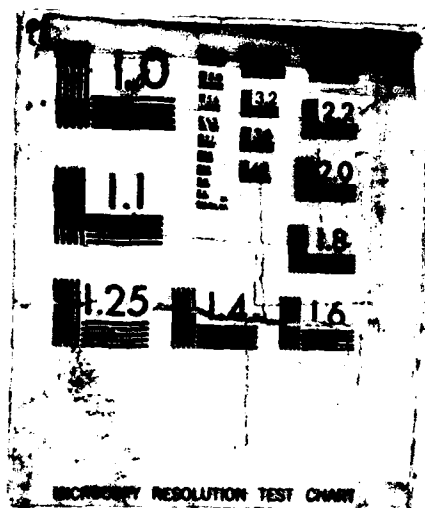


UNCLASSIFIED

A WORKSHOP ON 3-5 SEMICONDUCTOR: METAL INTERFACIAL
CHEMISTRY AND ITS EFFECTS (U) STANFORD UNIV CA
H E SPICER ET AL. 05 NOV 86 N00014-87-G-0038

NI

F/G 20/12



DTIC FILE COPY



AD-A183 158

A Workshop on 3-5 Semiconductor: Metal Interfacial
Chemistry and Its Effect on Electrical Properties

Sponsored by
Stanford University
and
ONR

November 3-5, 1986

W. E. Spicer
Larry Cooper

Contract N00014-87-G-0038

DTIC
ELECTE
JUL 30 1987
S D

DISTRIBUTION STATEMENT A
Approved for public release
Distribution Unlimited

87 7 14 084

Program

A Workshop on 3-5 Semiconductor: Metal Interfacial Chemistry and Its Effect on Electrical Properties

Monday, November 3rd

Chairman: W. E. Spicer - Stanford University

↓
This workshop discusses

8:00 - 8:30	Continental breakfast	
8:30 - 8:35	Introduction - Chairman	
8:35 - 9:05	R. Stanley Williams UCLA	"The Thermodynamics of Bulk Metal: III-V Systems Related to Interfacial Chemistry"
9:05 - 9:10	Questions	
9:10 - 9:30	Ki Bum Kim Stanford University	"Thermodynamic Considerations of Metal-GaAs Reactions plus TEM Results"
9:30 - 9:35	Questions	
9:35 - 9:55	M. Kniffin/C. Robert Helms Stanford University	"Chemistry of Ti:GaAs Interfaces"
9:55 - 10:00	Questions	
10:00 - 10:20	General discussion of all papers in session	
10:20 - 10:35	Coffee	
<u>Chairman: Thomas C. McGill, CALTECH</u>		
10:35 - 10:55	William E. Spicer Stanford University	"Questions Concerning Interfacial Chemistry, Equilibrium, and Electrical Properties"
10:55 - 11:00	Questions	
11:00 - 11:25	John Weaver University of Minnesota	"The Chemistry and Morphology of Metal/ III-V Semiconductor Interfaces"
11:25 - 11:30	Questions	
11:30 - 11:50	Tomasz Kendelewicz Stanford University	"Schottky Barriers on InP(110); Comparison to GaAs(110) Interface"
11:50 - 11:55	Questions	
11:55 - 12:20	Discussion of all preceding papers in Workshop	
12:20 - 1:40	Luncheon - Durand 450	



1
Approved for Public Release. Distribution Unlimited.
Per Dr. Larry Cooper, ONR/Code 1114

over →

per phonecon

Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

Monday, November 3rd
Chairman: Dr. Larry Cooper. ONR

1:40 - 2:00 Tim Sands
Bell Communications
Research

"Stable Phases at Reactive Metal/Compound
Semiconductor Interfaces"

2:00 - 2:05 Questions

2:05 - 2:25 Masanori Murakami
IBM Yorktown Heights

"Thermally Stable Ohmic Contact to n-type
GaAs"

2:25 - 2:30 Questions

2:30 - 2:50 Thomas McGill
CALTECH

"Effects in Ohmic Contacts"

2:50 - 2:55 Questions

2:55 - 3:15 S. S. Lau
UC - San Diego

"Non-Alloyed Ohmic Contacts by Solid State
Reactions"

3:15 - 3:20 Questions

3:20 - 3:40 Discussion of all papers in session

3:40 - 3:55 Coffee

Chairman: Jack Dew, Notre Dame University

3:55 - 4:15 James Waldrop
Rockwell International

"Large Variations of GaAs Schottky Barrier
Height by Interface Layers"

4:15 - 4:20 Questions

4:20 - 4:40 Edgar Krut
Rockwell International/
Walter Harrison, Stanford

"Effects on Schottky Barriers of Metal
Substitution in Semiconductors"

4:40 - 4:45 Questions

4:45 - 5:05 Giorgio Margaritondo
University of Wisconsin

"III-V Interfaces: Schottky Barriers vs.
Heterojunctions"

5:05 - 5:10 Questions

5:10 - 5:40 General discussion - including all material presented this day

Tuesday, November 4th
Chairman, Pierre Petroff - U.C. Santa Barbara

8:00 - 8:30 Continental Breakfast

8:30 - 8:50

Chris Palmström
Rutgers University
and Bell Labs

"A Comparison between Conventional and *in-situ* UHV Processing for Ge/GaAs and Co/GaAs Structures"

8:50 - 8:55

Questions

8:55 - 9:20

Nathan Newman
Stanford University

"Electrical Study of Schottky Barriers on Atomically Clean 3-5(110) Surfaces; A Comparison to the Results of Studies Using Surface Sensitive Techniques and Au-GaAs Ohmic Contacts"

9:20 - 9:25

Questions

9:25 - 9:55

Z. Liliental-Weber
UC-Berkeley

"The Structure of Au/GaAs and Al/GaAs Interfaces"

9:55 - 10:00

Questions

10:00 - 10:35

Discussion of three papers of this session

10:35 - 10:50

Coffee

Chairman: Paul Ho, IBM, Yorktown Heights

10:50 - 11:10

Thomas Jackson
IBM-Yorktown Heights

"Refractory Silicide Contacts for Self-Aligned GaAs MESFETs"

11:10 - 11:15

Questions

11:15 - 11:35

Tom Knech
IBM - Yorktown Heights

"Heterojunction Growth and Impurity Incorporation During Vapor Growth of Compound Semiconductors"

11:35 - 11:40

Questions

11:40 - 12:00

Bruce Bunker
Notre Dame University

"Reflection EXAFS Studies of Semiconductor-Metal Interfaces"

12:00 - 12:05

Questions

12:05 - 12:30

General discussion of preceding papers

12:30 - 1:30

Luncheon, Demand 450

Tuesday, November 4th

Chairman: Ron Grant, Rockwell International

1:30 - 1:50	Harry Wieder UC-San Diego	"Composition Dependence of Metal $\text{In}_x\text{Al}_{1-x}\text{As}$ Barrier Height and Its Applications"
1:50 - 1:55	Questions	
1:55 - 2:15	Steven Wright IBM-Yorktown Heights	" <i>In-situ</i> Contacts to GaAs Based on InAs"
2:15 - 2:20	Questions	
2:20 - 2:40	Jerry Tersoff IBM-Yorktown Heights	"Intrinsic Mechanisms for Fermi-level Pinning at Surfaces and Interfaces"
2:40 - 2:45	Questions	
2:45 - 3:10	General discussion of preceding papers	
3:10 - 3:30	Coffee	

Chairman: Ingrid Linden, Stanford University

3:30 - 3:50	Leonard J. Brillson Xerox Corporation	"Recent Photoemission and Cathodoluminescence Spectroscopy Studies of III-V Semiconductor- Metal Interfaces"
3:50 - 3:55	Questions	
3:55 - 4:15	Jack Dow Notre Dame University	"Antisite Defects and Schottky Barriers"
4:15 - 4:20	Questions	
4:20 - 4:40	Paul Ho IBM-Yorktown Heights	"Direct Measurements of Electronic States at Metal/GaAs Interfaces"
4:40 - 4:45	Questions	
4:45 - 5:05	Discussion of preceding papers	
5:05 - 5:45	General discussion of all papers presented at meeting	
6:00 - 7:00	Stanford Faculty Club - no host cocktail party	
7:00	Dinner - Stanford Faculty Club	

Wednesday, November 5th
Chairman, Harry Wieder, U.C. San Diego

8:00 - 8:30	Continental breakfast	
8:30 - 8:50	Rudolf Ludeke IBM-Yorktown Heights	"The Role of Transition Metal Impurity States in Schottky Barrier Formation"
8:50 - 8:55	Questions	
8:55 - 9:15	Walter Harrison Stanford University	"Effects of Coverages, Relaxation, and Screening at Interfaces"
9:15 - 9:20	Questions	
9:20 - 9:40	Jerry M. Woodall IBM-Yorktown Heights	"Unpinned GaAs Surfaces by Photochemistry"
9:40 - 9:45	Questions	
9:45 - 10:05	Discussion of preceding papers	
10:05 - 10:25	Coffee	

Chairman, Piero Pianetta, Stanford University

10:25 - 10:45	Antoine Kahn Princeton University	"Kinetics of Schottky Barrier Formation: Metals on Low Temperature GaAs (110)"
10:45 - 10:50	Questions	
10:50 - 11:10	Seb Doniach Stanford	"Microscopic Metal Clusters and Schottky Barrier Formation"
11:10 - 11:15	Questions	
11:15 - 11:35	Discussion of papers of this day	
11:35 - 12:15	General discussion of workshop	

Workshop attendees

Ludeke, Dr. Rudolf
IBM Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, NY 10598
(914) 945-2591

Woodall, Dr. Jerry
IBM Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, NY 10598
(914) 945-1568

Lau, Dr. S. S.
University of California-San Diego
P.O. Box 109
LaJolla, CA 92037
(619) 534-6940

Wieder, Dr. Harry
University of California-San Diego
Department of Electrical Engineering
P.O. Box 109
LaJolla, CA 92037
(619) 534-3546

Liliental-Weber, Dr. Zuzanna
University of California
Lawrence Berkeley Laboratory
1 Cyclotron Road 622-203
Berkeley, CA 94720
(415) 486-6276

Weber, Dr. Eicke
University of California
Hearst Mining Building
Berkeley, CA 94720
(415) 624-3801

Weaver, Prof. John
University of Minnesota
Department of Chemical Engineering
and Materials Science
151 Washington S.E.
Amundson Hall 421
Minneapolis, MN 55455
(612) 625-6548

Dow, Dr. Jack
University of Notre Dame
Department of Physics
Notre Dame, IN 46556
(219) 239-6407
(219) 239-6386

Bunker, Dr. Bruce
University of Notre Dame
Department of Physics
Notre Dame, IN 46556
(219) 239-7219
(219) 239-6386

McGill, Dr. Thomas C. CALTECH Department of Applied Physics Mail Code 128-95 Pasadena, CA 91125	(818) 356-4849
Ho, Dr. Paul IBM Thomas J. Watson Research Center P.O. Box 218 Yorktown Heights, NY 10598	(914) 945-2007
Lindau, Dr. Ingolf Stanford Electronics Laboratories McCullough Building, Rm. 336 Stanford, CA 94305	(415) 723-1052
Helms, Dr. C. Robert Stanford Electronics Laboratories McCullough Building, Rm. 342 Stanford, CA 94305	(415) 723-0406
Harrison, Dr. Walter Department of Applied Physics Stanford University Stanford, CA 94305	(415) 723-4224
Kim, Mr. Ki Bum Department of Materials Science Stanford University Stanford, CA 94305	(415) 725-2648
Deal, Dr. Mike Department of Electrical Engineering McCullough Building Rm. 118 Stanford, CA 94305	(415) 725-0209
Sands, Dr. Tim Bell Communications Laboratories 331 Newman Springs Road Redbank, NJ 07701	(415) 486-6254
Margaritondo, Dr. Giorgio Department of Physics Synchrotron Radiation Center University of Wisconsin-Madison 3275 Schneider Drive Stoughton, WI 53589-3098	(608) 873-6651
Dr. Larry Cooper Electronic and Solid State Departments Office of Naval Research, Code 414 800 N. Quincy Avenue Arlington, VA 22217	(202) 696-4214

Brillson, Dr. Leonard
Xerox Corporation
800 Phillips Road
Webster, NY 14580

(716) 422-6468

Petroff, Dr. Pierre
Department of Materials Science and
Electrical Engineering
University of California-Santa Barbara
Goleta, CA 93106

(805) 961-8256

Williams, Dr. R. Stanley
University of California-Los Angeles
Department of Chemistry
Los Angeles, CA 90024

(213) 825-8818

Grant, Dr. Ronald W.
Rockwell International Science Center
1046 Camino Dos Rios
P.O. Box 1085
Thousand Oaks, CA 91360

(805) 373-4219

Waldrop, Dr. James
Rockwell International Science Center
1046 Camino Dos Rios
P.O. Box 1085
Thousand Oaks, CA 91360

(805) 373-4249

Kraut, Dr. Edgar
Rockwell International Science Center
1046 Camino Dos Rios
P.O. Box 1085
Thousand Oaks, CA 91360

(805) 373-4186

Kahn, Dr. Antoine
Department of Electrical Engineering
Princeton University
Princeton, NJ 08540

(609) 452-4642

Dr. Masano Murakami
IBM Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, NY 10598

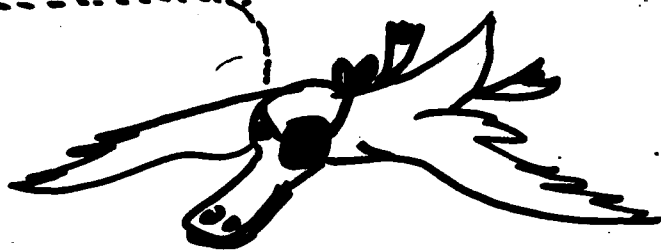
(914) 945-1865

Dr. Thomas Jackson
IBM Thomas J. Watson Research Center
P.O. Box 218
Yorktown Heights, NY 10598

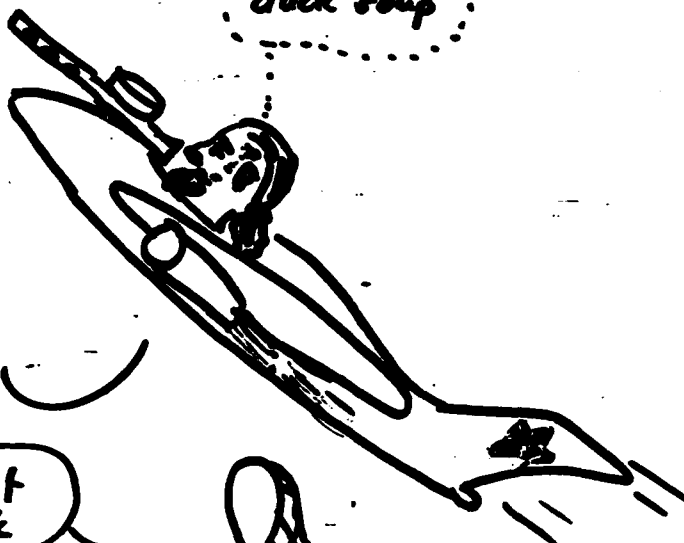
(914) 945-1947

Dr. Tom Kuech IBM Thomas J. Watson Research Center P.O. Box 218 Yorktown Heights, NY 10598	(914) 945-1644
Dr. Chris Palmstrøm Department of Physics SERIN Lab at Rutgers University P.O. Box 849 Piscataway, NJ 08854	(201) 699-2221
Tersoff, Dr. Jerry IBM Thomas J. Watson Research Center P.O. Box 218 Yorktown Heights, NY 10598	(914) 945-3128
Kim, Ki Bum Department of Materials Science Stanford University Stanford, CA 94305	(415) 725-2648
Beyers, Dr. Robert K-32-801 IBM Almaden Research Center 650 Harry Road San Jose, CA 95120-6099	(408) 927-2383
Wright, Dr. Steven IBM Thomas J. Watson Research Center P.O. Box 218 Yorktown Heights, NY 10598	(914) 945-3000
Spicer, Dr. William E. Department of Electrical Engineering/ Stanford Electronics Laboratories McCullough 238 Stanford, CA 94305	(415) 723-4639
Pianetta, Dr. Piero Stanford Electronics Laboratories McCullough 232 Stanford, CA 94305	(415) 723-1083
Doniach, Dr. Sebastian Department of Applied Physics Stanford University Stanford, CA 94305	(415) 723-4786

if it quacks...



duck soup



just a bit more junk



I thought I saw a quack



antisite?!

Uniformly Defective Missile

2

**The Thermodynamics of Bulk
Metal-III-V Systems
Related to Interfacial Chemistry**

R. Stanley Williams

**Department of Chemistry and Biochemistry
and
Solid State Science Center
UCLA**

11

**for the Workshop on III-V Semiconductor: Metal
Interfacial Chemistry and Its Effect on
Electrical Properties**

ACKNOWLEDGMENTS

Dr. Jeffrey R. Lince

C. Thomas Tsai

John H. Pugh

and

Office of Naval Research

California MICRO

Hughes Aircraft Corporation

Relevance of Bulk Thermodynamics to the Chemistry of Metal/Compound-Semiconductor Interfaces

1) BOUNDARY CONDITIONS

An interface cannot be stable if the bulk phases that are joined can react to form more stable products.

2) PHASE STABILITY

Determine the conditions under which two phases are stable with respect to one another.

3) REACTION SEQUENCES

Predict the equilibrium phases and the intermediate products that can form during a reaction.

4) STABLE INTERFACES

Deposit metals that are at chemical equilibrium under the conditions that the interface will experience.

Hasn't all of this been done already?

**Hasn't it been shown that
thermodynamic predictions
fail for thin metal films on
compound semiconductors ?**

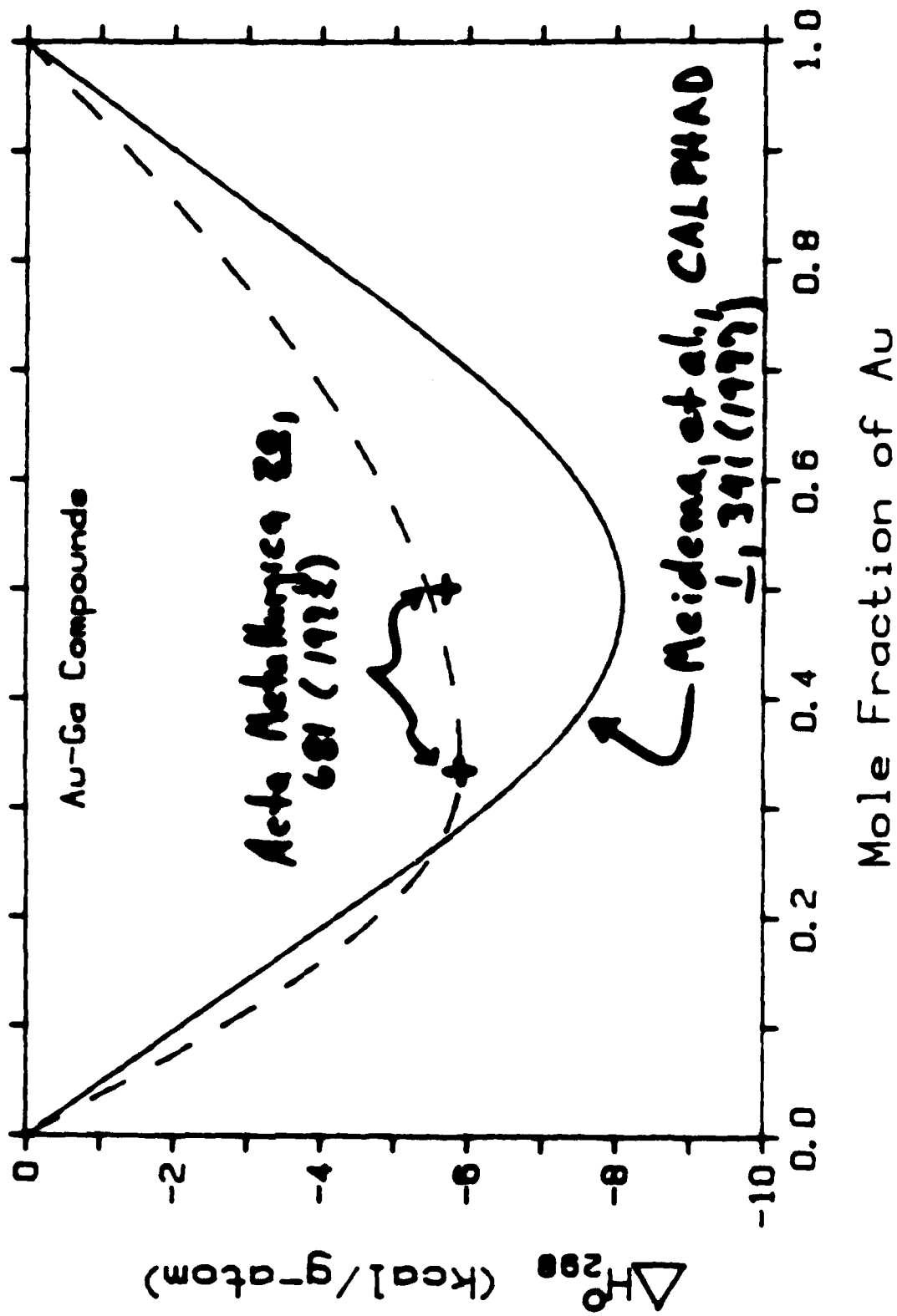
N O !

PREVIOUS WORK

Many investigators have calculated the change in *enthalpy* (ΔH_p) for possible reactions. These studies have had two basic problems:

- 1) Use of incorrect thermochemical data from Meidema et al., CALPHAD 1, 341 (1977).
 - a) Often the enthalpies were for mixing of liquids, which have little relation to the formation of solid compounds.
 - b) Meidema's predictions of enthalpies of formation for compounds with group III elements contain systematic errors
- 2) The equilibrium state of a system at constant pressure is determined by the Gibbs Free Energy, $G = H - TS$. The entropy is not negligible and cannot be ignored.
J.Mats.Res. 1, 343 (1966).

Enthalpy of formation vs. Au mole fraction

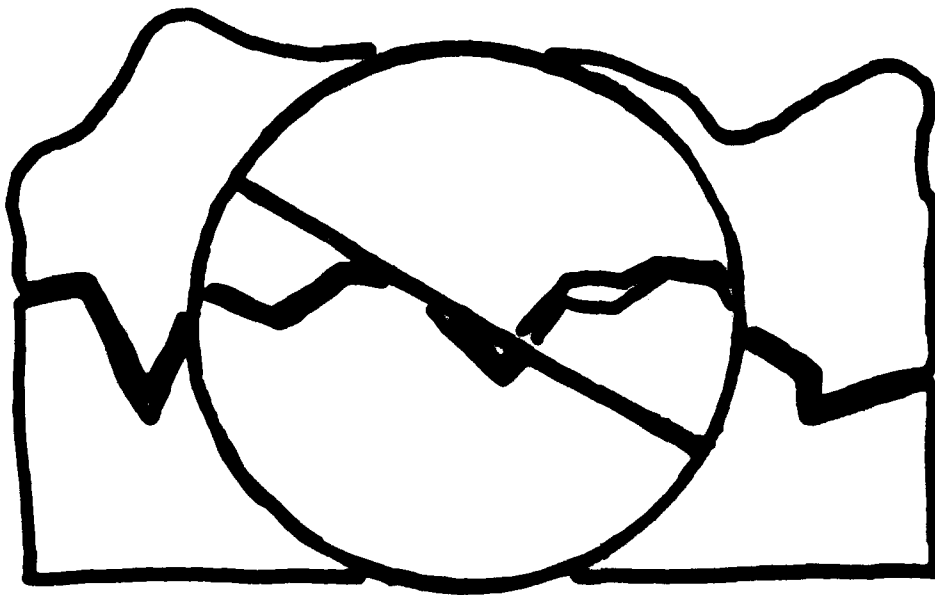


**Will not explain - -
Schottky barrier heights.**

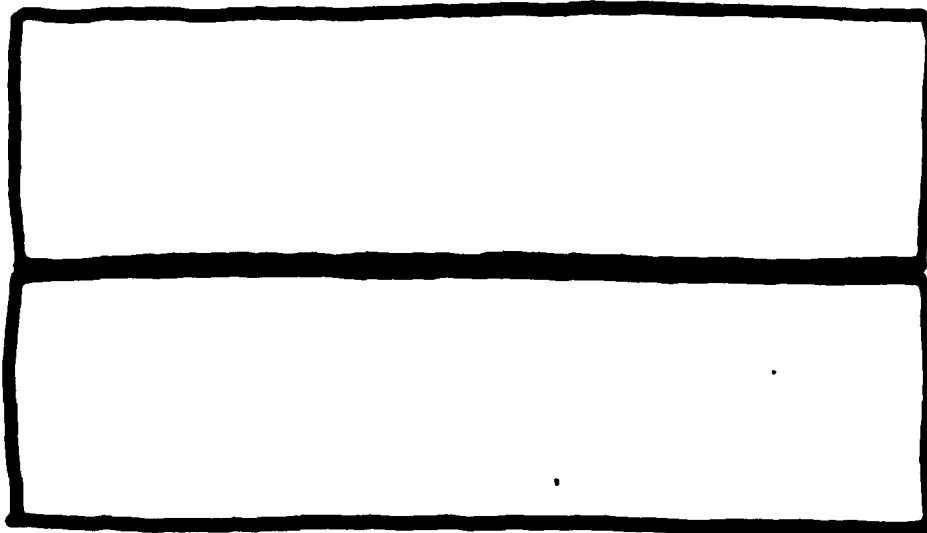
**Will not discuss - -
Submonolayer coverages.**

- Define
"Thermodynamically Stable"
- Examine
Bulk Phase Diagrams
- Analyze
Entropic Contributions
- Compare
Au/GaAs and AuGa₂/GaAs
- Summarize

Minimize Mass Transport



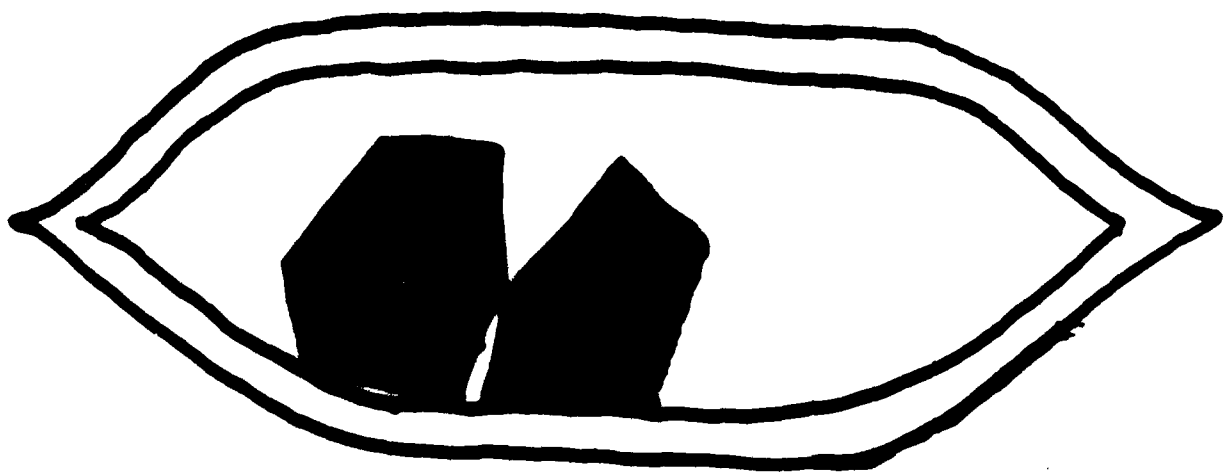
Rough



Abrupt

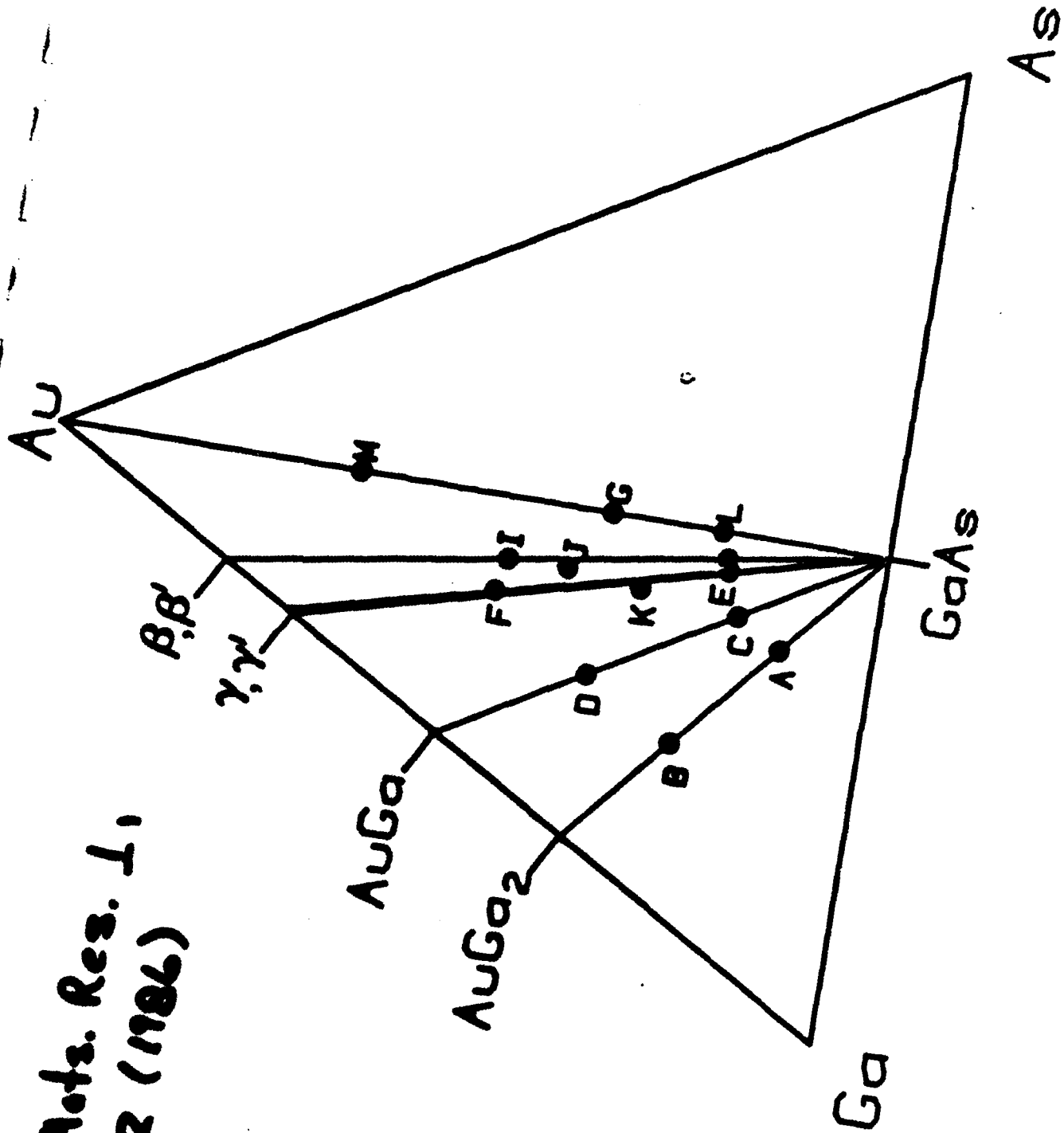
Minimize G

Experimental Determination of Bulk Phase Diagrams



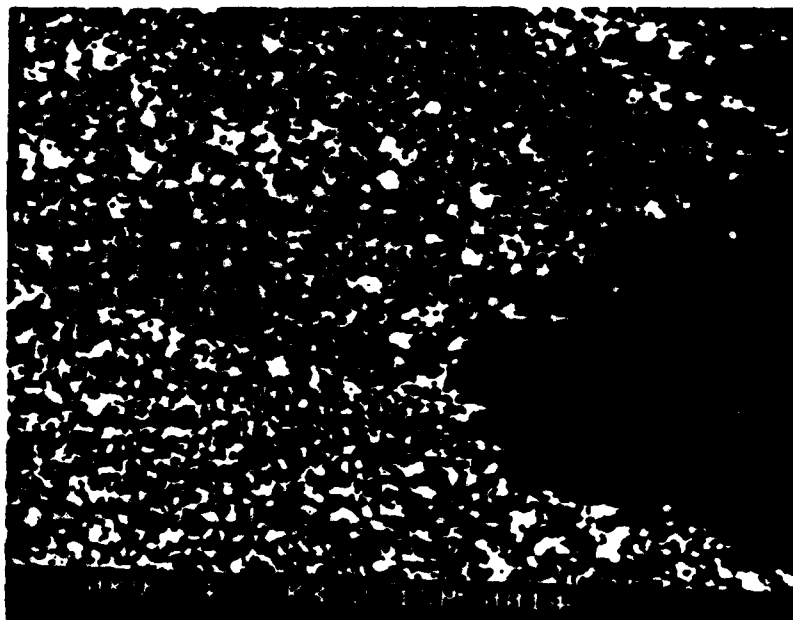
Sealed Capsule
(Nearly Ideal Closed
Thermodynamic System)

J. Appl. Res. 1,
352 (1986)



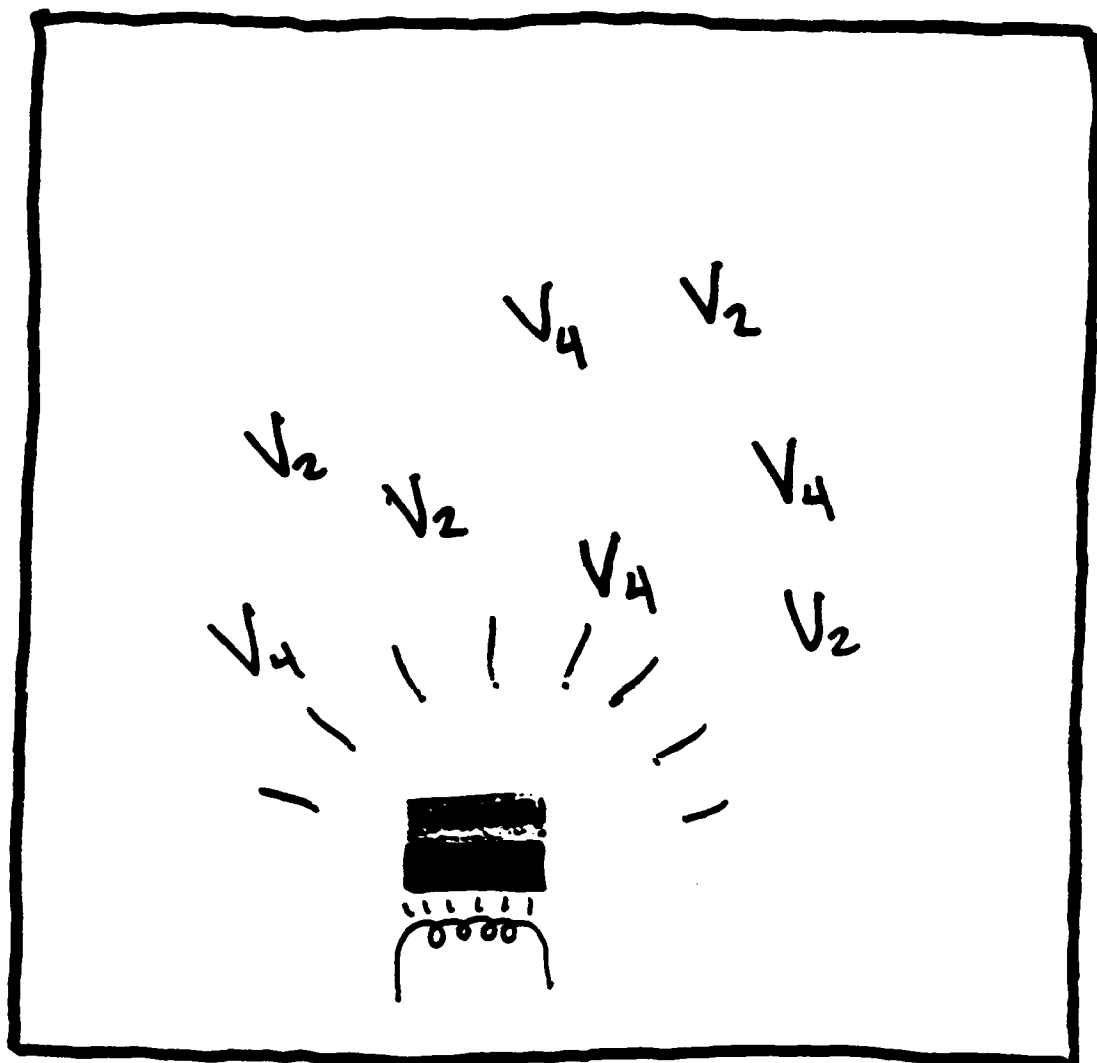
Au on GaAs

Room
Temp.



500°C





Open System:
ie. mass is not
necessarily constant

Solid State Electronics

22 (1979) 517.

DISSOCIATION OF GaAs AND Ga_{0.7}Al_{0.3}As DURING ALLOYING OF GOLD CONTACT FILMS

E. KINSEBORN, P. K. GALLAGHER and A. T. ENGLISH
Bell Laboratories, Murray Hill, NJ 07974, U.S.A.

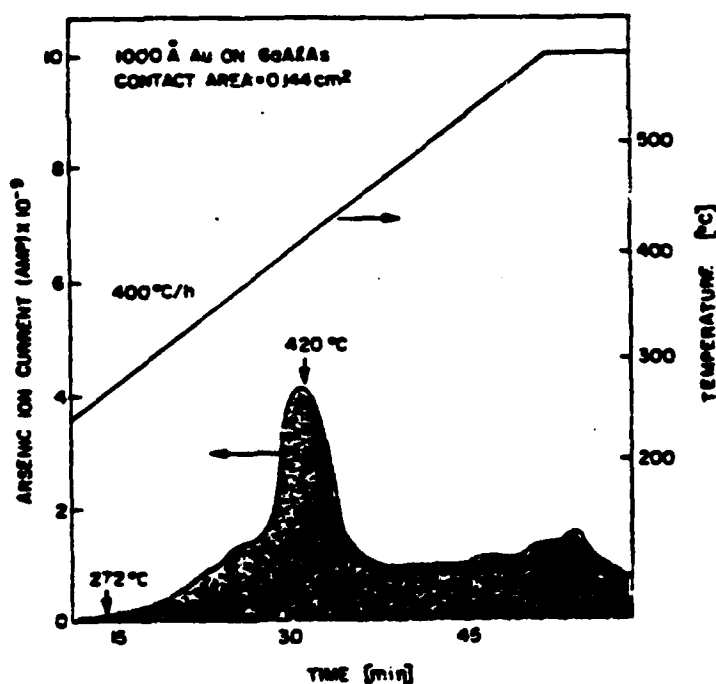
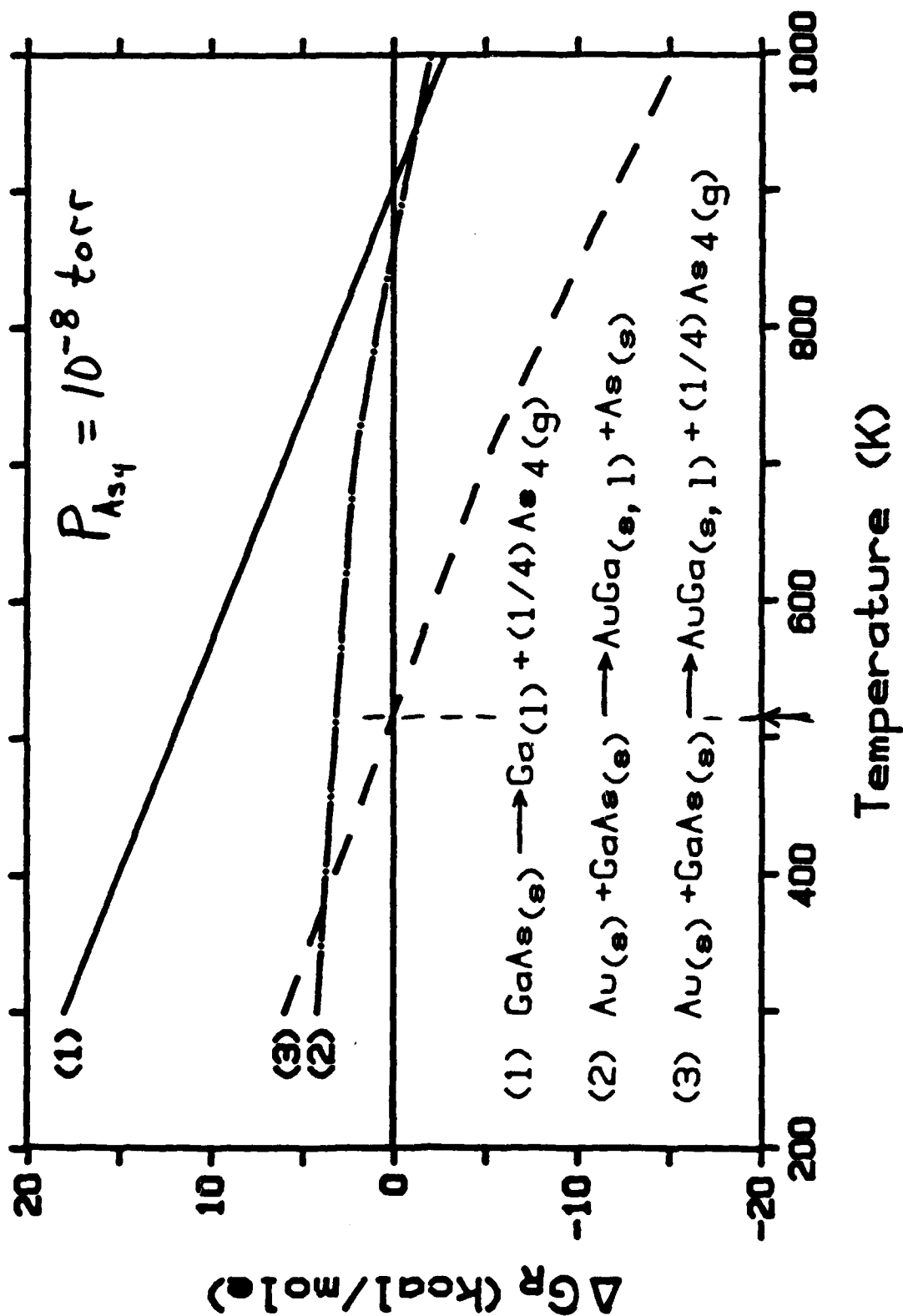


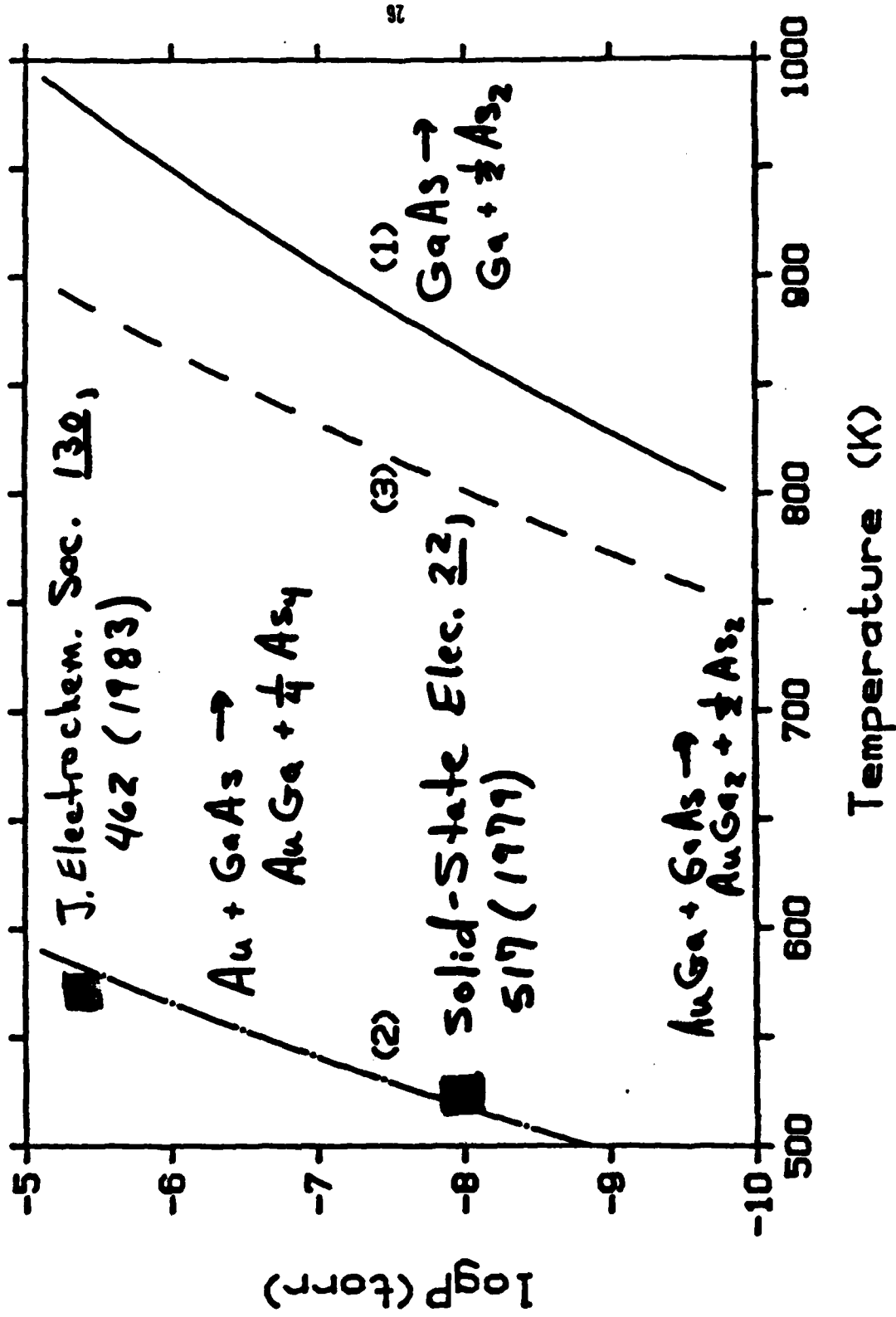
Fig. 1. The mass spectrometer output for a repeated scan through a short range around the As a.m.u. As starts to appear at -230°C and reaches a maximum rate of evolution at 420°C . Unreacted GaAs starts to decompose at -620°C .

