for new characterization and crystal growth methods to a comprehensive utilization of our techniques toward the establishment of growth-property relationships and the enhancement of the quality of bulk and epitaxial GaAs.

As the most significant and promising result of last year's research we consider the growth of electron trap-free bulk GaAs with extremely low density of dislocations. Bulk GaAs of such high electronic and structural quality (i.e., of epitaxially grown GaAs quality) has never been achieved in the past. In conjunction with this achievement the understanding of the effects of As pressure (or vacancies) on dislocation density and deep level concentration was substantially advanced.

In electroepitaxy we succeeded in developing a new growth configuration which eliminates the substrate back-contact. This new configuration can be extended to the simultaneous growth on many substrates with a thin solution layer sandwiched between any two of them. The significant reduction of Joule heating effects in the new configuration made it possible to realize for the first time in liquid phase epitaxy the in situ measurement of the layer thickness and the growth velocity.

Utilizing the advantages of electroepitaxy in achieving abrupt acceleration (or deceleration) of the 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 previous investigations.

Our electronic characterization facility was utilized to assess the quality of presently available melt-grown GaAs obtained from commercial suppliers and also for a detailed analysis of bulk and epitaxial GaAs grown in our laboratory. Our photo-electric characterization methods were extended to the study of GaAs-oxide interfaces which constitute one of the most challenging problems in device applications. We discovered a gigantic photoionization effect in the GaAs-oxide interface. Utilizing this phenomena we showed, for the first time, that both deep and shallow interface states can be

attributed to Ga and As vacancies. Furthermore, our findings make it possible to explain anomalous hysteresis and frequency response of GaAs MOS structures as non-equilibrium effects involving deep interface states.

INTRODUCTION

Our experimental and theoretical effort led to the development of unique crystal growth approaches, new effective techniques for electronic characterization on a macro- and micro-scale, and to the discovery of new phenomena and processes relevant to GaAs device applications. Table I summarizes the major developments achieved during the last four years. The most important results obtained during the last year (i.e., since April 1, 1980) are indicated in this table by shaded areas. Detailed discussion is given in our publications and our annual reports.

CRYSTAL GROWTH

Electroepitaxy

GaAs device technology relies--by necessity rather than choice--on epitaxial growth technology. Among various epitaxial techniques such as chemical vapor deposition (CVD), molecular beam epitaxy (MBE) or liquid phase epitaxy (LPE) we have chosen liquid phase epitaxy because of unique prospects in this technique for achieving precise control of the crystal growth process by simply controlling the electric current passing through the substrate-solution interface.

Our earlier experimental and theoretical investigations have led to the development of a theoretical model of the growth kinetics, impurity segregation and composition of multicomponent systems.[1-5] We have also demonstrated the unique advantages of electroepitaxy in achieving ideal surface morphology, reducing density of defects generated during the growth and/or outdiffusing from the substrate. Furthermore, high growth velocity achievable in electroepitaxy

TABLE I

PROGRESS TO DATE - SUMMARY OF MAJOR DEVELOPMENTS

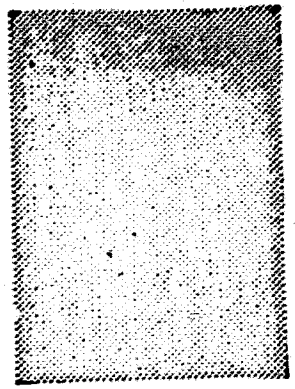
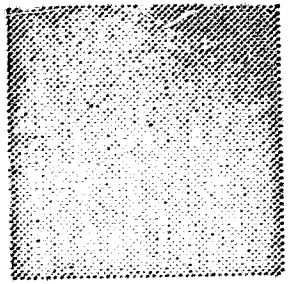
	Development	Comments	Reference
ELECTROEPITAXIAL GROWTH	1. Growth Kinetics Model 2. Dopant Segregation Model 3. Growth Model of Multicomponent Systems	Quantitative understanding of the role of electromigration and of the Peltier effect in the electroepitaxy of binary & multicomponent systems	1,2 3,4 5
	4. Improvement in Defect Structure and Electronic Characteristics	Reduction of micro-defect density has been achieved in electroepitaxial growth high growth rates	6
	5. Contactless Configuration	A new electroepitaxial configuration is introduced in which the practical problems related to the substrate back-contact are eliminated	7
	6. 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 and growth velocity	8
	7. 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.	9
	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	10
	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	11

TABLE I (continued)

	Development	Comments	Reference
CHARACTERIZATION	1. IR Scanning Absorption	Quantitative method was developed for microprofiling of carrier concentration & compensation ratio through free carrier absorption	12
	2. Derivative Surface Photovoltage Spectroscopy	A new approach was developed for the determination of deep levels, band structure & shallow impurities	13,14
	3. Derivative Photocapacitance Spectroscopy	Wavelength modulated photocapacitance spectroscopy was developed for the determination of deep levels	15
	4. Deep Level Transient Capacitance Spectroscopy	DLTS system was set up suitable for the determination of bulk levels & interface states	16
	5. Transport Techniques	New approach was developed for reliable determination of electron concentration & compensation ratio from electron mobility & free carrier absorption	17-19
	6. SEM-Cathodoluminescence	Advanced variable temperature system was set up for cathodoluminescence microprofiling of defects, impurities & carrier concentration	
	7. SEM-Electron Beam Induced Current	Variable temperature system was set up for instantaneous profiling of diffusion length	26
	8. Transient Photocapacitance	A transient photocapacitance technique was adopted for quantitative determination of dynamic parameters of deep levels (including electron and hole traps)	20
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	14,18,21,22
	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	23

TABLE I (continued)

	Development	Comments	Reference
PROPERTIES & PHENOMENA	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	24,25
	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 government by amphoteric doping & deviation from stoichiometry rather than impurity segregation	12
	5. Relationships between As Pressure & Structural Properties of Melt-Grown GaAs	A direct relationship was established between As pressure above the melt & the dislocation density as well as mobility, compensation ratio & deep level concentration in melt-grown GaAs	10-11
	6. Minority Carrier Mobility	Minority carrier mobility in p-type GaAs was computed as a function of carrier concentration and temperature	27
	7. 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	26
	8. Interface States	Surface states on GaAs-anodic oxide interface were determined with modified DLTS	16
	9. 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	27,28
	10. Optoelectronic Properties of InP	Cathodoluminescence studies of InP were completed	29

TABLE I (continued)

	Development	Comments	Reference
INTERACTION WITH INDUSTRIAL ORGANIZATIONS	1. Workshop	A workshop was held with representatives of leading industrial & educational institutions devoted to the assessment of present status, major problems & future prospects for GaAs growth & applications. A follow-up workshop is scheduled for March 11-13, 1981.	22
	2. Literature Survey	The literature survey on GaAs was updated identifying the leading organization and most important trends in GaAs research and development	
	3. Exposure of the Program to Scientific Community	The present program & 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, Kodak, etc.), presentations at scientific meetings and/or direct contacts with individual scientists	
	4. Working Contacts	Preliminary contacts were established with industrial organizations in the area of GaAs characterization, growth & device applications	

made this process comparable to melt growth and thus offers a unique possibility for obtaining sizeable "bulk" crystals of epitaxial quality.

During the last year our research on electroepitaxy was concencrated primarily on overcoming certain technical problems (e.g., electrical back-contact to the substrate) and also on the development of new advanced "state of art" systems for electroepitaxial growth of high quality heterostructures and for thick GaAs layers.

Contactless Configuration for Electroepitaxial Growth

We have introduced a new electroepitaxial configuration in which the problems related to the substrate back-contact are eliminated by positioning the substrate between two identical segments of the solution. Furthermore, with this configuration growth can take place simultaneously on many substrates positioned in the solution parallel to each other. In addition, growth as well as dissolution can be studied on the opposite sides of the same substrate.

In liquid phase electroepitaxy the growth is initiated and sustained by passing an electric current through the growth cell containing the solution and the substrate. In most instances the growth process is primarily controlled by the electromigration of a solute flux toward the substrate. Peltier cooling at the solution-substrate interface provides additional driving force for growth. The advantages of electroepitaxy in studying and controlling crystal growth are associated with the attainable very high growth rates and low supercooling localized at the interface. In practice, however, these advantages can be significantly attenuated by serious interference from the Joule heating at the substrate back-contact. Furthermore, theoretically predicted ideal surface morphology of electroepitaxial layers can also be affected by non-uniform electrical back-contacts to the substrate. A schematic illustration of the new configuration is shown in Fig. 1. A boron nitride slider divides the solution in two segments. With the aid of this slider the substrate is

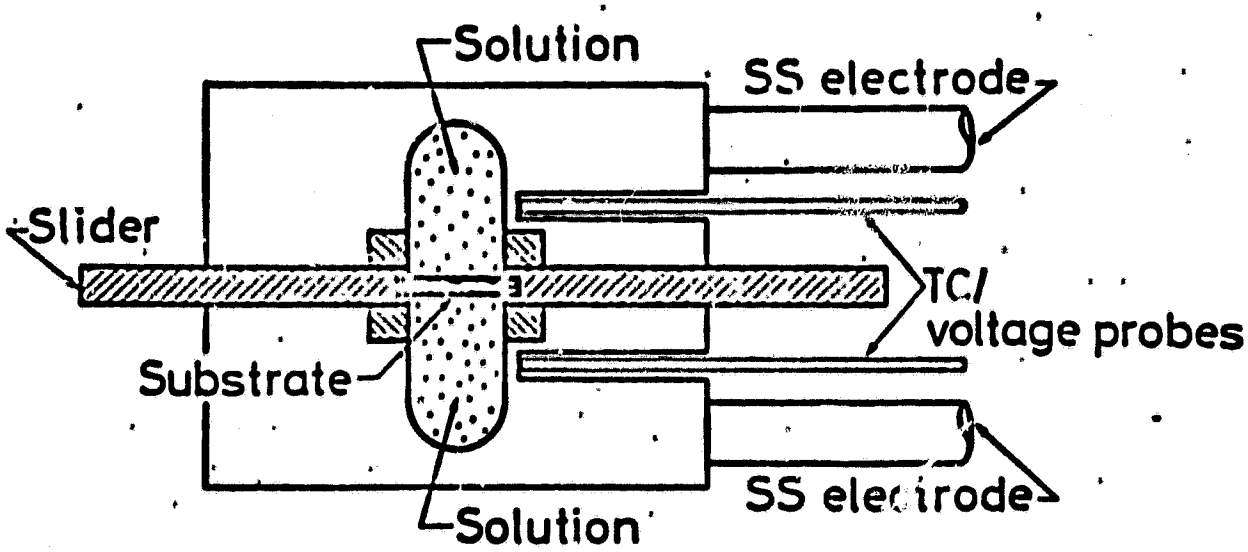


Fig. 1. Top view of apparatus for electroepitaxial growth without back-contact. Shaded parts are boron nitride. Others are graphite.