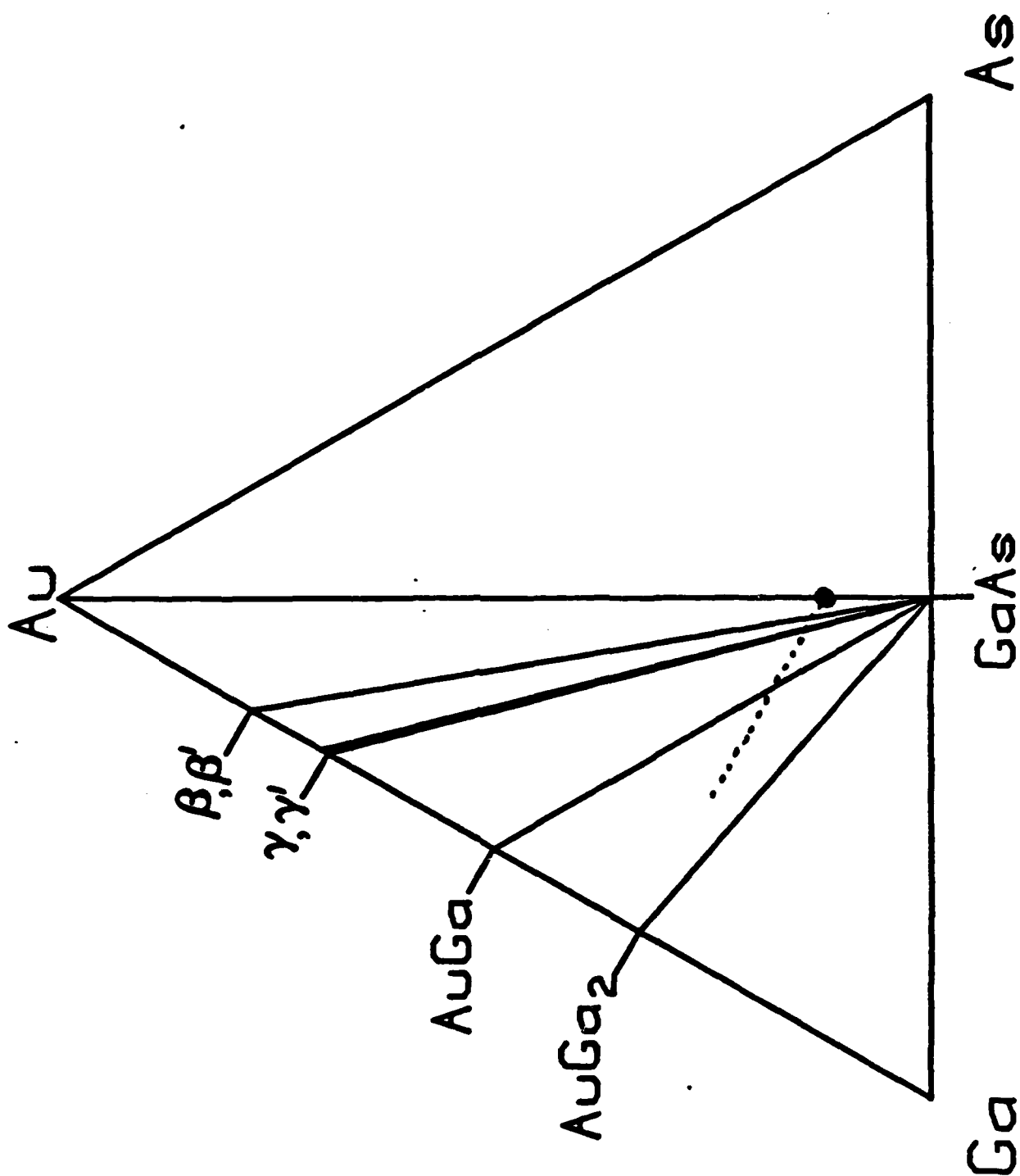
Gibbs Free Energy of Reaction



J. Mats. Res. L, 343 (1986)

As partial pressure vs temp.





Reaction Sequence



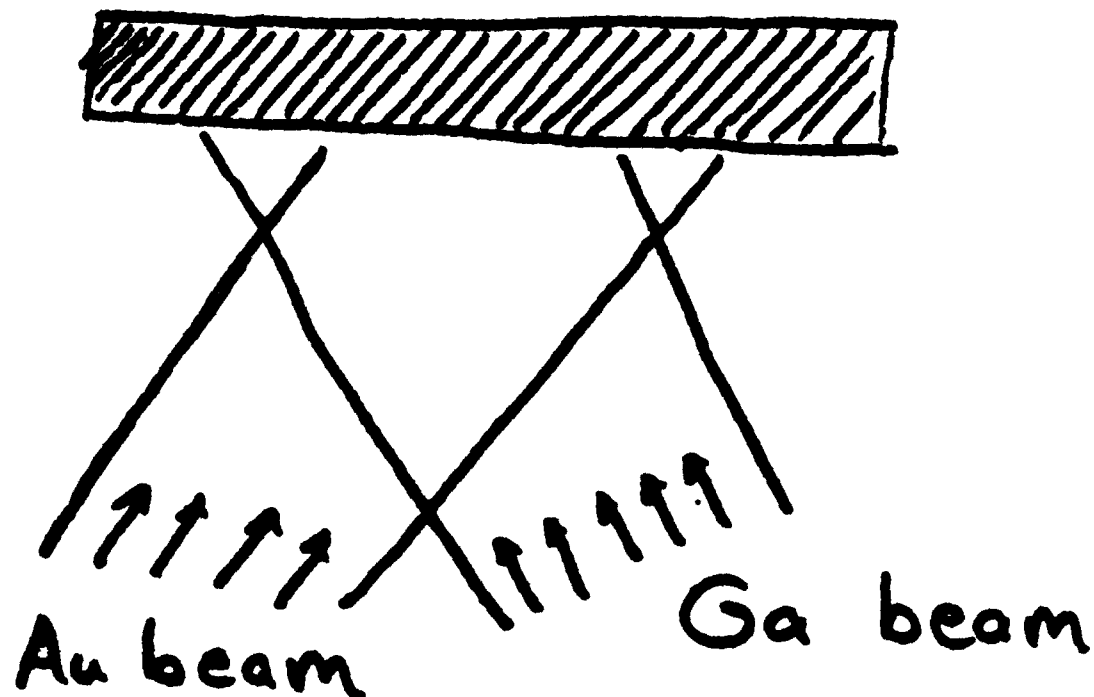
for all reactions, $\Delta H > 0$

but $\Delta G < 0$!

Au + Ga on GaAs



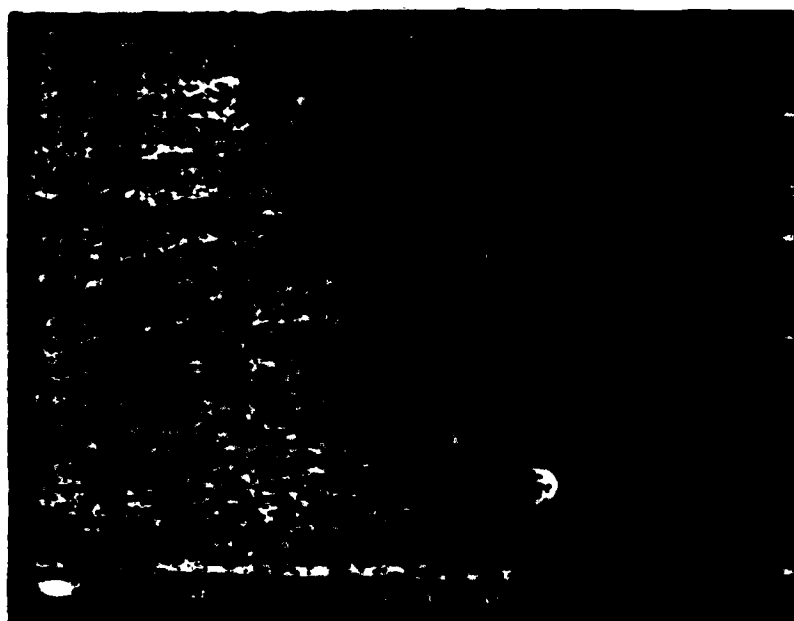
GaAs Substrate



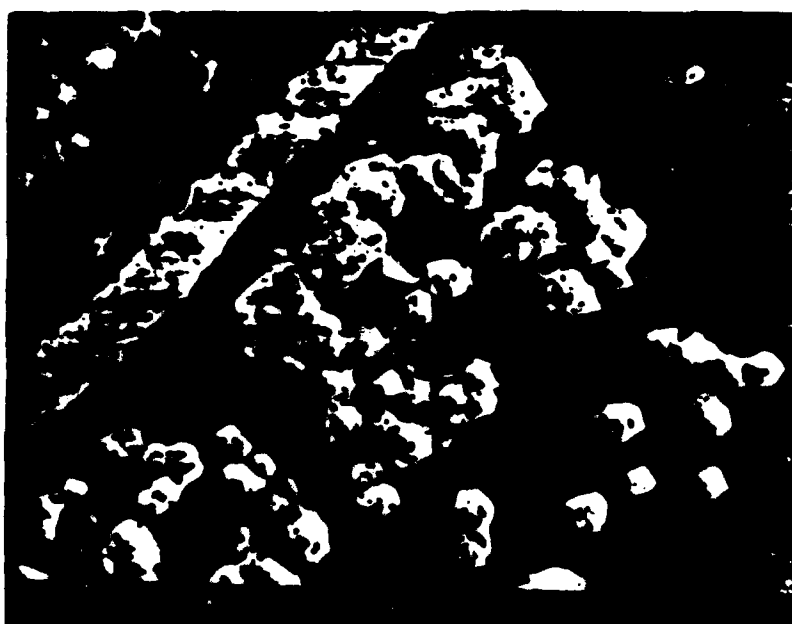
J. Appl. Phys. 61, 537 (1986)

2000Å Au on GaAs

Room
Temp.



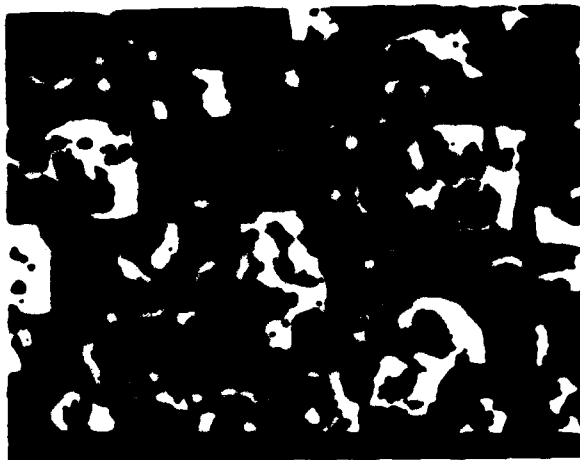
500°C



AuGa_2 on GaAs

a)

300°C



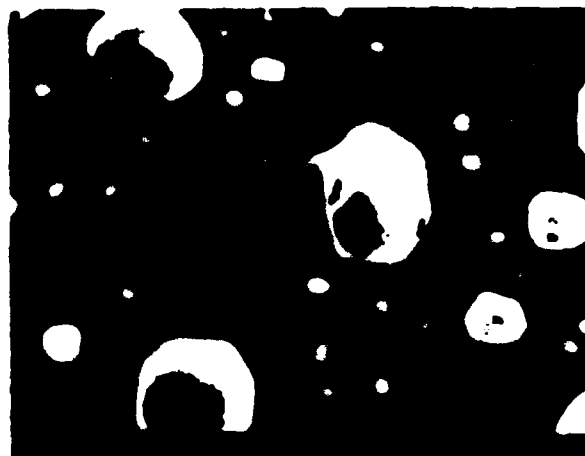
b)

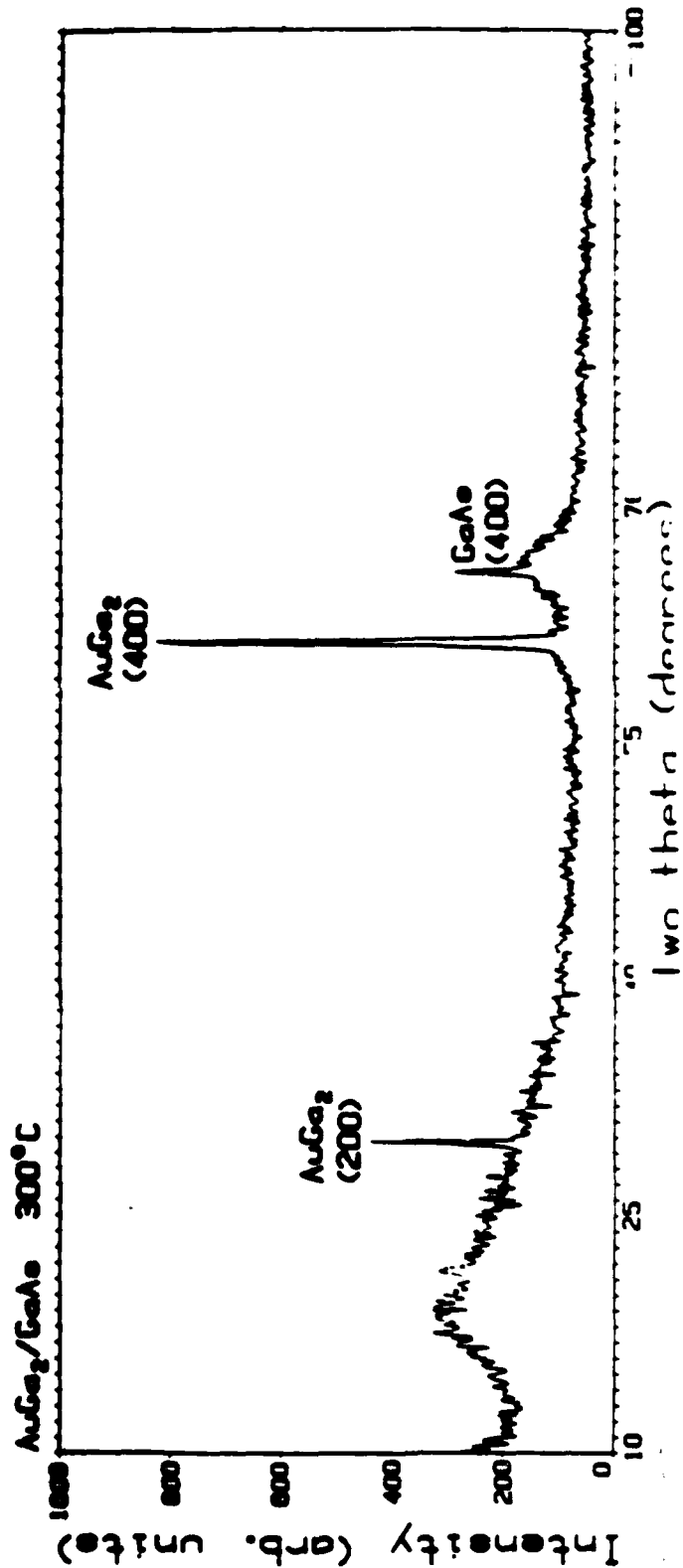
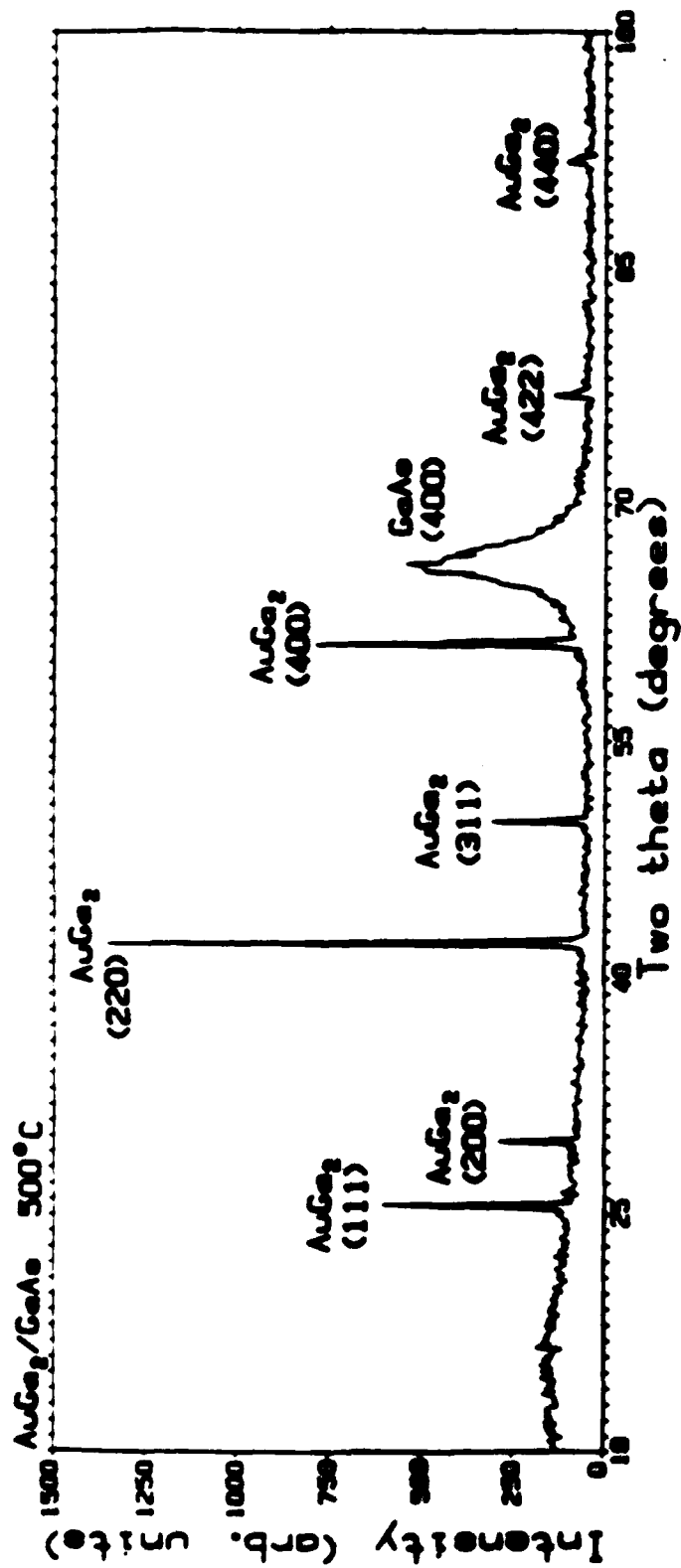
480°C



c)

500°C





Electrical Properties of Metal Contacts on GaAs

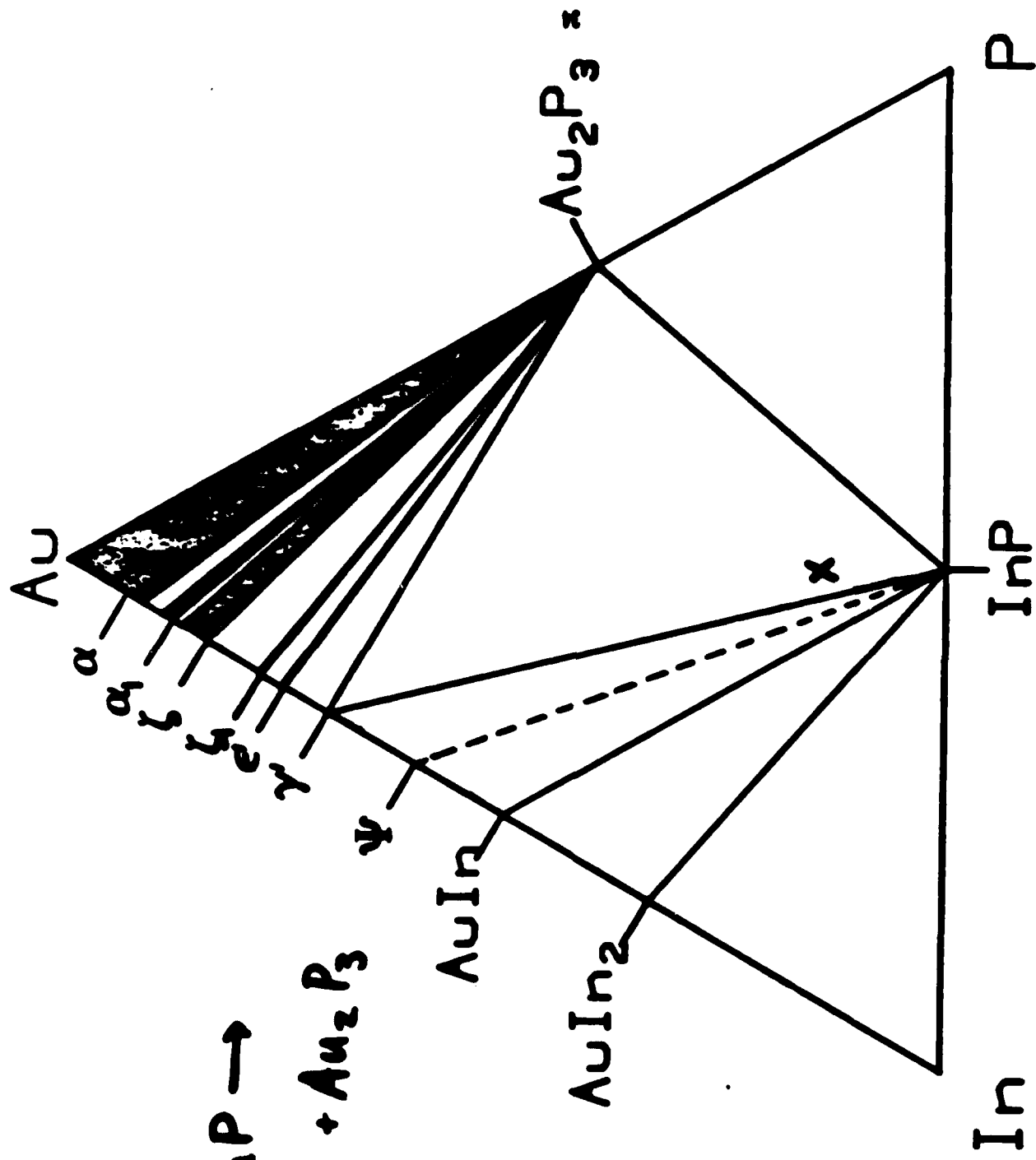
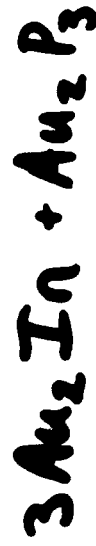
Leung, Yoshie, Bauer, and Milnes

J. Electrochem. Soc. 133, 898 (1985)

	As deposited	350°C Anneal				
	ϕ (eV)	n	V_B (volts)	ϕ	n	V_B^R
Au	0.95	1.05	33	-	ohmic -	

AuGa ₂	0.68	1.05	21	0.74	1.04	18

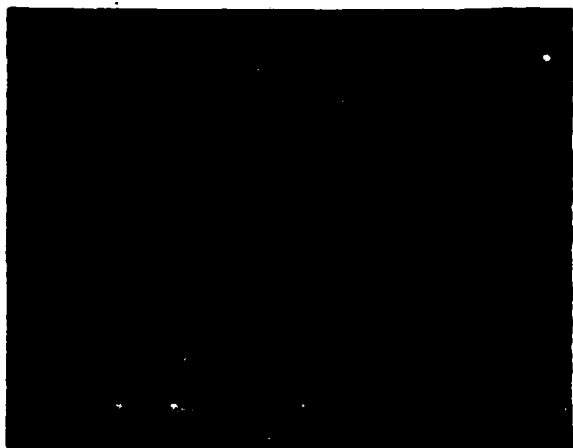
Predict



550 Å Au on InP(001)

Annealed under 1 Atm. Dry N₂

a)
R.T.
35 days

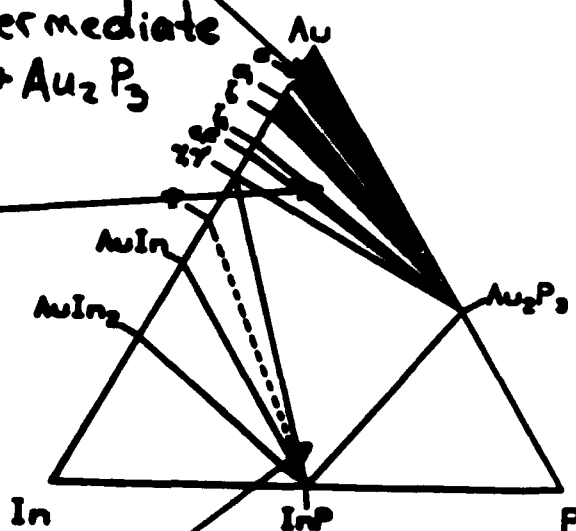


initial reaction stage
continuous film
 α phase

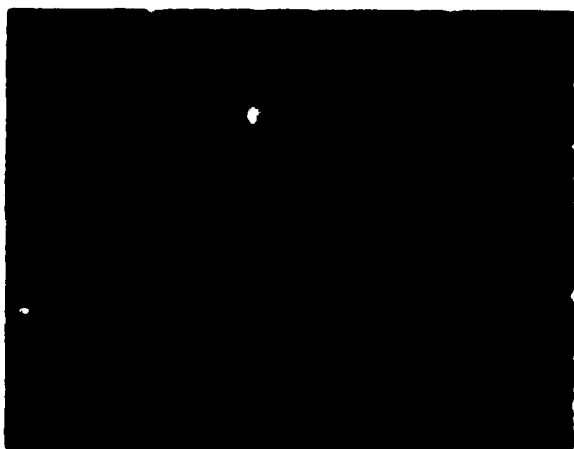
b)
365°C
10 min



intermediate
 $\zeta_1 + \text{Au}_2\text{P}_3$



c)
510°C
10 min



closed system equil.
islands
 $\gamma + \text{Au}_2\text{P}_3$

CONCLUSIONS

- 1) Bulk phase diagrams are guides to the understanding of interfacial chemistry.
- 2) Thermochemistry can be used to predict the end products of a chemical reaction, and provide information on the intermediates.
- 3) Entropy must be considered explicitly in reactions that can produce volatile group V products.
- 4) Thermodynamics cannot be used to predict how fast a reaction will proceed.
- 5) Chemically stable interfaces are also electrically stable.
- 6) Phase diagrams should be consulted before a metal/compound-semiconductor is designed.
- 7) The current thermochemical data base is inadequate for a broad understanding of metal/compound-semiconductor systems.

**Phase Equilibria in Metal-Gallium-Arsenic Systems:
Thermodynamic Considerations for Metallization Materials**

Robert Beyers*, Ki Bum Kim, and Robert Sinclair
Department of Materials Science and Engineering
Stanford University, Stanford, California 94305

Journal of Applied Physics (in press)

Abstract

We propose a classification scheme for phase equilibria in elemental metal-gallium-arsenic systems. Using available data we assign as many metals as possible to seven generic types of ternary phase diagrams. We describe how the phase diagrams can provide a framework for interpreting previous studies of metal reactions with GaAs substrates and for identifying stable materials for GaAs metallizations.

I. Introduction

One of the most challenging problems in GaAs integrated circuit fabrication is the formation of reliable metal contacts. This problem has resulted in numerous studies of metal reactions with GaAs substrates, which typically attempt to relate changes in the electrical properties of the contact to interdiffusion and reaction at the metal-semiconductor interface. Clearly, as device dimensions decrease in GaAs integrated circuits, it will become increasingly important to form uniform contact layers to GaAs with minimal substrate interaction.¹⁻³

While there have been many investigations of metal-GaAs chemistry, the results of these studies have been explained largely with empirical correlations, such as comparing the electronegativities of the elements involved⁴ or the heats of formation of the compounds involved.^{5, 6} Unfortunately, these correlations provide little or no framework for understanding actual processing problems or for choosing stable metallization materials because they disregard classical thermodynamic considerations, most notably the implications of the Gibbs phase rule. In contrast, metal-gallium-arsenic (M-Ga-As) ternary phase diagrams should provide just such a framework.⁷

Indeed, ternary diagrams have already been used to understand other aspects of GaAs processing. For instance, to assist in studies of dopant diffusion in GaAs and solution growth of doped GaAs crystals, Panish⁸⁻¹⁶ determined the liquidus and solidus data for numerous dopant-Ga-As diagrams. Similarly, Deal^{17, 18} recently determined the Cr-Ga-As diagram and resolved many ambiguities in previous studies of chromium solubility and diffusivity in GaAs. Moreover, Thurmond *et al.*¹⁹ used the Ga-As-O diagram to explain the phases formed during GaAs oxidation. However, the use of ternary phase equilibria to explain metallization processing problems in GaAs has only just begun, with the recent work by Williams *et al.*^{20,21} being the most notable example.

The purpose of the present article, then, is to describe how M-Ga-As phase diagrams can provide a framework for interpreting previous results and for identifying suitable materials for

stable contacts. We begin by outlining the seven generic M-Ga-As diagrams that are possible. For the four simplest types, we show how they can be identified in principle by a single experiment, and we point out which metal-containing phases will be stable contacts. Next, based on previously published studies, we identify metals that belong to each type. Finally, we describe how the phase diagrams can be used to search systematically for stable metallization materials.

II. CLASSIFICATION SCHEME

Because the thin-film reactions to be discussed involve three elements distributed in various phases, they should be described using ternary phase diagrams. At fixed temperature and pressure, the Gibbs phase rule predicts a maximum of three phases in equilibrium in any portion of the phase diagram. Regions of three-phase equilibrium form triangles in isothermal sections of the ternary phase diagram. The phases at the corners of a given triangle are thermodynamically stable in contact with each other. For metal-gallium-arsenic systems, this means that the chemical potential of the metal is the same in all three phases, and similarly for the gallium and the arsenic. If free energy data are available for all the phases, then the regions of three-phase equilibrium can be found by determining the stable two-phase tie-lines, which in turn are established by straightforward free energy calculations.²² Alternatively, the stable tie-lines and three-phase regions can be found experimentally by reacting various M-Ga-As compositions in closed, inert containers and identifying the phases formed. Through judicious use of the phase rule, the number of compositions that must be evaluated to determine the stable tie-lines and three-phase regions can be quite small. In particular, for some simple cases, the metal-containing phases with stable tie-lines to GaAs can be determined by a single experiment.

For understanding M-Ga-As chemistry, it is useful to classify the diagrams according to their key features, i.e., the disposition of their stable tie-lines. In practice, other aspects of the diagrams (solubility ranges, solidus and liquidus data) will be important for interpreting particular problems. Thus, we begin by classifying the diagrams according to their general features and then consider in

turn subtler factors that may be important for interpreting M-Ga-As thin-film reactions.

A. Simplest cases

For the moment, let us make the following assumptions and simplifications:

- (1) Assume just one MGa_x and one MAs_y binary compound exist.
- (2) Assume no MGa_xAs_y ternary phases exist.
- (3) Neglect the homogeneity range of each phase.
- (4) Neglect the formation of liquid phases.
- (5) Neglect arsenic sublimation.
- (6) Assume equilibrium between the solid phases is reached during processing.

(The converse of each of these simplifications will be considered in the next section.)

Given these simplifications, there are four possible types of M-Ga-As diagrams (Fig. 1a-d):

Type I: GaAs dominant. The most important feature of this diagram is the GaAs-M tie-line (Fig. 1a), which indicates that GaAs is stable in contact with the elemental metal. This is the only type of diagram in which the elemental metal can be in thermodynamic equilibrium with the semiconductor. In all other cases, heating the M-GaAs couple will result in a chemical reaction and the production of new phases. The simplest way to verify such a diagram is to heat a mixture of the elemental metal and GaAs in a closed, inert container. While some interdiffusion between the two phases will take place, no new phases will form. To further check this result, a $y:x$ mixture of $\text{MGa}_x\text{-MAs}_y$ can be heated in a closed, inert container. A solid-state reaction will occur, producing a mixture of the elemental metal and GaAs. For this type of diagram, MGa_x , MAs_y , and M are all stable with respect to new compound formation when in contact with GaAs.

Type II: MGa_x dominant. The key feature of this diagram is the $\text{MGa}_x\text{-As}$ tie-line (Fig. 1b). From the Gibbs phase rule, the presence of the $\text{MGa}_x\text{-As}$ tie-line precludes the existence of a GaAs-M tie-line. The elemental metal, therefore, cannot be stable in contact with GaAs. The simplest way to verify such a diagram is to heat a mixture of the elemental metal and a large excess

of GaAs in a closed, inert container. At equilibrium, the container will hold a mixture of MGa_x , elemental arsenic, and the excess GaAs. These phases can normally be identified by X-ray or electron diffraction techniques. For this type of diagram, MGa_x is the only metal-containing phase that is stable in contact with GaAs.

Type III: MAS_y dominant. This diagram is the complement of the Type II diagram. Its key feature is the MAS_y -Ga tie-line (Fig. 1c). As before, the simplest way to verify such a diagram is to heat a mixture of the elemental metal and a large excess of GaAs in a closed, inert container. At equilibrium, the container will hold a mixture of MAS_y , elemental gallium, and the excess GaAs. For this type of diagram, MAS_y is the only metal-containing phase that is stable in contact with GaAs.

Type IV: No phase dominant. The most important feature of this diagram is the lack of any tie-lines between a binary compound and the remaining third element (Fig. 1d). Once again, the simplest way to verify such a diagram is to heat a mixture of the elemental metal and a large excess of GaAs in a closed, inert container. At equilibrium, the container will hold a mixture of MGa_x , MAS_y , and the excess GaAs. For this type of diagram, both MGa_x and MAS_y are stable in contact with GaAs, but the elemental metal is not.

B. Complicating factors

In this section, we consider in turn the converse of each of the aforementioned simplifications.

(1) More than one MGa_x or MAS_y binary compound exists. Many metals have more than one MGa_x or MAS_y binary compound. This complication, however, does not change the two key ideas presented in the previous section. First, the reaction of the elemental metal with excess GaAs in a closed, inert container can still be used to determine to which type of diagram the metal belongs. Additional binary compounds may result in more intermediate phases forming in a M-GaAs ternary diffusion couple, but the end phases will remain the same (See Fig. 2.). Second,

for the purpose of materials selection, only the phases with tie-lines to GaAs warrant further study because only these phases can form thermodynamically stable contacts to GaAs (We are not considering materials stable by virtue of kinetic barriers in this analysis, even though they may be useful in practice.). Note that some metals do not form stable MGa_x or MAs_y binary compounds, thereby simplifying the phase diagram determination for these metals. Because our classification scheme is based on the presence of certain key tie-lines, no new categories are introduced by the existence of more than one MGa_x or MAs_y binary compound.

(2) MGa_xAs_y ternary phases exist. If ternary phases exist, then additional experiments will be required to determine the stable tie-lines in the diagram. The basic approach, however, remains the same: through judicious use of the phase rule, a small number of experiments can be performed to determine the stable tie-lines in the M-Ga-As diagram, and only those ternary phases with stable tie-lines to GaAs deserve further study as potential metallization materials. Fortunately, there appear to be few MGa_xAs_y ternary phases.

The presence of a ternary phase creates another category, which we have designated Type V. Although many new tie-line configurations become possible if ternary phases are present, further subclassification of these configurations is unwarranted for our purposes. In Fig. 1e, we have drawn the Type V diagram with a M_2GaAs ternary phase, since this is the most common type of ternary phase observed in M-GaAs reactions. The existence of a M_2GaAs phase implies that the elemental metal cannot be stable in contact with GaAs, i.e., there is no direct GaAs-M tie-line. Moreover, the M_2GaAs phase itself will be stable in contact with GaAs only if no MGa_x - MAs_y tie-line intervenes (Type IV).

(3) Each phase has a homogeneity range. Most $\text{M}(\text{Ga})$ solid solutions and some MGa_x and MAs_y phases have substantial homogeneity ranges. Thus, a pure, stoichiometric metal-containing phase cannot be at complete equilibrium with the GaAs substrate, even if there is a stable tie-line between the metal-containing phase and the GaAs. Metal atoms will diffuse from the pure phase into the GaAs until the solubility limit is reached, and similarly gallium and arsenic will diffuse into

the pure phase. Moreover, differences in the gallium and arsenic solubilities in the metal-containing phase can cause a third phase to form. If arsenic is less soluble than gallium in the metal-containing phase, then the excess arsenic will react to form the arsenic-rich phase adjacent in the M-Ga-As diagram to the metal-containing phase (See Fig. 3.). Conversely, if gallium is less soluble, then the gallium-rich phase adjacent to the metal-containing phase will form.

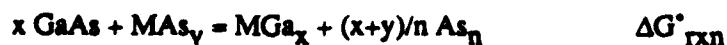
To minimize the net exchange of material between the metal-containing phase and the GaAs substrate, the metal-containing phase should be deposited with the maximum solubility of gallium and arsenic already incorporated in it, if this is feasible. Indeed, several researchers have found that codepositing (M + Ga) improved the contact stability of GaAs metallizations during subsequent high-temperature processing.²³⁻²⁶ Such a saturated film should also be a stable, more reproducible metal diffusion source for the GaAs substrate.

Lastly, note that some Group III-As and Ga-Group V compounds form a complete series of solid solutions with GaAs, thereby producing the final two categories of M-Ga-As phase diagrams, Types VI and VII (Figs. 1f, g).

(4) Liquid phase formation cannot be neglected. "Alloying" is commonly used to make ohmic contacts to GaAs.^{1, 27} The alloying process involves melting and resolidifying the metallization layer. While this process has been used successfully in low-density circuits, the morphological changes brought on by melting and resolidification will become unacceptable as device dimensions continue to shrink. Because liquid phase formation needs to be avoided, solidus data for the phases with stable tie-lines to GaAs need to be determined. This information can be readily obtained from differential thermal analysis experiments. Furthermore, since gallium melts at low temperatures, the composition of the thin film-substrate system must remain outside the three-phase region containing elemental gallium during processing. If liquid phase formation cannot be avoided, then both solidus and liquidus data will be required to explain the liquid and solid compositions and the resolidification path.

(5) Arsenic sublimation cannot be neglected. Because processing is typically done in an open system, there may be substantial arsenic loss to the gas phase as the M-Ga-As system continually tries to establish the equilibrium arsenic pressure.^{28, 29} This arsenic loss will result in varying proportions of the condensed phases in mutual equilibrium (if the overall composition remains in one three-phase region of the diagram) or a sequence of increasingly gallium-rich phases (if tie-lines are crossed). In this instance, the heat-treatment time and temperature are clearly critical to the observed products. Several methods are commonly used to minimize or eliminate arsenic loss to the vapor: an arsenic overpressure can be maintained in the annealing furnace,³⁰ an inert capping layer can be deposited over the wafer,³¹ or rapid thermal annealing can replace conventional furnace annealing.^{32, 33}

In addition, since arsenic must diffuse through the metallization layer prior to sublimation and since equilibrium between the metallization layer and the GaAs substrate fixes the equilibrium arsenic vapor pressure, the metallization material chosen will also affect the rate of arsenic loss. From the Gibbs phase rule, the equilibrium arsenic pressure is fixed in each three-phase region of the ternary diagram, being largest in the three-phase region containing elemental arsenic. If the free energy data are available, then the equilibrium arsenic pressure can be calculated. The partial pressure of each arsenic gas specie (As , As_2 , and As_4) in a particular three-phase region is determined by writing an equilibrium reaction between the arsenic gas specie and the condensed phases comprising the three-phase region.³⁴ For example, for the MGa_x - MAs_y -GaAs three-phase region in Fig. 1d, the reaction is



the As_n partial pressure is given by

$$P_{As_n} = \exp[-\Delta G^\circ_{rxn} / n(x+y)RT]$$

and the total arsenic pressure is the sum of the partial pressures. A similar analysis applies to the equilibrium vapor pressures of both gallium and the metal, but these pressures are typically much less than the arsenic pressure and will not be considered here.

If the most gallium-rich MGa_x phase having a stable tie-line to GaAs is chosen as the metallization material, then it will also have the lowest equilibrium arsenic vapor pressure and potentially lower arsenic losses.²⁰ Note, however, that arsenic sublimation from the GaAs substrate through this phase would result in the undesirable formation of liquid gallium.

(6) Equilibrium between the solid phases is not reached during processing. The time-temperature combinations used in processing may not be sufficient to reach equilibrium. In particular, metastable intermediates in M-GaAs ternary diffusion couples may form. This possibility can be checked by determining whether the same phases in a possible three-phase region are produced by different combinations of starting materials.

Thus, while many complicating factors can and do arise, the use of ternary diagrams to explain M-Ga-As thin-film reactions need not be abandoned. Quite the contrary, the ternary diagrams provide the simplest, most logical framework in which to explain the complications.

III. Specific systems

In this section, we attempt to assign as many metals as possible to the seven categories described in the preceding section. If a M-Ga-As diagram has been previously determined experimentally, then making this assignment is a simple matter. Similarly, if free energy data are available for all the phases in a particular M-Ga-As system, then the diagram can be easily calculated²² and classified. Unfortunately, for many metals, neither of these situations exist. Instead, the only information available for many metals are published studies of metal thin-film reactions with GaAs substrates. For these metals, we try to infer the stable tie-lines (and thus classify the diagram) from the reported reaction products. This method has been quite useful in

explaining ternary reactions involving silicon metallizations.^{35,36} For GaAs metallizations, however, arsenic volatilization can lead to incorrect conclusions using this method. Moreover, for many metal-GaAs thin-film reactions, the product phases have not been identified unambiguously using diffraction methods. For both of these reasons, the diagrams for such metals must be considered only tentative. If anything, this section points out the need to complement thin-film investigations of metal-GaAs reactions with bulk studies in closed systems.

The simplified diagrams in Figs. 4-9 show the equilibria between solid phases at typical processing temperatures. The diagrams are "pseudoisothermal" sections, meaning that changes in the tie-line configurations due to solid-state transformations (eutectoids, peritectoids, melting, etc.) with changing temperature are not explicitly shown.

A. Type I

Metals such as gold, silver, and tungsten have a Type I diagram.

Tsai and Williams²¹ recently determined the Au-Ga-As diagram. The fact that gold has long been employed in GaAs metallizations is consistent with its simplified diagram (Fig. 4a). The many technological problems associated with the use of gold, however, can be appreciated immediately from the exact Au-Ga-As diagram. Gold dissolves a substantial amount of gallium (~10%) and some arsenic (<1%) at a processing temperature of 300°C.³⁷ The metal composition in equilibrium with GaAs is a saturated ternary solid solution, whose composition changes with annealing temperature. Thus, when pure gold is annealed on GaAs, the substrate locally disintegrates, a ternary solid solution forms, and the excess arsenic crystallizes or sublimes. Several researchers have shown that this interdiffusion dramatically alters the microstructure and resulting electrical properties of the metal-semiconductor interface.^{26,38-40} From a thermodynamic perspective, the problem can be minimized either by depositing an alloy of suitable composition (or even one supersaturated with gallium and arsenic) or by substituting a Au-Ga compound for pure gold, as demonstrated by Guha *et al.*²⁶ and Williams *et al.*²⁰ respectively.

The simplified Ag-Ga-As diagram shown in Fig. 4b can be derived from Panish's work.¹³ The ϵ phase is stable only in the temperature range 446-582°C.⁴¹

Tungsten forms two compounds with arsenic⁴² — W_2As_3 and WAs_2 — but none with gallium. From available thermochemical data,⁴³ it can be shown that the W-GaAs tie-line is favored over the Ga- W_2As_3 tie-line and that therefore the former exists. Thus, we believe the W-Ga-As diagram is as shown in Fig. 4c. At first glance, a recent study⁴⁴ of SiO_2 -encapsulated W-GaAs diffusion couples would appear to contradict the existence of the W-GaAs tie-line. This study found that no new phases formed after annealing at 750°C, but a reaction producing W_2As_3 occurred at 900°C. However, greater gallium solubility in tungsten at higher temperatures and selective gallium loss through the SiO_2 encapsulant can explain this high-temperature instability. Thus, during high-temperature annealing, the composition of the system moved from the W-GaAs two-phase region to the W- W_2As_3 -GaAs three-phase region.

For completeness, we note that the semiconductors silicon, germanium, and tin also have Type I diagrams, as determined by Panish.^{8,11} Simplified diagrams for silicon and germanium are shown in Figs. 4d and 4e. Like tungsten, silicon and germanium have two arsenides, but no gallium-based phases. The mutual equilibrium of silicon and germanium with GaAs is expected from chemical considerations and is quite important technologically for heteroepitaxial growth of GaAs films on silicon substrates, and vice versa. Moreover, Kavanaugh *et al.*⁴⁵ have recently investigated the formation of thermally stable, degenerately doped polycrystalline silicon contacts to GaAs.

B. Types II and III.

Few metals have these types of diagrams since it is unusual for either elemental arsenic (Type II) or elemental gallium (Type III) to be in equilibrium with a complementary binary compound. Lahav and Eizenberg⁴⁶ reported that a thin film of tantalum reacts with GaAs at 650°C and produces TaAs and liquid gallium. Tantalum thus appears to have a Type III diagram. In

addition, x-ray photoemission spectroscopy has identified metal arsenides and "metallic" gallium as products of GaAs reactions with Re, Ir, Tb, Dy, and Er monolayers.^{47, 48} If "metallic" gallium corresponds to elemental gallium, then these metals also have MA_s dominant Type III diagrams. On the other hand, if "metallic" gallium corresponds to MGa_x compounds, then these metals belong to the no phase dominant Type IV category. Note that diffraction studies of thicker films would be simpler to perform, easier to interpret, and more representative of thin-film behavior in actual metallizations than spectroscopic studies of monolayer films. Based on published results of numerous M-GaAs thin-film reactions, there do not appear to be any metals which have Type II diagrams. However, studies of GaAs oxidation by Thurmond *et al.*¹⁹ have shown that the Ga-As-O diagram is basically of this type (Fig. 5).

C. Types IV and V.

The most commonly found M-Ga-As diagram is Type IV, no phase dominant. Copper, chromium, and platinum can definitely be assigned to this category, as can palladium, nickel, and cobalt at high temperatures. In Fig. 6, the copper diagram is established by Panish's work,¹³ the chromium diagram from an X-ray analysis by Deal,¹⁷ and the platinum diagram from thin film studies.⁴⁹⁻⁵²

The Pd-Ga-As diagram determined by El-Boragy and Schubert⁵³ (Fig. 7) can be used to explain several recent studies of Pd-GaAs thin-film diffusion couples.⁵⁴⁻⁵⁸ Their diagram predicts that the final products of a reaction between a thin film of palladium and a GaAs substrate should be a mixture of PdGa, PdAs₂, and excess GaAs. Moreover, their diagram predicts that several palladium-rich phases, including two ternary phases, may precede the formation of the final equilibrium products. In the thin-film studies, a ternary phase, designated "Phase I" by Sands *et al.*,⁵⁷ formed in the temperature range 25-250°C; Phase I was followed by a second ternary phase, designated "Phase II", between 250-500°C; and finally, a mixture of PdGa and PdAs₂ formed at 600°C.⁵⁸ The crystal structure, lattice parameters, and stoichiometry of Phase I

— hexagonal, $a_0 \sim 0.67$ nm and $c_0 \sim 0.37$ nm, $\sim \text{Pd}_{2.4}\text{GaAs}$ — match those of the ternary phase designated $\text{Pd}_2\text{Ga}_N\text{As}_{1-N}$ by El-Boragy and Schubert.⁵⁹ Similarly, Phase II — hexagonal, $a_0 \sim 0.9$ nm and $c_0 \sim 0.34$ nm, $\sim \text{Pd}_{3.3}\text{Ga}_{1.2}\text{As}_{0.8}$ — matches the phase designated $\text{Pd}_{12}\text{Ga}_5\text{As}_2$ by El-Boragy and Schubert.⁵³

Type V diagrams that have a ternary phase with the stoichiometry M_2GaAs might be regarded as a subset of Type IV since the ternary phase usually transforms to a mixture of MGa_x and MA_y after high-temperature annealing. Whether these ternary phases are metastable intermediates in M-GaAs diffusion couples or are stable, low-temperature phases with tie-lines to GaAs remains to be determined. Metals in this category include nickel^{60, 61} and perhaps cobalt⁶². The diagrams for these metals are drawn with dashed tie-lines to the ternary phase because of the present uncertainty about the stability of the ternary phase (Fig. 8).

D. Types VI and VII.

These diagrams exist for elements that can readily substitute for gallium or arsenic in the GaAs crystal structure, thereby forming ternary semiconductor compounds. Thus, aluminum and indium belong to Type VI, and phosphorus belongs to Type VII. While technological interest centers on their optical properties, one of the ternary semiconductors — $\text{In}_x\text{Ga}_{1-x}\text{As}$ — has also been suggested for use in graded heterojunction ohmic contacts.^{63, 64}

Photoemission studies of aluminum monolayer reactions with GaAs substrates are consistent with aluminum having a Type VI diagram. These studies⁶⁵⁻⁶⁸ have found that aluminum replaces gallium in the top layers of the GaAs substrate and that free gallium forms on the surface. For thicker aluminum films, the observed extent of reaction depends on the time-temperature combinations used and the amount of oxygen contamination present.⁶⁹⁻⁷²

IV. APPLICATIONS

The ideal metallization is a material that does almost nothing. It does not react with the substrate. It does not interdiffuse with the substrate. It does not react with other solids and gases with which it comes in contact. It does not melt during processing. Essentially all it does is conduct electricity well. Of course, actual metallization materials cannot satisfy all of these criteria, and compromises have to be made. Note, however, that ternary diagrams provide the basis for evaluating many of these criteria. The tie-lines in a ternary diagram indicate which phases will be stable in contact with GaAs. The solubility data show the maximum extent of interdiffusion as a function of temperature. The solidus data reveal the temperature at which melting begins for particular solid compositions.

Most materials comprising an integrated circuit are inherently in a metastable state. Short-time, low-temperature processing is used to prevent the materials from reaching a complete equilibrium state (and the undesirable properties associated with that state). For metallization materials, however, we suggest that a complementary approach may be useful: if the metallization is deposited with a composition that is already near equilibrium with the GaAs substrate, then minimal interaction between the metallization and the substrate will occur during subsequent processing. Thus, besides rapid thermal annealing, the composition of the as-deposited metallization layer can also be used to prevent solid-state reactions, to minimize interdiffusion, and to reduce arsenic sublimation.

If such an approach is adopted, then the following steps should be taken to identify optimal metallization materials. First, for a particular metal, the metal-containing phases with stable tie-lines to GaAs need to be determined. As shown in Section IIA, most of these phases can be deduced from the results of reacting the metal with excess GaAs in a closed, inert container. Second, the electrical properties of the stable phases have to be evaluated. Stable phases with high resistivities need not be examined further for use as metallizations. Third, for those stable phases with suitable electrical properties, the solubility and solidus data need to be measured to ascertain

the optimum as-deposited composition and the maximum allowable processing temperature. In addition to the thermodynamic and electrical data, kinetic and microstructural data also must be determined. The time-temperature combinations required to crystallize the as-deposited film, the crystallization path (i.e., the intermediate phases formed from the as-deposited film), and the resulting film morphology all must be established. Moreover, the diffusion of the metal into the substrate has to be quantified, as this diffusion will alter the electrical properties of the contact. Note also that the amount of metal diffusion will depend on which phase is used as the metal source.

The search for stable, low-resistivity GaAs metallizations need not be limited to M , MGa_x , and MAs_y phases: other phases can also be considered. Indeed, based on their low resistivity and high thermal stability on silicon, metal silicides are already being considered.⁷³⁻⁷⁷ It has been found that the silicide used on GaAs need not be the most silicon-rich silicide.⁷⁵ This result should not be considered surprising. While only the most silicon-rich silicide has a stable tie-line to silicon, several silicides can have stable tie-lines to GaAs. A partial thermodynamic analysis of the stability of silicides on GaAs has appeared recently.⁷⁸ However, a complete analysis requires determination of the stable tie-lines in the M -Si-Ga-As quaternary diagram. For example, using the Gibbs phase rule, it is straightforward to show that both WSi_2 and W_5Si_3 have stable tie-lines to GaAs in the W -Si-Ga-As diagram. Because tungsten and silicon also have stable tie-lines to GaAs, the relevant phase equilibria can be represented by a pseudoternary section of the isothermal quaternary diagram (See Fig.9.).

Finally, we note that the analysis outlined here can be applied to metallizations for any compound semiconductor. Our choice of a particular compound semiconductor, GaAs, was for illustrative purposes only.

V. CONCLUSIONS

We have proposed a classification scheme for phase equilibria in M-Ga-As systems. Through judicious use of the phase rule, a small number of experiments can be used to determine to which type of diagram a particular metal belongs. Moreover, phases that are stable in contact with GaAs can be rapidly identified. This approach may enable a more systematic search for stable metallizations. Using previously published phase diagrams, available free energy data, and reported products of metal thin film reactions with GaAs substrates, we have assigned as many elements as possible to the seven generic types. Many M-Ga-As diagrams, however, remain unknown, and some of the present ones cannot be regarded as definitive. Further studies in this area will aid in the production of reproducible and reliable GaAs metallizations.

Acknowledgements

Partial financial support from the NSF-MRL Program through the Center for Materials Research at Stanford University is gratefully acknowledged.

References

1. N. Braslau, J. Vac. Sci. Technol. **19**, 803 (1981).
2. N. Braslau, Thin Solid Films **104**, 391 (1983).
3. A. Piotrowska, A. Guivarc'h, and G. Pelous, Solid-State Electron. **26**, 179 (1983).
4. A.K. Sinha and J.M. Poate, in *Thin Films — Interdiffusion and Reactions*, edited by J.M. Poate, K.N. Tu, and J.W. Mayer (Wiley-Interscience, New York, 1978), p. 407.
5. L.J. Brillson, Phys. Rev. Lett. **40**, 260 (1978).
6. L.J. Brillson, Thin Solid Films **89**, 461 (1982).
7. For an overview, see F.N. Rhines, *Phase Diagrams in Metallurgy*, McGraw-Hill, New York (1956).
8. M.B. Panish, J. Less-Common Metals **10**, 416 (1966).
9. M.B. Panish, J. Phys. Chem. Solids **27**, 291 (1966).
10. M.B. Panish, J. Electrochem. Soc. **113**, 861 (1966).
11. M.B. Panish, J. Electrochem. Soc. **113**, 1226 (1966).
12. M.B. Panish, J. Electrochem. Soc. **114**, 91 (1967).
13. M.B. Panish, J. Electrochem. Soc. **114**, 516 (1967).
14. M.B. Panish, J. Phys. Chem. Solids **30**, 129 (1969).
15. M.B. Panish, J. Electrochem. Soc. **117**, 1202 (1970).
16. M.B. Panish and M. Ilegems, Prog. in Solid State Chem. **7**, 39 (1972).
17. M.D. Deal, Ph.D. Thesis, Stanford University (1983).
18. M.D. Deal and D.A. Stevenson, J. Electrochem. Soc. **131**, 2343 (1984).
19. C.D. Thurmond, G.P. Schwartz, G.W. Kammlott, and B. Schwartz, J. Electrochem. Soc. **127**, 1366 (1980).
20. R.S. Williams, J.R. Lince, T.C. Tsai, and J.H. Pugh, Mat. Res. Soc. Symp. Proc., 1986 (in press).
21. C.T. Tsai and R.S. Williams, J. Mater. Res. **1**, 352 (1986).
22. R. Beyers, J. Appl. Phys. **56**, 147 (1984).

23. T. Sebestyen, H.L. Hartnagel, and L.H. Herron, *IEEE Trans. Electron Devices* ED-22, 1073 (1975).
24. T. Sebestyen, I. Mojzes, and D. Szigethy, *Electronics Lett.* 16, 504 (1980).
25. I. Mojzes, T. Sebestyen, P.B. Barna, G. Gergely, and D. Szigethy, *Thin Solid Films* 61, 27 (1979).
26. S. Guha, B.M. Arora, and V.P. Salvi, *Solid-State Electron.* 20, 431 (1977).
27. N. Braslau, J.B. Gunn, and J.L. Staples, *Solid-State Electron.* 10, 381 (1967).
28. E. Kinsbron, P.K. Gallagher, and A.T. English, *Solid-State Electron.* 22, 517 (1979).
29. I. Mojzes, T. Sebestyen, and D. Szigethy, *Solid-State Electron.* 25, 449 (1982).
30. C.T. Lee, *Appl. Phys. Lett.* 46, 554 (1985).
31. A.A. Lakhani, L.C. Oliver, E.F. Dvorsky, and E.U. Hempfling, *IEEE Electron Device Lett.* EDL-6, 586 (1985).
32. S.J. Pearton, K.D. Cummings, and G.P. Vella-Coleiro, *J. Electrochem. Soc.* 132, 2743 (1985).
33. M. Kuzuhara, T. Nozaki, and H. Kohzu, *J. Appl. Phys.* 58, 1204 (1985).
34. N.A. Godshall, I.D. Raistrick, and R.A. Huggins, *J. Electrochem. Soc.* 131, 543 (1984).
35. R. Beyers, R. Sinclair, and M.E. Thomas, *J. Vac. Sci. Technol. B* 2, 781 (1984).
36. R. Beyers, *Mat. Res. Soc. Symp. Proc.* 47, 143 (1985).
37. C.J. Cooke and W. Hume-Rothery, *J. Less-Common Metals* 10, 42 (1966).
38. J. Gyulai, J.W. Mayer, V. Rodriguez, A.Y.C. Yu, and H.J. Gopen, *J. Appl. Phys.* 42, 3578 (1971).
39. K. Kumar, *Jap. J. Appl. Phys.* 18, 713 (1979).
40. W.G. Petro, I.A. Babalola, T. Kendelewicz, I. Lindau, and W.E. Spicer, *J. Vac. Sci. Technol. A* 1, 1181 (1983).
41. R.P. Elliott, *Constitution of Binary Alloys, First Supplement* (McGraw-Hill, New York, 1965), p. 2.
42. J.B. Taylor, L.D. Calvert, and M.R. Hunt, *Can. J. Chem.* 43, 3045 (1965).
43. J.J. Murray, P.L. Mart, and J.B. Taylor, *J. Less-Common Metals* 64, 45 (1979).

44. S.K. Cheung, K.-M. Yu, T. Sands, N.W. Cheung, J.M. Jaklevic, and E.E. Haller, *Mat. Res. Soc. Symp. Proc., Compound Semiconductor Materials, Spring Meeting, 1986* (in press).
45. K.L. Kavanagh, J.W. Mayer, C.W. Magee, J. Sheets, J. Tong, P.D. Kirchner, J.M. Woodall, and I. Haller, *J. Electrochem. Soc.* **133**, 1176 (1986).
46. A. Lahav and M. Eizenberg, *Appl. Phys. Lett.* **46**, 430 (1985).
47. J.R. Waldrop, S.P. Kowalczyk, and R.W. Grant, *J. Vac. Sci. Technol.* **21**, 607 (1982).
48. J.R. Waldrop, *Appl. Phys. Lett.* **46**, 864 (1985).
49. V. Kumar, *J. Phys. Chem. Solids* **36**, 535 (1975).
50. S.P. Murarka, *Solid-State Electron.* **17**, 869 (1974).
51. A.K. Sinha, *Appl. Phys. Lett.* **26**, 171 (1975).
52. C. Fontaine, T. Okumura, and K.N. Tu, *J. Appl. Phys.* **54**, 1404 (1983).
53. M. El-Boragy and K. Schubert, *Z. Metallkde.* **72**, 279 (1981).
54. P. Oelhafen, J.L. Freeouf, T.S. Kuan, T.N. Jackson, and P.E. Batson, *J. Vac. Sci. Technol. B* **1**, 588 (1983).
55. T.S. Kuan, J.L. Freeouf, P.E. Batson, and E.L. Wilkie, *J. Appl. Phys.* **58**, 1519 (1985).
56. T. Sands, V.G. Keramidas, R. Gronsky, and J. Washburn, *Materials Lett.* **3**, 409 (1985).
57. T. Sands, V.G. Keramidas, A.J. Yu, K.-M. Yu, R. Gronsky, and J. Washburn, *J. Mater. Res.*, 1986 (in press).
58. K.-M. Yu, J.M. Jaklevic, and E.E. Haller, *Mat. Res. Soc. Symp. Proc., Materials Characterization, Spring Meeting, 1986* (in press).
59. M. El-Boragy and K. Schubert, *Z. Metallkde.* **61**, 579 (1970).
60. M. Ogawa, *Thin Solid Films* **70**, 181 (1980).
61. T. Sands, V.G. Keramidas, J. Washburn, and R. Gronsky, *Appl. Phys. Lett.* **48**, 402 (1986).
62. A.J. Yu, G.J. Galvin, C.J. Palmstrom, and J.W. Mayer, *Appl. Phys. Lett.* **47**, 934 (1985).
63. A.A. Lakhani, *J. Appl. Phys.* **56**, 1888 (1984).
64. D.C. Marvin, N.A. Ives, and M.S. Leung, *J. Appl. Phys.* **58**, 2659 (1985).

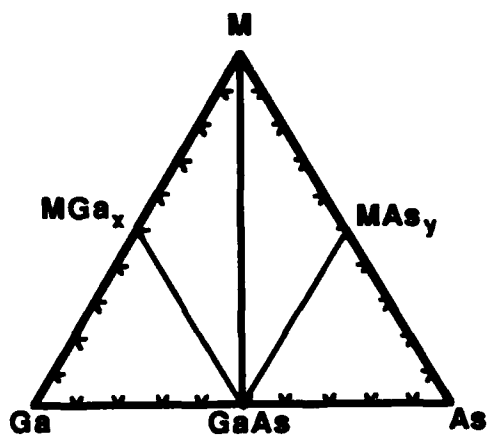
65. R.Z. Bachrach, J. Vac. Sci. Technol. **15**, 1340 (1978).
66. L.J. Brillson, R.Z. Bachrach, R.S. Bauer, and J. McMnamin, Phys. Rev.Lett. **42**, 397 (1979).
67. P. Skeath, I. Lindau, P. Pianetta, P.W. Chye, C.Y. Su, and W.E. Spicer, J. Elect. Spectr. Relat. Phenom. **17**, 259 (1979).
68. A. Khan, L.J. Brillson, A.D. Katnani, and G. Margaritondo, Solid State Comm. **38**, 1269 (1981).
69. N.M. Johnson, T.J. Magee, and J. Peng, J. Vac. Sci. Technol. **13**, 838 (1976).
70. A. Christou and H.M. Day, J. Appl. Phys. **47**, 4217 (1976).
71. A. Christou, J.E. Davey, H.M. Day, and A.C. Macpherson, J. Appl. Phys. **50**, 1139 (1979).
72. A.K. Srivastava and B.M. Arora, Solid-State Electron. **24**, 1049 (1981).
73. N. Yokoyama, T. Ohnishi, K. Odani, H. Onodera, and M. Abe, IEEE Trans. Electron Devices **ED-29**, 1541 (1982).
74. W.F. Tseng, B. Zhang, D. Scott, S.S. Lau, A. Christou, and B.R. Wilkins, IEEE Electron Device Lett. **EDL-4**, 207 (1983).
75. T. Ohnishi, N. Yokoyama, H. Onodera, S. Suzuki, and A. Shibatomi, Appl. Phys. Lett. **43**, 600 (1983).
76. J.K. Truman and P.H. Holloway, J. Vac. Sci. Technol. A **3**, 992 (1985).
77. S.S. Gill, G.J. Pryce, and J. Woodward, Physica **129B**, 430 (1985).
78. S.S. Lau, W.X. Chen, E.D. Marshall, and C.S. Pai, Appl. Phys. Lett. **47**, 1298 (1985).

Figure Captions

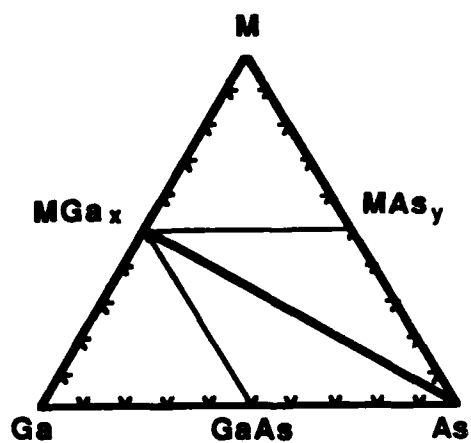
1. The seven basic types of M-Ga-As phase diagrams. Key tie-lines in the diagrams are emboldened. In (f) and (g), the one-phase and two-phase regions have been expanded for clarity.
2. Interpretation of the M-excess GaAs reaction when more than one MGa_x and/or MAs_y compound exists. "X" marks the three-phase region the system will be in when equilibrium is reached. "⊗" denotes the phases that will be stable with respect to new compound formation when in contact with GaAs.
3. Interpretation of the Type I M-GaAs diffusion couple when the metal has a large gallium solubility, but little arsenic solubility. The arsenic-rich phase (elemental arsenic in this example) adjacent to the metal-containing phase (elemental metal in this example) forms, and the system composition lies in the M(Ga)-As-GaAs three-phase region at equilibrium.
4. Pseudoisothermal sections of elements with Type I diagrams: (a) gold, (b) silver, (c) tungsten, (d) silicon, and (e) germanium.
5. A schematic of the Ga-As-O diagram of Thurmond *et al.*¹⁹

6. Pseudoisothermal sections of metals with Type IV diagrams: (a) copper, (b) chromium, and (c) platinum. In the copper diagram, Panish's work¹³ indicates that the Cu_3As - Cu_9Ga_4 tie-line exists at $\sim 600^\circ\text{C}$, but the Cu_8As - GaAs tie-line may exist at lower temperatures ($\sim 400^\circ\text{C}$). To account for this possibility, both of these tie-lines are drawn with dashes.
7. A schematic of the Pd-Ga-As diagram of El-Boragy and Schubert.⁵³ $T = 600^\circ\text{C}$.
8. Pseudoisothermal sections for (a) nickel and (b) cobalt. The diagrams for these metals are drawn with dashed tie-lines to the ternary phase because of the present uncertainty about the stability of the ternary phase.
9. (a) Quaternary and (b) pseudoternary representations of silicide equilibria with GaAs in the W-Si-Ga-As system.

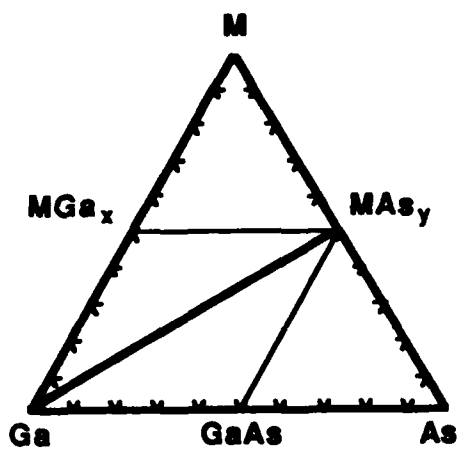
(a)



(b)



(c)



(d)

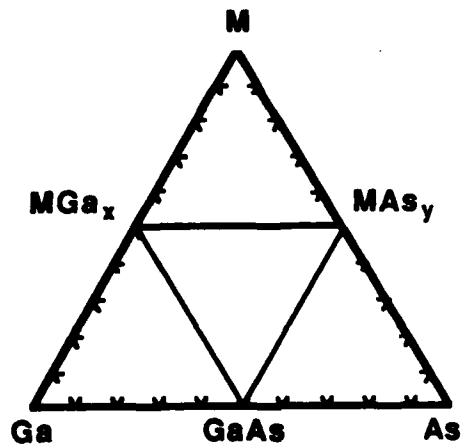
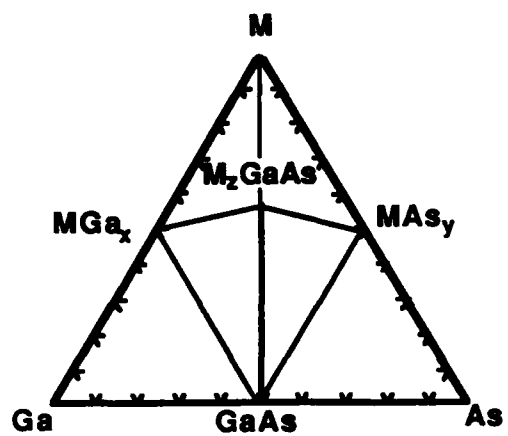
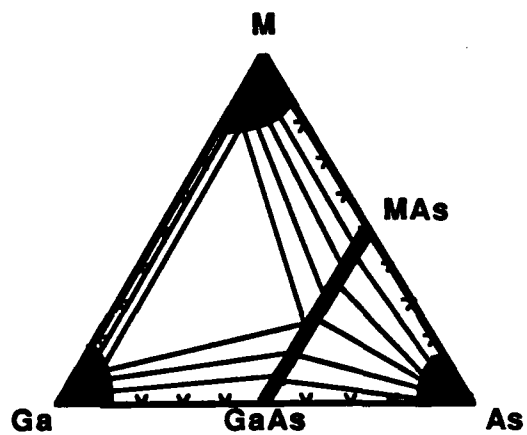


Fig. 1

(e)



(f)



(g)

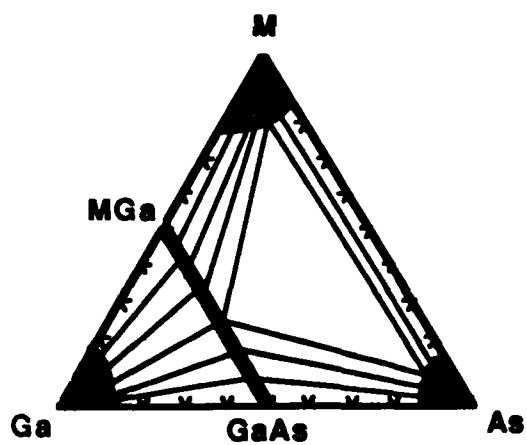


Fig. 1

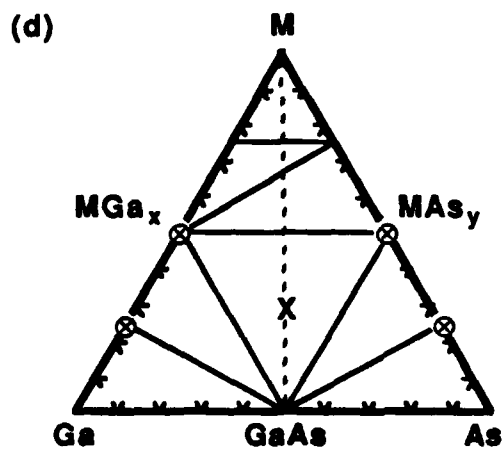
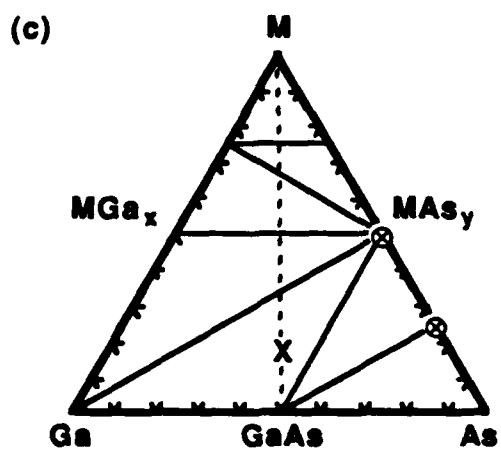
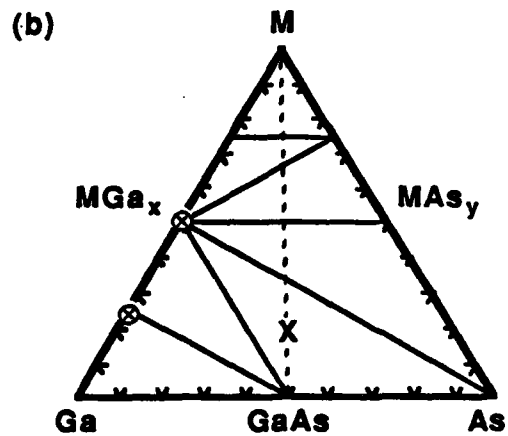
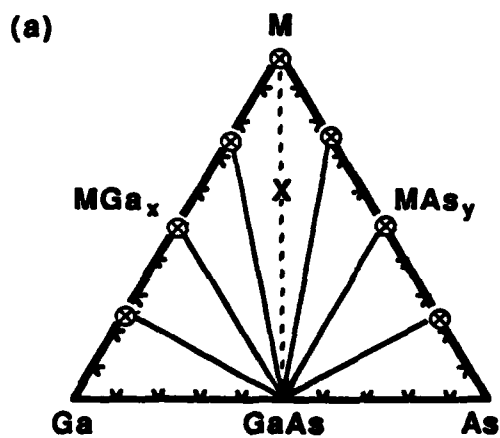


Fig. 2

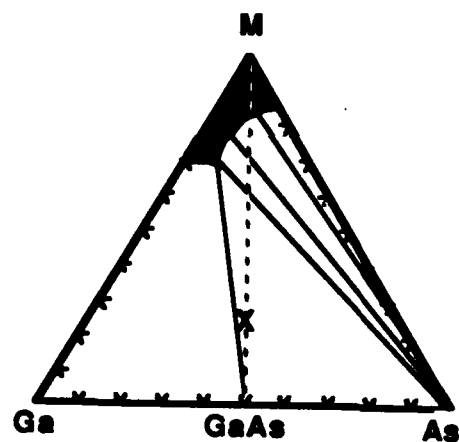
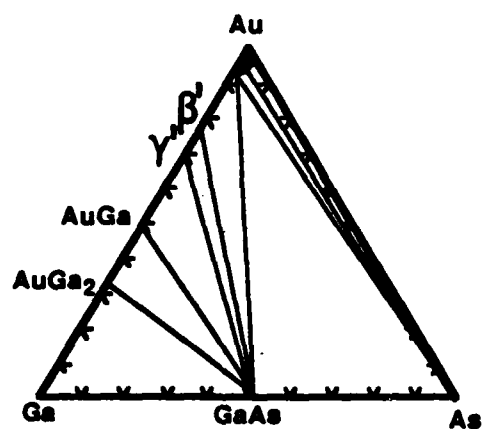
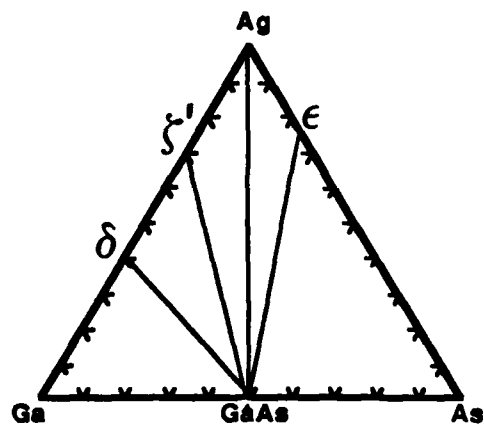


Fig. 3 11

(a)



(b)



(c)

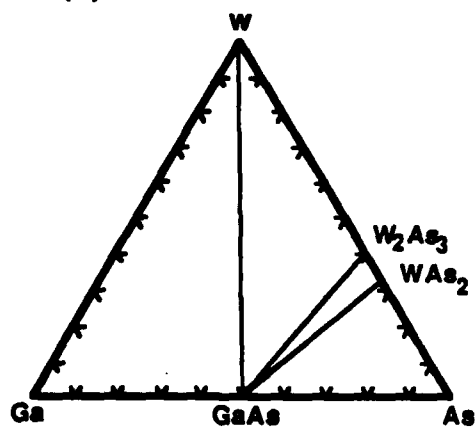
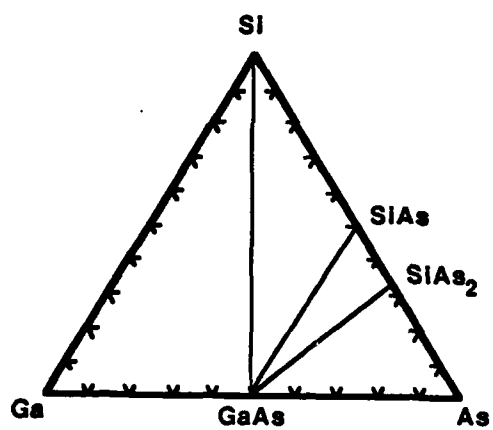


Fig. 4

(d)



(e)

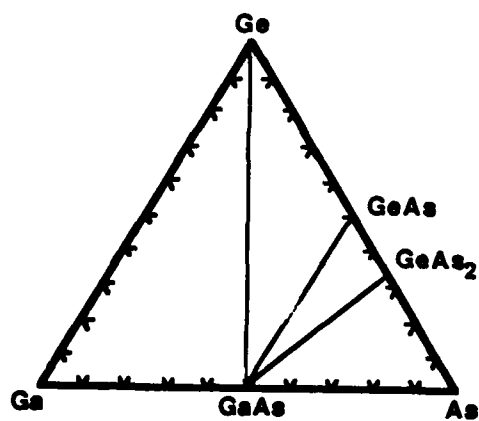


Fig. 4

Type II

Ga-As-O

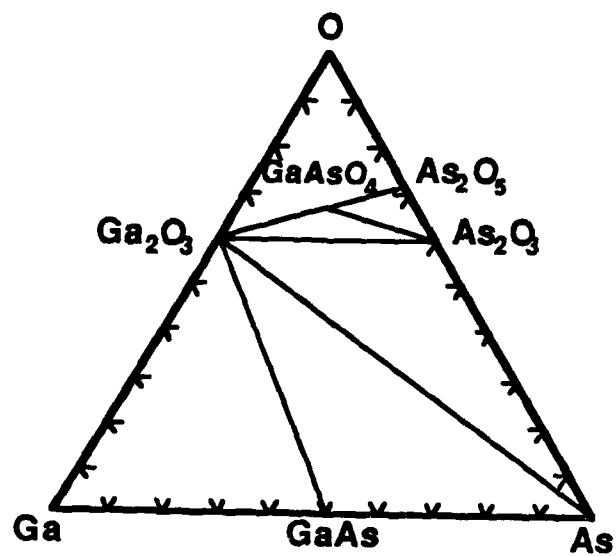
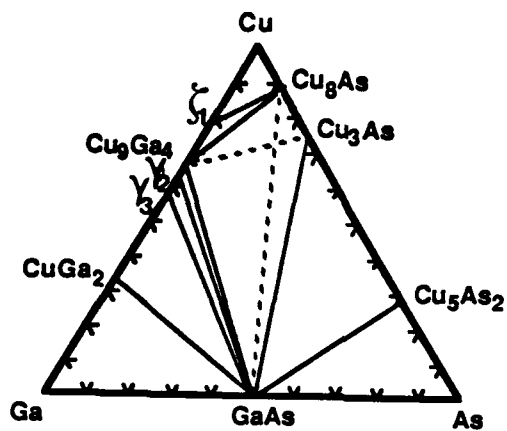
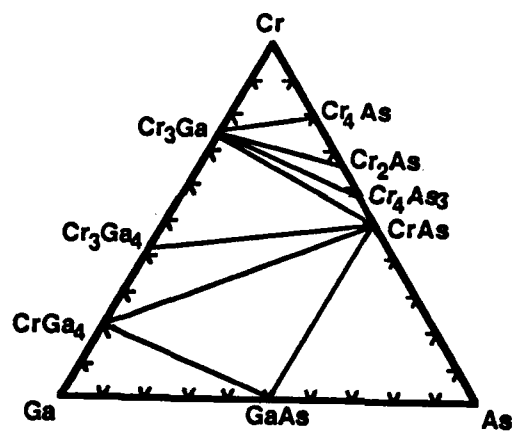


Fig. 5

(a)



(b)



(c)

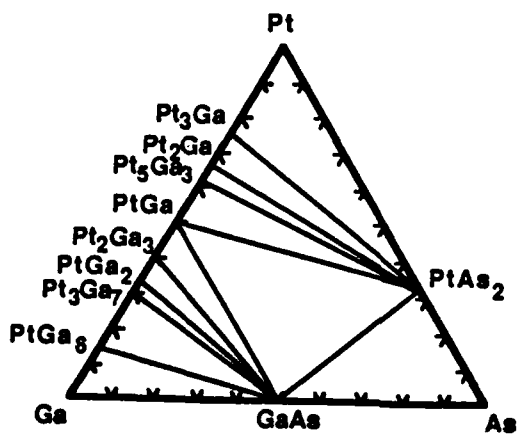


Fig. 6

Pd-Ga-As

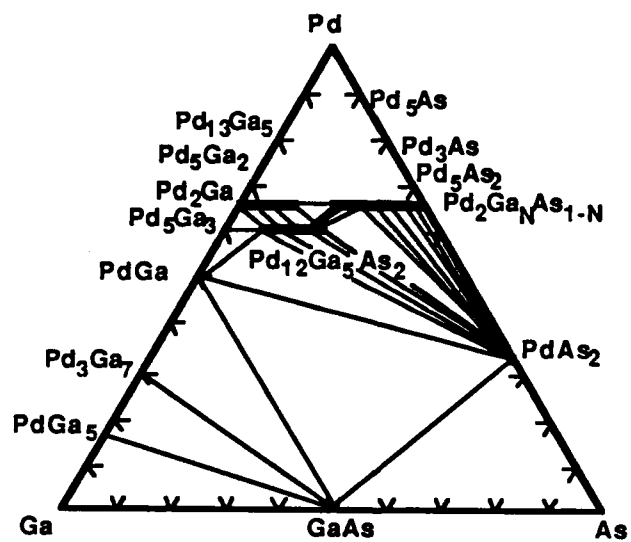
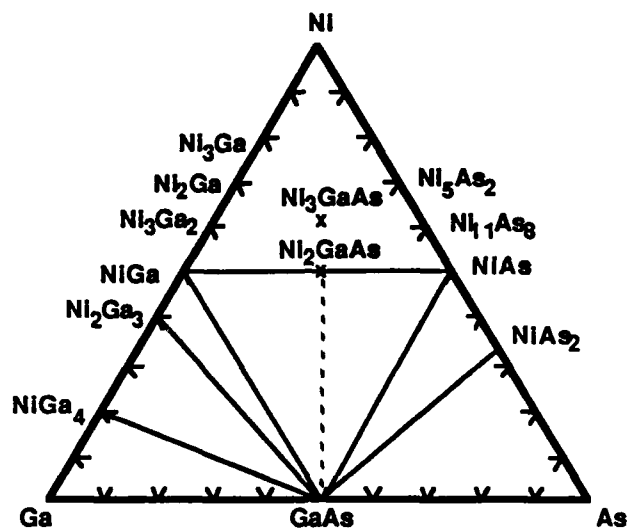


Fig. 7 . 68

Ni-Ga-As



Co-Ga-As

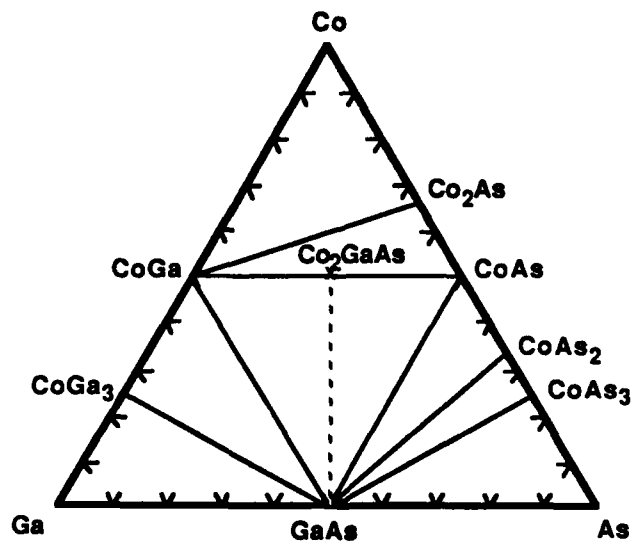
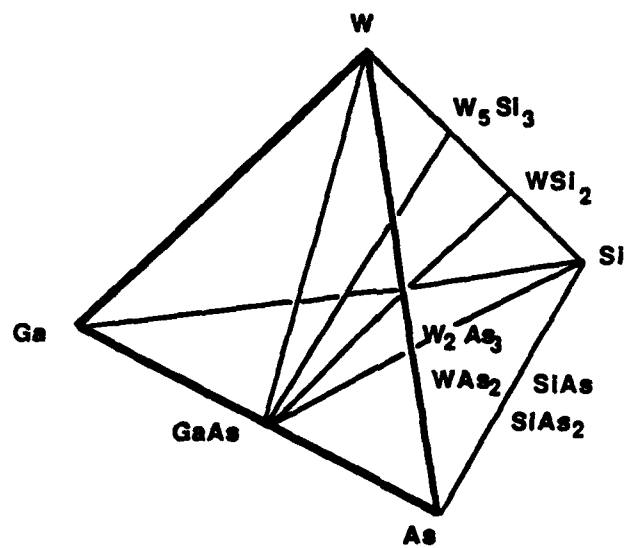