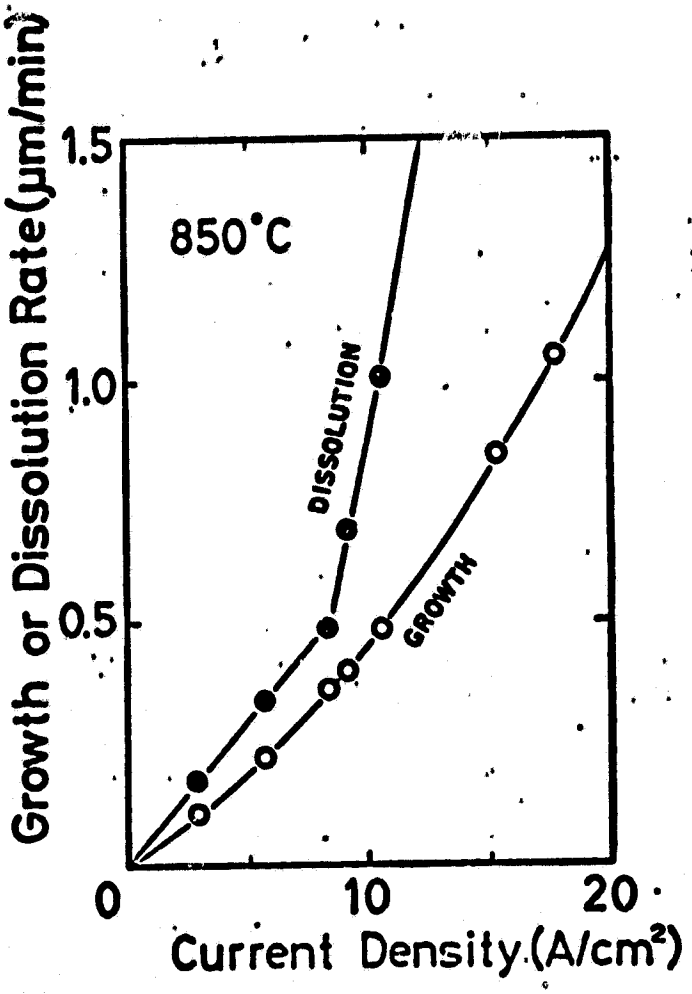


Fig. 2. Dependence of growth and dissolution rates on current density.

positioned between the two solution-segments. A stainless steel current electrode is inserted into the graphite walls of each solution segment together with thermocouples and voltage probes.

Experiments with Cr-doped and n^+ GaAs substrates were carried out at 850°C. The electric current passing through the two segments of the solutions and, thus, through the substrate resulted in growth on one side of the substrate and simultaneous dissolution on the other. For n^+ (Si-doped) substrate the growth rate was found to exceed only slightly the dissolution rate. Such behavior is consistent with a model assuming a dominant role of solute electromigration in both growth and dissolution. In contrast, higher dissolution rates than growth rates were observed in the case of Cr-doped substrate. As shown in Fig. 2, for low current densities, the difference between these two rates is relatively small; however, it becomes significant at higher current densities due to the rapid increase of the average dissolution rate. This behavior is apparently associated with pronounced convective flow caused by localized Joule heating at the substrate; the resistance of the Cr-doped substrates (active area 0.71 cm^2, thickness 500 μm) was 5.8×10^{-3} ohms, whereas that of the Si-doped substrates (active area 0.71 cm^2, thickness 340 μm was only 0.6×10^{-3} ohms. Non-uniform dissolution was further evidence of convective flow near the substrate-solution interface.

As pointed out in our previous studies, convective flow can be reduced by decreasing the solution thickness. Accordingly, in the present configuration, a multi-wafers arrangement, with a thin solution layer sandwiched between substrates, is a promising means to prevent convective flow at high current densities. It should be noted that the dissolution rate in the low current density region (Fig. 2) depends linearly on applied current and strongly suggests electromigration limited behavior. Thus, with a sandwich-type arrangement,

electromigration limited growth on Cr-doped substrate should be possible even at high current density.

In Situ Measurement of Growth Kinetics

The significant reduction of contact resistance and, thus, of Joule heating effects brought about by the new growth configuration, made it possible to achieve, for the first time, the "In Situ" monitoring of the LPE growth rate and the layer thickness. These measurements are based on monitoring the total resistance of the substrate and the growing layer. Typical results of thickness vs. time as measured for an undoped GaAs layer grown at 650°C on N^+ substrate are shown in Fig. 3. Fig. 4 illustrates a typical electroepitaxial transient induced by pulsing of an electric current. It should be emphasized that in addition to the evident practical importance, these in situ measurements of growth kinetics constitute an extremely valuable tool in studying growth-property relationships.

Advanced Apparatus for Electroepitaxy

During the last year we essentially completed construction of a highly advanced system for electroepitaxial growth of improved quality heterostructure layers. This system combines our own experience in current-controlled LPE with the advanced know-how of industrial organizations (RCA, Nippon T & T, Fujitsu Lab s) leading in the field of thermal LPE. Three subsystems of the new apparatus, ie., electronics system, the ambient gas system, and the electroepitaxial boat, were already tested. The first series of growth experiments will be completed before March 31, and the results will be discussed in our annual report.

Our second electroepitaxial system for the growth of thick GaAs layers in a Czochralski-type arrangement has been utilized in a series of exploratory experiments. The possibility for growing layers of a thickness of 1 mm or

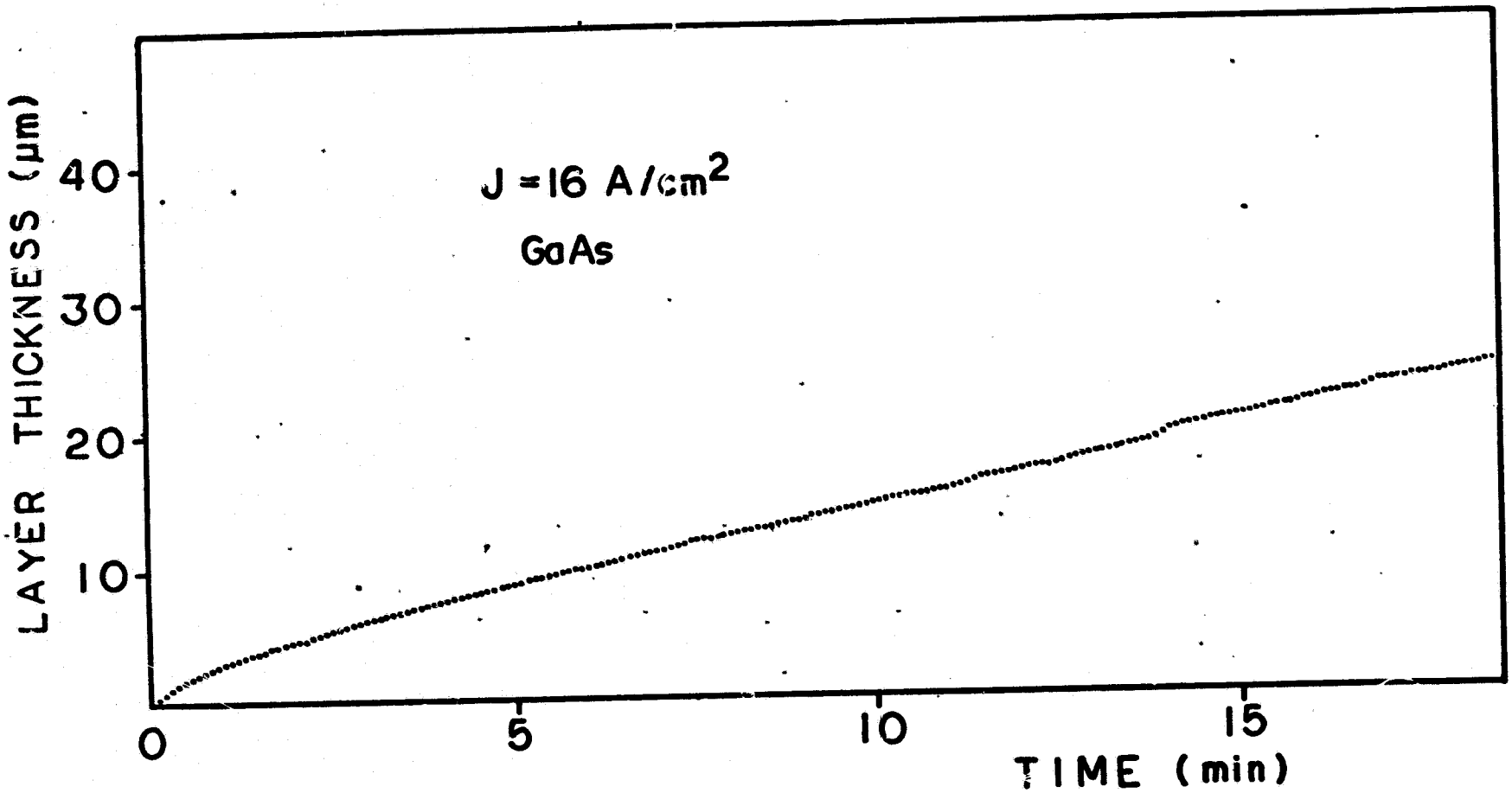


Fig. 3. In situ-monitored growth kinetics for electroepitaxial growth of GaAs with a current density J = 16 A/cm^2.