Fig. 8

W-Si-Ga-As



W-Si-GaAs

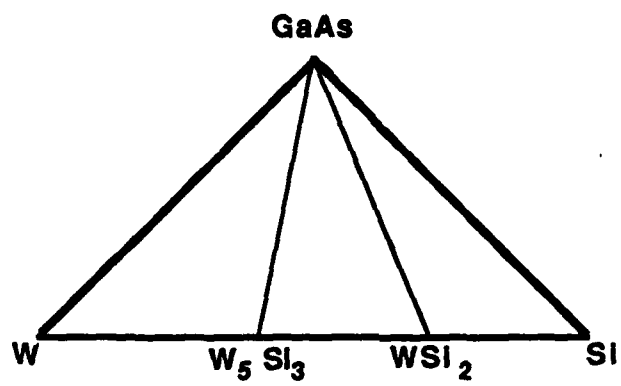


Fig. 9 70

slide #1

**Phase Equilibria in Metal-Gallium-Arsenic Systems:
Thermodynamic Considerations for Metallization Materials**

**KI Bum Kim, Robert Beyers* and Robert Sinclair
Department of Materials Science and Engineering
Stanford University, Stanford**

***present address: IBM Almaden Research Center**



slide #2

Outline

Thermodynamics

Simplest Cases - Idealized systems

Complicating Factors - real systems

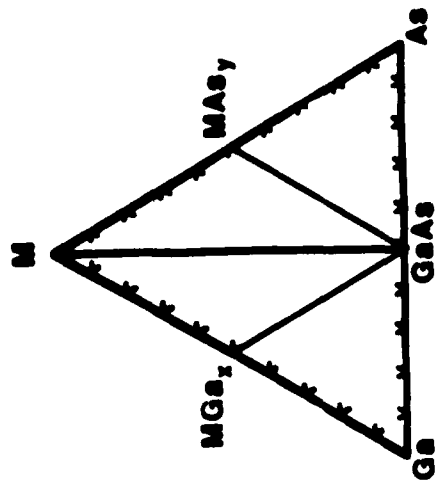
Applications

Conclusions

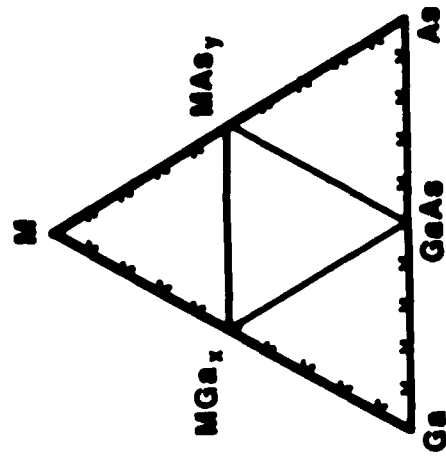
slide #3

Simplest Cases

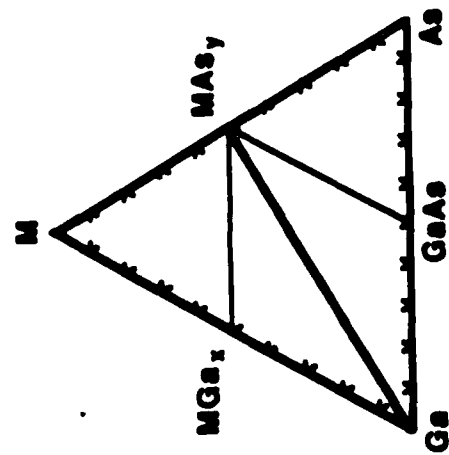
Type I: GaAs dominant



Type IV: no phase dominant



Type III: MA_y dominant

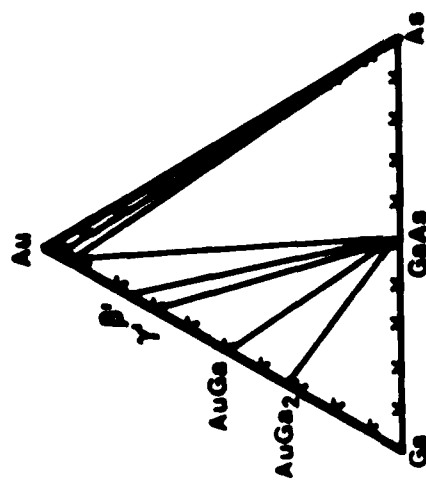


slide #4

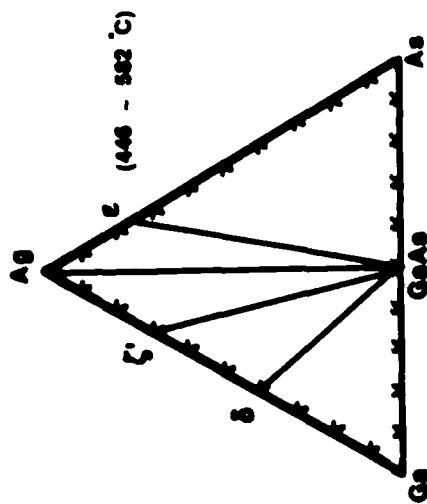
Complicating Factors

Type I

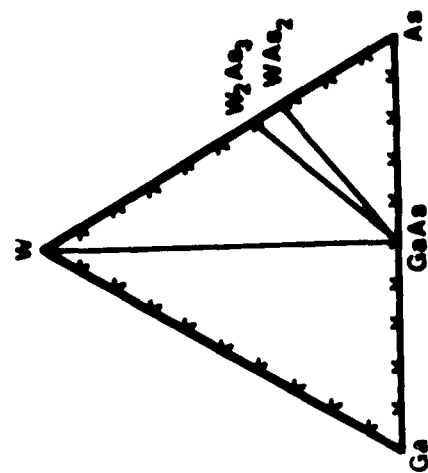
Au-Ga-As



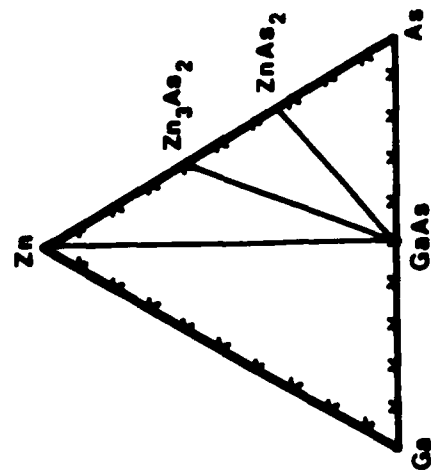
Ag-Ga-As



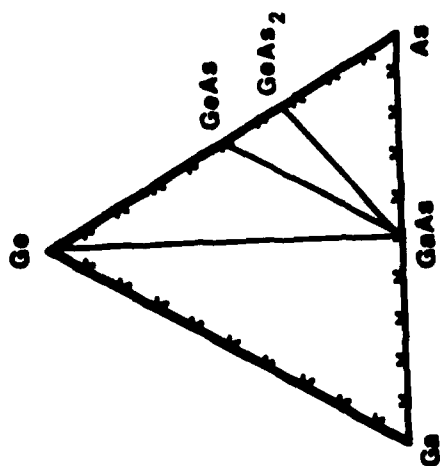
W-Ga-As



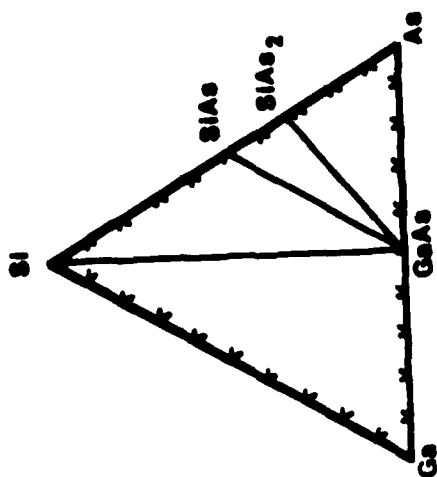
Zn-Ga-As



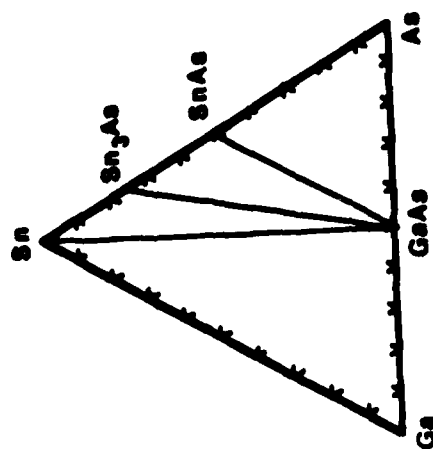
Ge-Ga-As



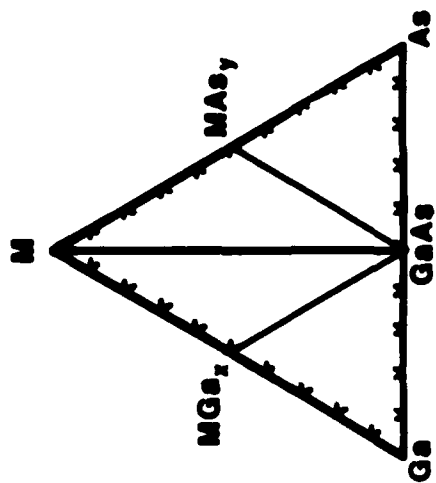
Si-Ga-As



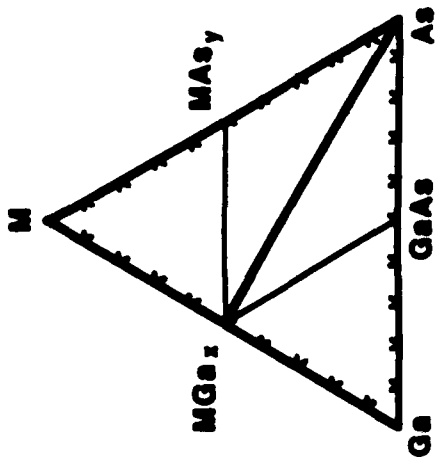
Sn-Ga-As



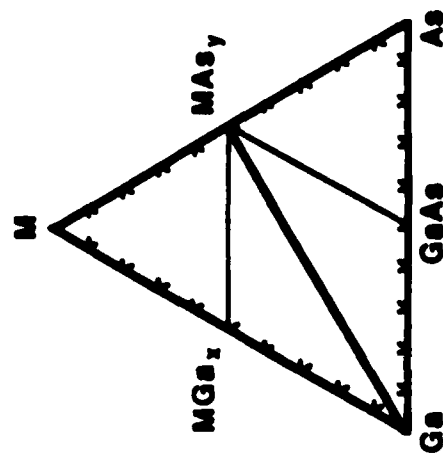
Type I: GaAs dominant



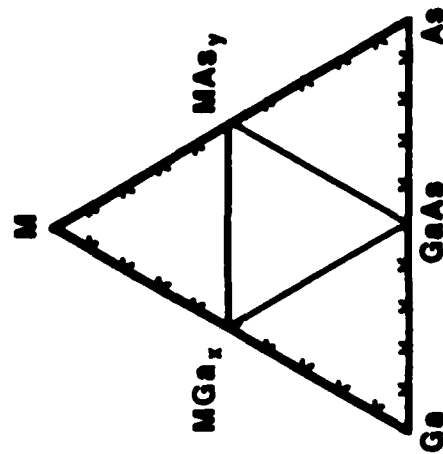
Type II: MGa_z dominant



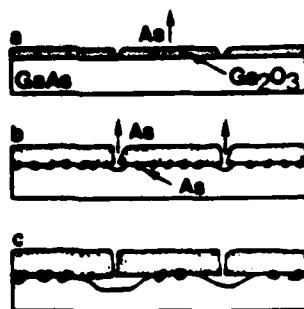
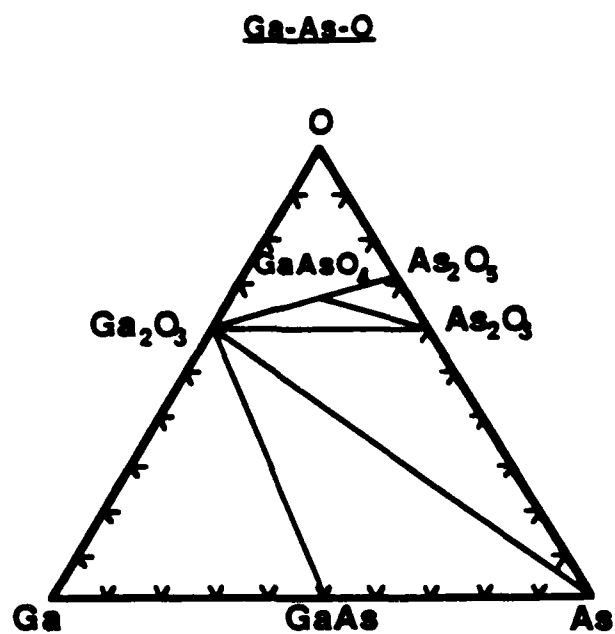
Type III: MAS_y dominant



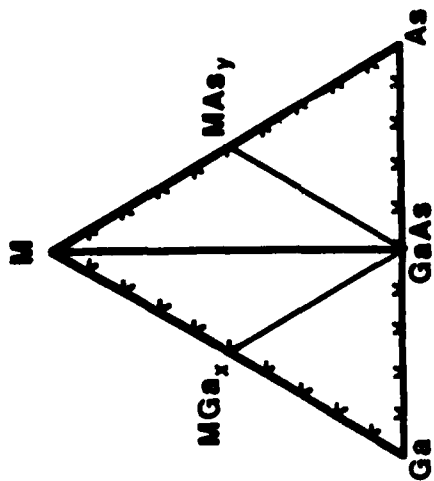
Type IV: no phase dominant



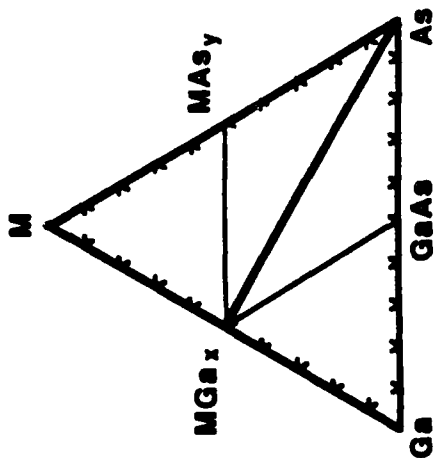
Type II



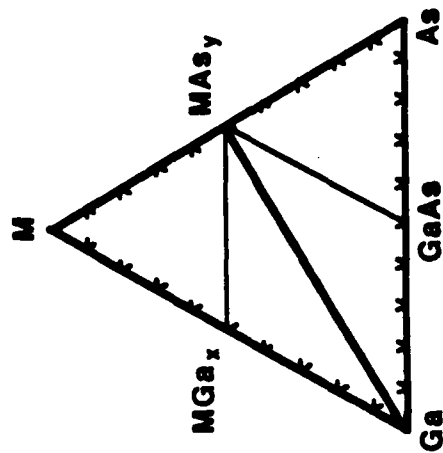
Type I: GaAs dominant



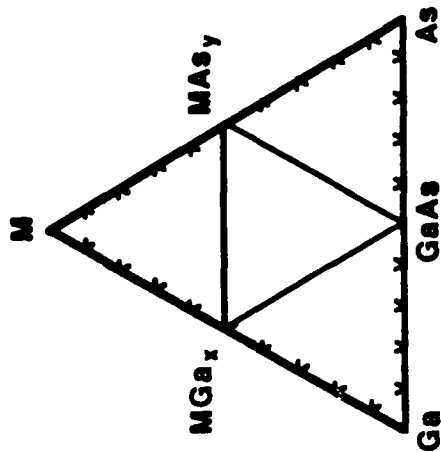
Type II: MGa_x dominant



Type III: MAs_y dominant

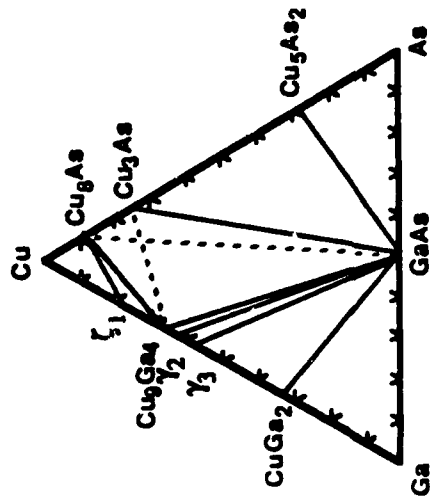


Type IV: no phase dominant

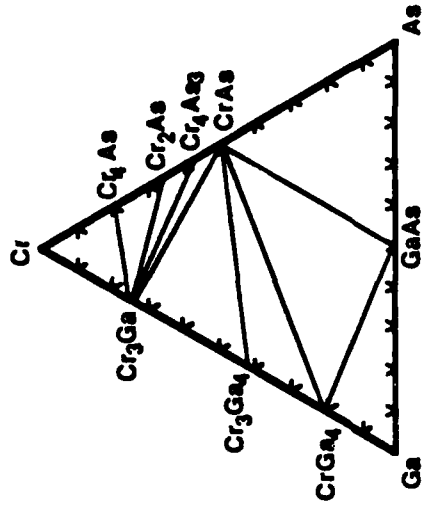


Type IV:

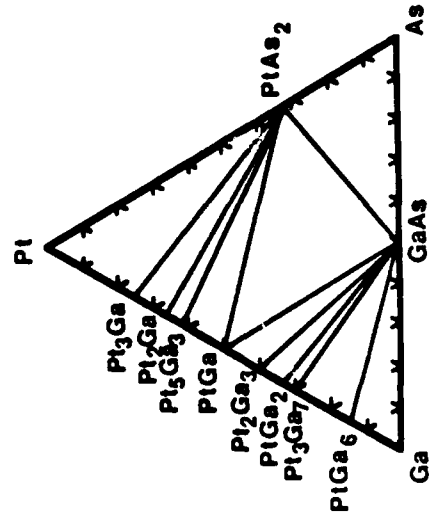
Cu-Ga-As

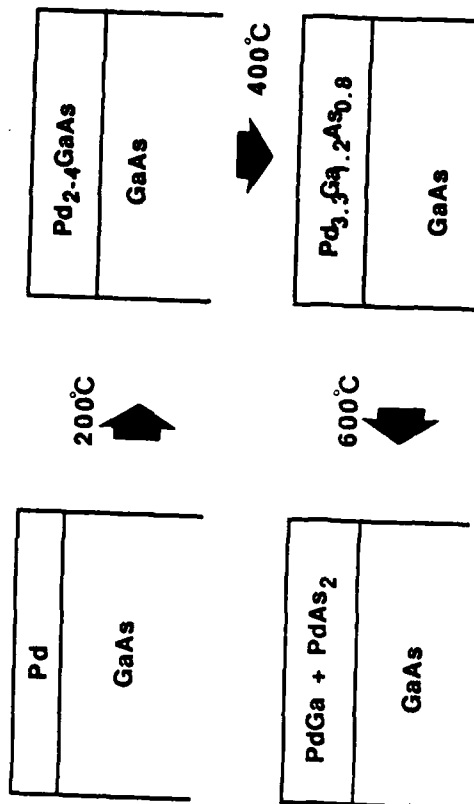


Cr-Ga-As

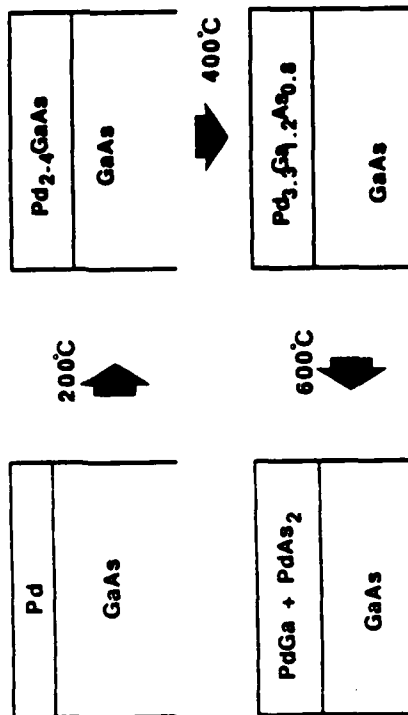
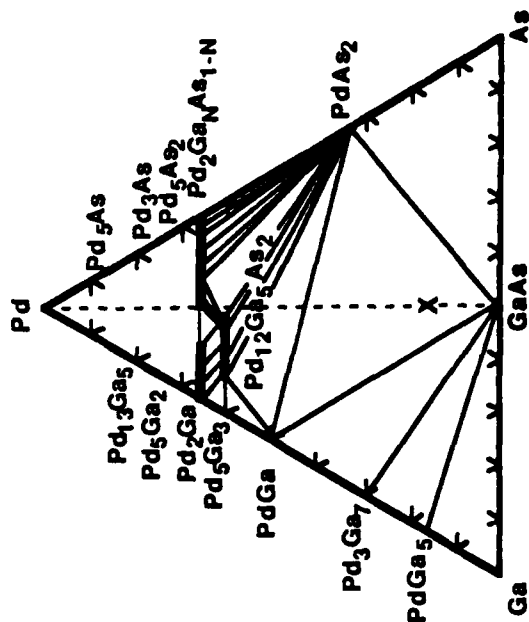


Pt-Ga-As

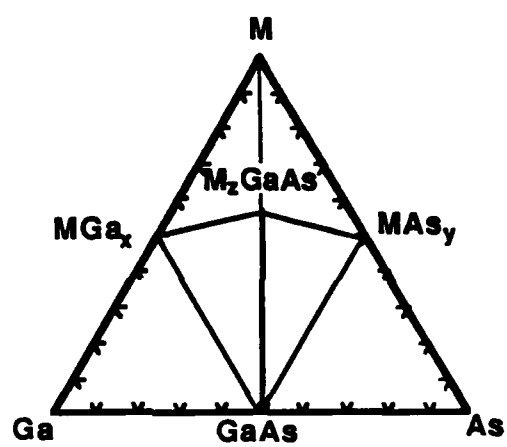




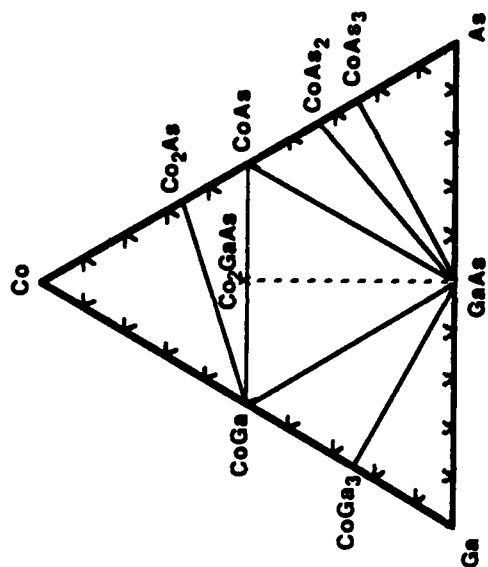
Pd-Ga-As



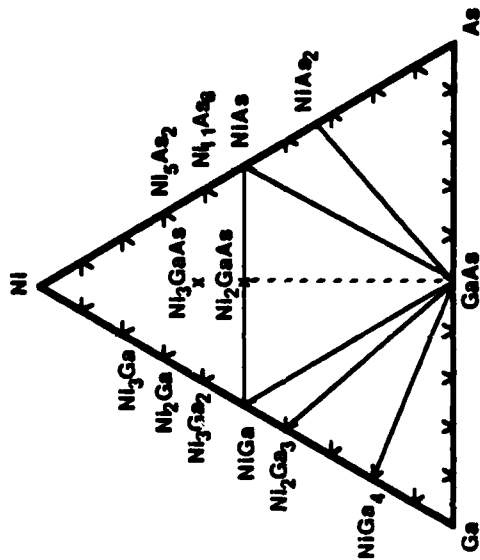
Type V: Ternary phase

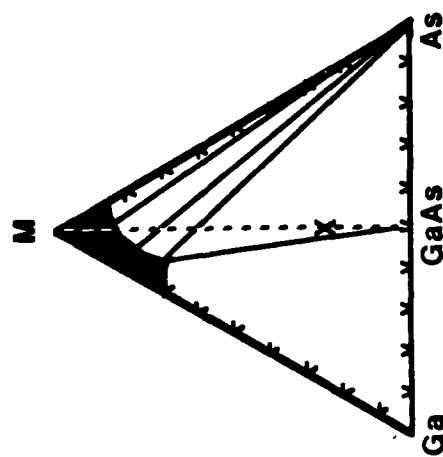
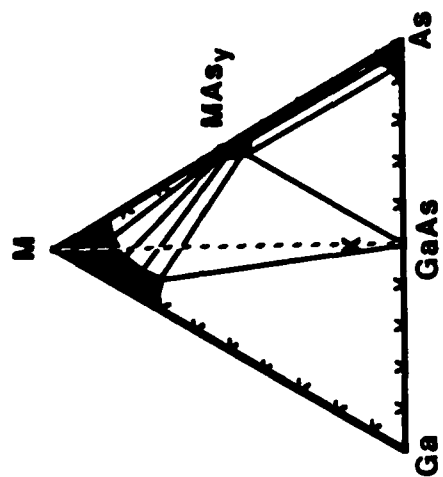


Co-Ga-As

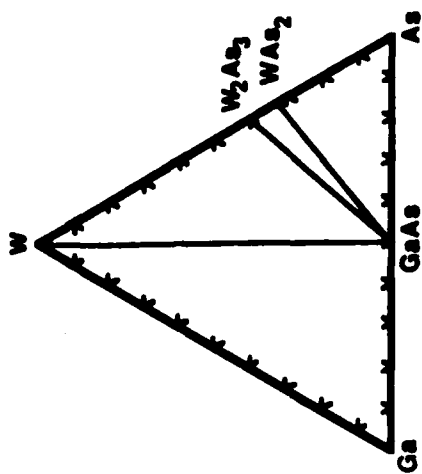


Ni-Ga-As

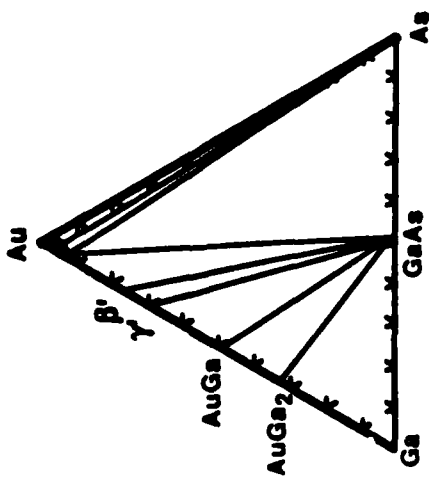




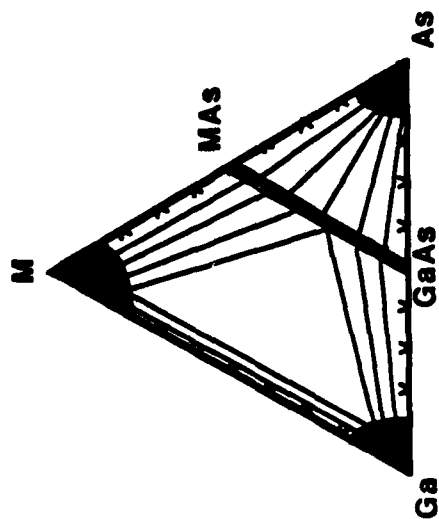
W-Ga-As



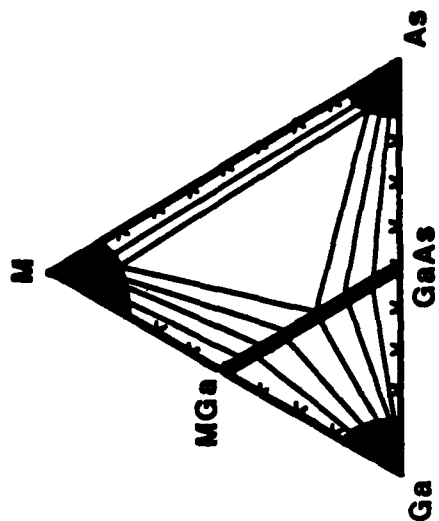
Au-Ga-As



Type VI: Solid Solubility

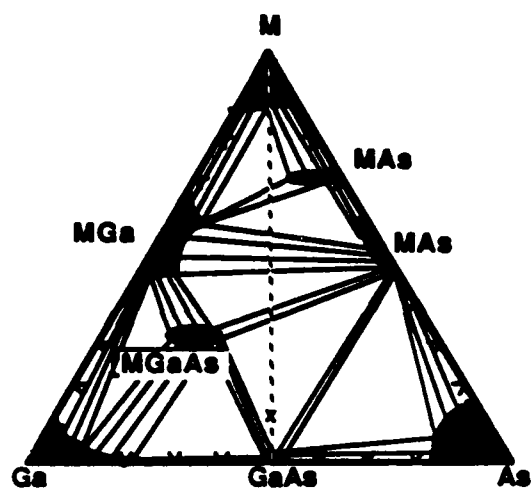


Type VII: Solid Solubility

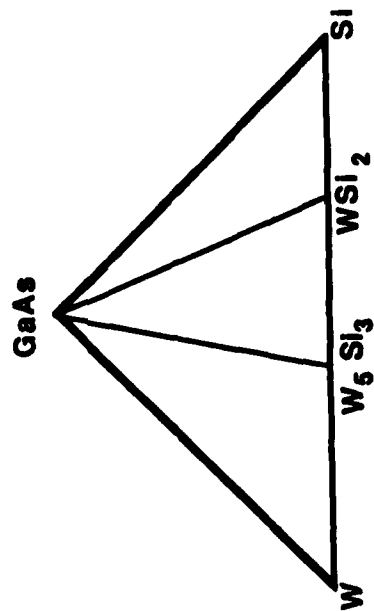


slide #5

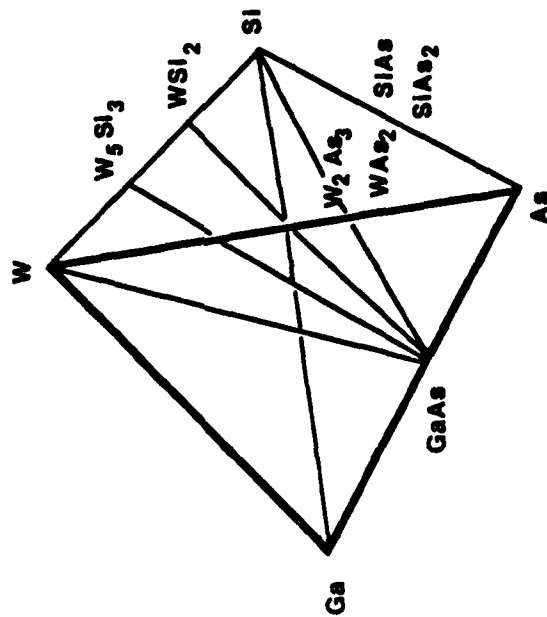
Applications



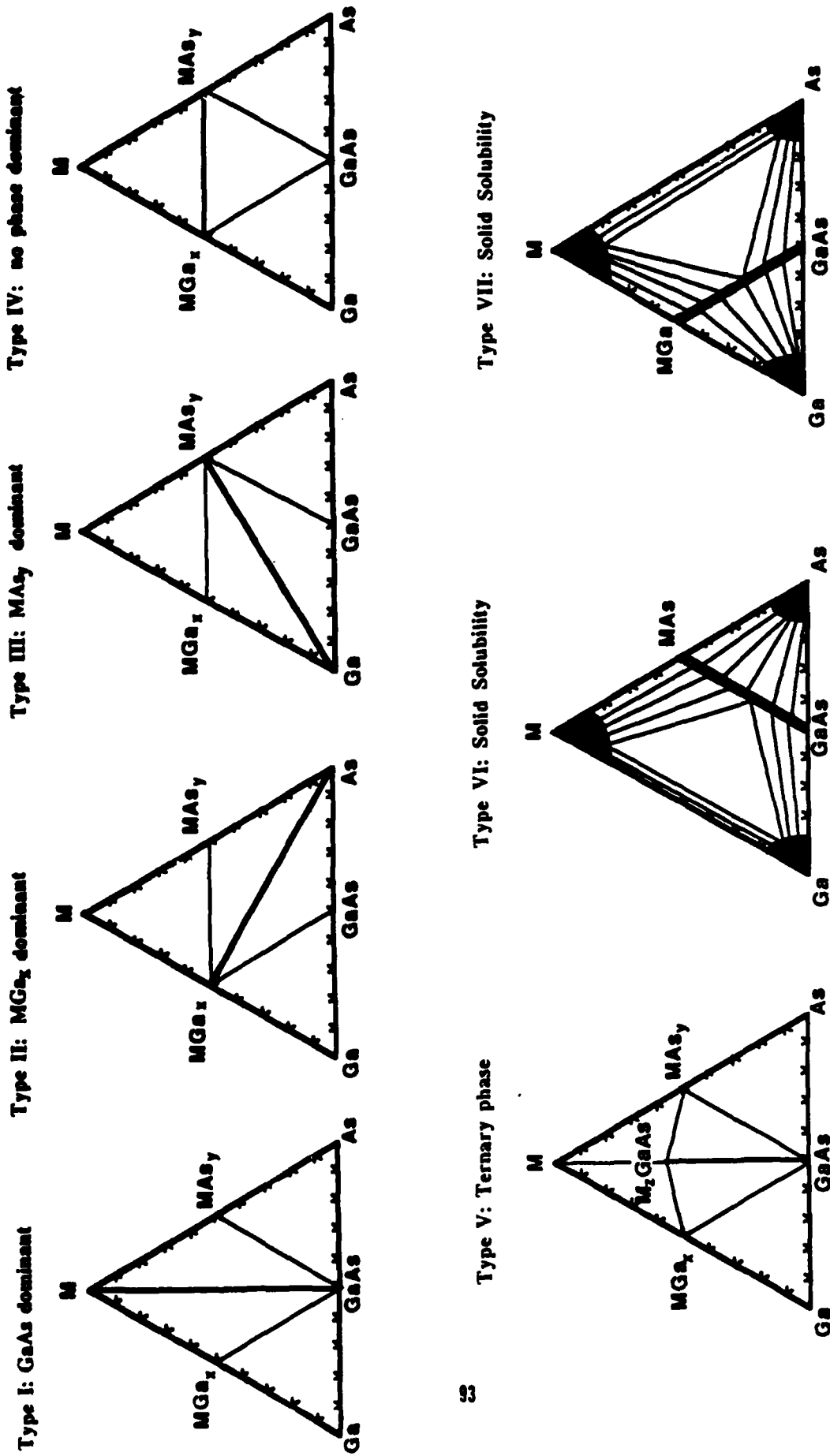
W-Si-GaAs



W-Si-Ga-As



Conclusions



CHEMISTRY OF Ti:GaAs INTERFACES

M. KNIFFIN, C. R. HELMS

K. B. KIM, R. L. SINCLAIR

BACKGROUND - Ti:Si SYSTEM

GaAs SURFACE PREPARATION EFFECTS

**EFFECT OF ANNEALING ON
CHEMISTRY/ BARRIER HEIGHT**

MODEL FOR KINETICS OF Ti:GaAs REACTIONS

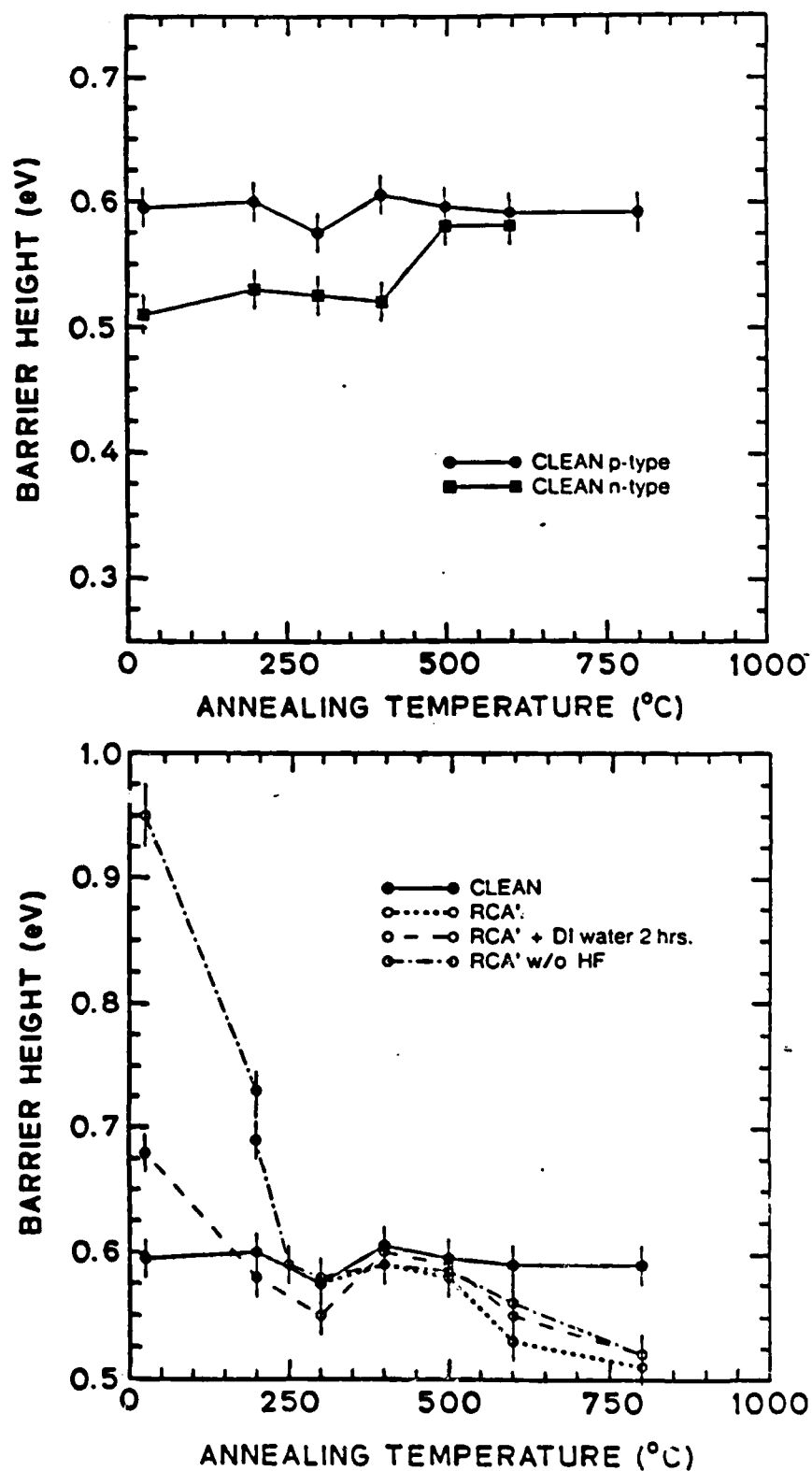


Figure 5.10: Barrier height as a function of annealing temperature for a variety of chemical procedures on *p*-Si. Procedures: Clean, RCA', RCA' + 2 hours in DI water, RCA' w/o HF. The RCA' w/o HF sample was reannealed for 10 min at 200°C.

AD-A183 158

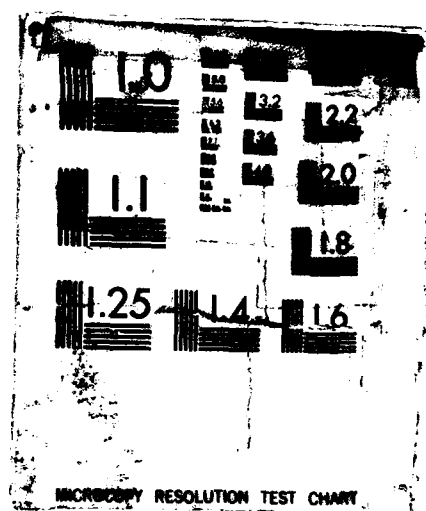
A WORKSHOP ON 3-5 SEMICONDUCTOR: METAL INTERFACIAL
CHEMISTRY AND ITS LIFE (U) STANFORD UNIV CA
W E SPICER ET AL. 85 NOV 86 N00014-87-G-0038

2/7

UNCLASSIFIED

F/G 20/12 NL





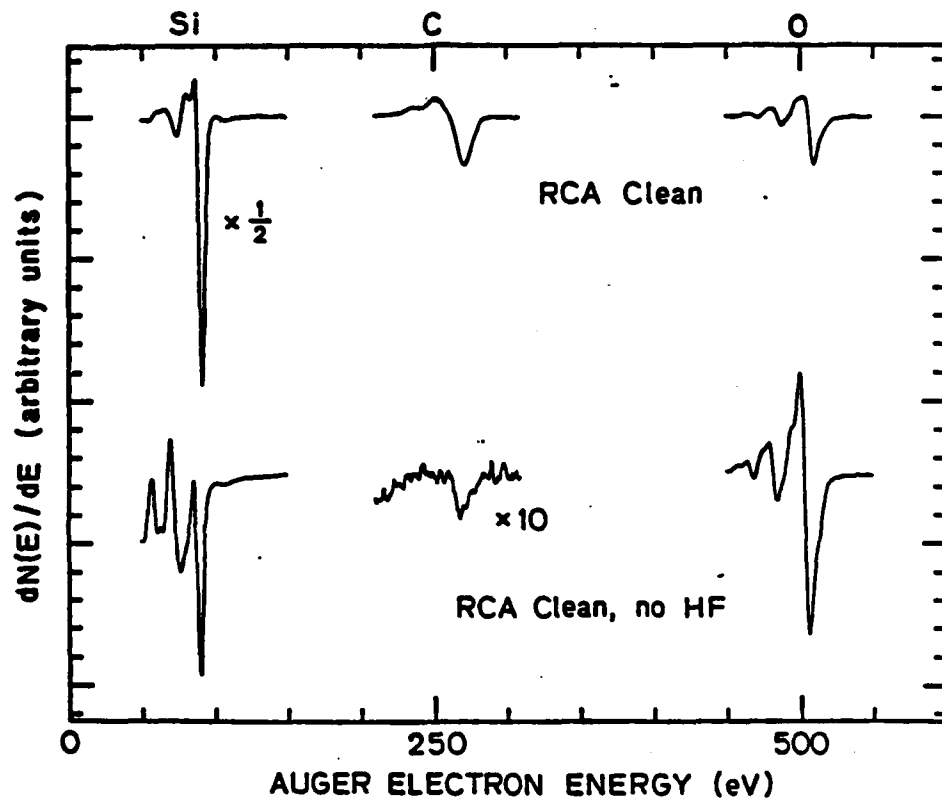


Figure 3.1: AES spectra of two chemical cleaning procedures: RCA' and RCA' w/o HF.

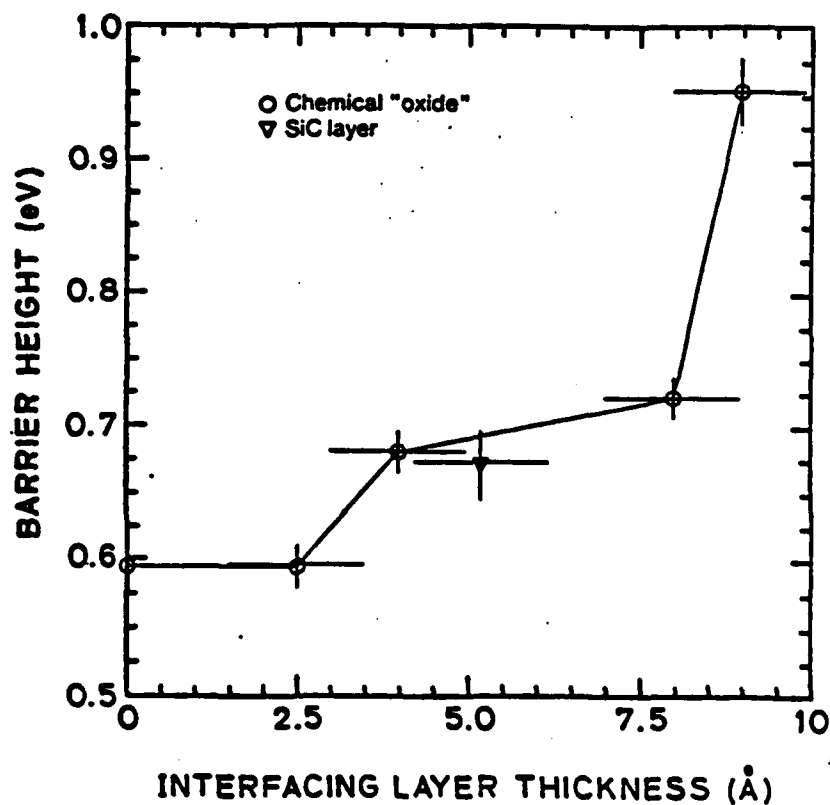


Figure 5.9: Schottky barrier height as a function of interfacial layer thickness for p-Si. Preparations used in order of increasing thickness: sputter/annealed, RCA', RCA' + 2 hours DI water, RCA' w/o HF*, RCA' w/o HF. Also shown is one point for the SiC layer.

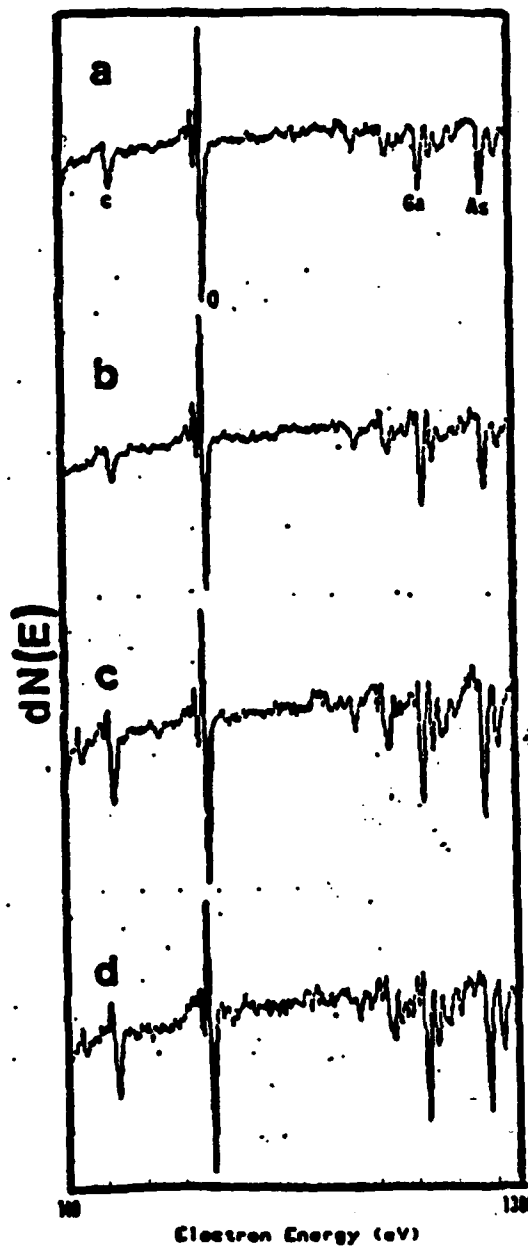
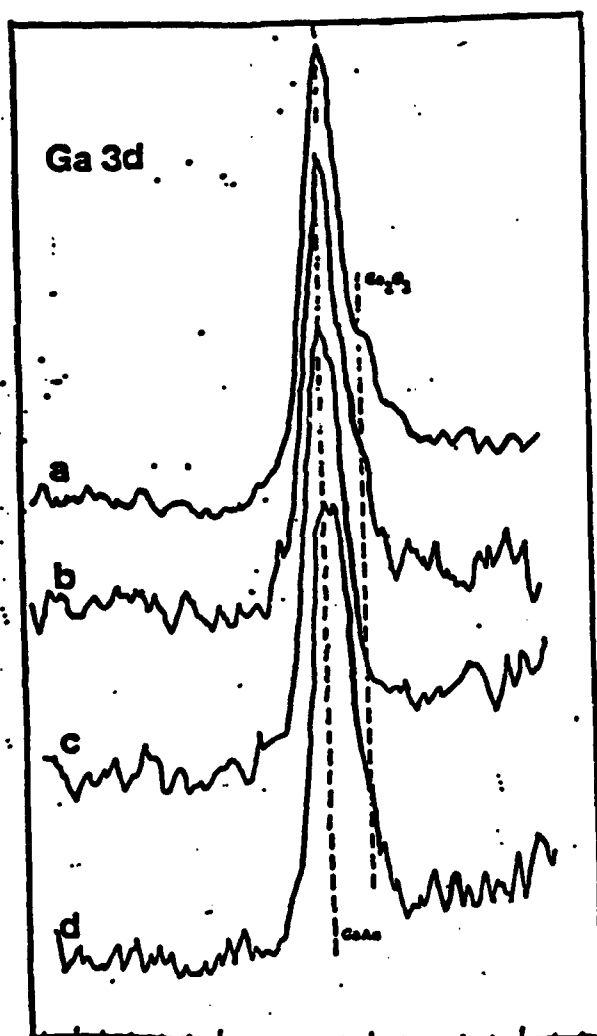
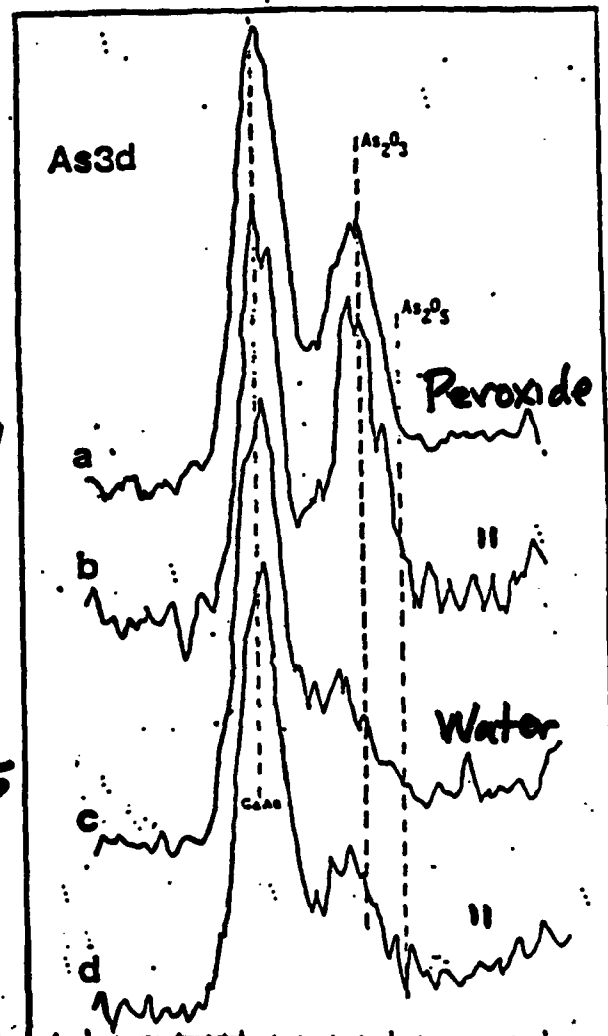


FIGURE 1.1: AES SPECTRA OF GAAS SURFACE FOR FOUR CLEANING PROCEDURES:

- (A) $H_2SO_4:H_2O_2:H_2O(5:1:1)$
- (B) $NH_4OH:H_2O_2:H_2O(1:1:10)$
- (c) $HCl:H_2O(1:1)$
- (c) $NH_4OH:H_2O(1:10)$



B.E. [eV]



B.E. [eV]

Φ_B :

.71eV

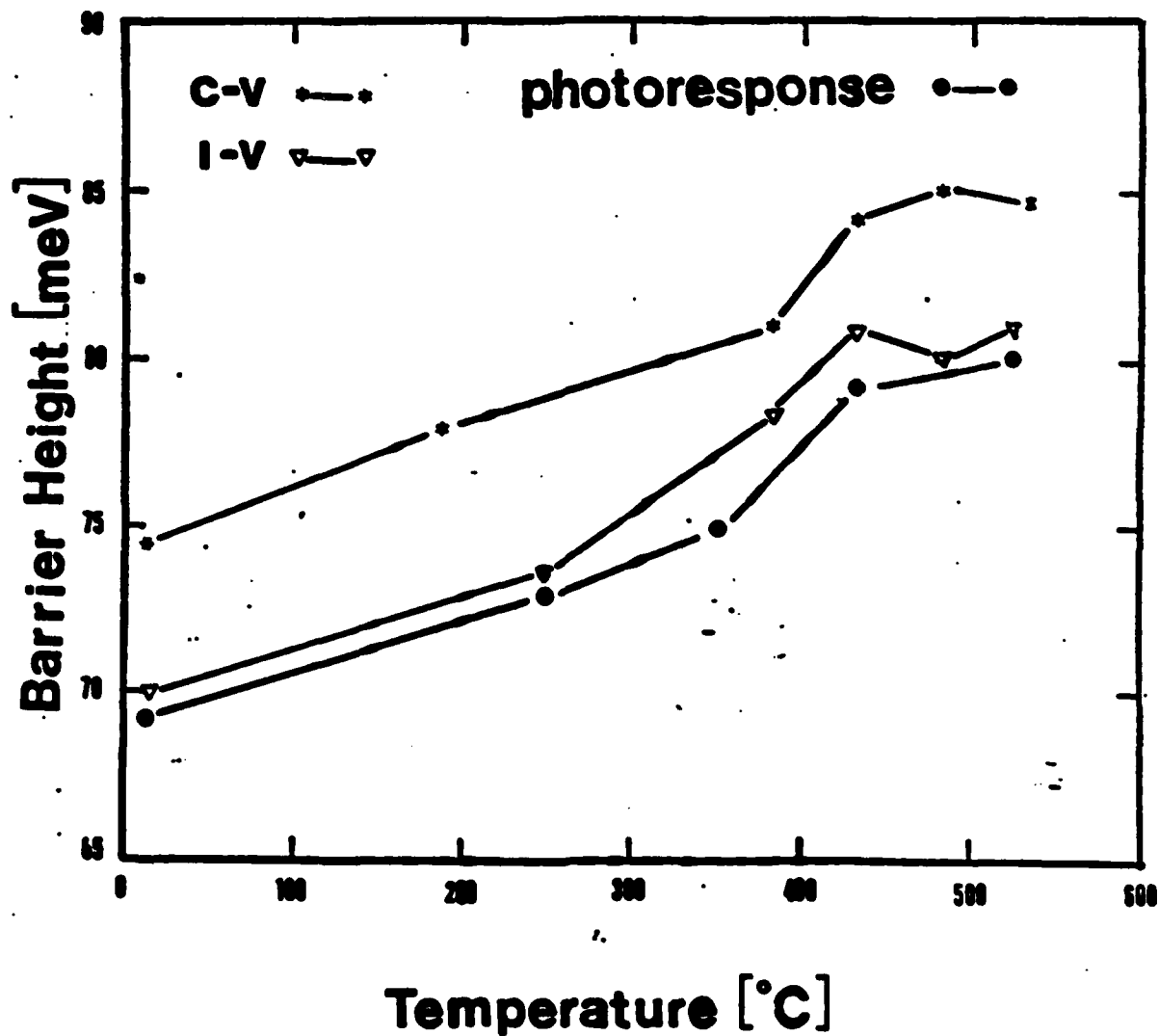
.69

.725

.69

Effect of Surface Clean on
Ga As Surface

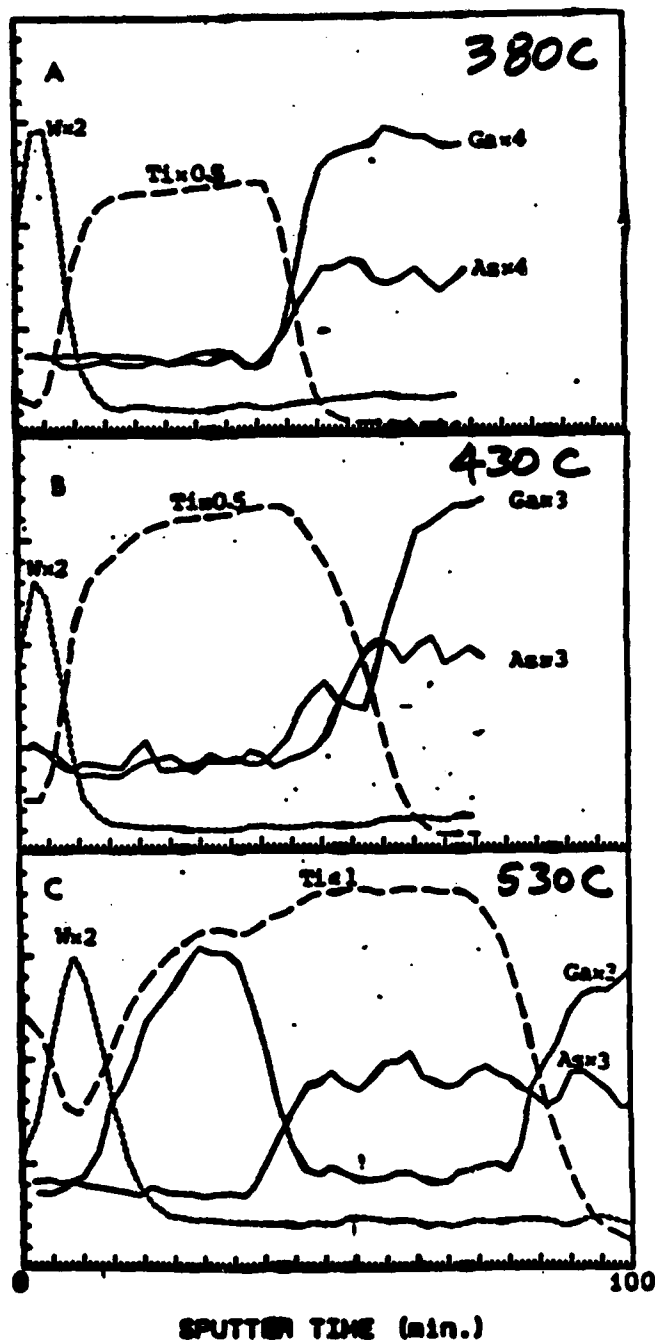
SCHOTTKY BARRIER HEIGHT OF Ti: GaAs INTERFACES VERSUS ANNEALING TEMPERATURE*



***MEASUREMENTS DONE IN SPICER/HELMS ELECTRICAL CHARACTERIZATION FACILITIES**

EFFECT OF ANNEALING ON W:Ti:GaAs LAYERED STRUCTURE*

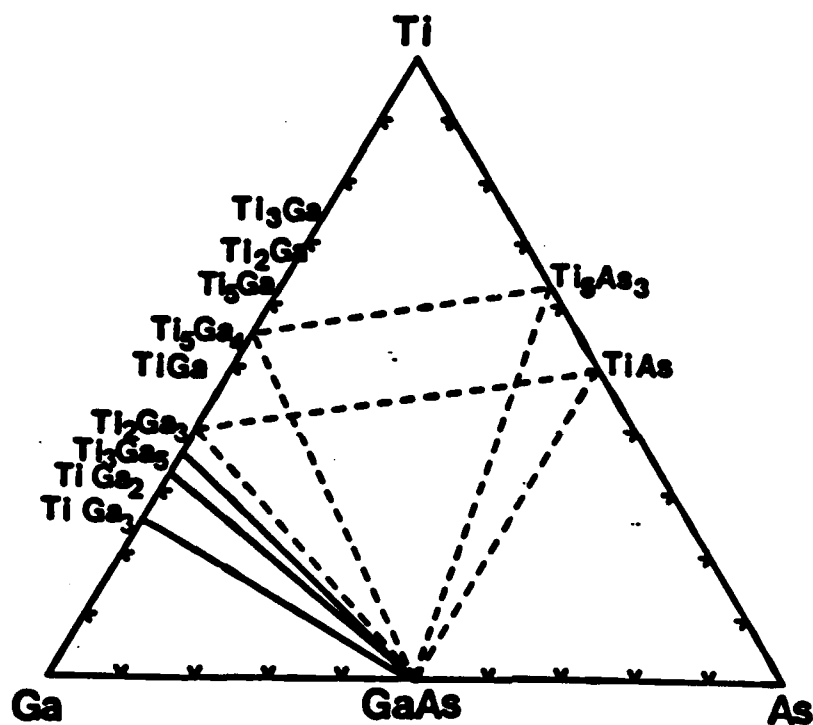
AUGER P-P SIGNAL (arb. units)

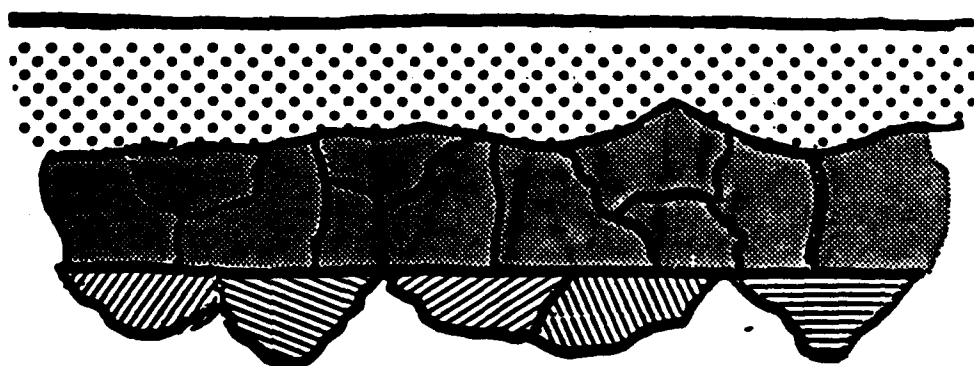


*AUGER SPUTTER PROFILING PERFORMED IN SYSTEM
PARTIALLY OBTAINED WITH CMR FUNDS

PRELIMINARY Ti-Ga-As PHASE DIAGRAM

(KIM, SINCLAIR)





GaAs

-  Ti:O
-  Ti:As
-  Ti:Ga

W. E. Spicer

"Questions Concerning Interfacial Chemistry, Equilibrium, and Electrical Properties"

Outline

1. PES examination of chemistry near interface due to deposition of metal
 - What is Chemistry?
 - Is Chemistry governed by bulk thermodynamics?
 - Is Chemistry the dominant factor in determining electrical properties of Schottky barrier
2. Study of Annealing Au on GaAs (N. Newman)
 - Decrease of Schottky barrier height (SBH) under Au dot (0.9 --> 0.8 eV)
 - Ohmic at perimeter - morphology
3. Study of Annealing Al on GaAs (N. Newman)
 - $\text{Al} + \text{GaAs} \rightarrow \text{Al}_x\text{Ga}_{1-x}\text{As} + \text{Ga}_y\text{Al}$
 - SBH increases 0.8 --> 0.89 eV

Study (PES) Annealing In on GaAs (K. Chin)

 - Melting point of In, InAs formed
 - Correlates with ohmic contact
4. Conclusions

1
Is "Chemistry" on deposition of metals in agreement with bulk thermodynamics?

Or is it controlled by kinetics of ^s Surface or ^t Interface Thermodynamics?

~~No ideal way to examine experimentally~~

However, ^p photoemission spectroscopy (PES) using synchrotron radiation gives a method for examining early stages of metal:3-5 interactions *due to metal deposition*

Characteristics of PES used here

1. Examine core states

For example	As-3d
	Ga-3d
	Au-4f

As deposited metal (e.g. Au) on clean semiconductor (e.g. GaAs) surface formed by cleaving ^{In situ} - diodes for electrical measurements made in the same way .

2. [^]Measure

- Binding Energy (B.E.) of core levels
Gives "Chemical Environment" of Atoms
- Intensity of Cores
Gives Chemical Composition of Layer Studied

Key to understanding this PES:

Sampling Depth is 5 to 10 Å, i.e. 2 to 10 Atomic Layers

Thus:

Thus, ^{1) F} form clean GaAs surface (usually by cleaving in UHV)

2) Examine spectrum of core levels after metals deposition

- Up to formation of metal layer several Å thick - look principally at substrate, i.e. GaAs
- With increasing metal coverage examine metal plus any Ga and As involved in " reactions"

By Core B.E. Shifts and

Relative Intensity Changes (e.g. does Ga to As intensity ratio change from that of GaAs)

— A look at changes in detail, can give insight into any new chemical species formed.

POSSIBLE COMPLICATIONS:

Metal may not deposit on GaAs in uniform way, layer by layer. Rather metal "islands" of various types may form.

But using both core shifts this complicates the analysis and intensities the effects can be sorted out

e.g.:

If large islands of metal formed leaving some GaAs exposed with no metal on it,

Would see GaAs after enough Au was deposited to completely cover GaAs if metal went down uniformly.

However, Ga and As

- Intensity ratio would be same as for GaAs
- Core level binding energies would be same as for GaAs

Thus, we see

1. Change in Ga to As intensity ratio and/or
2. New core shifts (particularly different As and Ga core shifts)

Have Strong Evidence that Chemical Reaction Has Taken Place

Now Illustrate with Data From Au on GaAs

NOTE:

1. For coverages greater than $8.7\text{\AA}$, intensity of As becomes increasingly larger than that of Ga
2. For coverages greater than $1.3\text{\AA}$ have:
 - Ga shift to lower B.E.
 - No shift in As peak but changes in shape at higher binding energies

Clear evidence that GaAs is being disassociated with Ga and As moving into new environment:

A shift suggests at least two new As configurations present possibilities:

- Elemental As, perhaps surface segregated
- As in or reacted with Au

Ga shift can be explained by alloying with Au

Calculation of Ga3d shift due to alloying with deposited metal
(also done for In 4d - InP case)

1. A recent article describes method to predict core shifts with respect to Ga metal, then can relate to the shift in GaAs. ↩

Based on: P. Steiner and S. Hufner, Act. Metall. 29, 1885 (1981) and B. Johansson and N. Martensson, Phys. Rev. B 21, 4427 (1980).

(J. Nogami, T. Kendelewicz, I. Lindau, and W. E. Spicer, Phys. Rev. B 34, 669 (1986).

$$\Delta E_A(x) = E(A; A_x B_{1-x}) - E(A+1; A_x B_{1-x}) + E(A+1; A)$$

Take dilute limit, i.e. $\Delta E_A(x)$ as $x \rightarrow 0$

Compare to experimental shift with lowest Ga intensity (e.g. large coverages)

$E(A;M)$ is partial heat of solution of A in M: A+1 denotes element to right of A in periodic table

$\Delta E_A(x)$ positive - increase in B.E. with respect to Ga in Ga metal

(6)

$\Delta E = G = S_{\text{u}} - E$ Due to Alloying
 ΔE with respect to G in $G = \text{As}$

Metal	ΔE^{exp} (eV)	ΔE^{cal} (eV)	PES ~~evapor~~ of evaluation Chemistry
Au	-0.4	-0.38	Strong disruption of GaAs As surface segregation?
Cu	-0.8	-0.83	Strong disruption of GaAs
Ag	----	-0.79	No GaAs disruption No <u>alloying</u> No reaction
Ni	-0.7	-0.60	Strong disruption of GaAs As outdiffusion Ni/Ga/As phase?
Pd	-0.7	-0.30	B.E. still decreasing at 50Å Pd As surface segregation, arsenide formation
Cr	-1.25	-1.05	Strong disruption of GaAs, Strong As out-diffusion
Ti	-1.8	-1.43	Strong disruption of GaAs

Overall Conclusions: on deposit of metal on GaAs (or InP) at room temperature reactions can take place which are not predicted by bulk thermodynamics

Suggest these due to:

Non-equilibrium conditions; i.e. kinetic process

Consider, e.g., heat released due to condensation of metal on GaAs

Annealing will take interface toward thermodynamic equilibrium

(Another possibility to consider, interfacial or surface thermodynamics)

For annealing:

- If reactions go to completion

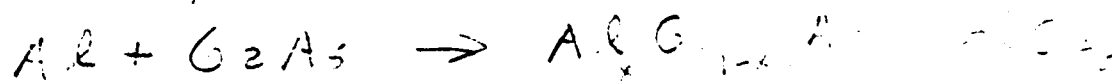
For example:



So that all Au converted uniformly to GaAu_x
Bulk Thermodynamics seems to predict

- However, many interfacial reactions approach to be kinetically or diffusion limited

For example:



Al_xGa_{1-x}As where can't go to completion

See "Chemistry" of various types, using PES.

9

What effect on Electrical Properties:

1) Seen via PES (Very Thin Films) - (0.1 to ~10 Å)

2) Seen via electrical measurements on "thick" (~1000 Å) films ~~PES and IV and/or~~

CV
3) *in general, PES and electrical measurements agree*
For example,

Have different chemistry on deposition for Au, ^{Au}Co, and Pd on GaAs - but all give similar Schottky barrier heights:
~0.9 on n-type

Variation from Metal to Metal correlates more strongly with electronegativity than other criteria including chemical activity

High electronegativity: higher barrier height on n-type GaAs

However, Chemistry can be important on annealing

Chemistry doesn't seem to be the key to understanding Schottky barrier height *metal deposition*

Much more likely to be important for:

Changes on order of 0.1 eV of the Schottky barrier height on annealing at moderate temperatures

Complete Loss of Schottky barrier on annealing at very high temperatures

Look at two studies at Stanford and Berkeley (Newman, et al; Liliental-Weber, et al.)

Au and Al

Examine Au and then Al and In

Au + GaAs - Annealed

Can explain in terms of AuGa_x formed at the interface

Decreased electronegativity - thus decrease Schottky barrier height

Questions:

1. Model predicts p-type barrier must increase by amount n-decreases must check -
2. Need direct evidence of significant Ga concentration in Au at interface. Difficult to determine if very near interface. Evidence to date is not conclusive.
3. What happens to As if Ga builds up?

Examine TEM lattice image (Liliental-Weber)

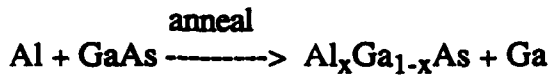
1. 5/6 Lattice mismatch (affect Schottky barrier height (SBH)?)
2. Defects in GaAs beneath the interface

Other Liliental-Weber Electronic Microscopic Studies

1. GaAs near ($\sim 25\text{-}50\text{\AA}$) interface As rich
2. Au-Ga + As; more Ga but measurements at limits of technique
Al:GaAs for comparison

Tentative Conclusion:

Defects and "impurities" (Ga in Au or excess As in GaAs) at interface may be important
Finally: Effect of Oxidation TEM



show PES results

SBH increases 0.8 $\longrightarrow$ 0.89 eV on annealing to 360°

stable to 565°

(Think loss of rectification at higher temperatures due to Al melting and/or GaAs dissociating - more study necessary)

Thought explanation of increase of Schottky barrier heights was alloy formation with larger E_g - But would predict that sum of (SBH) Schottky barrier heights on annealed n- and p-type would be greater than E_g

Newman's experiments to date don't agree - find Σ Schottky barrier heights = E_g

Suggestion of Eicke Weber: small fraction Al on As sides - doping p-type changes would be in the right direction.

Conclusions:

1. On deposition of the metal on to GaAs or InP, chemical reactions which are not predicted by bulk thermodynamics occur.
2. There does not seem to be a strong relationship between the type or extent of chemical reaction and the Schottky barrier height (SBH) on as deposited samples. (SBH correlates most strongly with electronegativity.)
3. "Chemistry" may be a key in determining changes in SBH due to annealing *but other factors important - must look at whole system.*
4. Much more to be done.

In on GaAs - gives Schottky barrier
 room temperature SBH = 0.76 eV

Anneal, etc - "ohmic"
 In + GaAs -----> $\text{In}_x\text{GaAs}_{1-x} + x\text{Ga}$

PES - Room Temperature see In metal
 anneal above melting point of In (see In in InGaAs)

Fermi level unchanged

Consistent with "ohmic" behavior due to InGaAs alloy

Problem - only Ga in GaAs detected using photoemission

not metallic Ga (little metallic In)

could be due to island formation but have not conclusively established this

The Chemistry and Morphology
of
Metal / III-V Semiconductor Interfaces

J. H. Weaver

Dept. Chem. Eng. + Materials Science

Univ. Minnesota

Coworkers

M. Grioni
J. J. Joyce
M. del Giudice
M. Ruckman
S. A. Chambers
F. Boscherini
Xu Fang

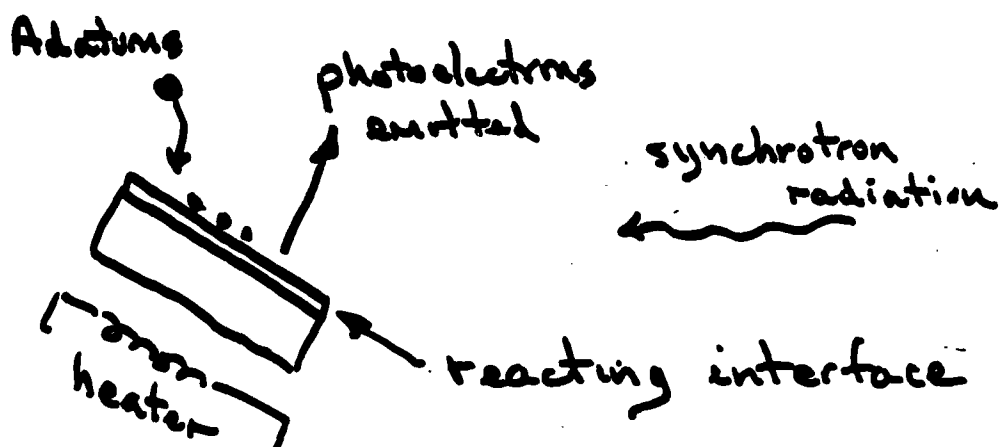
Support

ONR
Minnesota Microelectronics Center

Metal / Semiconductor interface formation

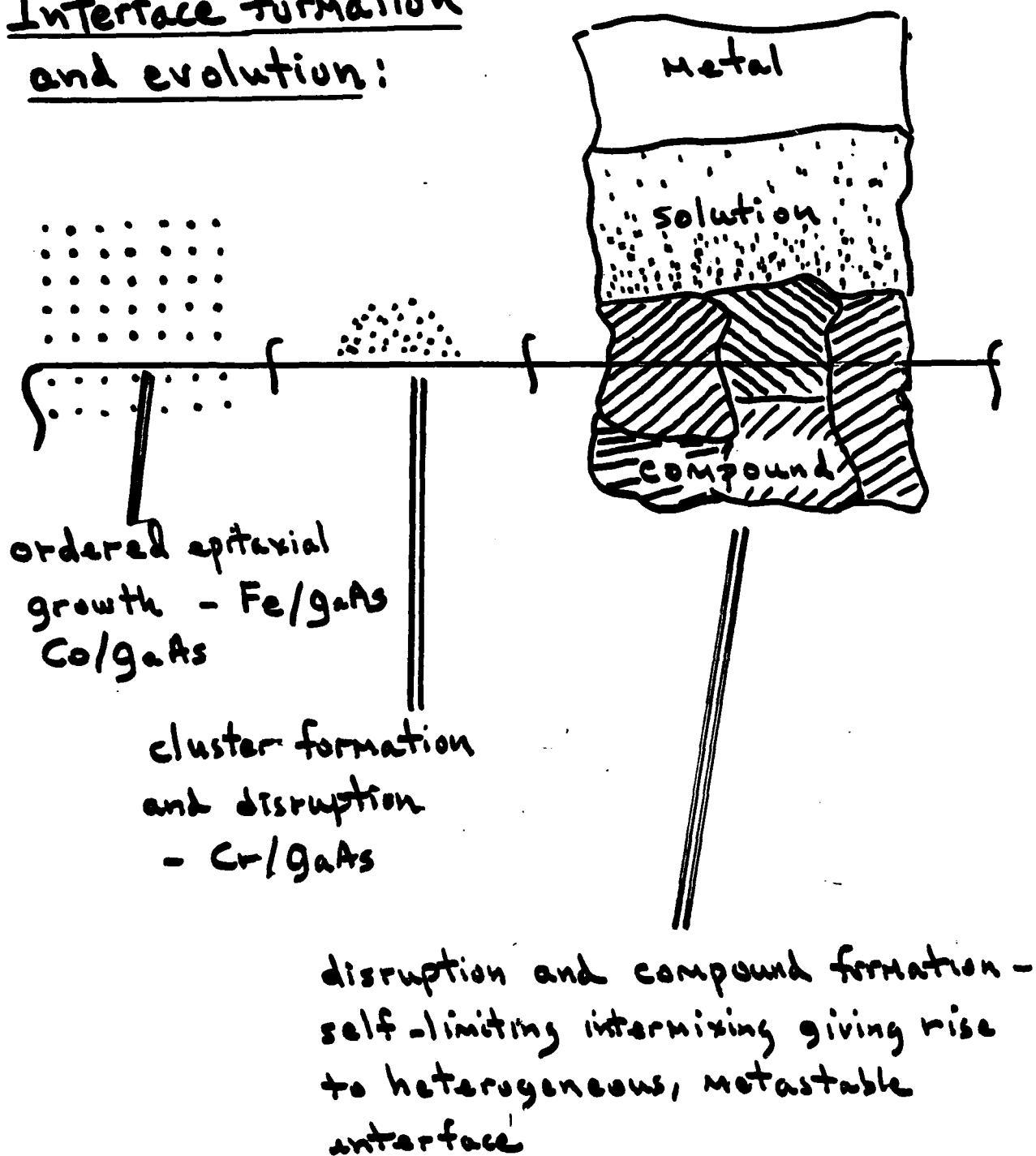
Goal: to understand the chemistry & physics of interfaces

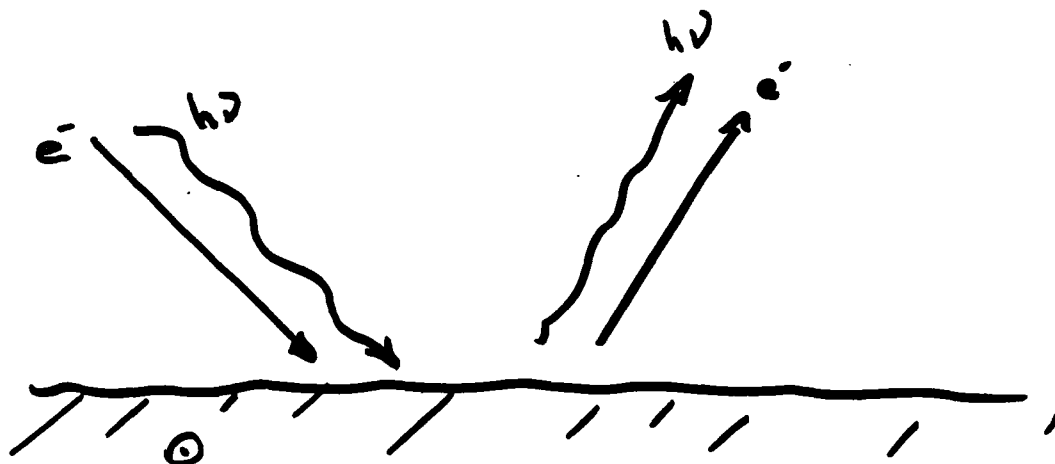
- dimensional constraints
- metastable
- local chemistry



1. What products form? Are they distinct in terms of stoichiometry? stability?
2. Role of kinetics
3. Role of reaction barriers & diffusion barriers
4. Role of clusters

Interface formation and evolution:





Photoemission : photons in, electrons out
 Auger : electrons in, electrons out
 LEED : electrons in, spots
 Inverse photoemission : electrons in, photons out
 (STM)

Co/GaAs > Excellent lattice
Fe/GaAs match

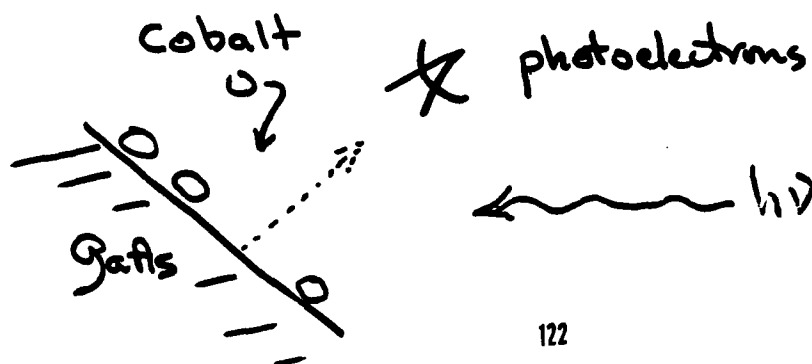
Q: can epitaxial layers be grown?

Yes. Prinz et al. NRL

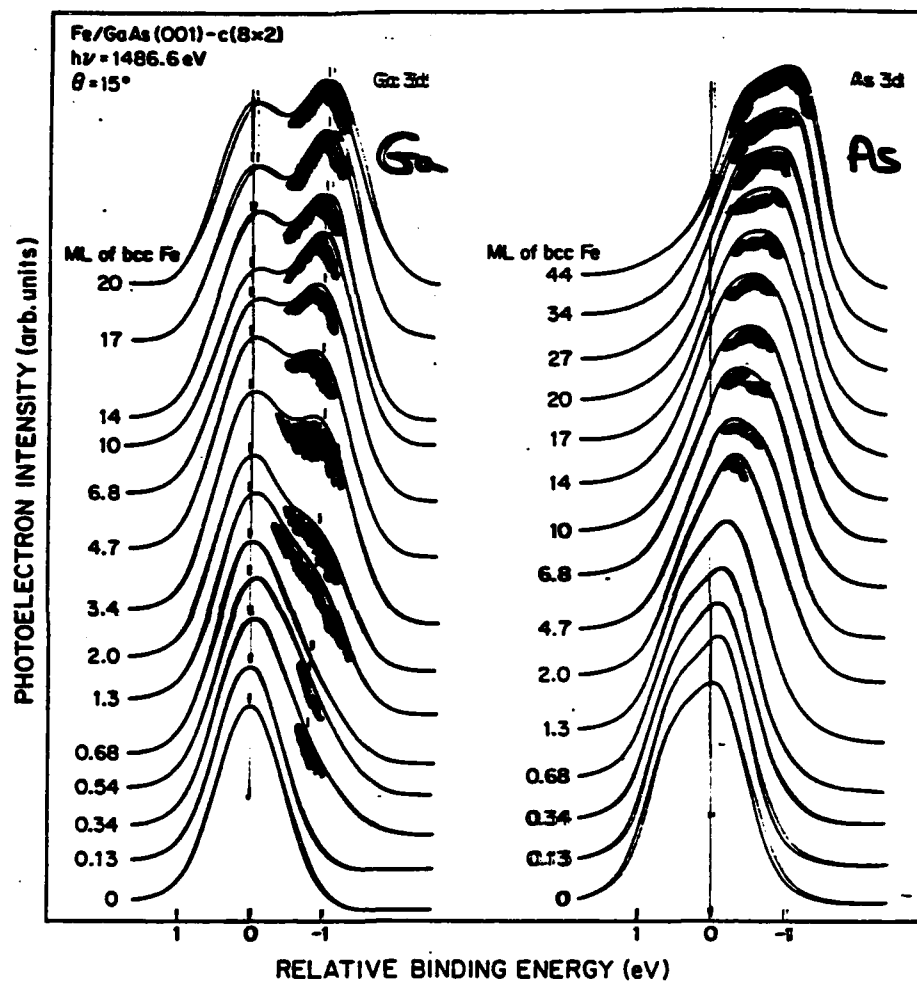
Q: Why? (Most metals induce disruption - will there be disruption?)