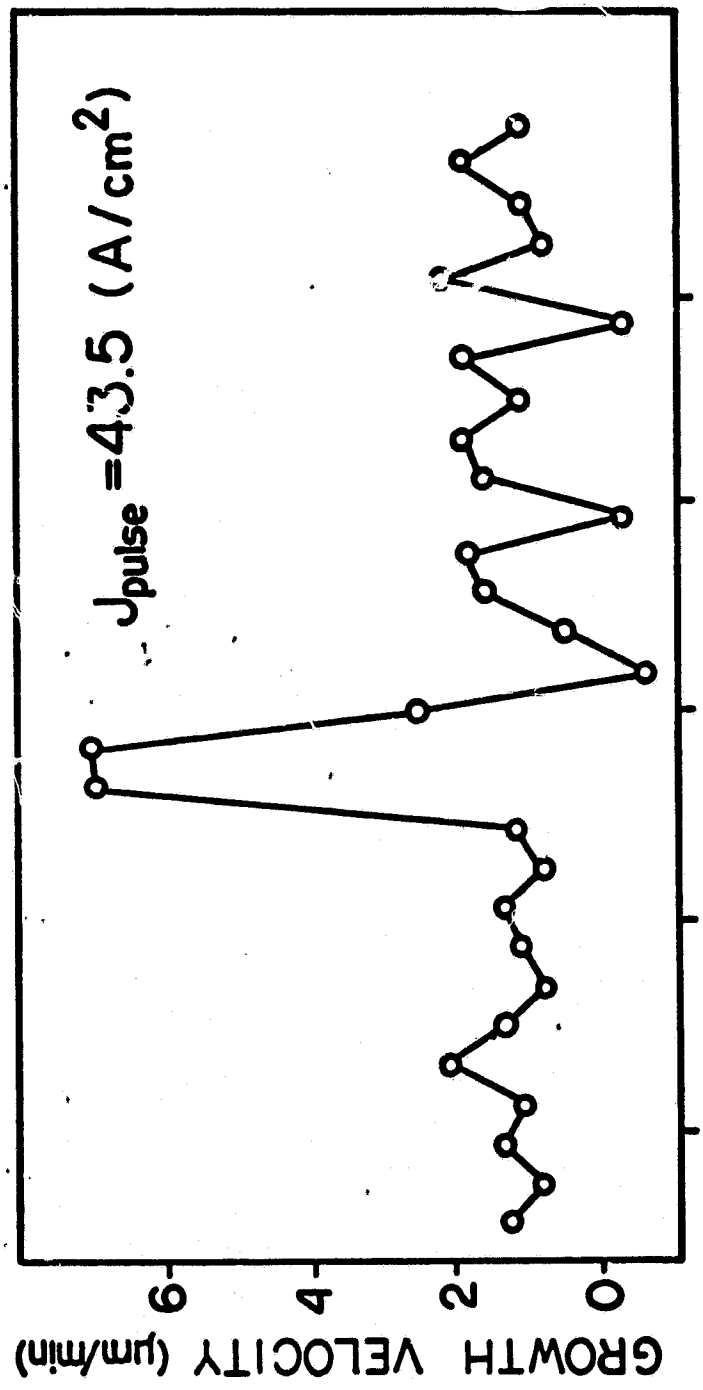


Fig. 4. In situ-monitored growth velocity change induced by a pulse of an electric current, 43.5 A/cm^2.

greater was demonstrated. However, we have also identified practical problems related to Joule heating and inadequate thermal characteristics of the furnace utilized in a prototype apparatus. Extensive work on improvement of the apparatus to overcome Joule heating effects is currently in progress.

Melt Growth

Our unique Bridgman-type apparatus for the study of growth-property relationships[9] has been utilized to establish the effect of As pressure on structural and electronic properties of GaAs. The results of these studies surpassed our expectations, as they led to the establishment of growth conditions yielding undoped dislocation-free GaAs and also, for the first time, electron trap-free GaAs.

Growth of "Dislocation-Free" Undoped GaAs

The dependence of structural properties of GaAs on the arsenic pressure, P_{As}, above the melt was studied employing a horizontal Bridgman furnace with precision-controlled thermal characteristics. Changes in P_{As} were introduced during crystal growth by varying the "cold" zone temperature (controlled by a sodium heat pipe) over the range 612°C to 620°C. This temperature range corresponds to approximately 0.17 atm changes about the 1 atm P_{As}. A series of <111>oriented cross-sections 1 mm thick were cut from the crystal grown under controlled changes of P_{As}; they were etched in molten KOH for etch-pit density (EPD) evaluation.

In the seeding region of the crystal, a relatively high dislocation density of about $10^4 cm^{-2}$ was typically observed. Owing to the design of the quartz boat in the seeding region, these dislocations are confined preferentially in the upper half of the growing crystal. Thus, as shown in Fig. 5, the density of dislocations drastically reduces as growth proceeds. The dislocation density in the further portion of the crystal is influenced by

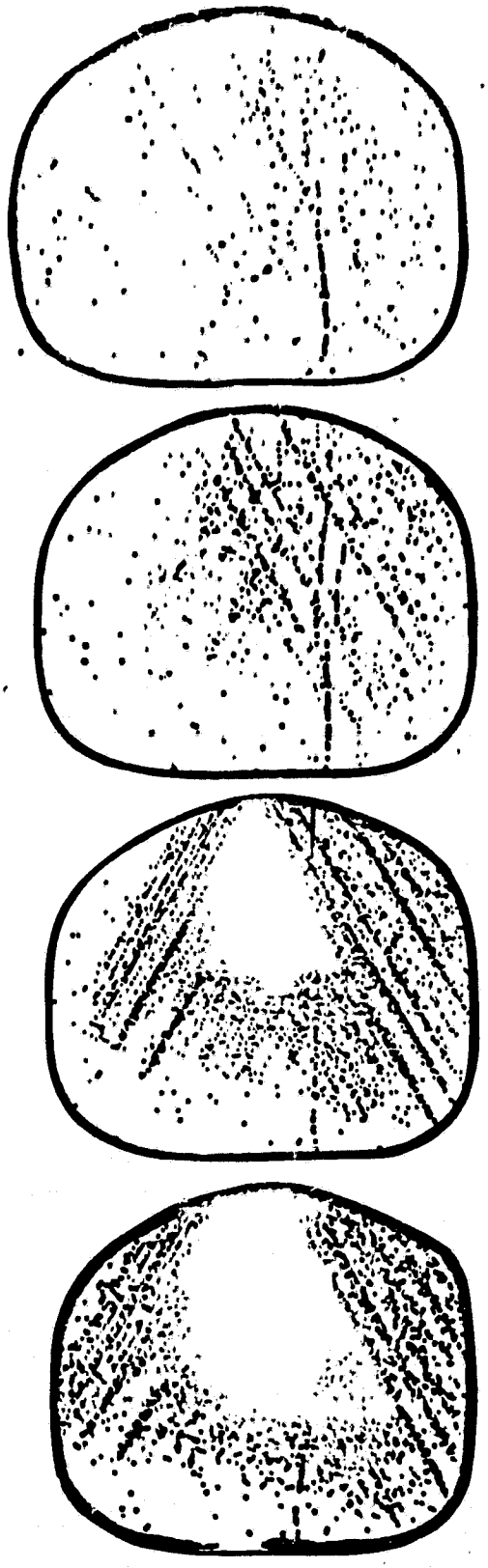


Fig. 5. Series of <111> oriented cross-sections of melt-grown GaAs crystal etched in molten KOH. Note diminishing of dislocation densities as growth proceeds (from bottom to top).

arsenic pressure. As shown in Fig. 6, it reaches a minimum value (EPD below 100 cm^{-2}) for an optimum P_{As} corresponding to a temperature at the cold zone of approximately 617°C.

For the above temperature of 617°C we achieved reproducible growth of undoped GaAs with dislocation density below 100 cm^{-2}, i.e., essentially "dislocation-free material".

Reports on low density dislocation GaAs crystals grown by Czochralski-type methods indicated the importance of necking techniques, low temperature gradient at the solid-liquid interface, and the dislocation density of the seed material. Sumitomo Electric Industries recently reported the effect of "impurity hardening" whereby a sharp decrease of dislocation densities was observed as the GaAs was doped with Si at concentrations greater than $2x10^{18} cm^{-3}$.

The present results indicate the importance of arsenic partial pressure control for reproducible growth of dislocation-free GaAs. This implies that generation of growth of dislocations are directly related to the presence of point defects. Elimination of "wetting" of the quartz boat by the melt was found to be another important factor in horizontal Bridgman growth. Elimination of wetting was achieved by certain design features of the boat and by careful preparation of the quartz boat surface. Control of dislocation generation in the seeding region during seeding process appears to be more important than dislocation density of the seed.