Q: Can we use these systems to gain insight into more complex interfaces?

e.g. epi. vs. disruption.
atom profiles



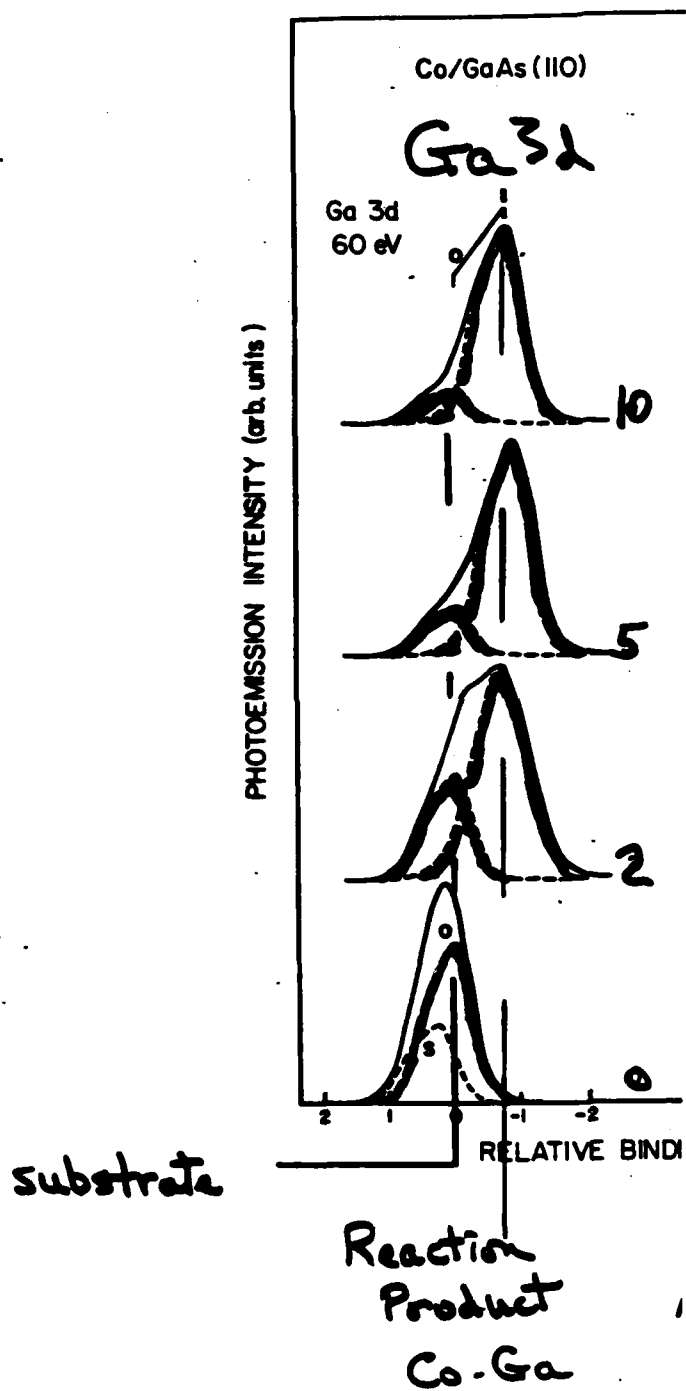
XPS Fe/GaAs(100)
 $h\nu = 1486.6 \text{ eV}$ Modest resolution



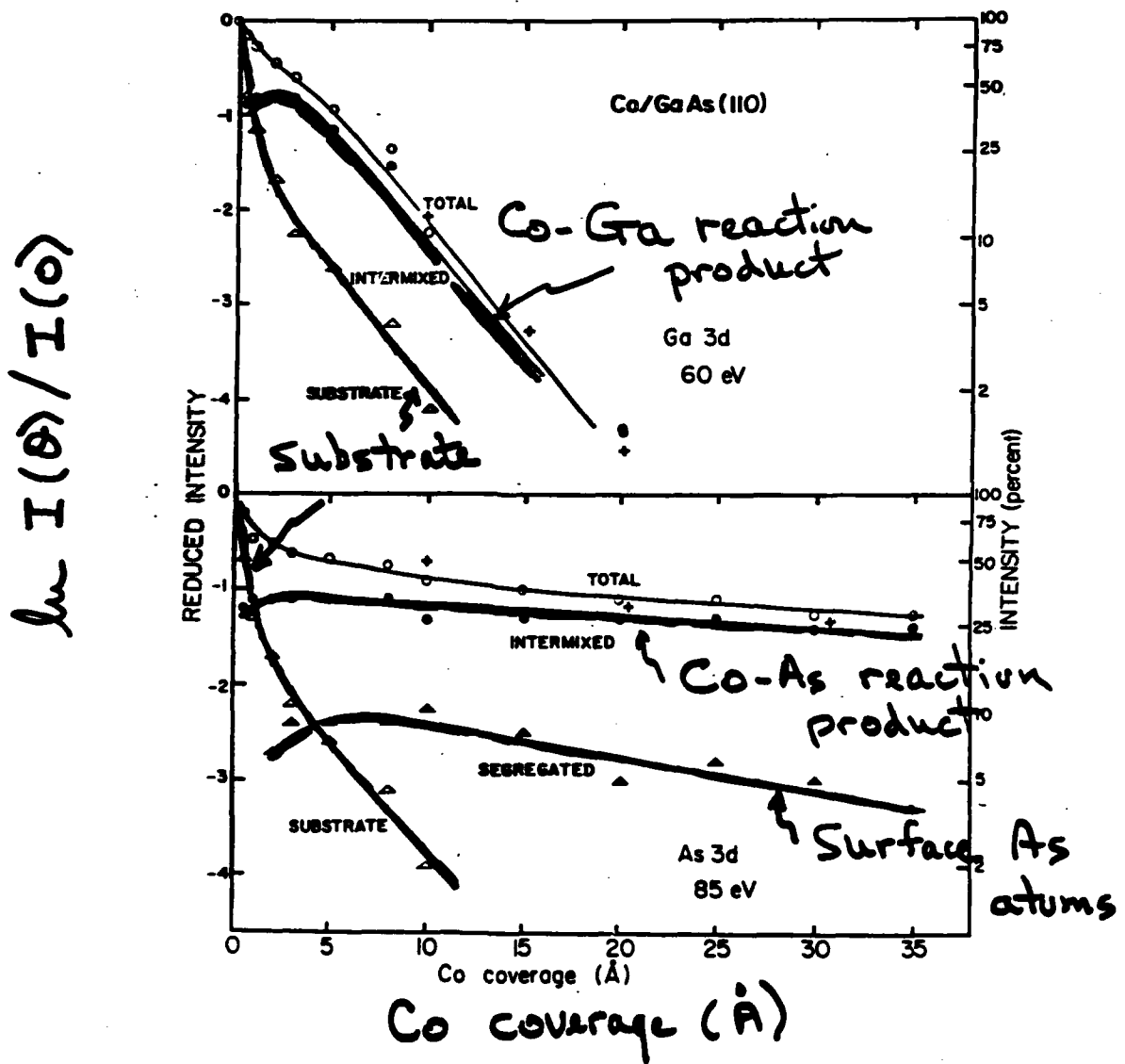
↑ reaction products
 ↑ substrate

Fig. 6

Co/GaAs (110)



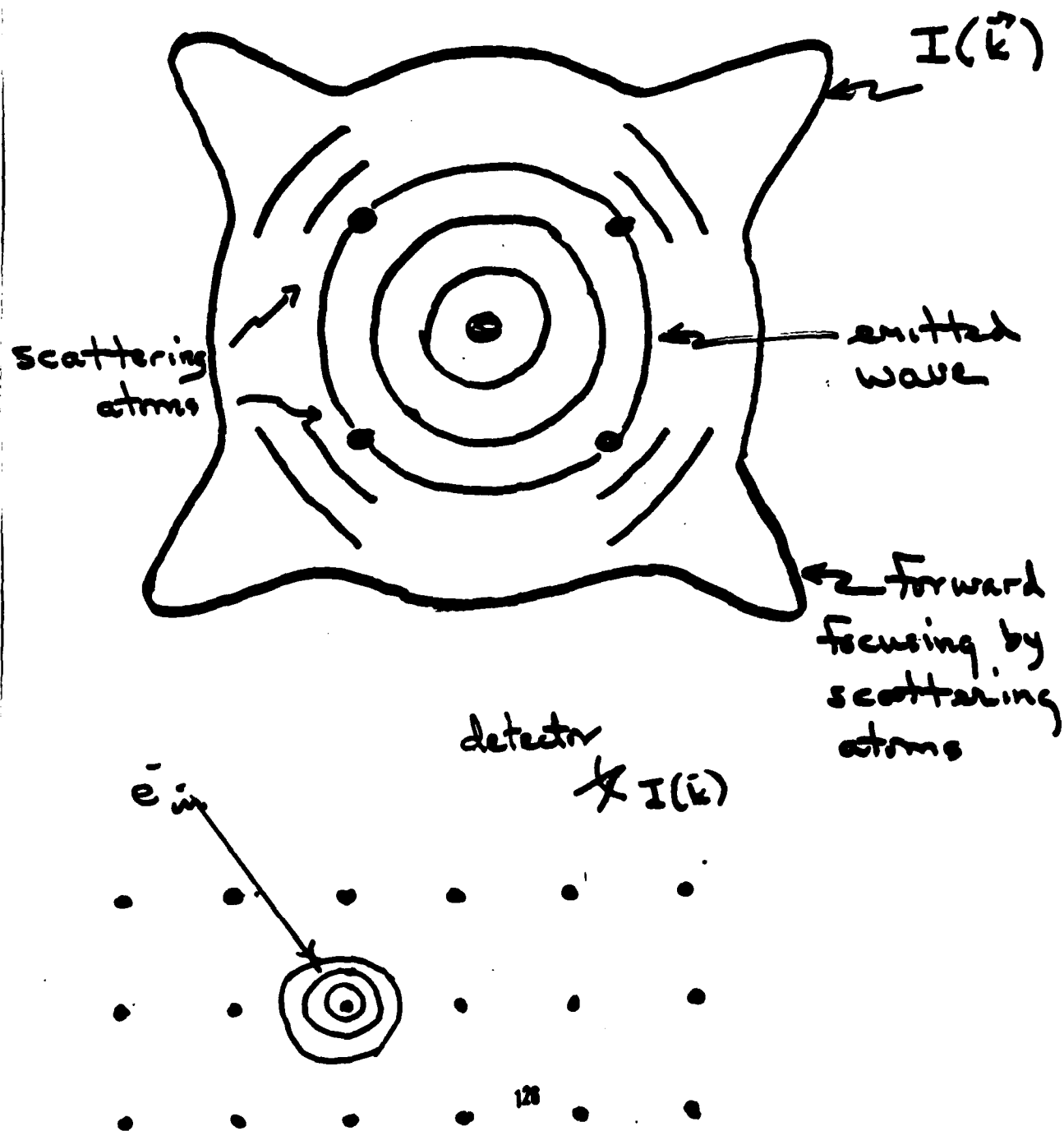
Co/GaAs (110)



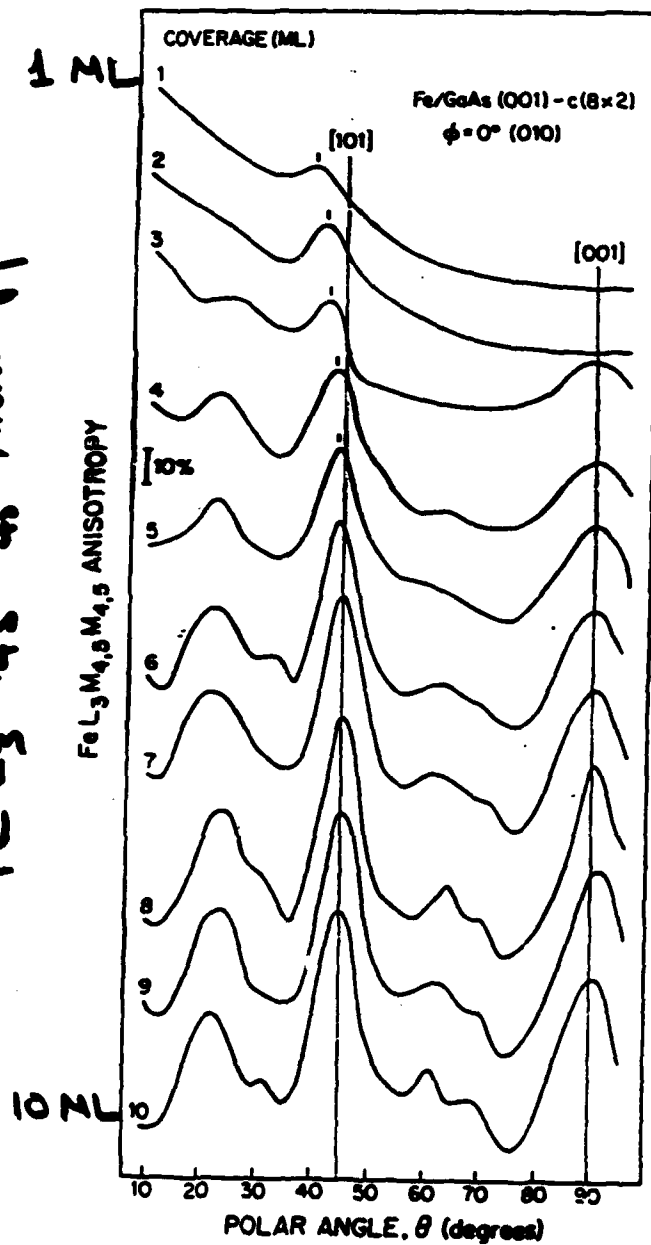
Conclusion: there is reaction and intermixing

Q: Is there epitaxy?

Angle-resolved Auger electron diffraction:
(Structural probe)



Fe L₃ M_{4,5} Anisotropy



polar angle

evolving epitaxial
bcc Fe on GaAs(100)

Fig. 2

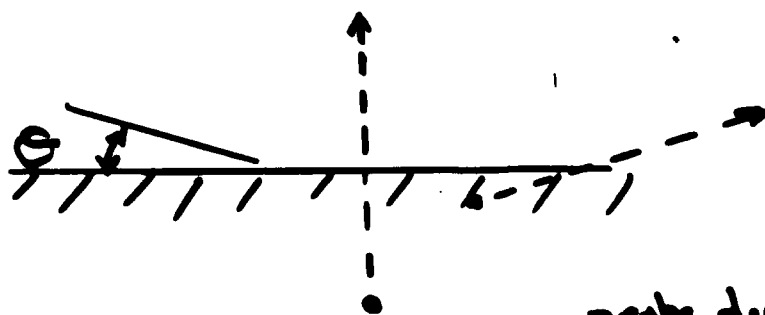
Conclusion: Excellent epitaxy.

So far:

1. Surface sensitive photoemission shows copious amounts of As at and near vacuum surface $\Rightarrow$ disruption of GaAs by Co
2. Auger diffraction shows nearly perfect epitaxy, starting at low coverage

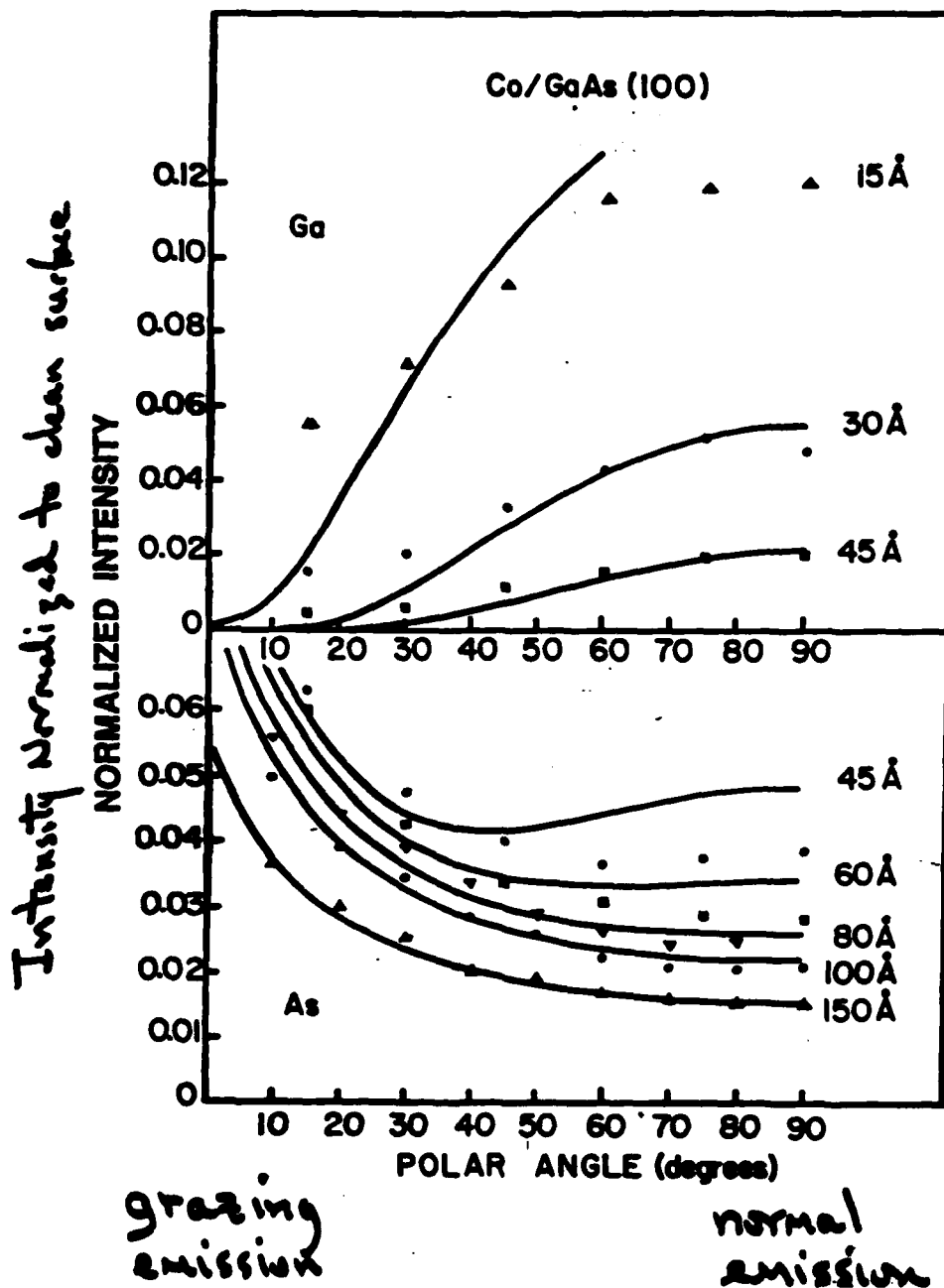
Q: What is the distribution of Ga and As in the overlayer?

$\Rightarrow$ Nondestructive depth profiling with polar-angle-dependent XPS



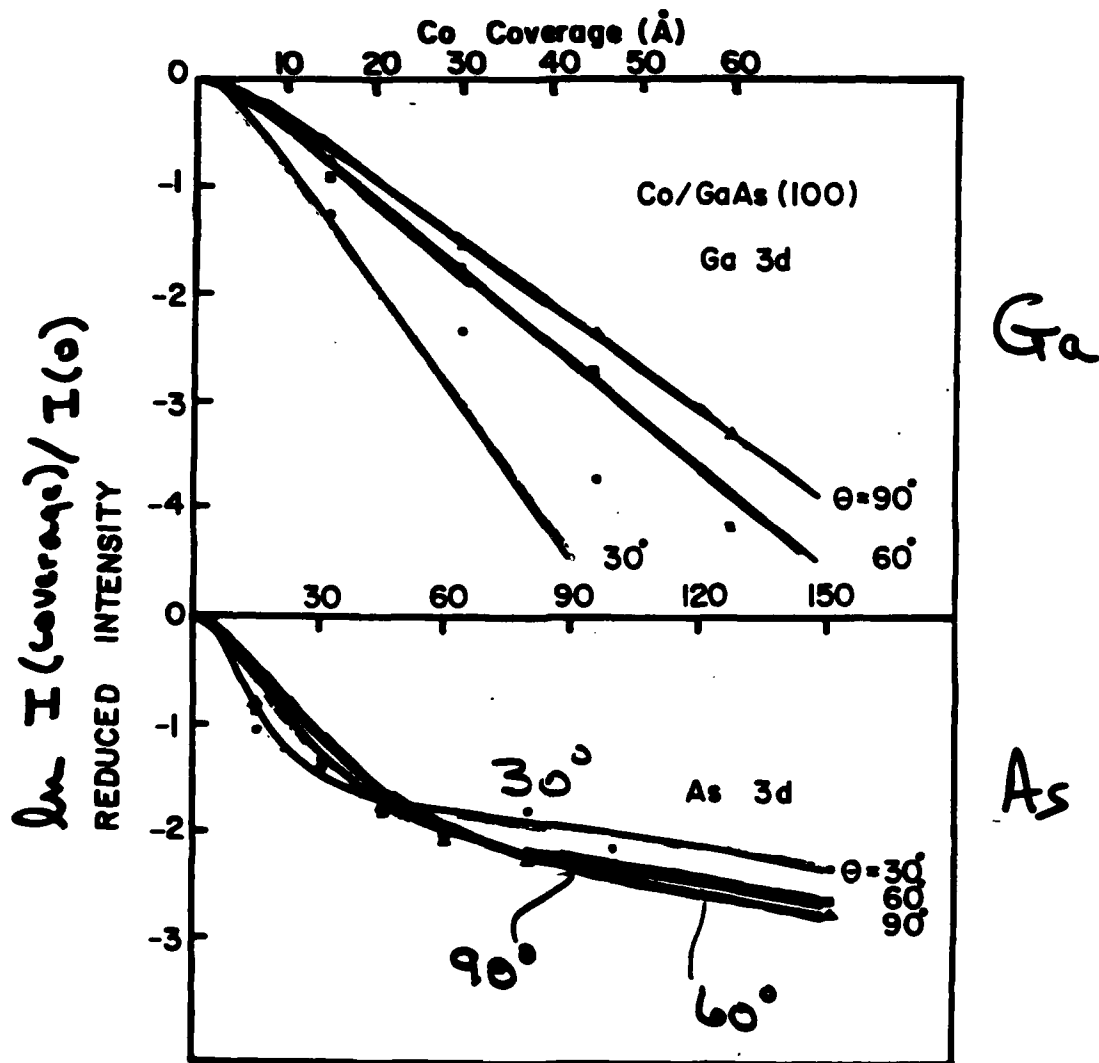
probe depth $\sim \lambda \sin \theta$

Polar-angle-dependent XPS Co / GaAs (100)



⇒ As segregation! (on a reactive metal surface)

Attenuation Curves:
polar-angle-dependent xPS
Co/GaAs(100)

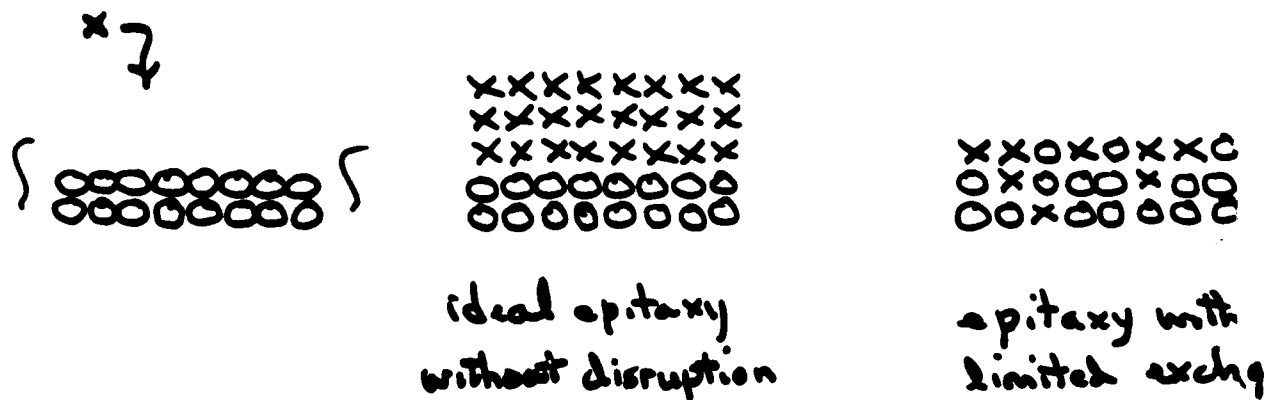


Conclusion: significant segregation to surface
and near-surface

Why does interface develop in this fashion?

What are the important parameters?

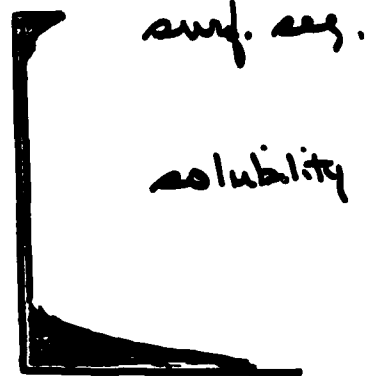
Evolution: Generic M/SC Interface



What if solubility is very low?



thin overlayer



thick overlayer

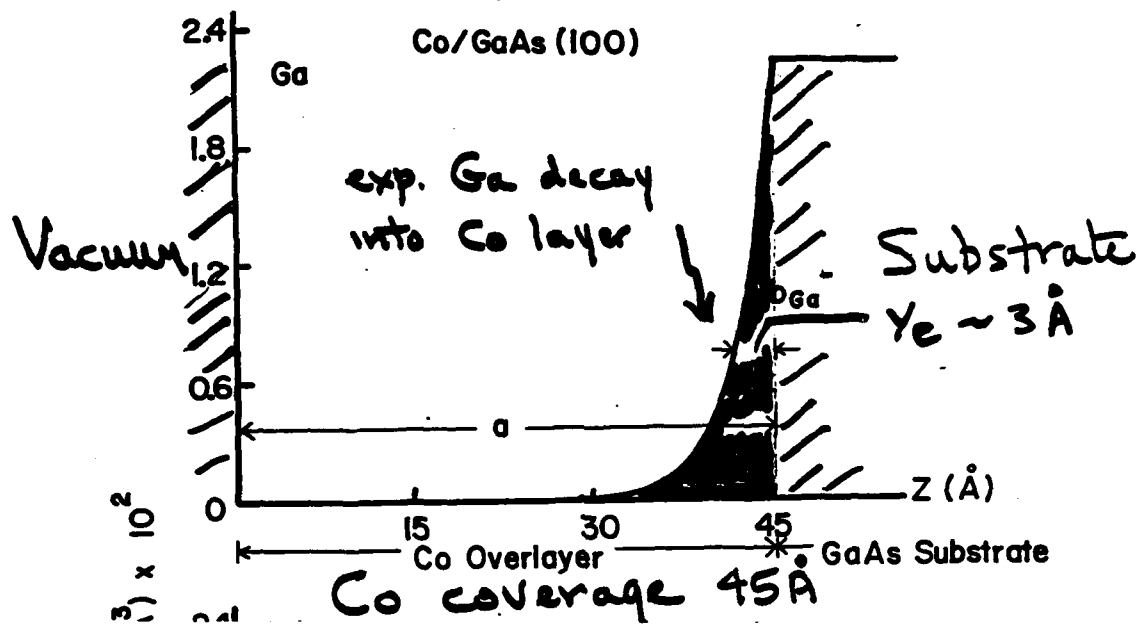
Photoemission intensity of element A detected
at an angle θ wrt surface is

$$I_A(\theta) = \underbrace{\sigma_A}_{\text{photoemission cross section}} \underbrace{I_0(\theta)}_{\text{clean surface}} \underbrace{S}_{\text{spot size}} \int_0^{\infty} \underbrace{\rho_A(z)}_{\text{density } f^{\text{A}} \text{ of element A}} e^{-\frac{z}{\lambda \sin \theta}} dz$$

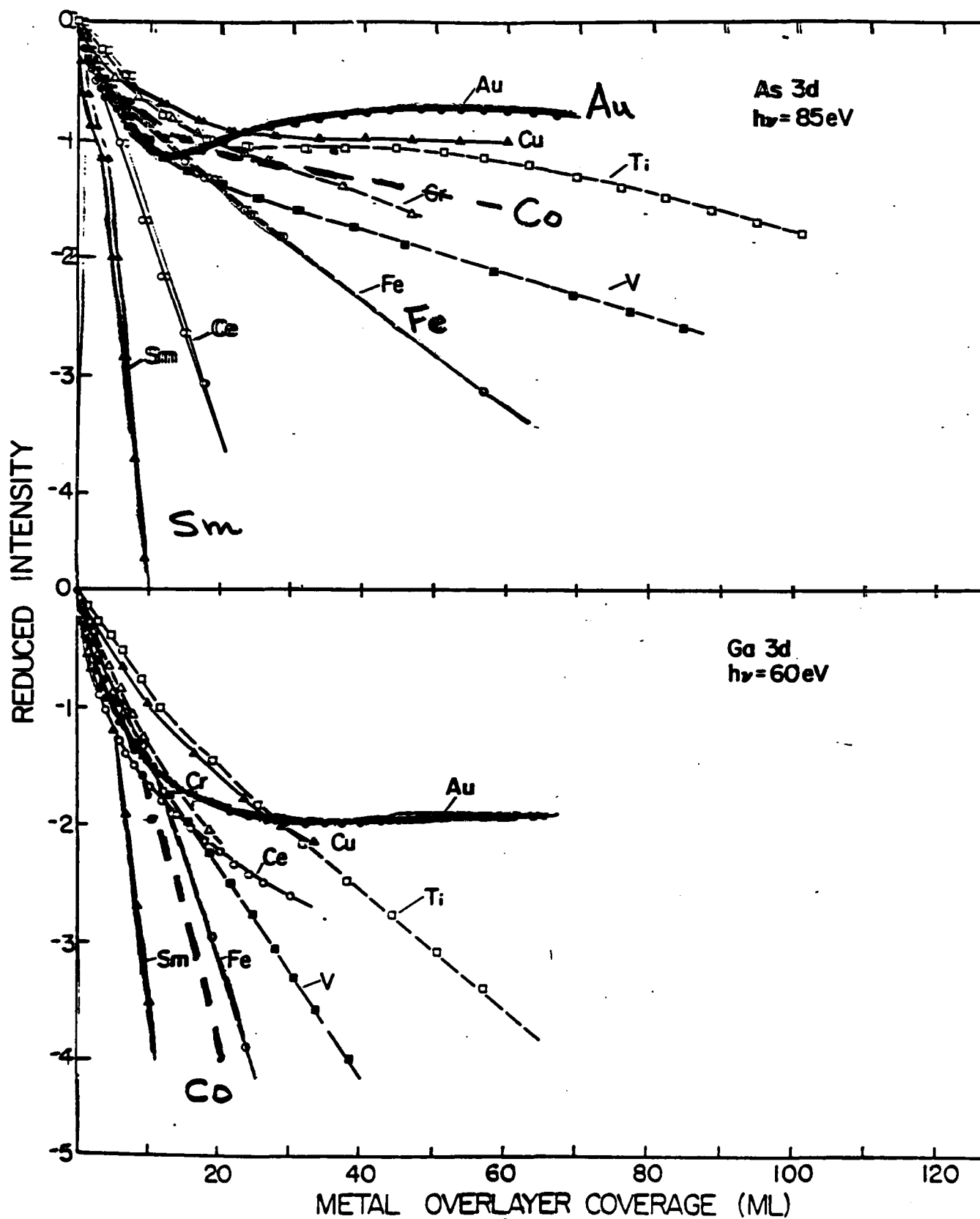
Unknown

Atom Profiles :

Co / GaAs (100)



How abrupt are interfaces?



Similar picture for Au/GaAs

$\frac{1}{e}$ values $\sim 3 \text{ \AA}$

$\rho^{\text{sol}} \sim 0.2 \text{ at. \%}$

Segregated Ga and As (amount depends
on surface)

For GaAs (100), $\sim 2 \text{ ML}$ of disruption.

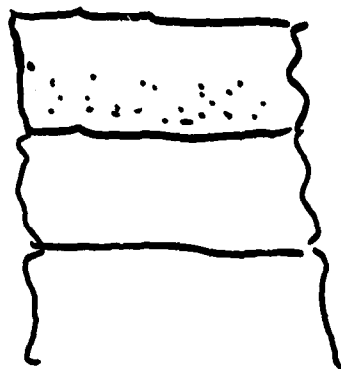
then $\sim \text{Au layer}$

For GaAs (110), As signal rises for

coverages $\geq 10 \text{ ML}$, then decreases

very slowly

What if compound formation occurs
during early stages of reaction?



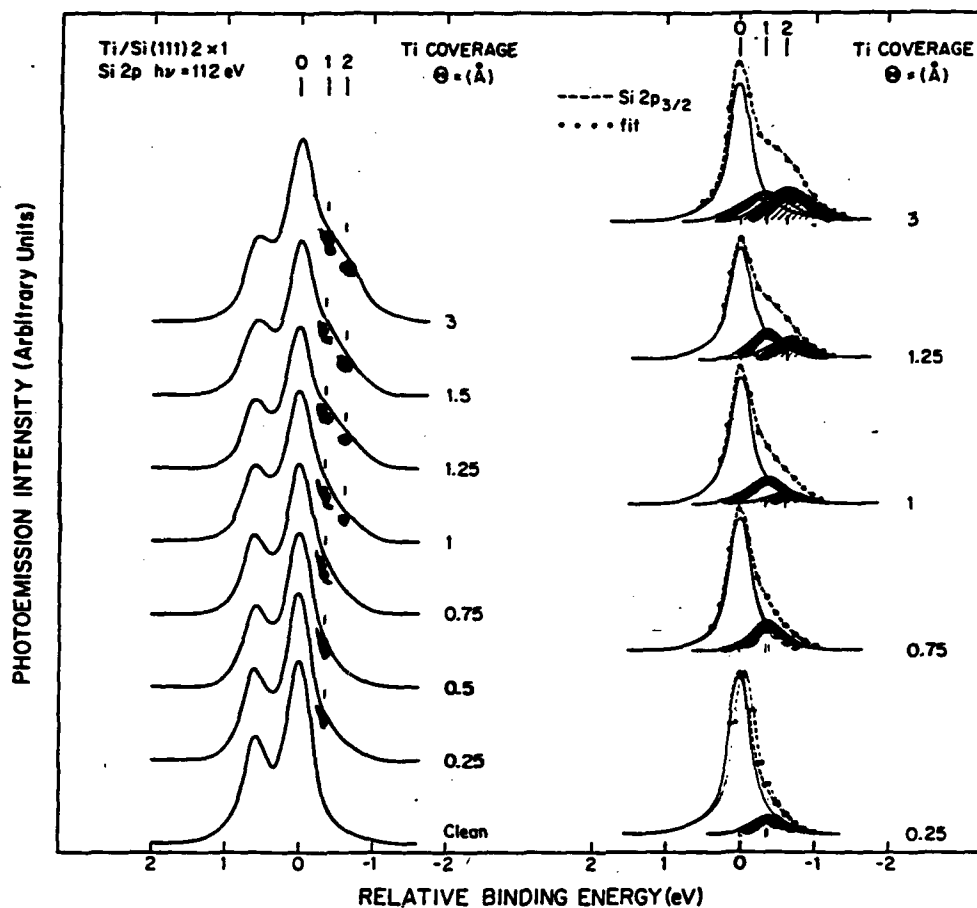
Metal overlayer with solution

reaction product(s) $\leftrightarrow xM + yS \rightarrow M_xS_y$

substrate

Example Ti / Si
Ti / GaAs
Ce / GaAs
V / Ge
⋮

Ti/Si(111) $h\nu = 112\text{ eV}$



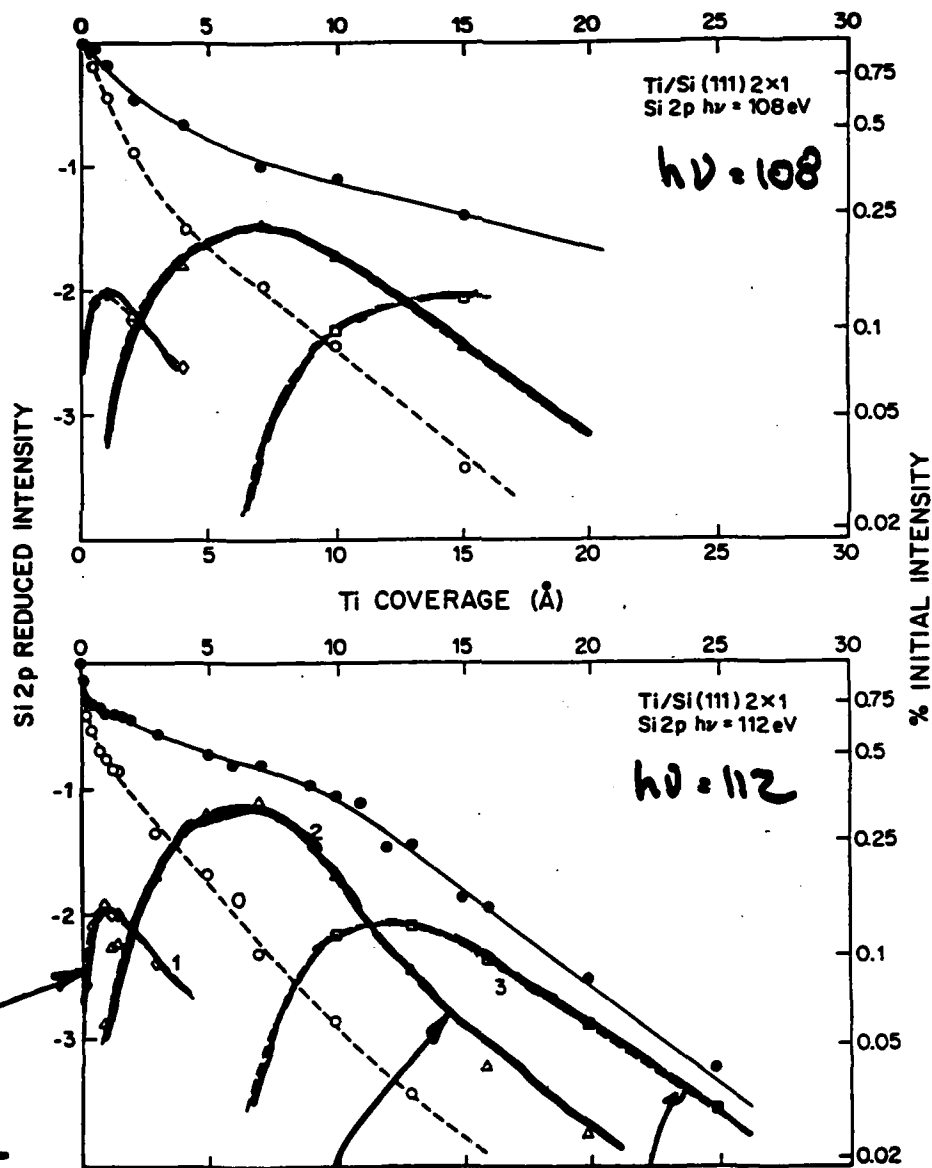
Si-2p_{1/2,3/2}

2p_{3/2}

Fig. 3

→ complex reaction products

Ti/Si(111)

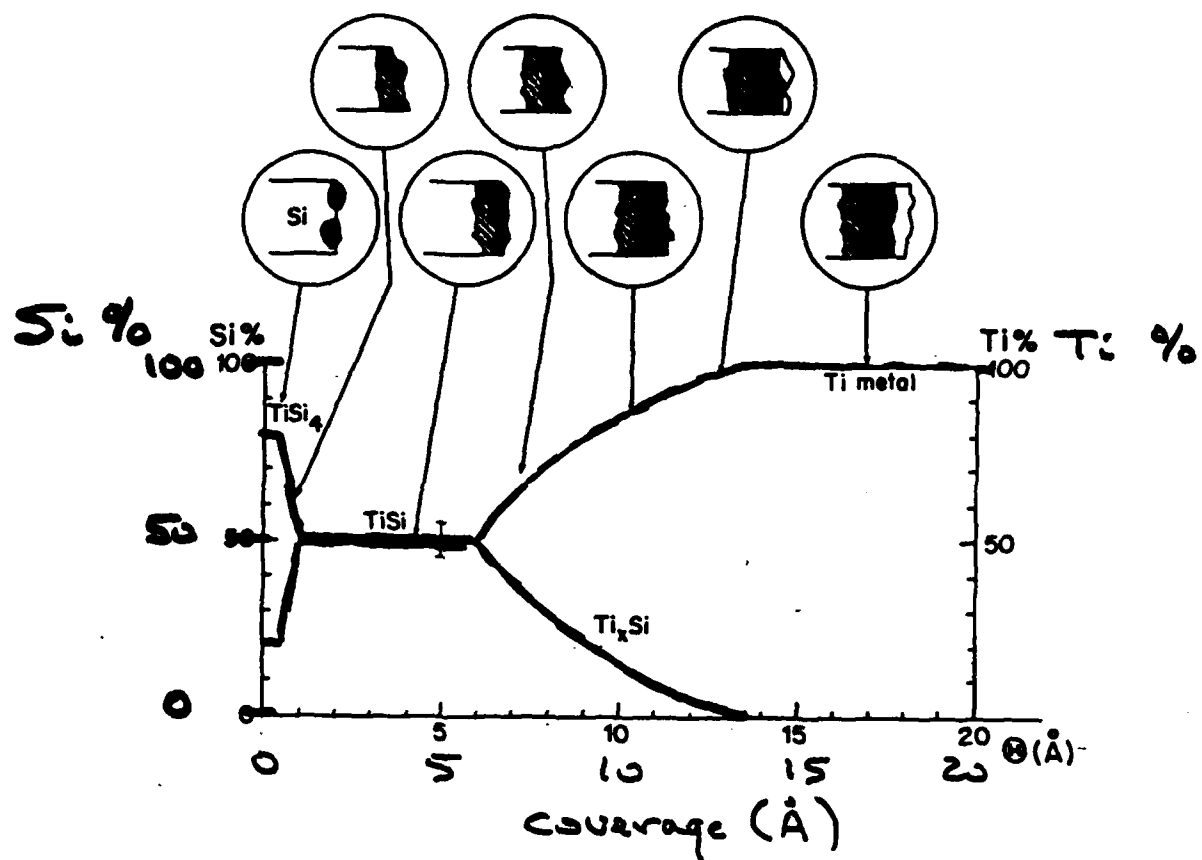


ultra thin
'transition
region

Ti-Si
reaction product

Si in solution
in Ti

Fig. 5



Metastable Ti/Si interface Fig. 6

Ti-Si acts to regulate its own growth through kinetics

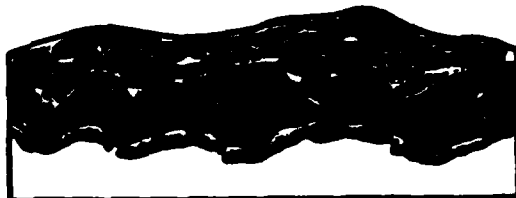
Modeling gives stoichiometry. Temp dependences give D_0 and activation energy

Interface Evolution

Convergence
to metal
overlayer



5. Metal overlayer growth on a complex, multiphase system

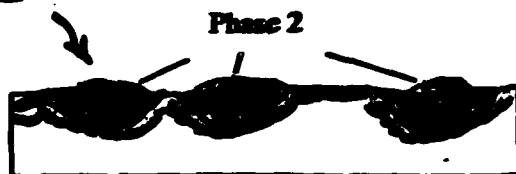


4. Complete coverage by final reaction product



3. Both reaction products grow as overlayer thickness increases

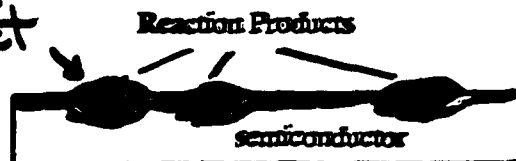
Phase 2



2. Onset of mixed phase growth

Reaction product

substrate



1. Heterogeneous formation of reaction products (islands)

Schematic of evolving metal/semiconductor interfaces showing heterogeneous, metastable growth with spatial dimensions approaching atomic scale. Modifying the physics and chemistry of bulk solids to be applicable to these dimensionally-constrained systems is a major challenge.

Room Temperature Chemical Reactions and Schottky Barrier Formation at the Metal/InP(110) Interfaces : Comparison to Si and GaAs Interfaces.

T. Kendelewicz, SEL, Stanford University,

**K. A. Bertness
K. K. Chin
R. S. List
P. H. Mahowald
C. E. McCants
N. Newman
M. D. Williams**

**I. Lindau
W. E. Spicer**

Outline:

- 1. Introduction and experimental approach**
- 2. Systematics of chemical reactions at the M/InP interfaces**
- 3. Submonolayer band bending vs band bending for thick interfaces. Is there a correlation between barrier height and chemistry?**
- 4. Implications on models of Schottky barrier formation**

Experimental approach

Use high resolution surface sensitive core level photoemission spectroscopy to study metal/InP interfaces built in a layer by layer fashion in UHV.

Get information on:

- 1. Evolution of the band bending with metal thickness.
(from shifts of the substrate components of the core levels)**
- 2. Chemical reactions between the substrate and the overlayer
(from the chemically shifted peaks).**
- 3. Overlayer growth mode (from intensities).**

XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

Studies were performed in UHV on clean cleaved InP(110) surfaces exposed to controlled amounts of metals deposited by resistive heating from in situ cleaned sources (deposition rates of about 1Å/min, pressure during evaporations about 10^{-10} Torr).

Advantage of the technique:

- 1. Surface sensitivity- allows one to study the very beginning of the chemical reactions and initial band bending.**
- 2. Photon energy tunability - allows modeling of interfaces.**
- 3. Atomic specificity - possibility to independently study the reactions of all the species building the interface.**
- 4. Control of contamination- possibility to detect contaminants (O, C etc.)**

Limitation of PES:

- 1. Does not provide information on buried interfaces**
- 2. Has to be combined with other techniques (ex I-V or C-V) to compare submonolayer band bending with thick devices barrier heights**
- 3. Often requires computer fitting of the data to separate band bending (error bar 0.1 eV) and model chemistry**

1 27 H																	2 He														
3 24 B	4 39 K															5 49 B	6 47 C	7 30 N	8 35 O	9 39 F	10 Ne										
11 23 Na	12 36 Ar															13 27 Al	14 28 Si	15 31 P	16 32 S	17 35 Cl	18 Ar										
19 39 K	20 40 Ca	21 39 K	22 38 Ti	23 41 V	24 46 Cr	25 38 Mn	26 43 Fe	27 44 Co	28 45 Ni	29 44 Cu	30 42 Zn	31 40 Ga	32 48 Ge	33 51 As	34 47 Se	35 48 Br	36 Kr														
37 85 Rb	38 88 Sr	39 87 Y	40 90 Zr	41 91 Nb	42 92 Mo	43 93 Tc	44 94 Ru	45 95 Rh	46 96 Pd	47 97 Ag	48 98 Cd	49 99 In	50 100 Sn	51 101 Sb	52 102 Te	53 103 I	54 104 Xe														
55 87 Cs	56 89 Ba	57 90 La	58 91 Ce	59 92 Pr	60 93 Nd	61 94 Pm	62 95 Sm	63 96 Eu	64 97 Gd	65 98 Tb	66 99 Dy	67 100 Ho	68 101 Er	69 102 Tm	70 103 Yb	71 104 Lu	72 105 Hf	73 106 Ta	74 107 W	75 108 Re	76 109 Os	77 110 Ir	78 111 Pt	79 112 Au	80 113 Hg	81 114 Tl	82 115 Pb	83 116 Bi	84 117 Po	85 118 At	86 119 Rn
87 87 Fr	88 88 Ra	89 89 Ac																													
			90 90 Th	91 91 Pa	92 92 U																										
			90 90 Th	91 91 Pa	92 92 U																										

Atomic Number

Work Function* [eV]

Electronegativity**

Valence Electron Configuration

3 2.4

10 Li

1s² 2s¹

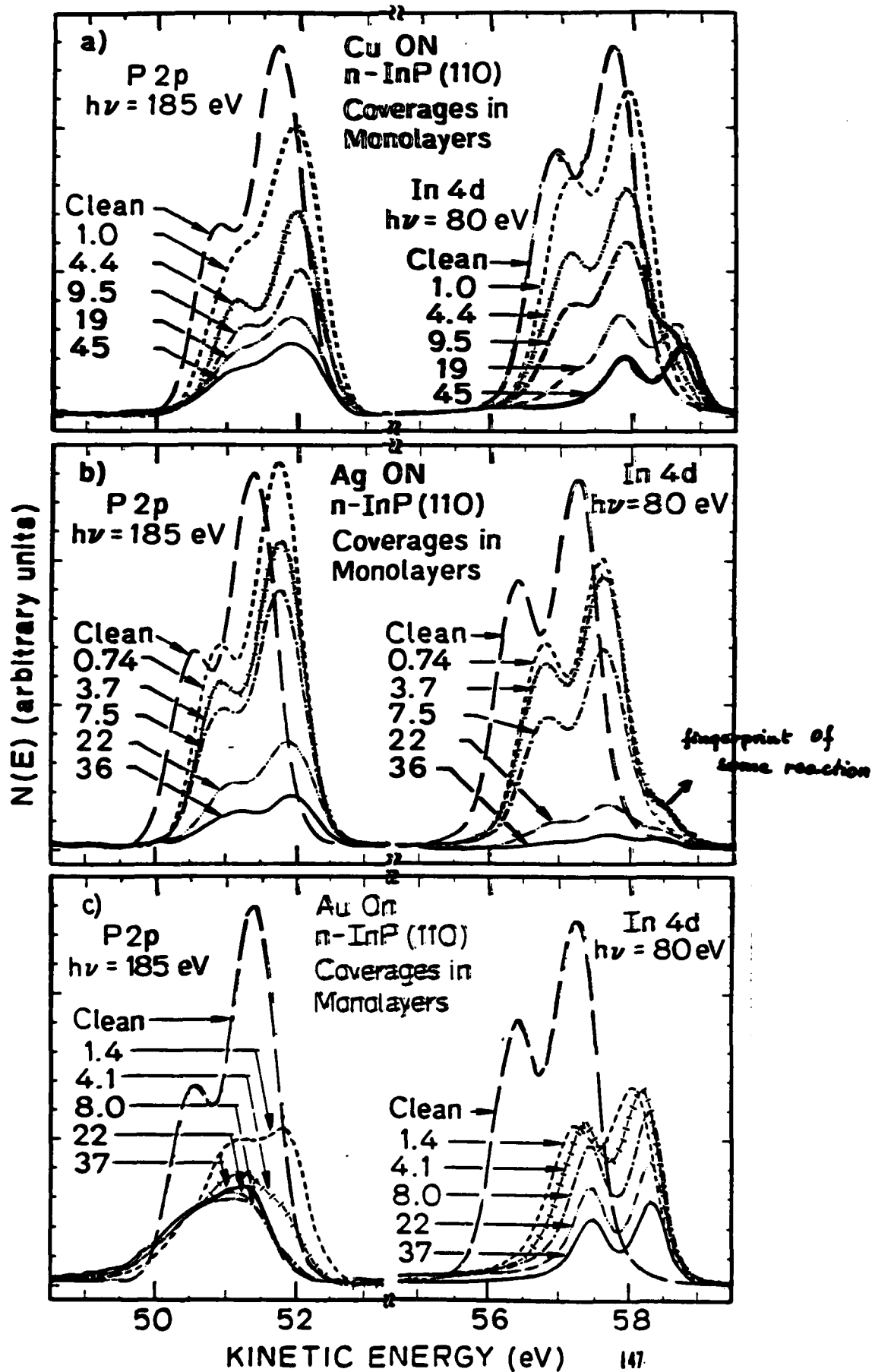
* Recommended by V. S. Fomenko, *Handbook of Thermodynamic Properties*, ed. G. V. Samsonov (Plenum Press, New York 1966).

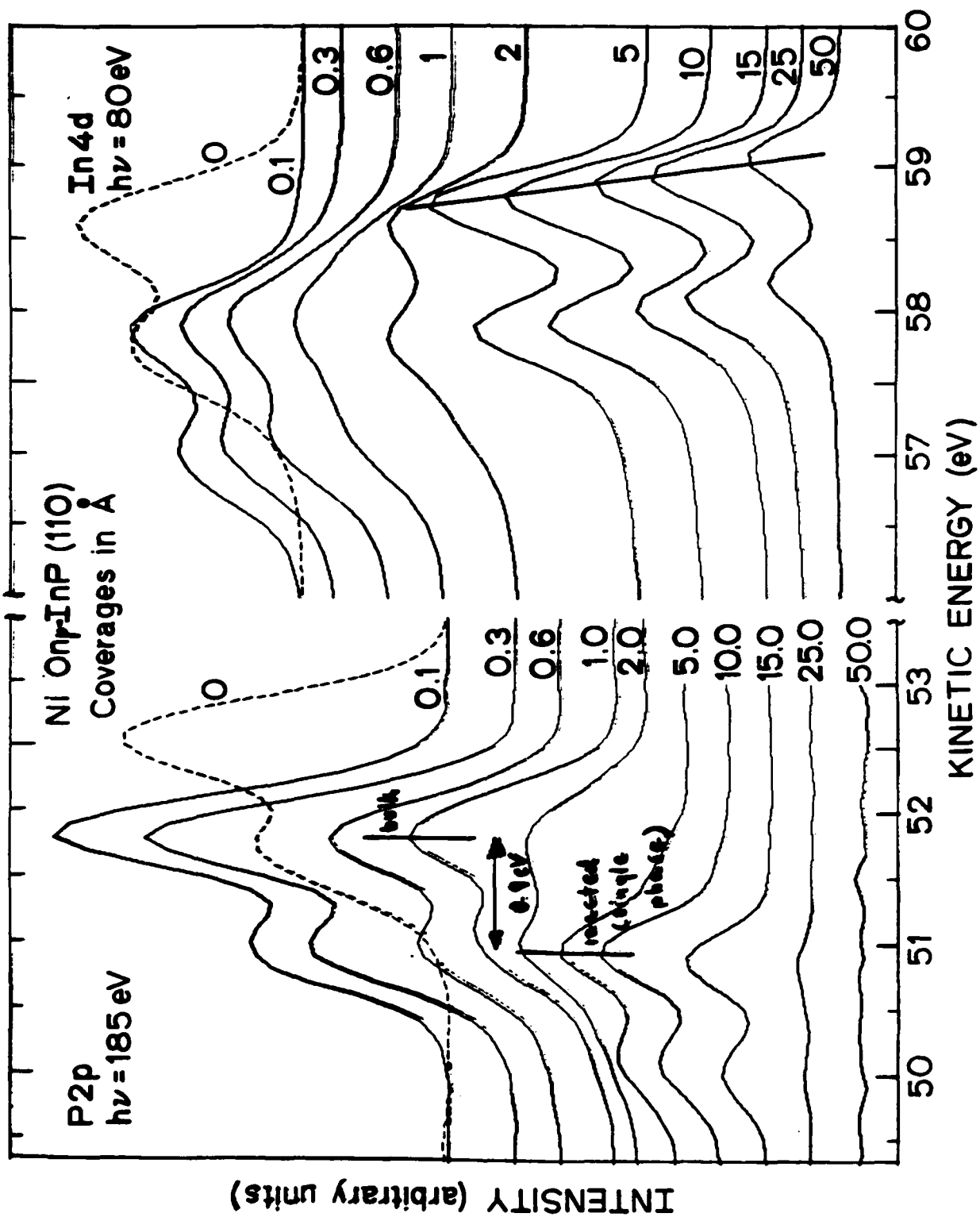
** Recommended by M. G. Evans, M. L. Eyring, J. Chem. Phys. 3, 426 (1935).

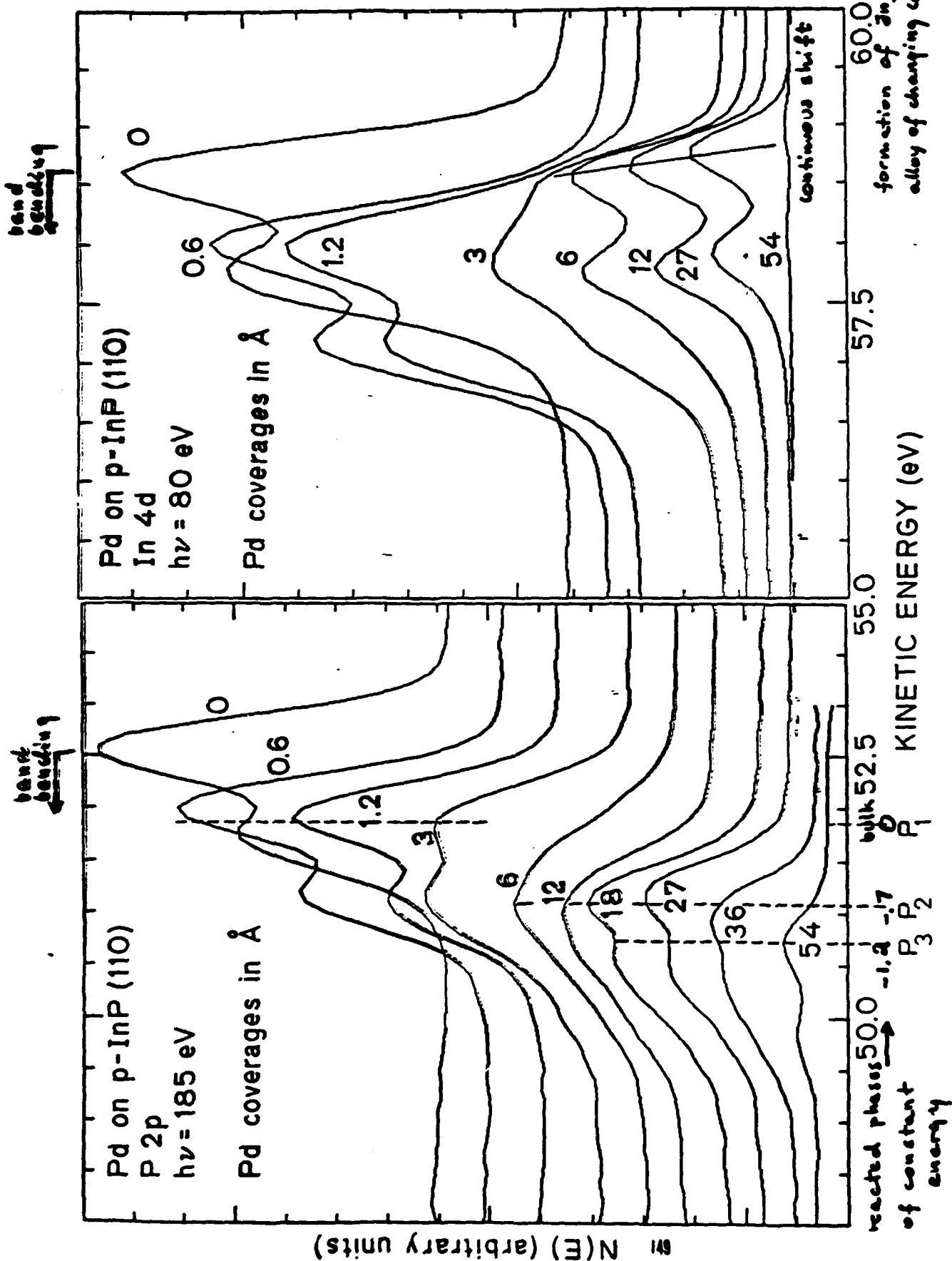
* Recommended by V S Fomenko: *Handbook of Thermodynamic Properties*, ed G. V. Samsonov (Plenum Press, New York 1986)
 ** Recommended by W. Gordy, W. J. O. Thomas: *J Chem Phys* 24 439 (1955)

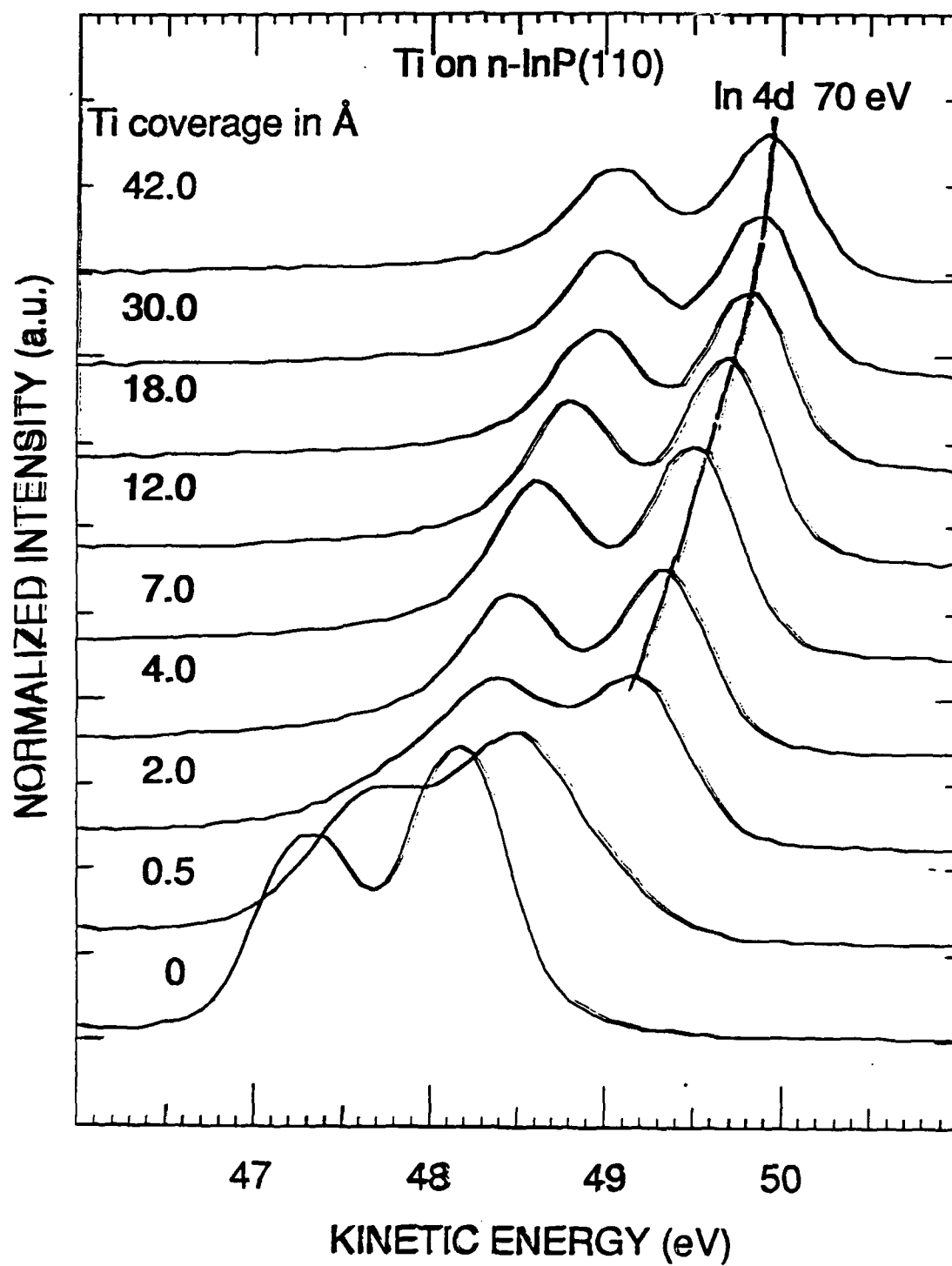
Description of chemical reactions at the M/InP interfaces

- 1. 3d transition metals (Ti, V, Cr, Mn, Co, Ni)- strongly reactive, multiphase reactions, uniform overlayers (no clustering).**
- 2. Near noble metals (Ni, Pd, Pt)- strength of the reaction decreases in the sequence Ni-Pd-Pt, clustering for Pt.**
- 3. Noble metals - much less reactive than transition metals. Reaction switches from mostly M-P for Cu to mostly M-In for Au. Ag- one of the least reactive metals.**
- 4. Column III simple metals (Al, Ga, In, Tl)- Limited exchange reaction for Al and Ga, with exception of Tl tendency to cluster.**
- 5. Column IV elements (Si, Ge, Sn)- Considerably less reactive than transition metals or Al. However, some outdiffusion of substrate species clearly observed. Typically form uniform overlayers (no clustering).**









General trends in reactivity (comparison with GaAs and Si)

1. All metals studied react with the InP surface. A truly nonreactive and sharp interface was not found. Ag closest to ideal.

2. In reactions

In is diluted into the overlayer. The changing stoichiometry of the alloy is reflected in the binding energy shifts of the In 4d core level. Trends in data understood in terms of the model calculations using Born-Haber cycle and heats of solution from Miedema.

Similar behavior as for M/GaAs interfaces.

3. P reactions

P is involved in single (Ni) or multiphase (Pd,Ti) reactions. Binding energies of these phases are constant through the interface evolution indicating well defined reaction products.

Similar behavior as for M/GaAs interfaces.

4. There seems to be no indication for ternary reaction products.

5. For strongly reactive interfaces P containing phases are trapped at the interface and In strongly outdiffuses (In signal often detected for overlayers thicker than 100Å).

Opposite trend observed for M/GaAs interfaces. The differences may be related to larger heats of compound formation for phosphides.

6. Trends in reactions are remarkably similar to those detected for M/Si interfaces with P playing the role of Si in the reaction

products and In segregating out. This observation seems to be true (to some extent) for M/GaAs interfaces.

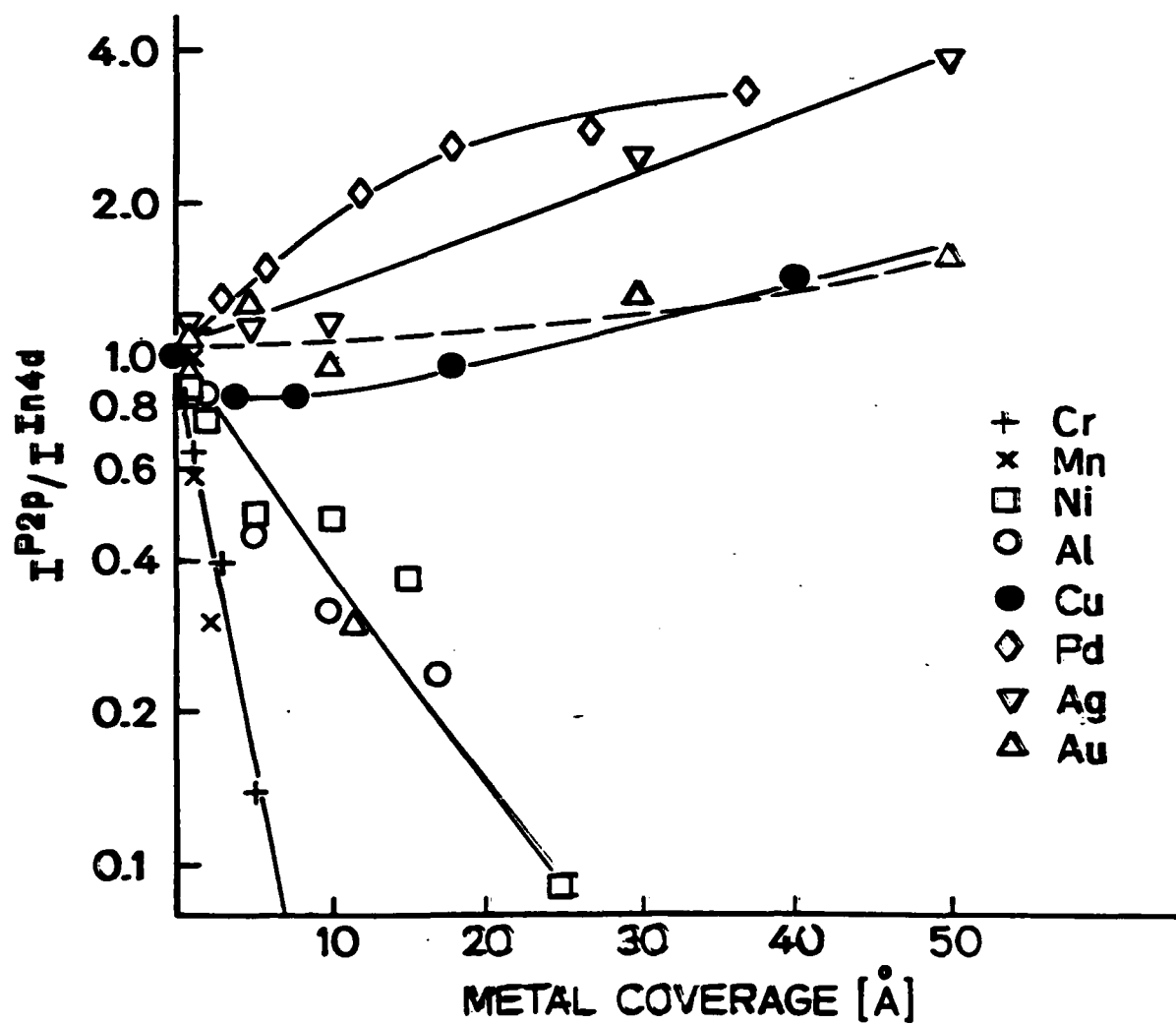
7. The data pin point the important role played by unfilled d shells in the interfacial reactions. The metals with unfilled d-shells react particularly strongly with InP (p-d hybridization).

8. Bulk thermodynamics is quite useful in predicting or accounting for interfacial reactions. However, at RT the interfaces are not in equilibrium and kinetics has to be considered.

INTIMATE SCHOTTKY BARRIERS ON CLEAVED n-InP(110)

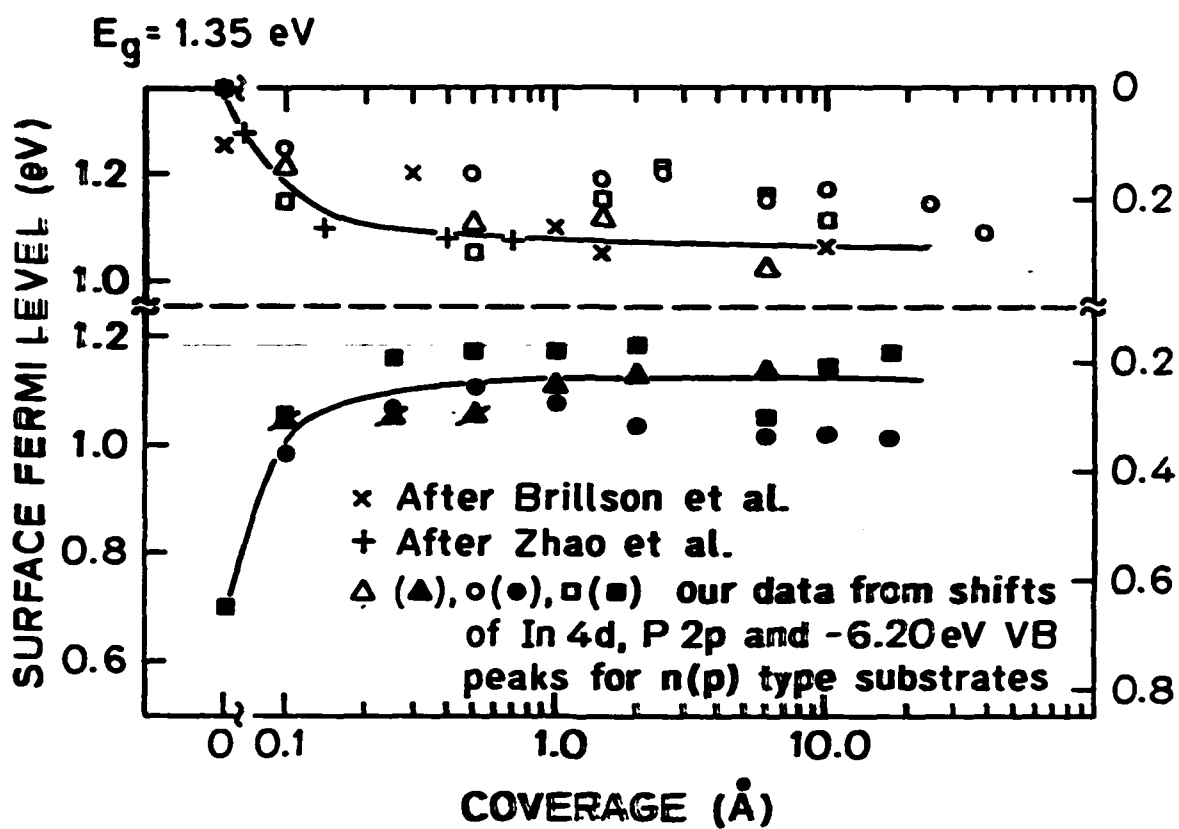
Metal	I-V Measurements		Fermi Level Pinning from PES*	
	Our Data Barrier Height (eV)	Ideality Factor	Our Data $\pm 0.1\text{eV}$	Brillson et al.
Ag	0.54	1.02 ± 0.02	0.45	0.45
Cr	0.45	1.10 ± 0.10	> 0.40	-
Cu	0.42	1.03 ± 0.05	0.65	0.70
Au	0.42	1.03 ± 0.03	0.40	0.40
Pd	0.41	1.03 ± 0.07	0.40	0.30
Mn	0.35	1.1 ± 0.3	0.40	-
Sn	0.35	1.04 ± 0.15	0.30	-
Al	0.33	1.0 ± 0.4	0.30	0.30
Ni	0.32	1.0 ± 0.3	0.30	0.20

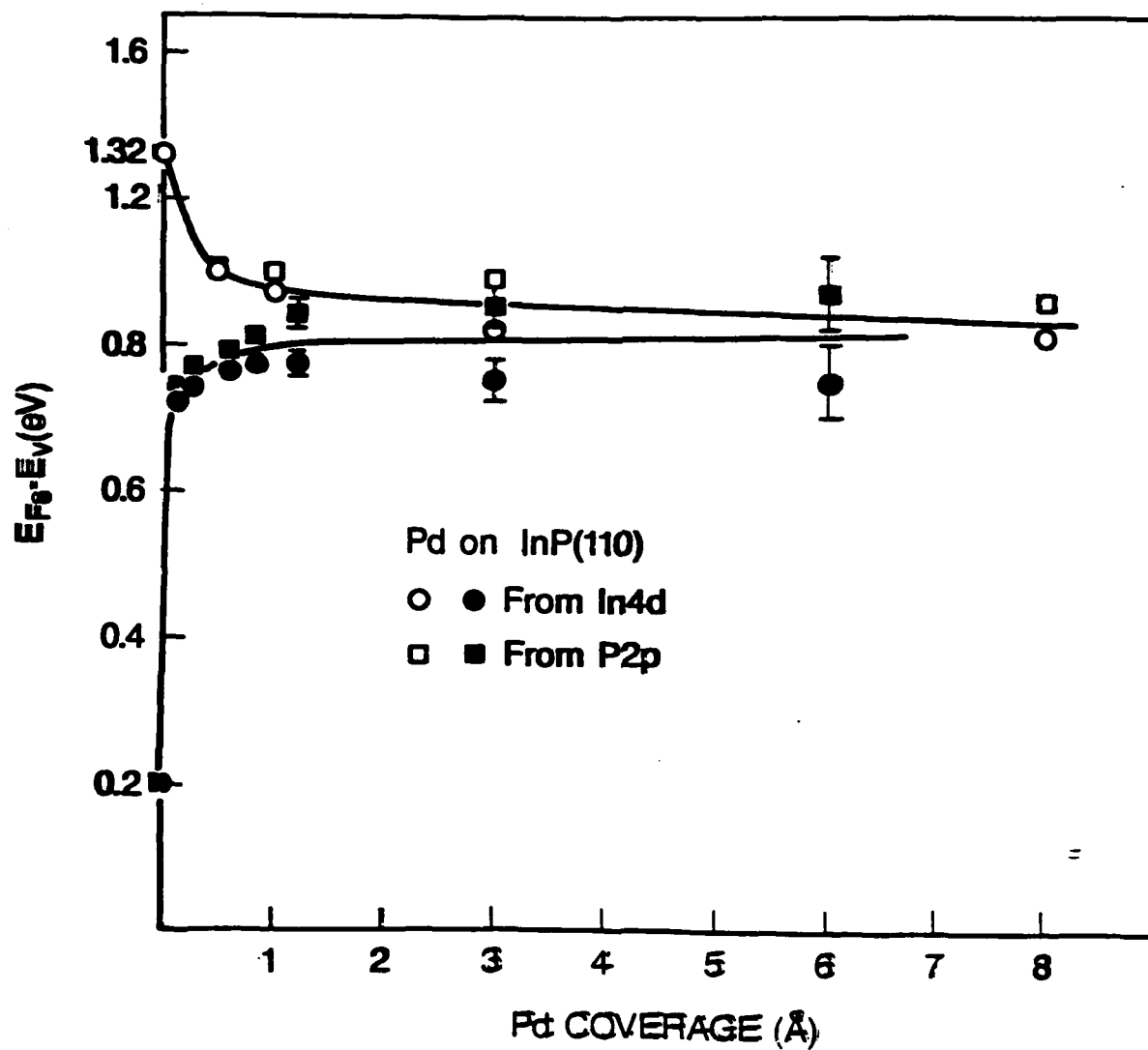
*Pinning established from original data for coverages below $10\text{\AA}$



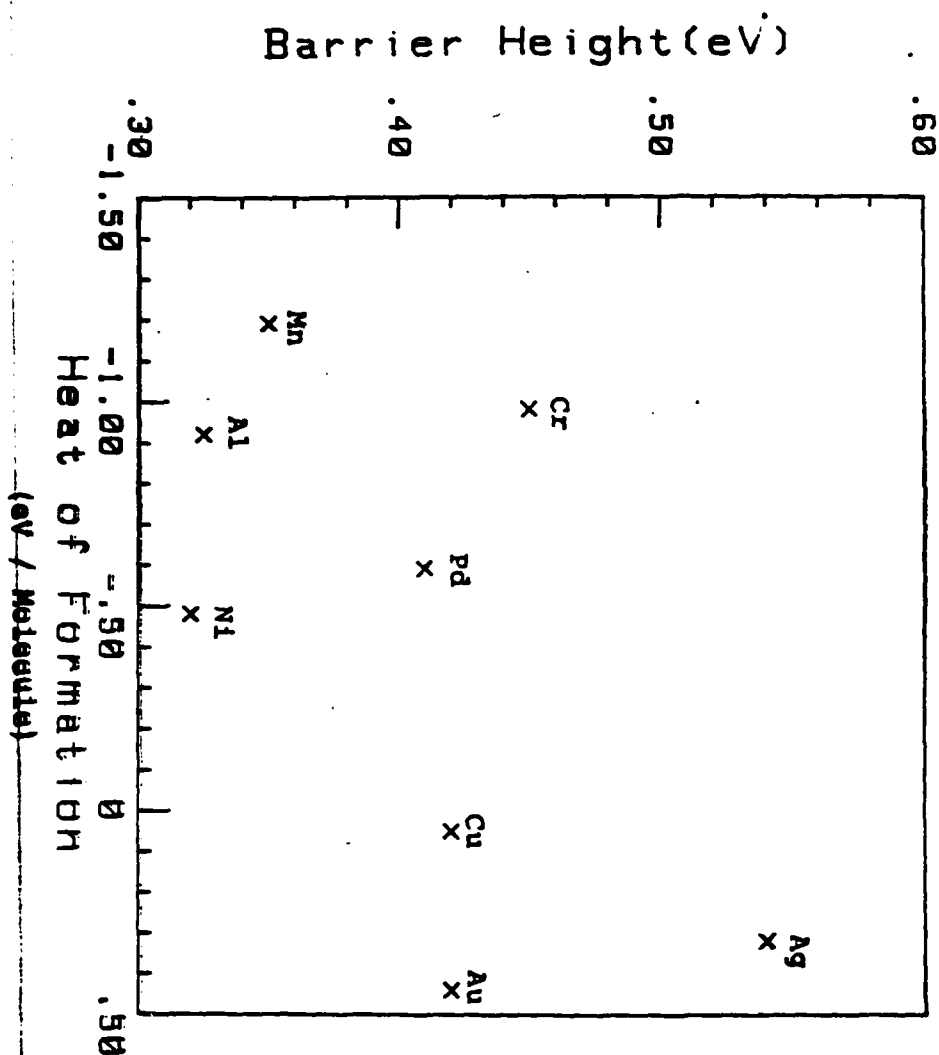
Band bending

- 1. Fermi level is pinned very rapidly. In the extreme case of transition metals, only a small fraction of a monolayer is necessary to complete the band bending.**
- 2. Pinning level is independent on the type of doping (including ex. Al overlayers).**
- 3. Pinning in the submonolayer coverage range agrees very well with barrier heights for diodes measured with I-V.**
- 4. Barrier heights for all metals studied are between 0.3 and 0.6 eV (n-type) and certainly DO NOT correlate with chemistry. There seems to be some dependence on electronegativity (work function). This point is in disagreement with older studies which suggested possible correlation with reactivity.**
- 5. Trends for InP and GaAs are very similar which indicates similar basic mechanisms.**





INP I-V



STABLE PHASES AT **REACTIVE METAL**

COMPOUND SEMICONDUCTOR **INTERFACES**

T. Sands
Bell Communications Research, Inc.

Contributors:

V. G. Keramidas and C. C. Chang
Bellcore

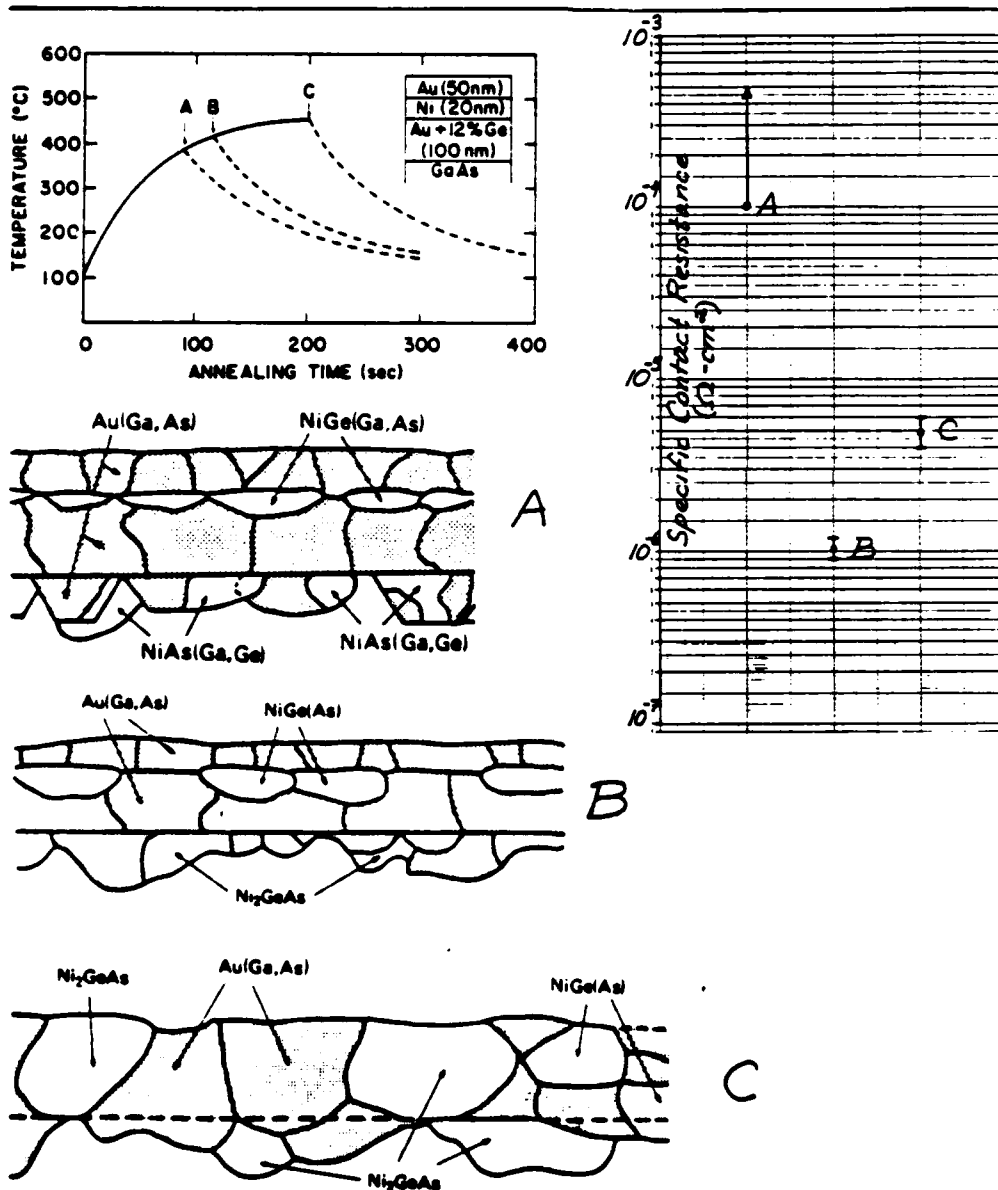
J. Ding, K-M. Yu, J. Washburn, K. Krishnan and R. Gronsky
LBL

A. J. Yu
Cornell

- o **Motivation for M/AB studies**
- o **Application of bulk equilibrium M-A-B phase diagrams to M/AB reactions:**
 - o **In/GaAs, a "success"**
 - o **Pd/GaAs, a "failure"**
- o **An example of uncharted territory:
the Ni/InP reaction**
- o **Conclusions**

Electron microscope studies of an alloyed Au/Ni/Au-Ge ohmic contact to GaAs JAP 54 (1983) 6952

T. S. Kuan, P. E. Batson, T. N. Jackson, H. Rupprecht, and E. L. Wilkie
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598



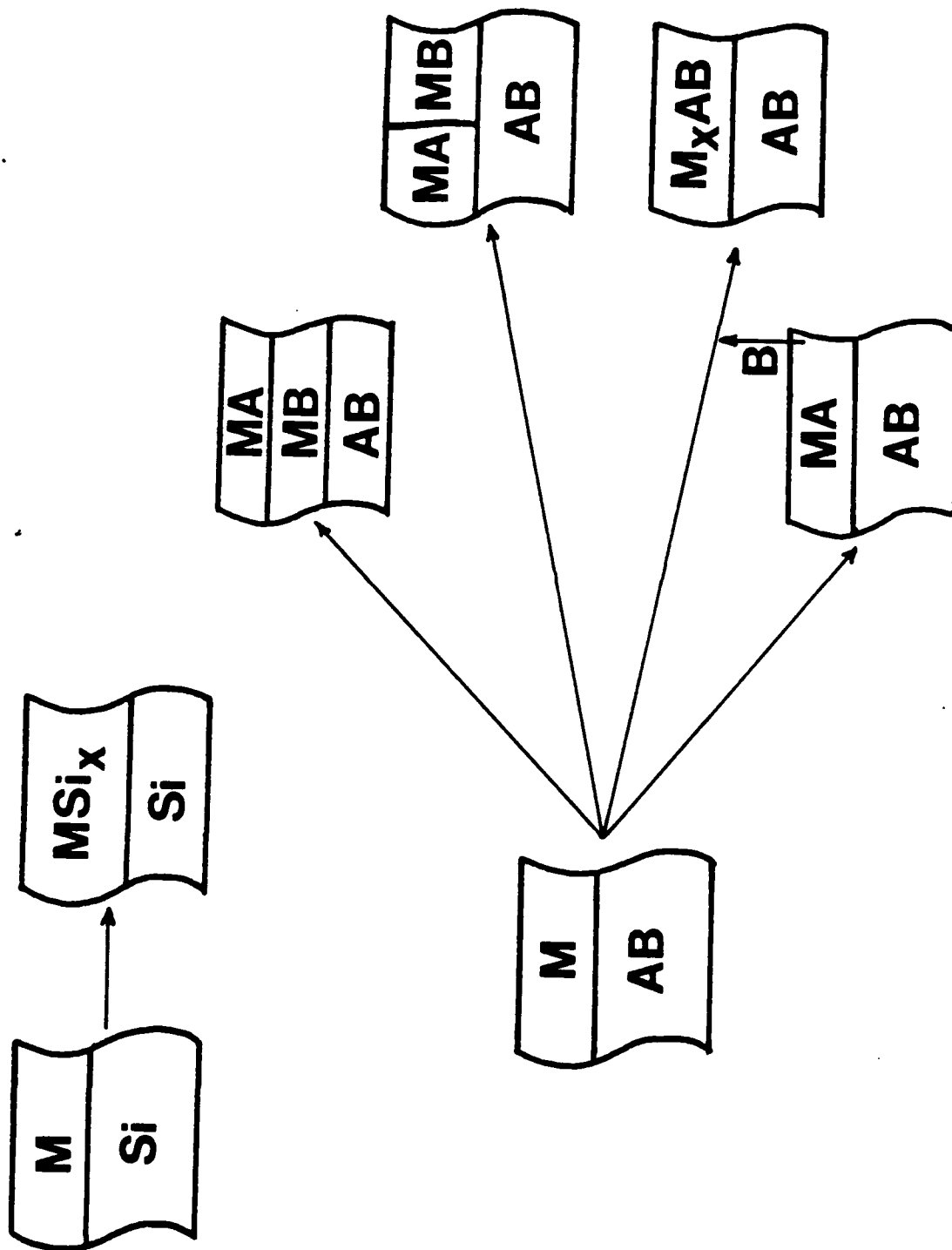
Why study M/AB reactions?