Dependence of Electronic Properties on As Pressure

We have found that the "optimum As pressure" condition which leads to dislocation-free material also yields GaAs with optimum electronic properties; i.e., highest mobility, smallest compensation ratio, and lowest concentration of electron traps. Typical variations of the electron trap concentrations induced by a slight change of P_{As} (1°C change of a temperature of the cold

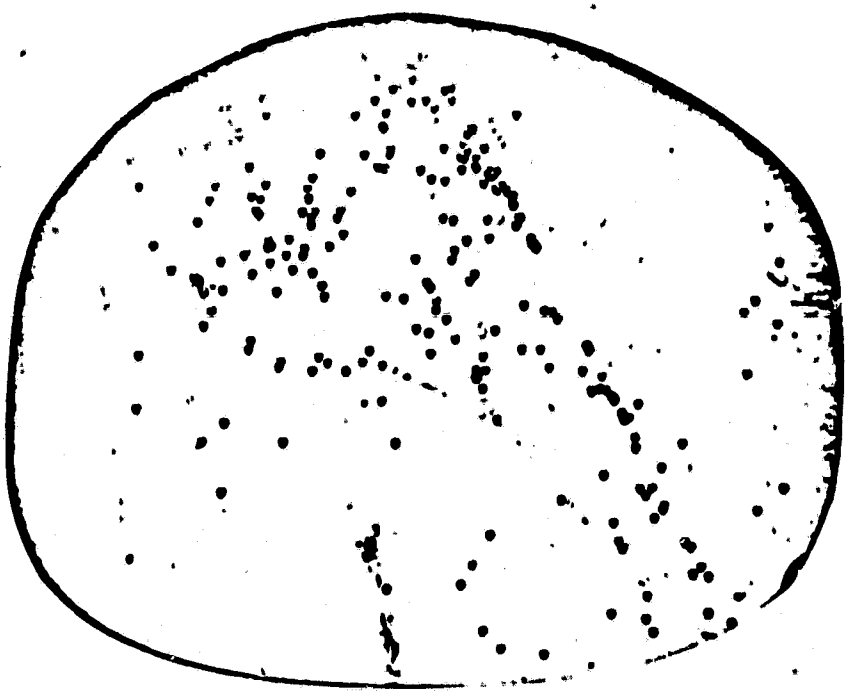


Fig. 6. Dislocation etch-pits in a crystal grown under optimum As pressure.

zone) is shown in Fig. 7.

Growth of Electron Trap-Free GaAs

The availability of high quality bulk crystals is paramount to realizing the full potential of GaAs in electronic applications. Thus far, high quality material has been produced only in thin layers by epitaxial techniques. Commercially grown bulk GaAs exhibits significant concentrations of structural defects and deep states which act as trapping or recombination centers precluding most of its direct applications on an active device material.

We showed recently, for the first time, that melt growth of electron trap-free GaAs can be reproducibly achieved through high precision control of the As vapor pressure over the melt and by doping the melt with minute amounts of Ga_2O_3.

As is seen from typical DLTS spectra in Fig. 8, crystals doped with Ga_2O_3 and grown under optimum As pressure exhibit two deep levels near the seed; as growth proceeds the concentration of these levels decreases to values below the detectability limits (approximately 10^{-4} of free carrier concentration, i.e., $10^{13} cm^{-3}$ in the present case). It should be noted that only two electron traps are initially present in this material (0.7 eV and 0.40 eV below the conduction band edge) in contrast to three to five deep states typically found in bulk GaAs, and also in GaAs grown under optimum P_{As} but without Ga_2O_3 doping.

Photocapacitance measurements also confirmed the absence of electron traps and revealed a single hole trap at about 0.4 eV above the valence band with a concentration of about $3 \times 10^{15} cm^{-3}$ (i.e., less than 1% of carrier concentration). In contrast, the high quality of LPE GaAs often contains two hole traps of comparable relative concentrations.

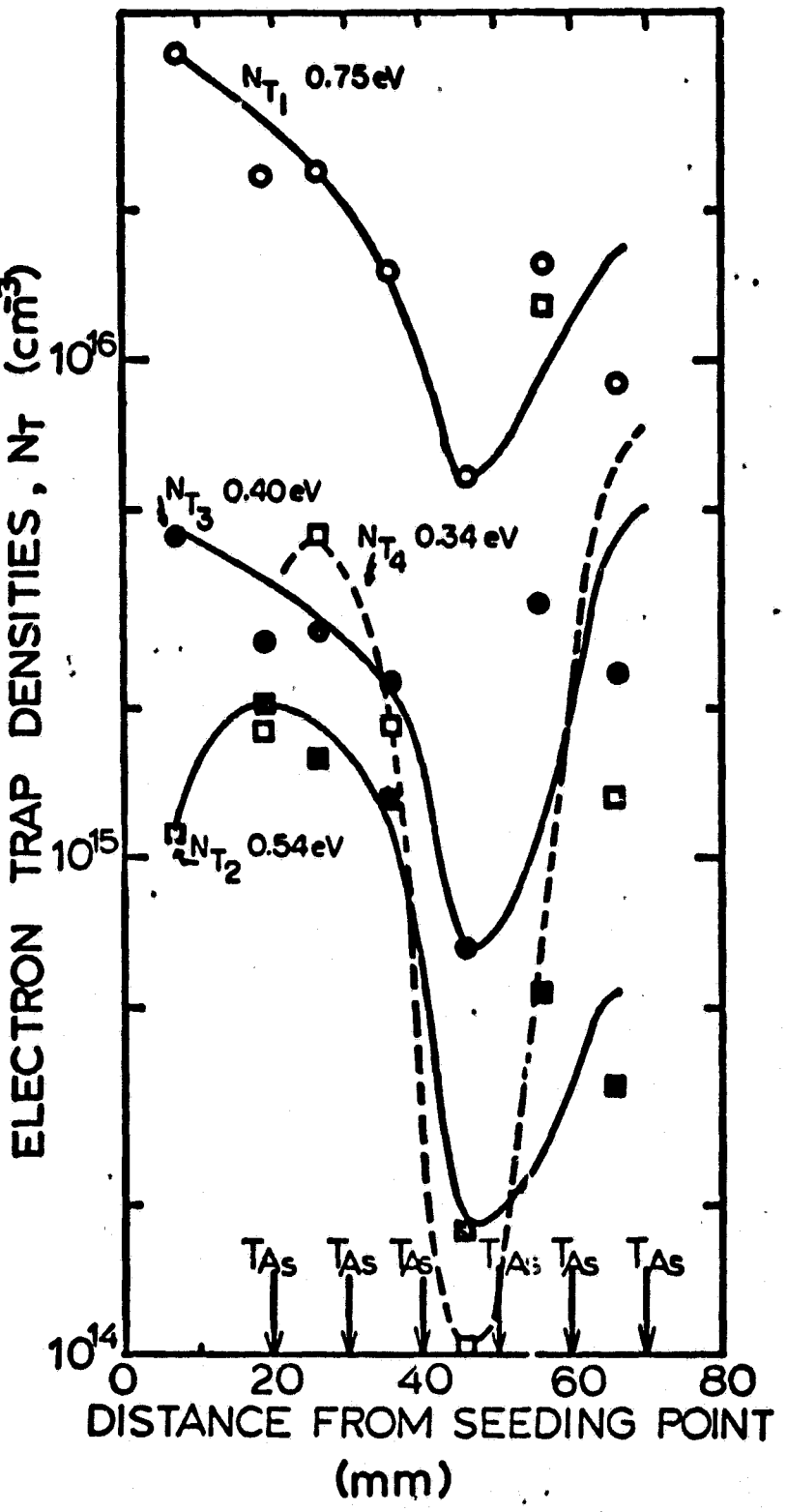


Fig. 7. Variation in electron trap concentrations along the growth direction; the positions of arsenic pressure change are indicated by arrows.

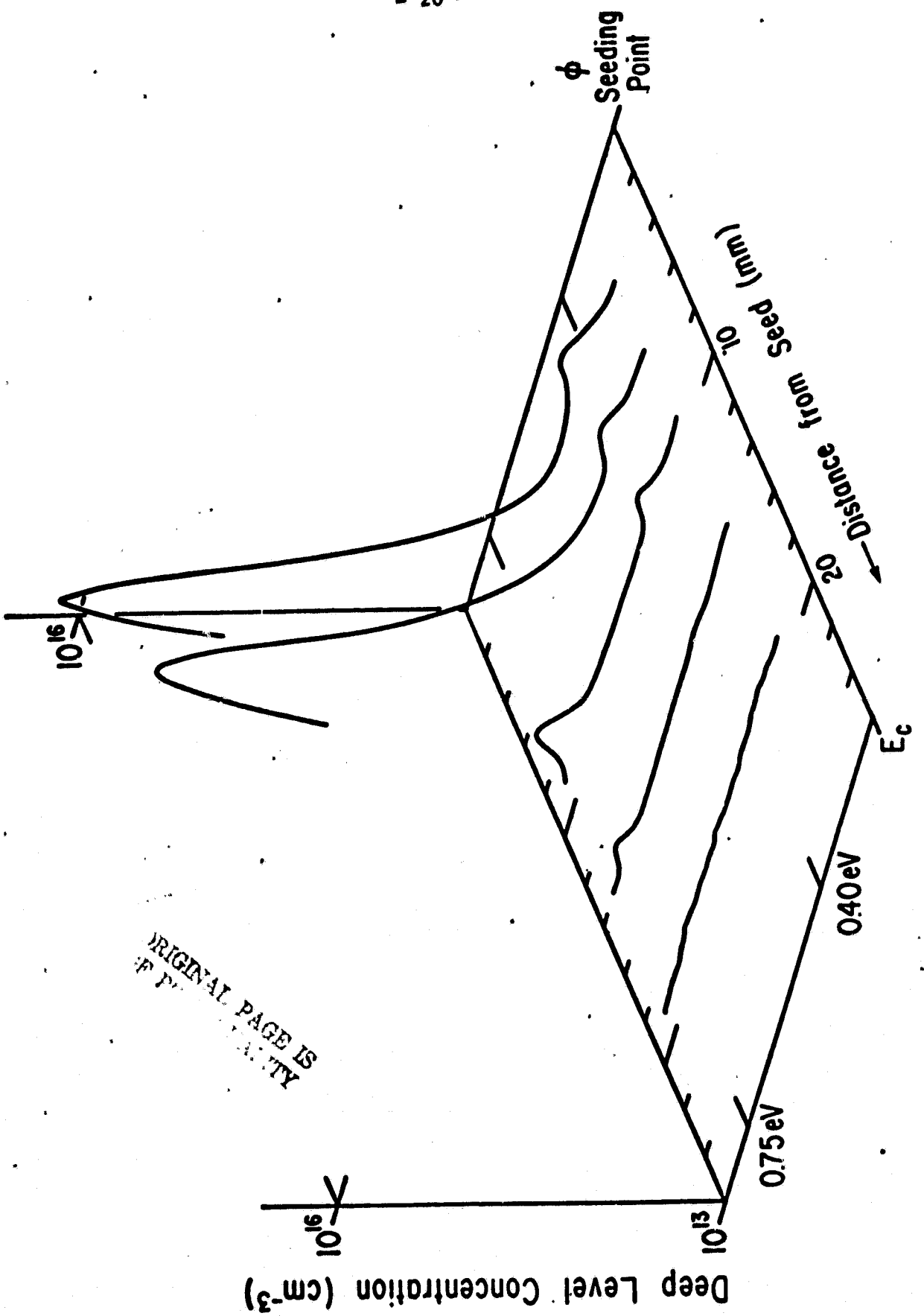


Fig. 8. DLTS spectra as a function of distance from the seed. Note total elimination of deep traps at a distance of about 2 cm.

The highly beneficial effect of Ga_2O_3 doping is further evidenced in Table II where typical properties of GaAs crystals grown under optimum As pressure with and without Ga_2O_3 doping are presented. Remarkably, the crystal grown with Ga_2O_3 exhibits a much larger value of the minority carrier diffusion length (as determined from photovoltage and SEM-EBIC measurements) and has a minority carrier lifetime which is close to the radiative recombination limit. The crystals grown in the absence of Ga_2O_3 reveal significant concentration of deep states and the minority carrier lifetime is nearly 25 times smaller than in electron trap-free GaAs.

It is thus evident that the outstanding quality of GaAs achieved results from the combined effects of minute additions of Ga_2O_3 in the melt and of the precisely controlled "optimum" arsenic vapor pressure.

At present, we do not fully understand the mechanisms by which oxygen in conjunction with precise arsenic vapor pressure control leads to the elimination of dislocations and deep levels in GaAs. However, this process is reproducible under stringently controlled growth conditions. Further studies on low carrier concentration electron trap-free bulk GaAs should enhance the understanding of the role of oxygen and other growth parameters on the materials properties of melt-grown GaAs.

PROPERTIES AND PHENOMENA

Electronic Properties of Commercially Available Bulk GaAs

During the last year we performed detailed macro- and micro-scale analysis of the electronic properties of the "state of art" melt-grown GaAs produced by one of the major commercial suppliers of GaAs. Some representative results of our studies are given in Figures 9-11. Thus, a typical electron concentration microprofile obtained with our IR laser scanning technique (Fig. 9) clearly shows the presence of inhomogeneities which appear to be related to turbulent convection in the melt caused by thermal asymmetry enhanced by the viewing window of the growth apparatus. As shown in Fig. 10, high resolution SEM

TABLE II

PROPERTIES OF GaAs GROWN UNDER OPTIMUM As PRESSURE WITH AND WITHOUT Ga_2O_3 DOPING

MATERIAL	DISLOCATION DENSITY (cm^{-2})	CARRIER CONCENTRATION (cm^{-3})	COMPENSATION RATIO (N_A/N_D)	MOBILITY ($cm^2/V\text{-}s$)	MINORITY CARRIER DIFFUSION LENGTH (μm)	MINORITY CARRIER LIFETIME (sec)
Ga_2O_3 added	<500	1.8×10^{17}	0.58	2400	5	3.2×10^{-8}
Ga_2O_3 free	<500	6.2×10^{16}	0.68	3300	1	1.3×10^{-9}

	ELECTRON TRAP CONCENTRATION (cm^{-3})				
	0.75	0.54	0.40	0.34	0.25 (eV)
Ga_2O_3 added	N/D	N/D	N/D	N/D	N/D
Ga_2O_3 free	2.3×10^{16}	6.8×10^{14}	3.1×10^{15}	6.6×10^{15}	N/D

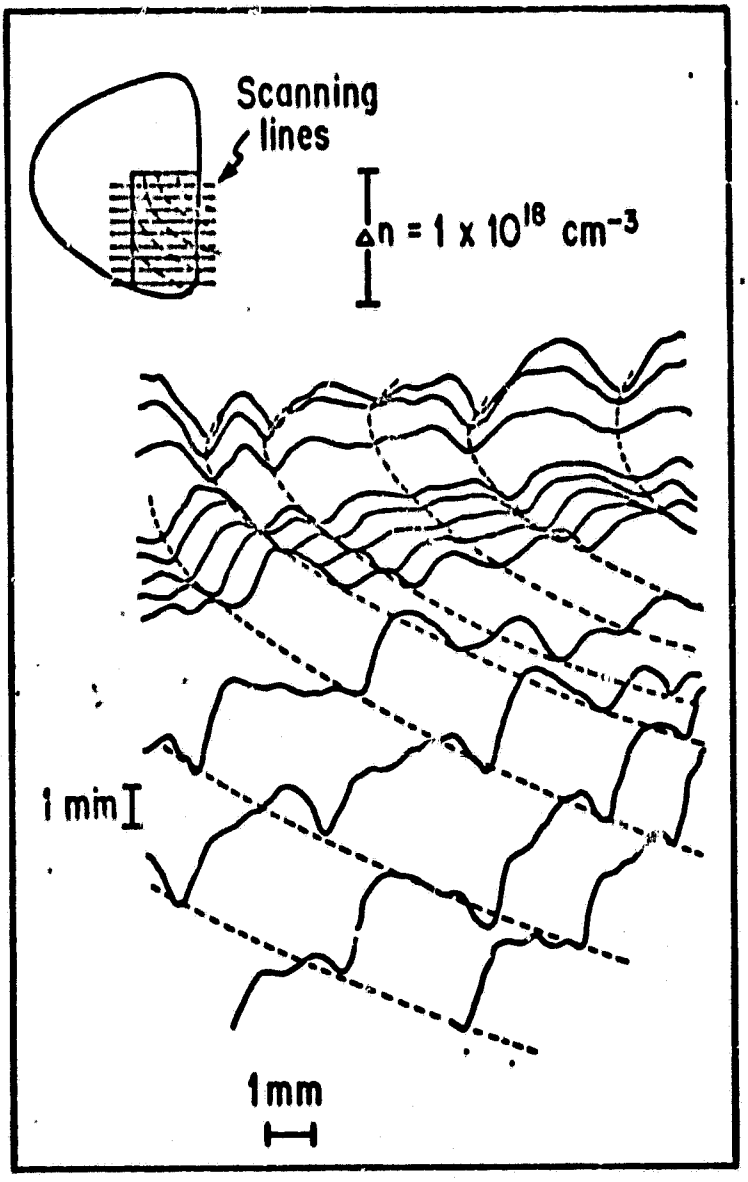


Fig. 9. Electron concentration microprofile of melt-grown commercial GaAs obtained with IR absorption scanning.

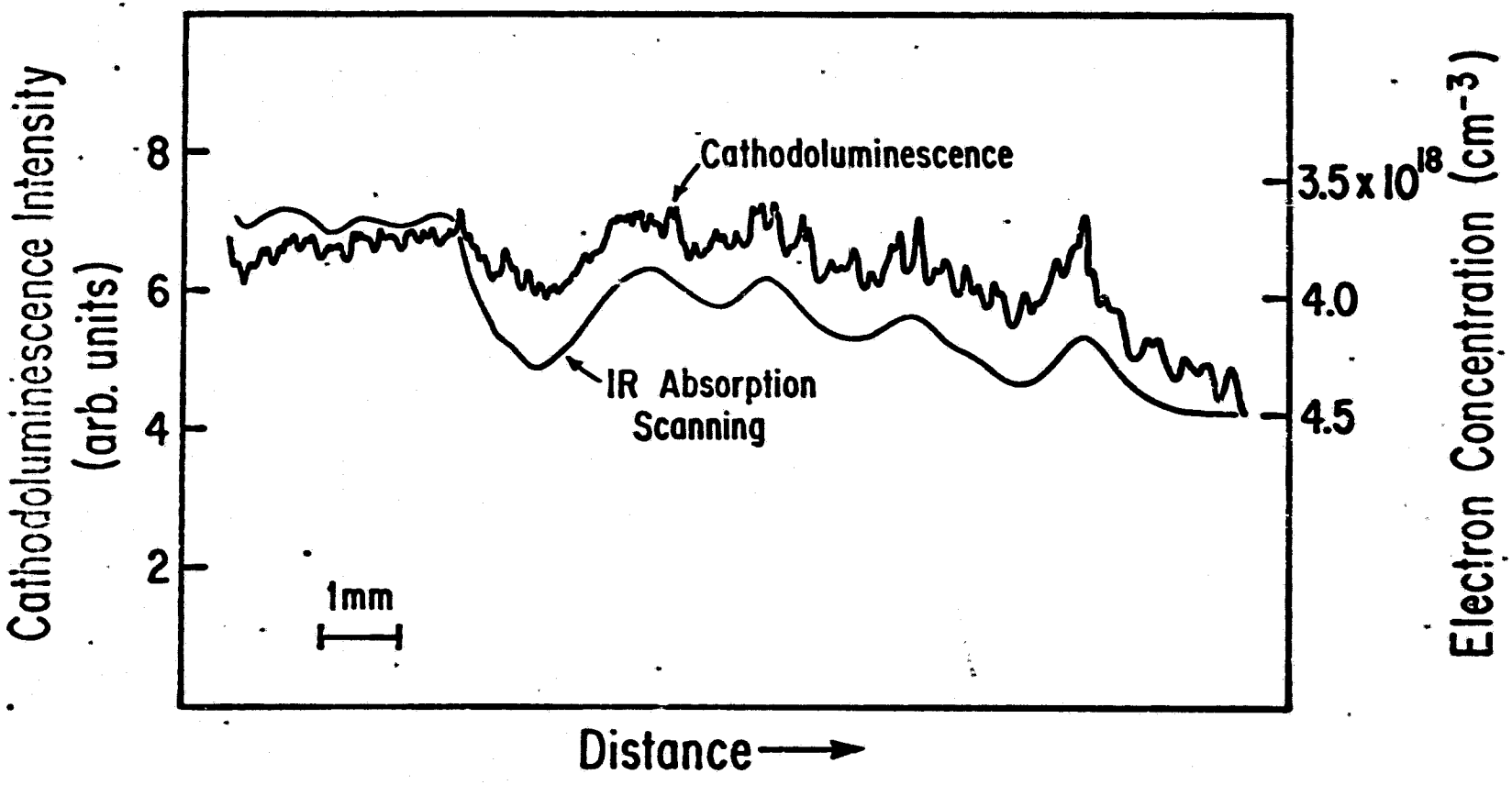


Fig. 10. IR absorption microprofile and corresponding SEM-cathodoluminescence microprofile of Si-doped commercial GaAs.

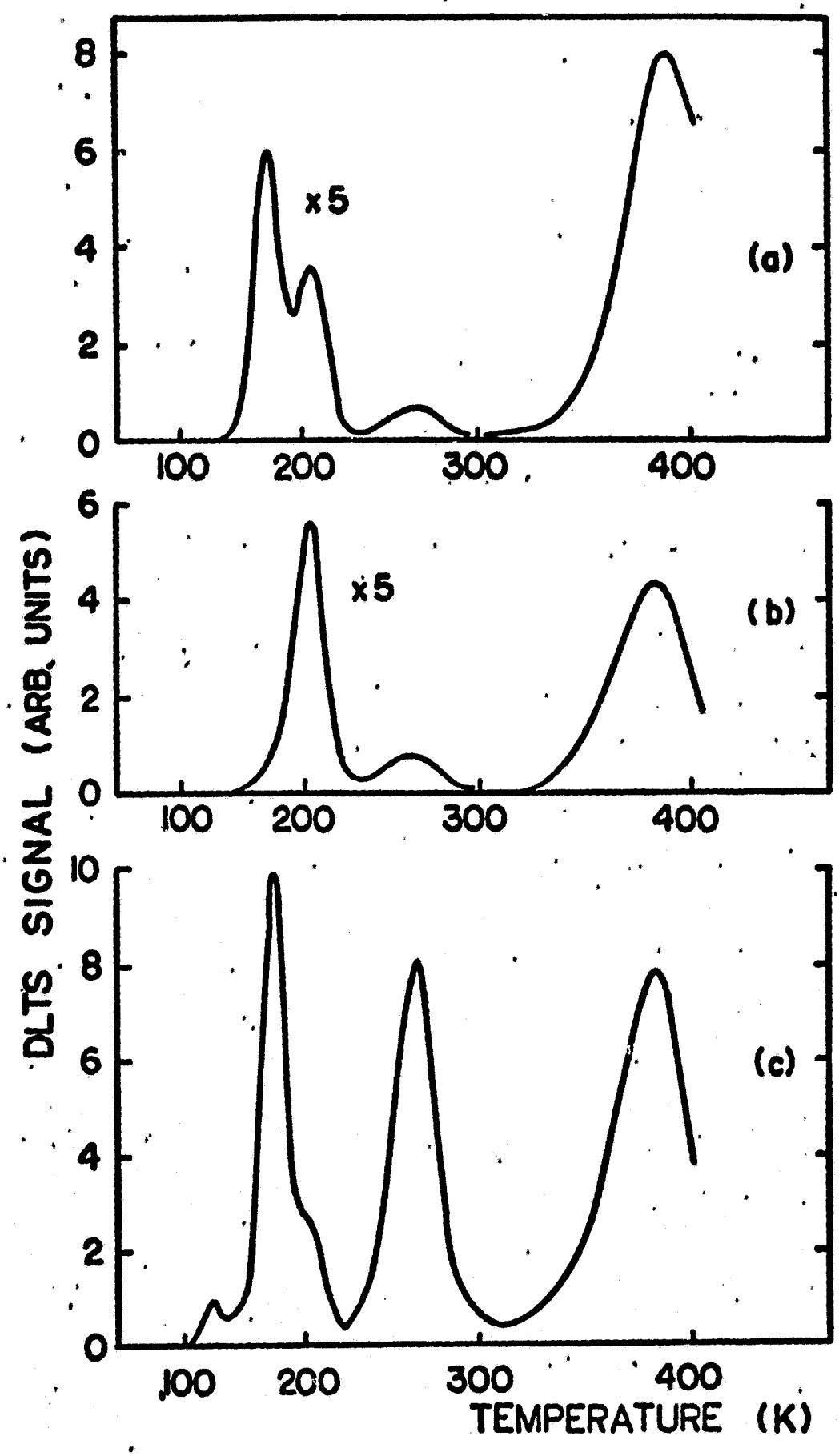


Fig. 11. Electron trap DLTS spectra of melt-grown GaAs; (a) presently grown undoped GaAs ; (b) presently grown GaAs heavily doped with Ga_2O_3; (c) commercial undoped GaAs.

cathodoluminescence scanning measurements have revealed the presence of low magnitude closely spaced fluctuations of electron concentration which are superimposed to a large magnitude, lower frequency fluctuations observed also in IR scanning measurements. It is important to note that none of these inhomogeneities were present in GaAs grown with our horizontal Bridgman apparatus in which thermal symmetry was minimized.

The commercial n-type GaAs exhibited typically 4 to 5 electron traps as determined by DLTS measurements (Fig. 11). Within a given wafer the concentration of deep levels exhibited remarkable variations, from point to point (see Table III) of a relative amplitude clearly exceeding the respective changes in electron concentrati These results do not show any correlation between dislocation density and the density of deep traps. It is also evident that variations of the concentrations of deep levels do not show any systematic trends. These results are markedly different than the results obtained with our crystals grown under precisely controlled growth conditions (see below), whereby all deep level concentrations varied with changes of As pressure in a similar manner. It is thus apparent that thermal fluctuations at the growth interface present in a commercial growth system have particularly adverse effects on deep levels and carrier concentration inhomogeneities.

Recombination Centers in LPE GaAs

We have utilized electroepitaxy in introducing controlled growth velocity changes during LPE growth of GaAs from Ga-rich solutions and to assess their role in the formation of recombination centers. The changes in concentration of recombination centers were measured by the minority carrier lifetime micro-profiling of the grown layers, utilizing SEM-electron beam-induced current (EBIC) techniques. Representative experimental results showing the effect of growth velocity changes on EBIC collection efficiency are given in Figures 12 and 13.

TABLE III

ELECTRON TRAPS IN COMMERCIAL GaAs
(Undoped)

Sample	N_A-N_A (cm^{-3})	Dislocation Density (cm^{-2})	Electron Trap Concentration (cm^{-3}) E1=0.75 eV	E2=0.54 eV	E3=0.40 eV	E4=0.34 eV	E4=0.25 eV
A.1	3.2×10^{16}	--	3×10^{15}	1.4×10^{15}	--	1.4×10^{16}	4.5×10^{14}
A.2	2.6×10^{16}	--	3.6×10^{15}	2.9×10^{14}	--	1.2×10^{16}	--
A.3	2.5×10^{16}	2100	8.8×10^{16}	1.6×10^{15}	--	1.8×10^{16}	--
A.4	1.7×10^{16}	1500	5.4×10^{16}	1.3×10^{15}	--	1.2×10^{16}	--
C.1	2.8×10^{16}	7200	3.3×10^{15}	3.6×10^{15}	7×10^{14}	4.3×10^{15}	4.8×10^{14}
C.2	2.8×10^{16}	2200	2.6×10^{15}	3.7×10^{15}	9×10^{15}	1.4×10^{16}	7×10^{14}
C.3	1.8×10^{16}	200	4.7×10^{15}	1.3×10^{15}	--	1.5×10^{16}	--

(It should be noted that the collection efficiency decreases when the concentration of recombination centers increases.)

It is evident from Fig. 12a that an abrupt increase of growth velocity from 2 to 4 μm/min produces a pronounced minimum in collection efficiency in the corresponding transition region. Higher growth velocity changes (from 2 to 14 μm/min; or from 8 to 20 μm/min) reduce the collection efficiency by as much as 30%. It should be pointed out that the recovery of the collection efficiency (concentration of recombination centers) following the step-like change in growth velocity indicates that the acceleration of the growth (dV/dt) rather than the absolute value of growth velocity (V) is responsible for the formation of recombination centers. This conclusion is confirmed by the results of Fig. 12b, whereby the growth velocity was changed from 8 to 20 μm/min, however, not instantaneously but during a period of 10 seconds. In this case no noticeable amount of recombination centers was introduced.

The results shown on the right-hand side of Fig. 12 (a,b) indicate that the effect of deceleration of the growth on recombination centers is about one order of magnitude smaller than that of acceleration of the growth.

Experiments, as discussed above, were also carried out with substrates of different thickness, and thus under different current-induced changes of the interface temperature. No significant differences were observed from the results of Fig.12 obtained with thin substrates. Apparently, changes in interface temperature are of secondary importance compared to changes in growth velocity.

Typical results regarding the effect of backmelting on the formation of recombination centers are shown in Fig. 13. In the upper portion of Fig. 13 backmelting is introduced with 1 sec electric current pulse of polarity opposite than required for growth. It is seen that a minimum in collection efficiency is introduced by this pulse.

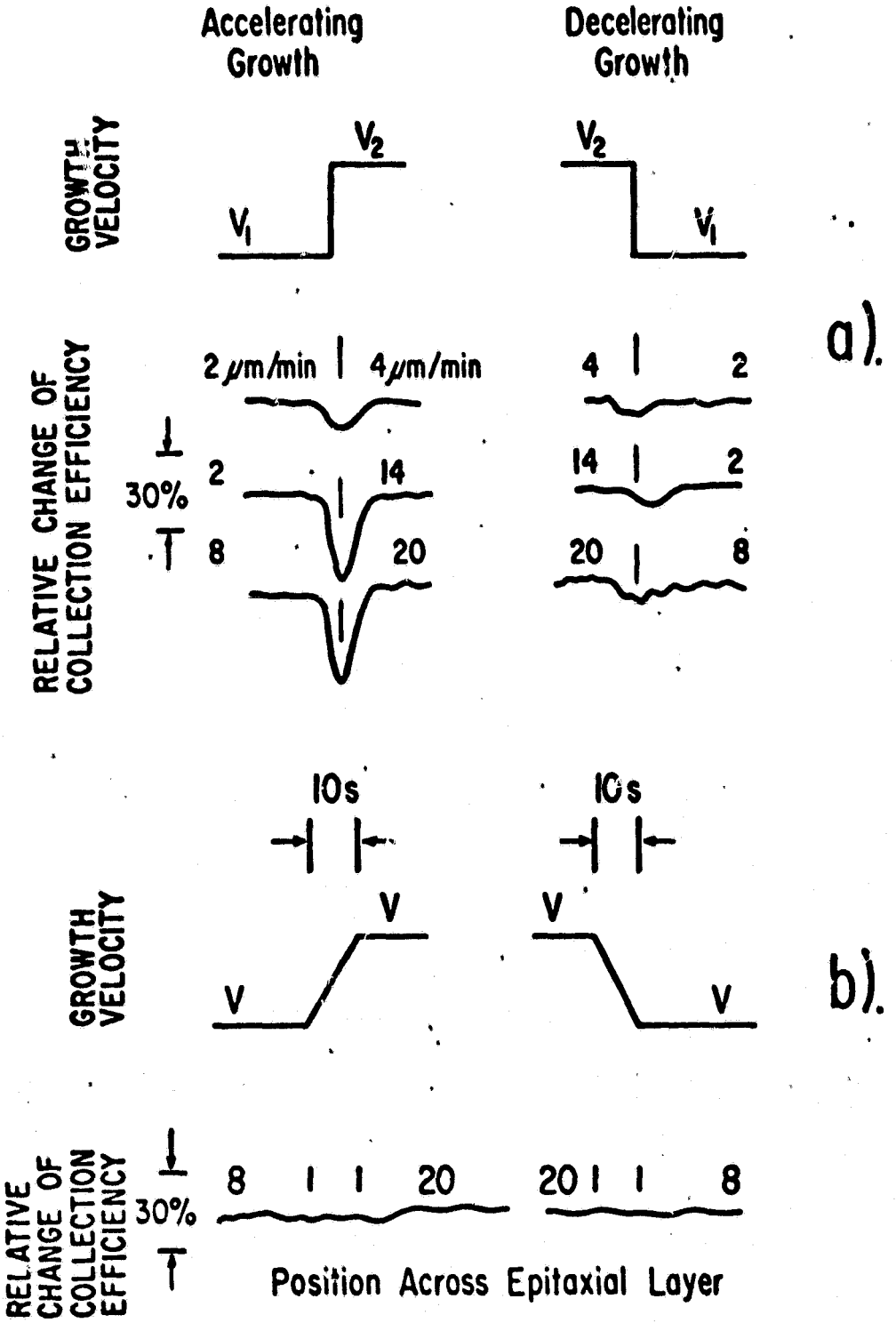


Fig. 12. EBIC microprofiles reflecting formation of recombination centers upon abrupt changes of growth velocity (a) and upon similar changes spread over a period of 10 seconds (b).

In order to verify whether the observed increase in concentration of recombination centers is caused by phenomena taking place during backmelting of the grown crystal or by the subsequent increase of the growth velocity to the original value of 8 μm/min, the following experiments were carried out: Growth was arrested for an extended period and then it was abruptly increased to 8 μm/min. In addition, the growth was interrupted for 1 sec and then restored abruptly to its original value of 8 μm/min. As seen in the lower part of Fig. B, the results are the same as those obtained for backmelting (upper part of Fig. B). Thus, it is concluded that the recombination centers introduced into the epitaxial layer during backmelting are formed primarily by the acceleration of the growth following backmelting.

In summary, we have demonstrated the importance of growth dynamics, and in particular, the importance of the acceleration of growth in the formation of recombination centers during liquid phase epitaxy. It is likely that these recombination centers originate from point defects generated at the growth interface in response to abrupt increases in growth velocity (abrupt deviations from steady state growth conditions). It is apparent that surface nucleation effects commonly considered of no significance in the LPE process with slowly varying growth velocity can in fact be of primary importance in the case of abrupt increases in growth velocity.

Cathodoluminescence of InP

Cathodoluminescence studies were carried out on p-type InP with carrier concentrations ranging from 7.2×10^{16} to $7.4 \times 10^{18} cm^3$ in the temperature range of 80 to 580 K. It was found that low temperature spectra exhibited peaks at 1.41 and 1.38 eV. These peaks were attributed to band-to-band transitions, respectively. The dependence of the band-to-band peak on temperature was used to extend the temperature dependence of the energy gap

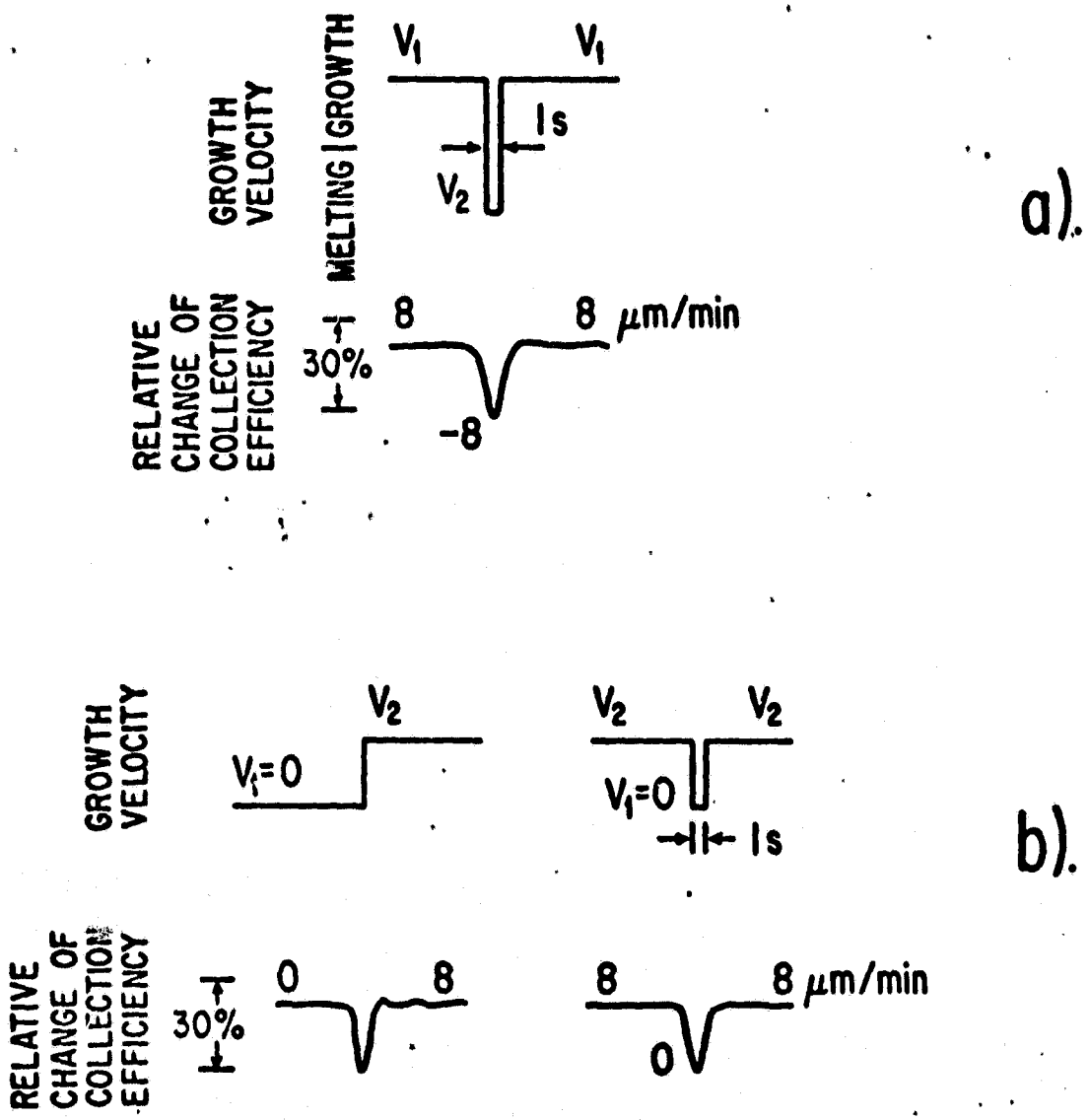


Fig. 13. EBIC microprofiles corresponding to backmelting (a) and to abrupt changes of growth velocity without backmelting (b).

of InP to 550 K. It was shown that the half width of the cathodoluminescence peak can be used for the determination of carrier concentration and carrier concentration inhomogeneities in the material. The variations of the cathodoluminescence peak height with temperature indicated the possibility of Auger recombination for high carrier concentrations ($7.4 \times 10^{18} cm^3$) at temperatures above 450 K. A more detailed account of these studies will be presented in our annual report.

GaAs-Oxide Interface

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 photoionization 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, shown schematically in Fig. 14. 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 previous theoretical predictions. It was shown that not only deep levels, but also shallow donor and acceptor levels at the GaAs-oxide interface can be assigned to Ga and As vacancies.

We have also utilized the photoionization discharge of GaAs-oxide interfaces in conjunction with capacitance measurements and thermal emission

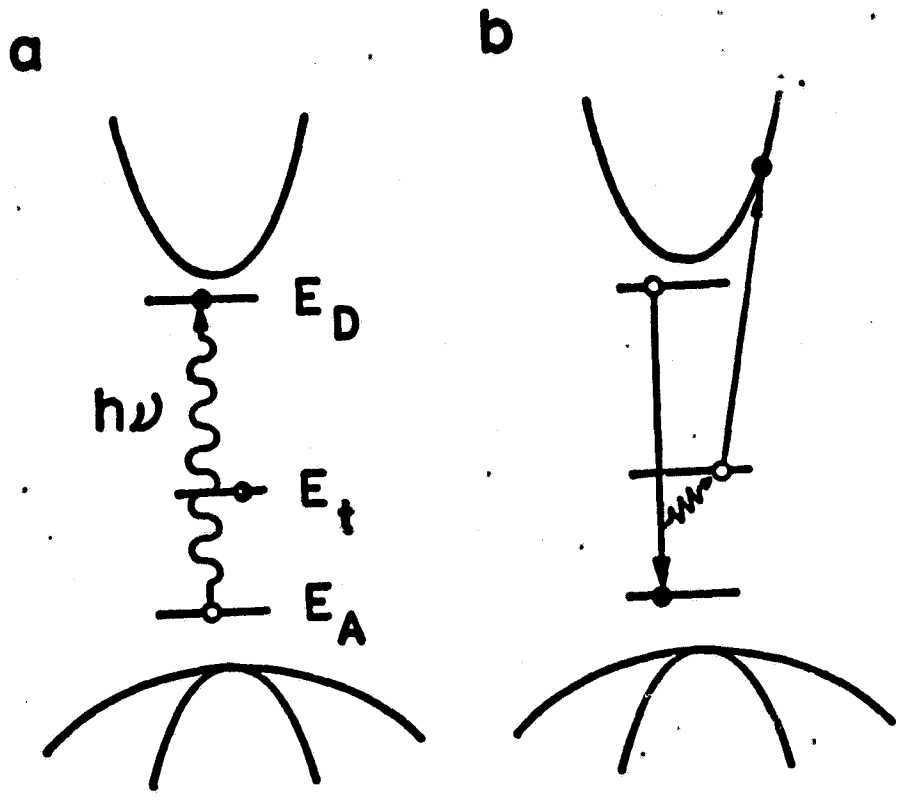


Fig. 14. Schematic representation of an Auger-like mechanism of the gigantic photoionization effect: (a) photoexcitation of donor-acceptor pair; (b) energy transfer to a deep state and ejection of an electron to conduction band.

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 doe not obey equilibrium characteristics (determined by Fermi level position at the surface) which leads at low temperatures to very large C-V hysteresis. Photoionization discharge of interface states which is far more efficient than thermal emission brings the occupation to equilibrium and thus eliminates the C-V hysteresis. Photoionization also reduces the frequency dispersion of C-V characteristics. It increases the contribution from interface states capacitance and makes it possible to reach the oxide capacitance for lower values of positive bias on the metal or for higher frequencies. These findings indicate that anomalous frequency dispersion is also associated with low thermal emission of interface states. However, in this case the thermal emission limits the frequency response of interface states and thus their contribution to the overall capacitance. The present findings clearly show that all essential features of GaAs-MOS characteristics can be adequately explained as non-equilibrium effects involving discrete interface states. This non-equilibrium character dictated by the large separation of states from the conduction band seems to constitute a major difference between GaAs and Si which has not been explicitly recognized in previous studies.

References

1. L. Jastrzebski, J. Lagowski, H.C. Gatos and A.F. Witt, "Model of Liquid Phase Electroepitaxial Growth: GaAs," presented at Fourth American Conf. on Crystal Growth, July 1978, Gaithersburg, Maryland.

2. L. Jastrzebski, J. Lagowski, H.C. Gatos and A.F. Witt, "Liquid-Phase Electroepitaxy: Growth Kinetics," J. Appl. Phys. 49, 5909 (1978).

3. L. Jastrzebski, J. Lagowski, H.C. Gatos and A.F. Witt, "Dopant Segregration in Liquid Phase Electroepitaxy; GaAs," presented at Fourth American Conf. on Crystal Growth, July 1978, Gaithersburg, Maryland.

4. J. Lagowski, L. Jastrzebski and H.C. Gatos, "Liquid Phase Electroepitaxy: Dopant Segregation," J. Appl. Phys. 51, 364 (1980).

5. T. Bryskiewicz, J. Lagowski and H.C. Gatos, "Electroepitaxy of Multicomponent Systems," J. Appl. Phys. 51, 988 (1980).

6. Y. Imamura, L. Jastrzebski and H.C. Gatos, "Defect Structure and Electronic Characteristics of GaAs Layers Grown by Electroepitaxy and Thermal LPE," J. Electrochem. Soc. 126, 1381 (1979).

7. S. Isozumi, C. Herman, A. Okamoto, J. Lagowski and H.C. Gatos, "A New Approach to Liquid Phase Electroepitaxy", to be published in J. Electrochem. Soc.

8. A. Okamoto, S. Isozumi, J. Lagowski and H.C. Gatos, "In Situ Monitoring of GaAs LPE Growth Rate", to be published in J. Electrochem. Soc.

9. J. Parsey, Y. Nanishi, J. Lagowski and H.C. Gatos, "Bridgman-type Apparatus for the Study of Growth-Property Relationships", to be published in J. Electrochem. Soc.

10. Y. Nanishi, J. Parsey, J. Lagowski and H.C. Gatos, "Dislocation-Free Undoped GaAs by Controlled Horizontal Bridgman Method", to be published in J. Electrochem. Soc.

11. J. Parsey, Y. Nanishi, J. Lagowski and H.C. Gatos, "Electron Trap-Free GaAs", to be published in J. Electrochem. Soc.

12. L. Jastrzebski, J. Lagowski, W. Walukiewicz and H.C. Gatos, "Determination of Carrier Concentration and Compensation Microprofiles in GaAs," J. Appl. Phys. 51, 2301 (1980).

13. J. Lagowski, W. Walukiewicz, M.M.G. Slusarczuk and H.C. Gatos, "Derivative Surface Photovoltage Spectroscopy; A New Approach to the Study of Absorption in Semiconductors; GaAs", J. Appl. Phys. 50, 5059 (1979).

14. M.M.G. Slusarczuk, "Study of Electronic and Optical Properties of Gallium Arsenide Surfaces and Interfaces", Doctor's Thesis, MIT, 1979.

15. E. Kamieniecki, J. Lagowski and H.C. Gatos, "Wavelength Modulated Photocapacitance Spectroscopy", J. Appl. Phys. 51, 1863 (1980).

16. E. Kamieniecki, T.E. Kazior, J. Lagowski and H.C. Gatos, "A Study of GaAs-Native Oxide Interface States by Transient Capacitance", presented at 7th Annual Conf. on the Physics of Compound Semiconductor Interfaces, Estes Park, Colorado, January 1980; J. Vac. Science & Technol. 17, 1041 (1980).

17. W. Walukiewicz, J. Lagowski, L. Jastrzebski, M. Lichtensteiger and H.C. Gatos, "Determination of Compensation Ratios in Semiconductors from Electron Mobility and Free Carrier Absorption; GaAs", 153d Electrochem. Soc. Meeting, Seattle, Washington, 1978.

18. W. Walukiewicz, J. Lagowski, L. Jastrzebski, M. Lichtensteiger and H.C. Gatos, "Electron Mobility and Free-Carrier Absorption in GaAs: Determination of the Compensation Ratio", J. Appl. Phys. 50, 899 (1979).

19. W. Walukiewicz, J. Lagowski, L. Jastrzebski, P. Rava, M. Lichtensteiger, C.H. Gatos and H.C. Gatos, "Electron Mobility and Free-Carrier Absorption in InP; Determination of the Compensation Ratio", J. Appl. Phys. 51, 2659 (1980).

20. M. Kaminska, J. Lagowski and H.C. Gatos, "Deep Levels in Melt-Grown GaAs; The Role of Oxygen", to be published in J. Appl. Phys.

21. J. Lagowski, "Microcharacterization of GaAs for Device Applications", Proc. 3rd Biennial Univ./Industry/Gov. Microelectronic Symp., May 1979, Lubbock, Texas, IEEE Conf. Record, p. 1.

22. H.C. Gatos, J. Lagowski and L. Jastrzebski, "Present Status of GaAs", NASA Contractor Report 3093, Jan. 1979.

23. L. Jastrzebski, J. Lagowski and H.C. Gatos, "Outdiffusion of Recombination Centers from the Substrate into LPE Layers; GaAs", J. Electrochem. Soc. 126, 2231 (1979).

24. L. Jastrzebski, J. Lagowski and H.C. Gatos, "Effect of Growth Kinetics on Formation of Recombination Centers in GaAs", presented at 155th Annual Meeting of Electrochem. Soc., May 1979, Boston.

25. L. Jastrzebski, J. Lagowski and H.C. Gatos, "Formation of Recombination Centers in Epitaxial GaAs Due to Rapid Changes of the Growth Velocity", J. Electrochem. Soc., 1980, in press.

26. W. Walukiewicz, J. Lagowski, L. Jastrzebski and H.C. Gatos, "Minority-Carrier Mobility in p-Type GaAs", J. Appl. Phys. 50, 5040 (1979); "Electron Scattering on the Short-Range Potentials in GaAs", to be published in J. Appl. Phys.

27. J. Lagowski, W. Walukiewicz, T.E. Kazior, H.C. Gatos and J. Siejka, "GaAs-Oxide Interface States . . .", submitted to Phys. Rev. Letters.

28. J. Lagowski, T.E. Kazior, W. Walukiewicz, J. Siejka and H.C. Gatos, "GaAs Interface States, a Gigantic Photoionization Effect and Its Implication to the Origin of These States", 8th Conf. on the Physics of Comp. Sem. Interfaces, Williamsburg, Va., Jan., 1981.

29. C.H. Gatos, J.J. Vaughan, J. Lagowski and H.C. Gatos, "Cathodoluminescence of InP", J. Appl. Phys., in press.

30. A.F. Witt, H.C. Gatos, M. Lichtensteiger, M.C. Lavine and C.J. Herman, "Crystal Growth and Steady-State Segregation under Zero Gravity: InSb", J. Electrochem. Soc. 122, 276 (1975); also 125, 1832 (1978).

31. F.M. Eisen, "A Review of GaAs Materials Preparation for High Speed Logic", Electrochem. Soc. Meeting, Hollywood, Fla., October 1980, Ext. Abstracts, p. 470.

32. C.A. Liechti, "Pathways and Pitfalls for GaAs IC Technology", Electrochem. Soc. Meeting, Hollywood, Fla., October 1980, Ext. Abstracts, p. 1168.

APPENDIX

PUBLICATIONS

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