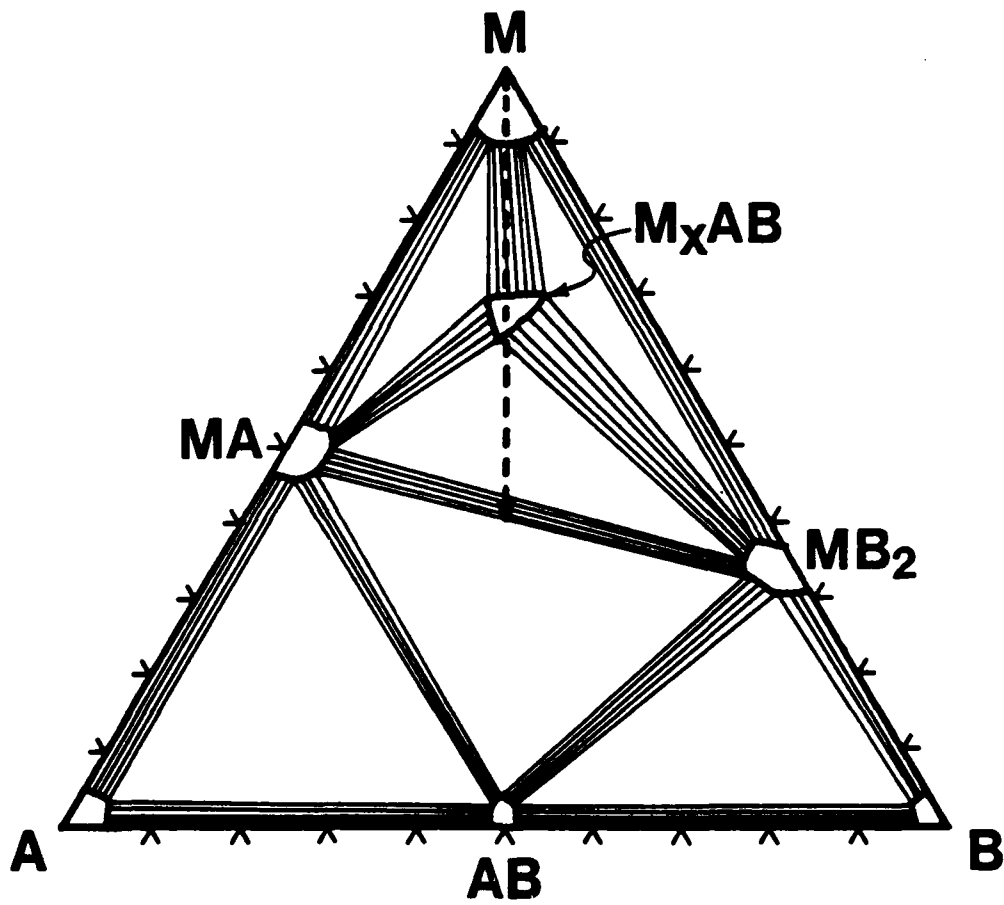
- Au-Ni-Ge/n-GaAs:**
- o low r_c but**
 - o difficult to reproduce**
 - o not stable at moderate T**
 - o lacks submicron lateral uniformity**

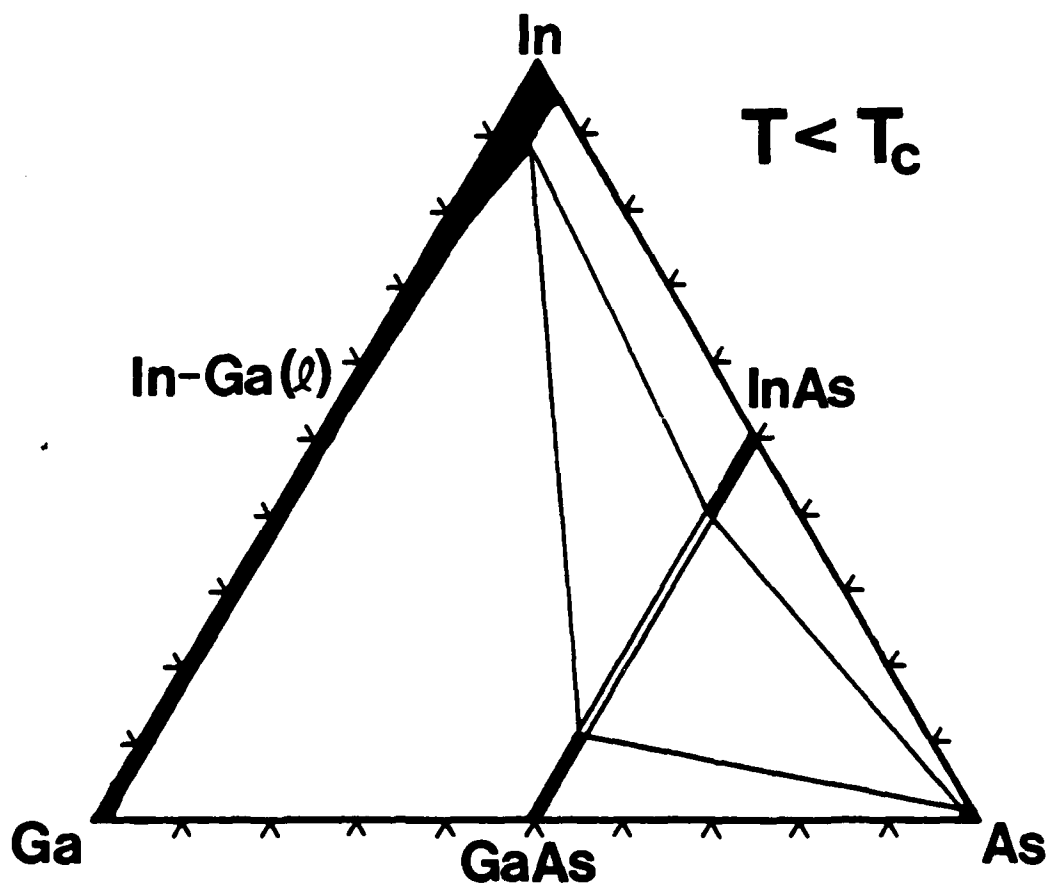
Design of contact metallizations which are compatible with future device requirements will require at least a rudimentary understanding of phase stability in M-A-B systems.

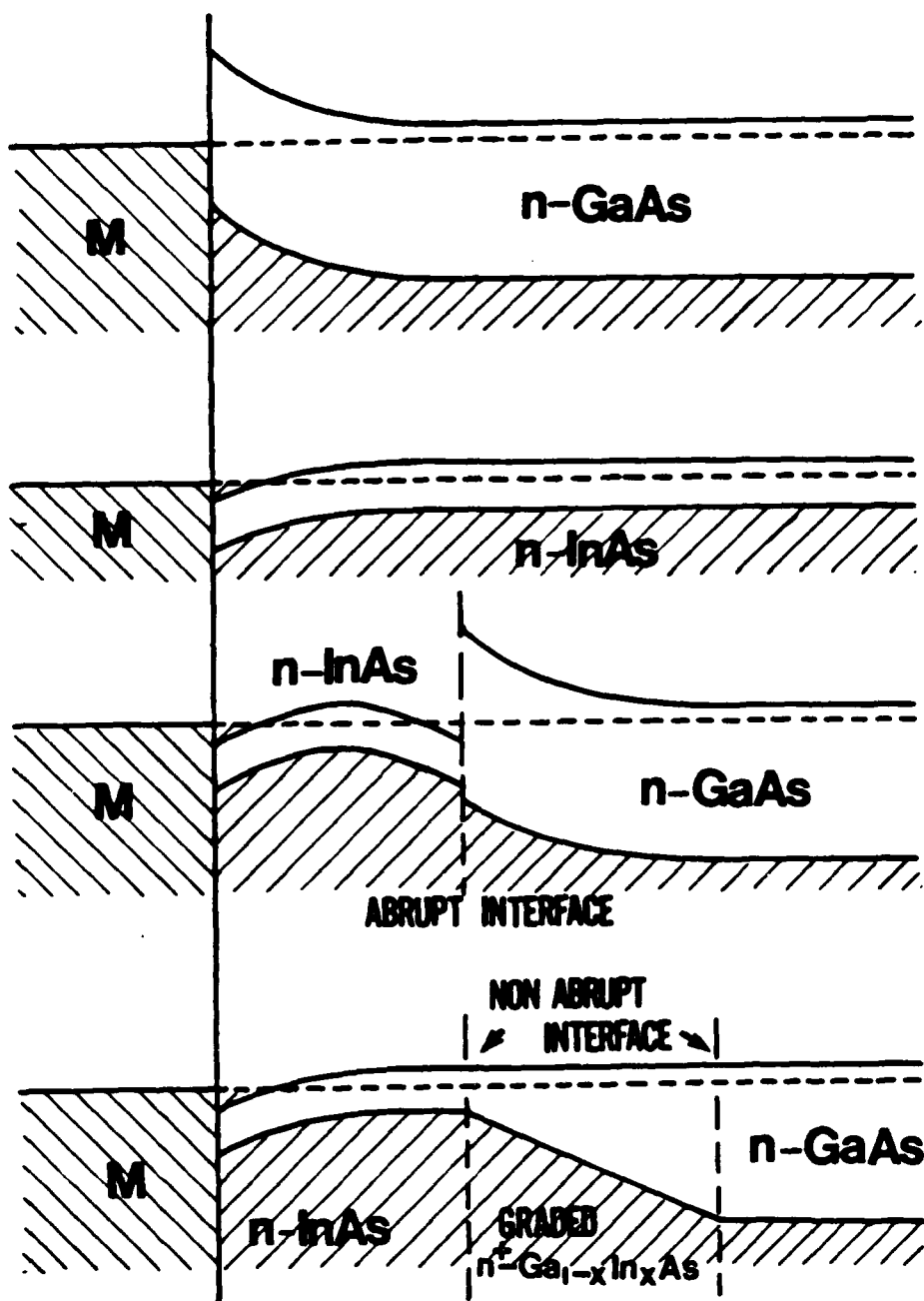
"If it ain't broke don't fix it ..."

... but if you know it's gonna break tomorrow, you better have your tools in your back pocket.



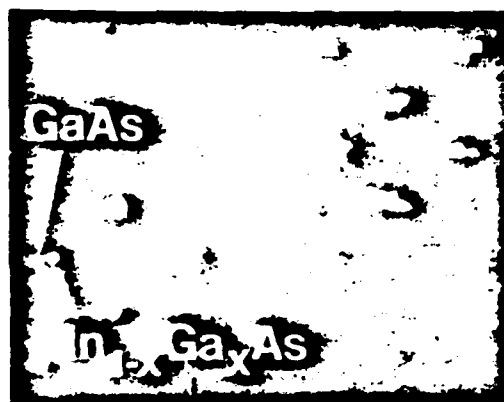
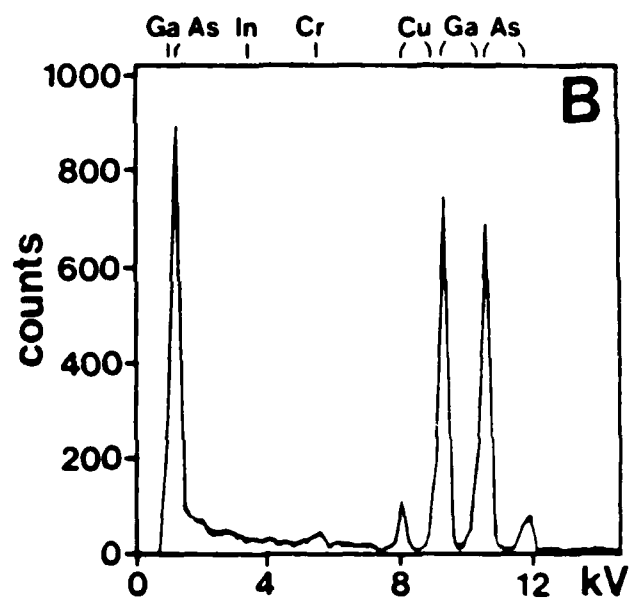
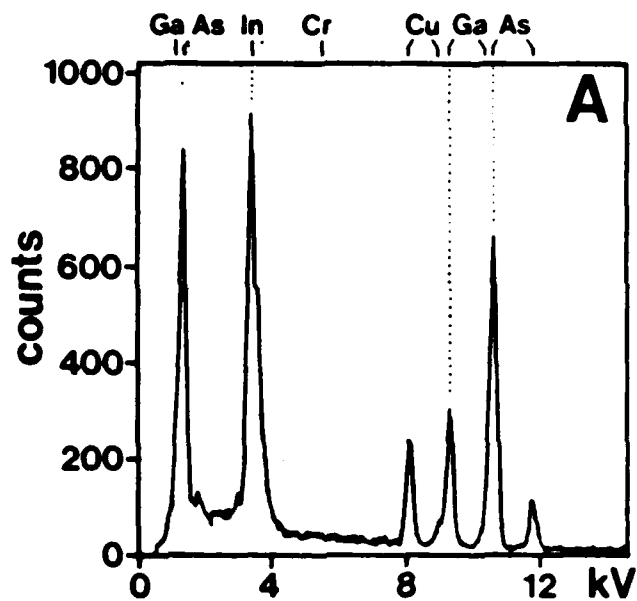




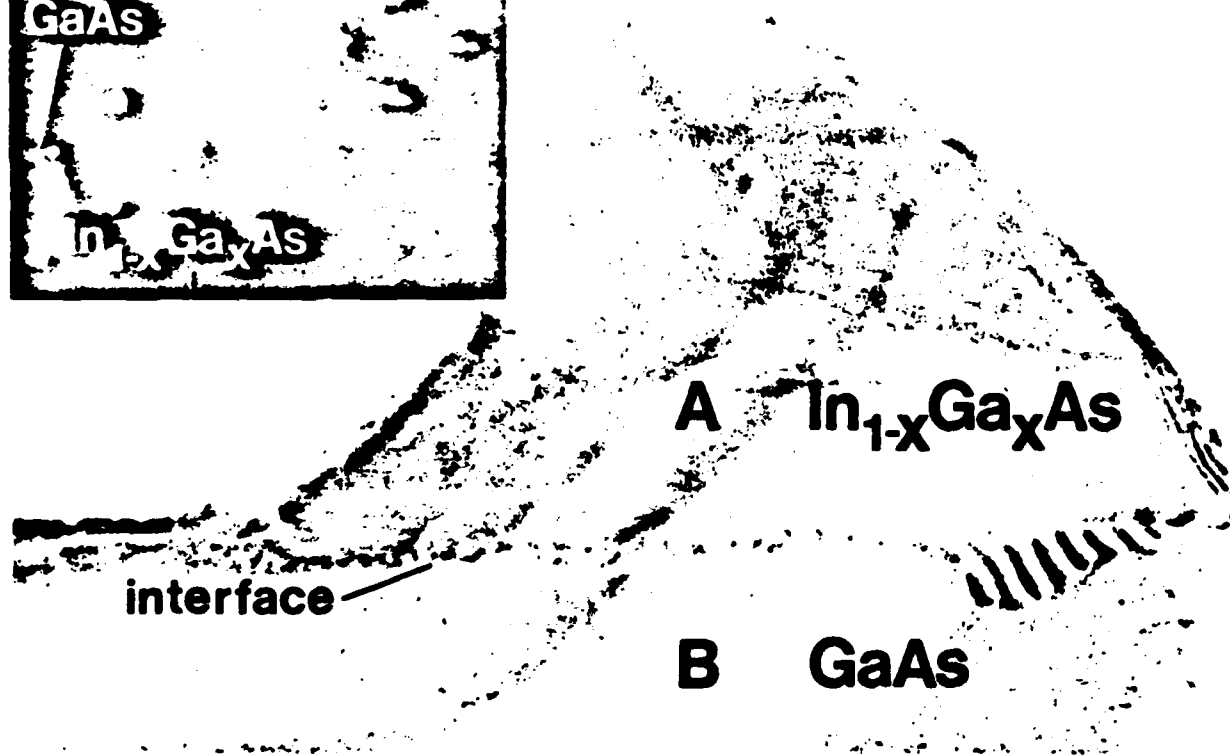


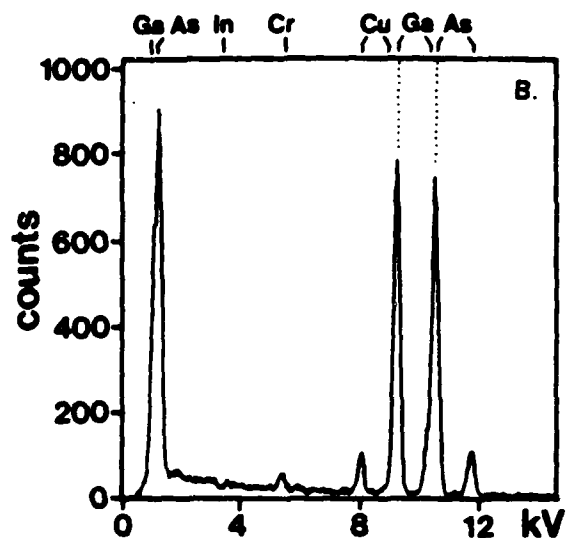
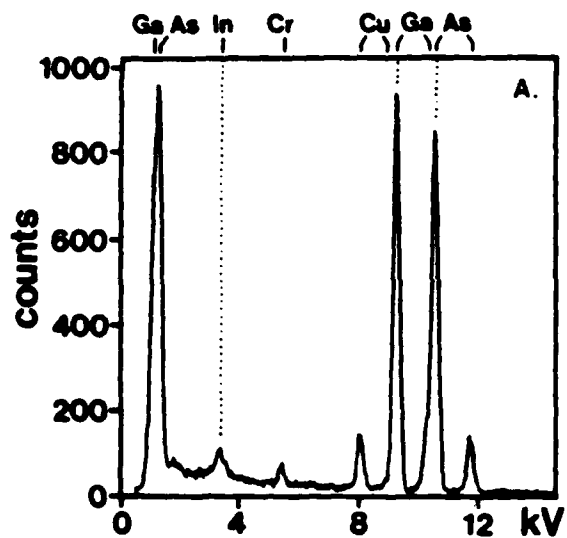
Woodall et al. JVST 1981 XBL 864-1319



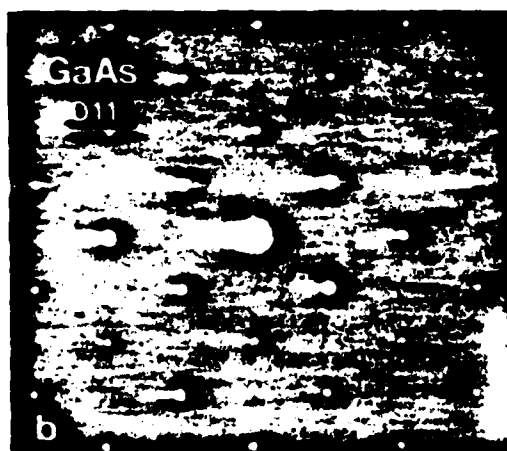


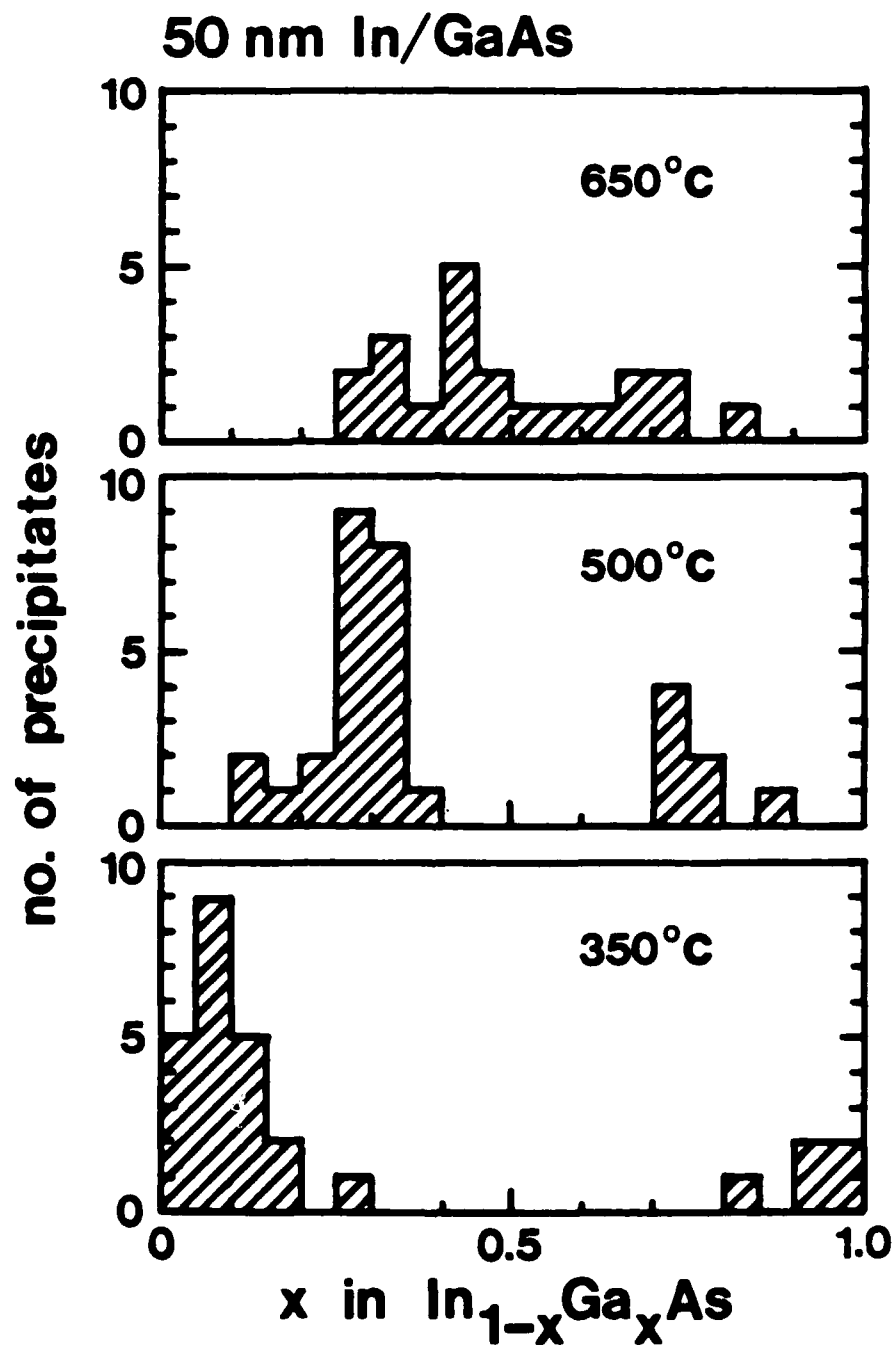
50 nm



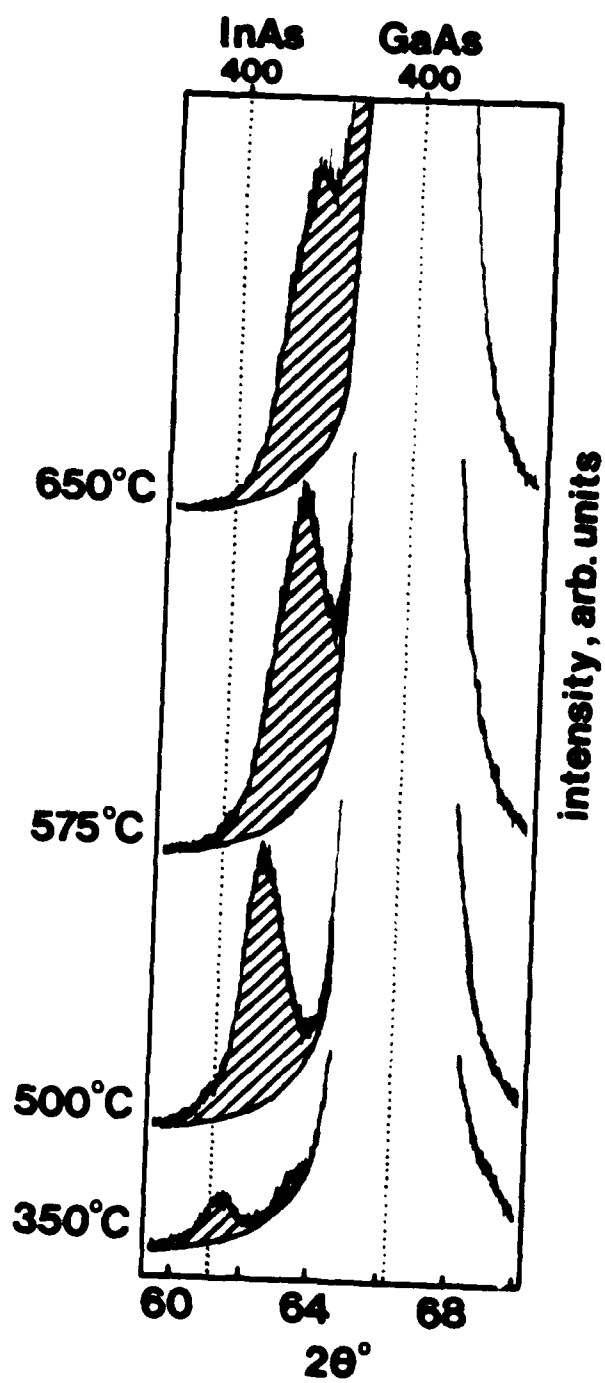


NO/A

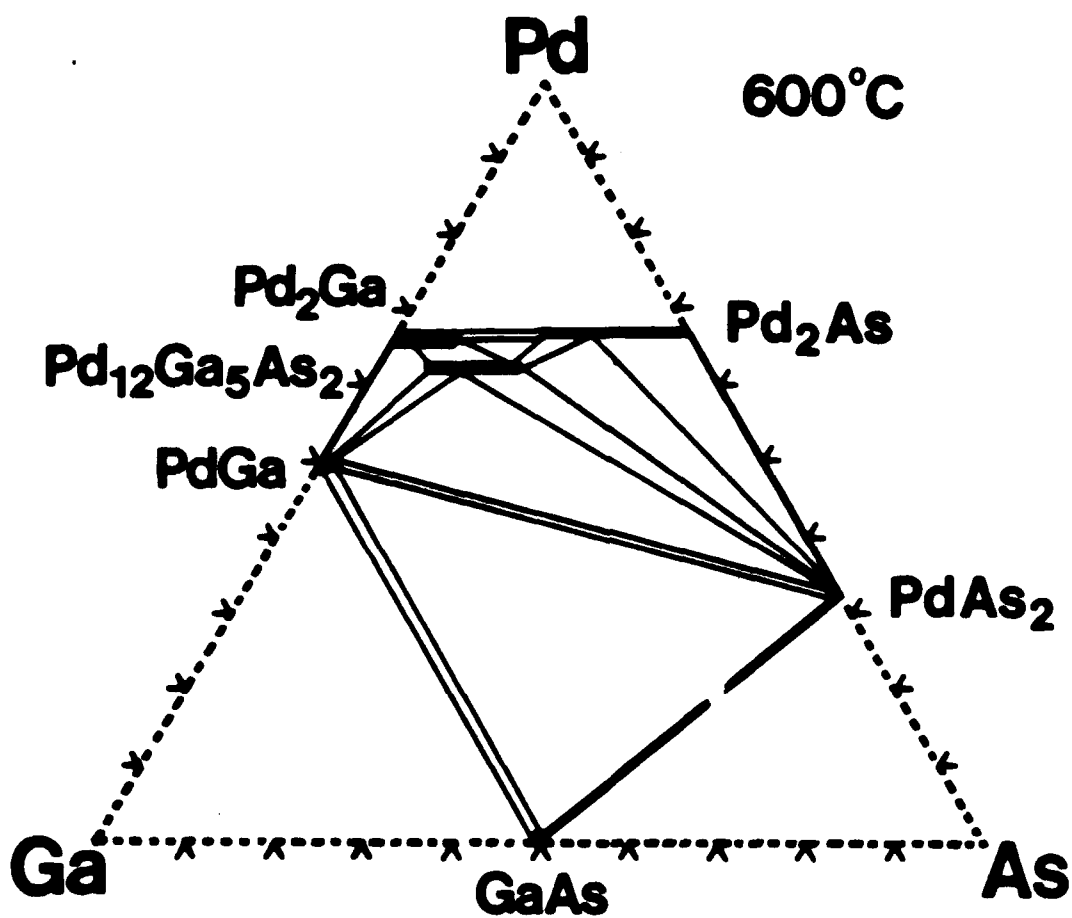




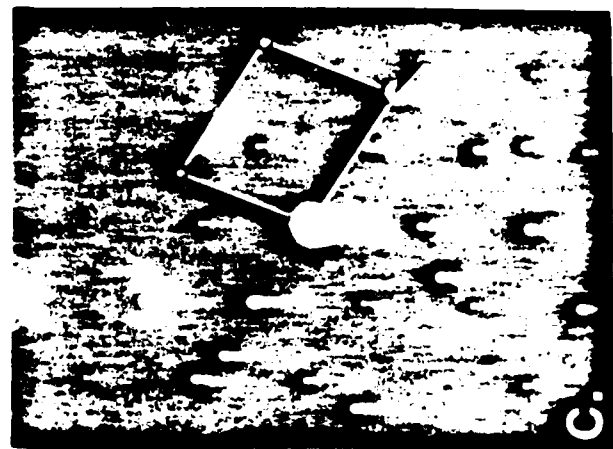
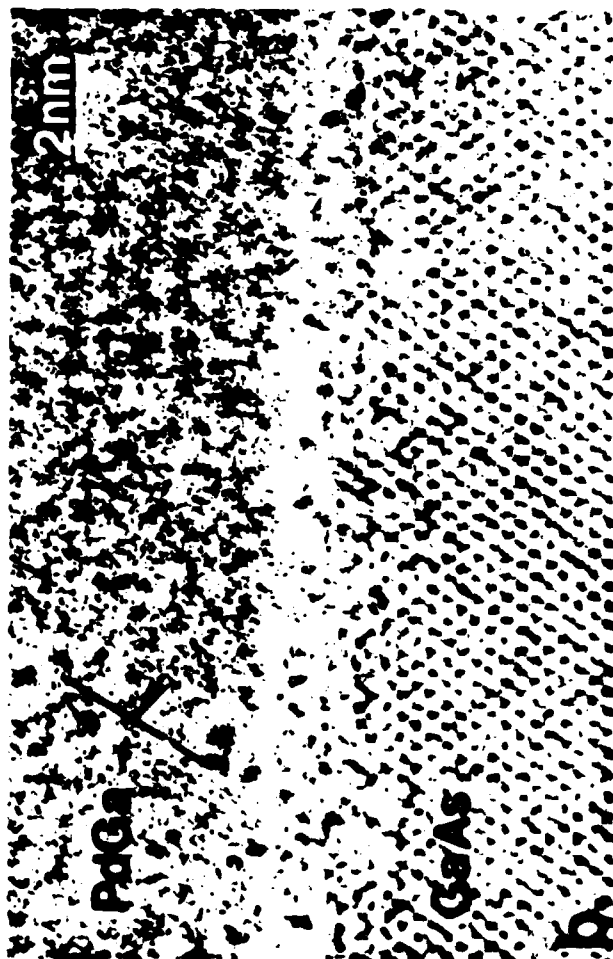
XBL 868-3109

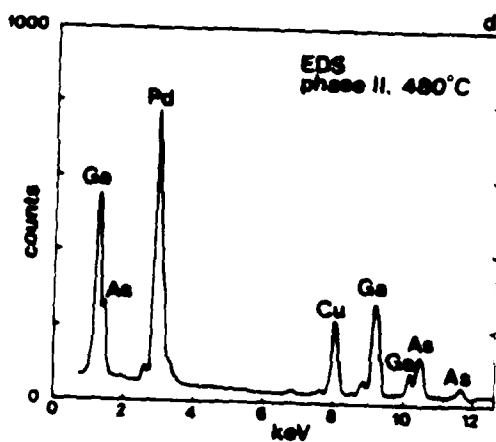
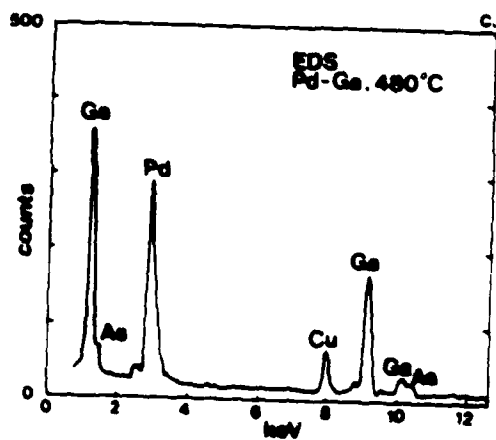
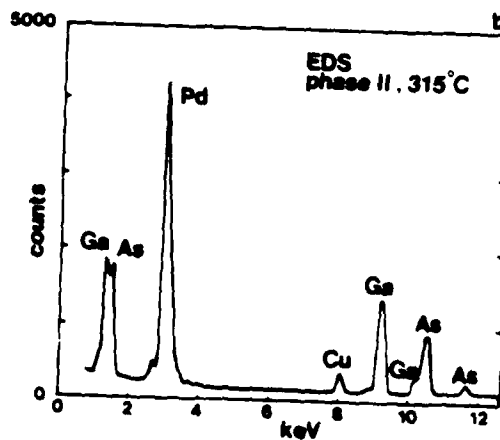
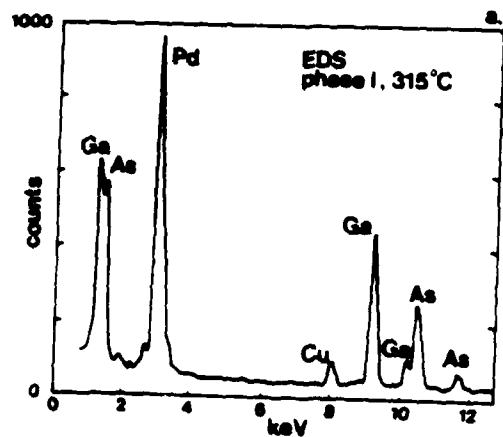


XBL 869-3272

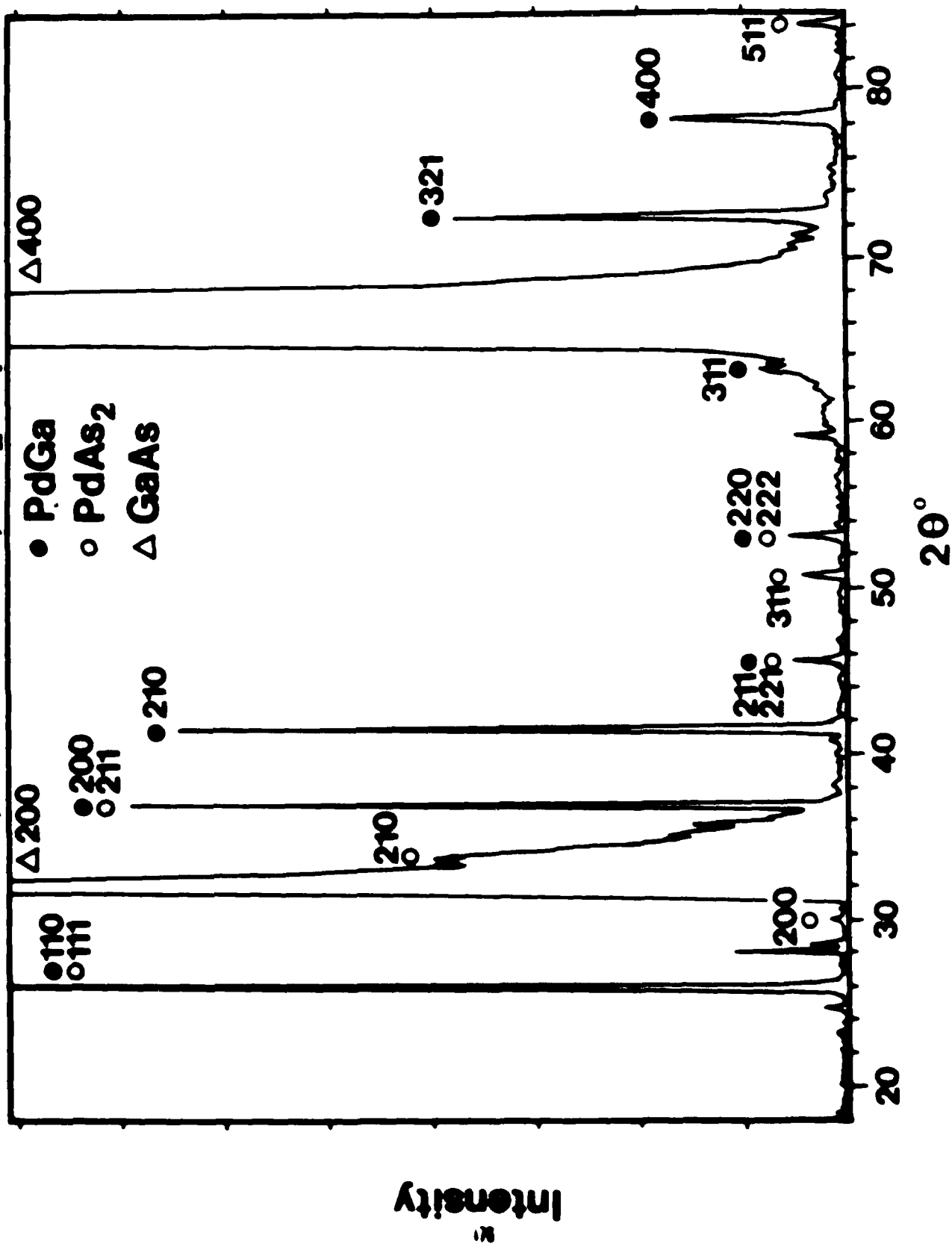


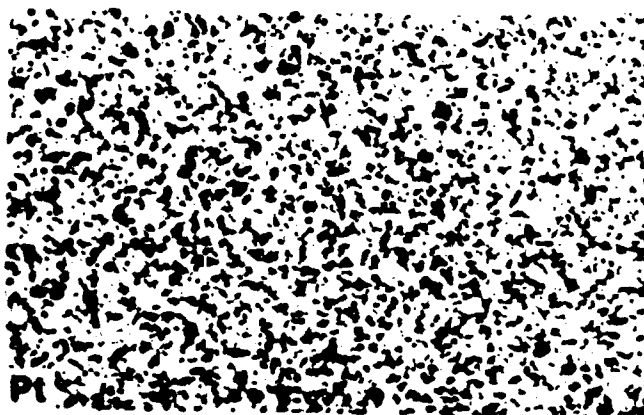
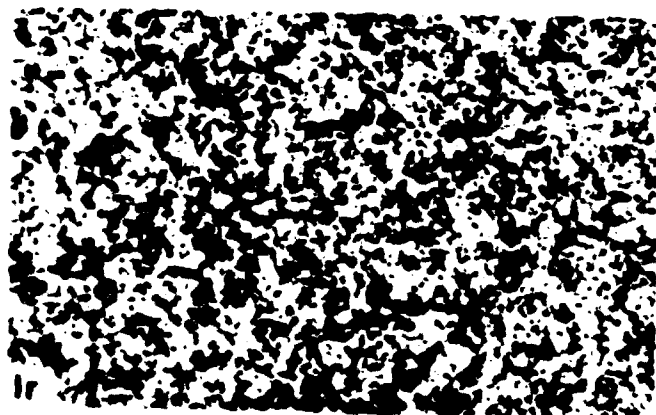
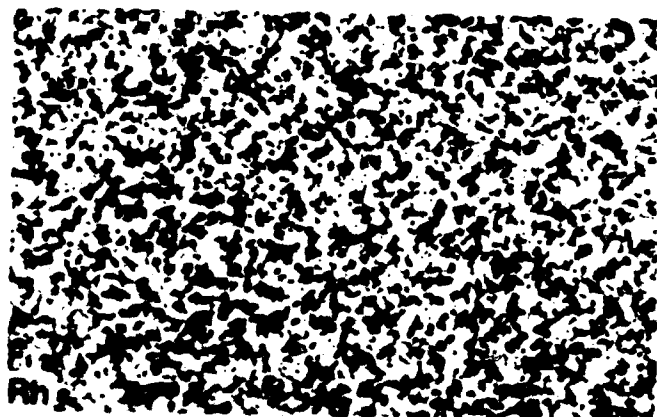
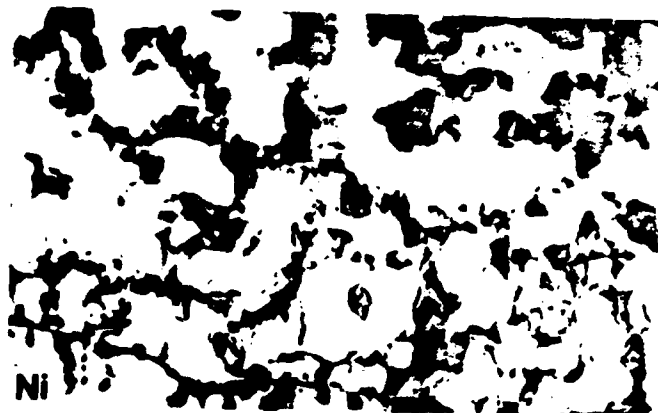
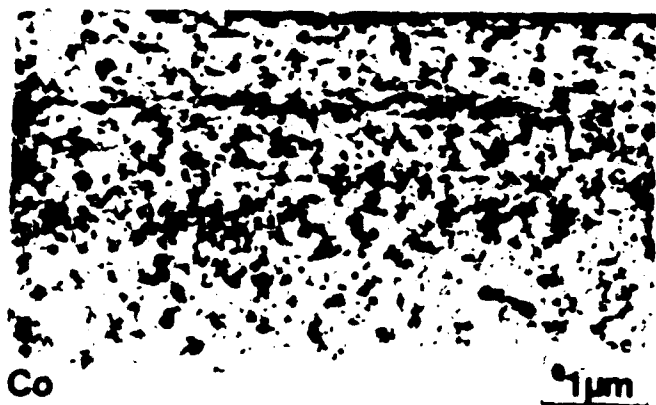
El-Boragy & Schubert, Z. Metall., 1981

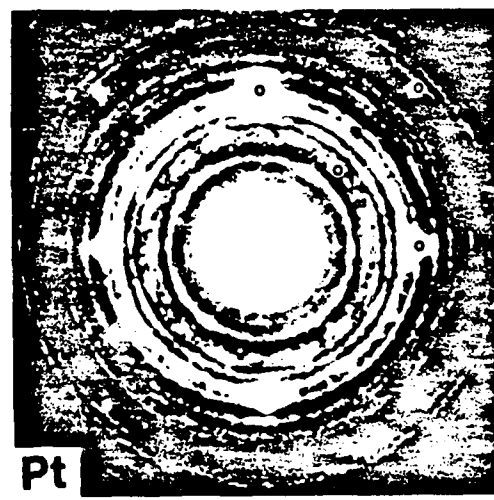
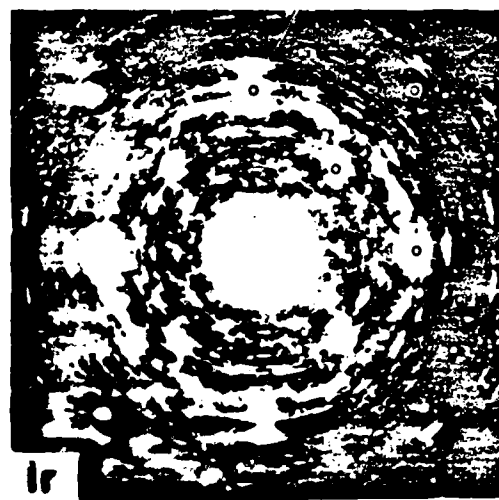
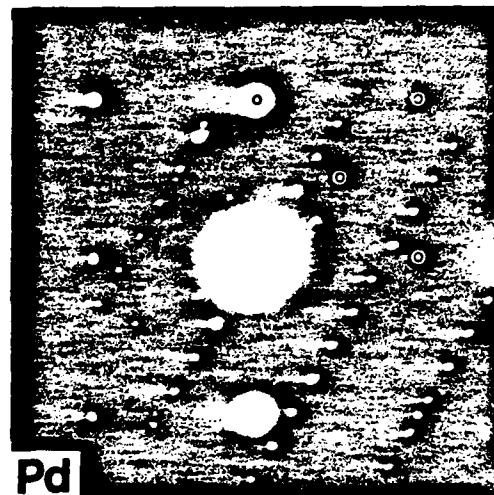
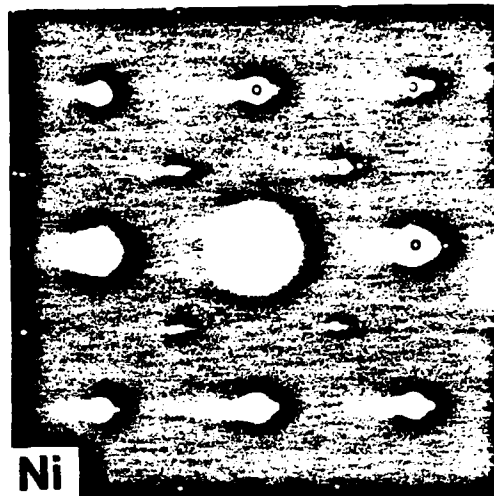
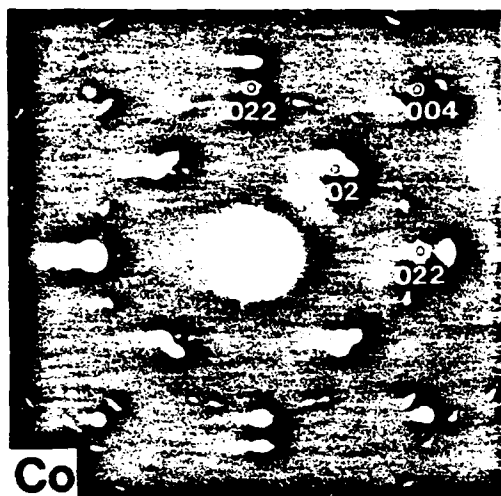


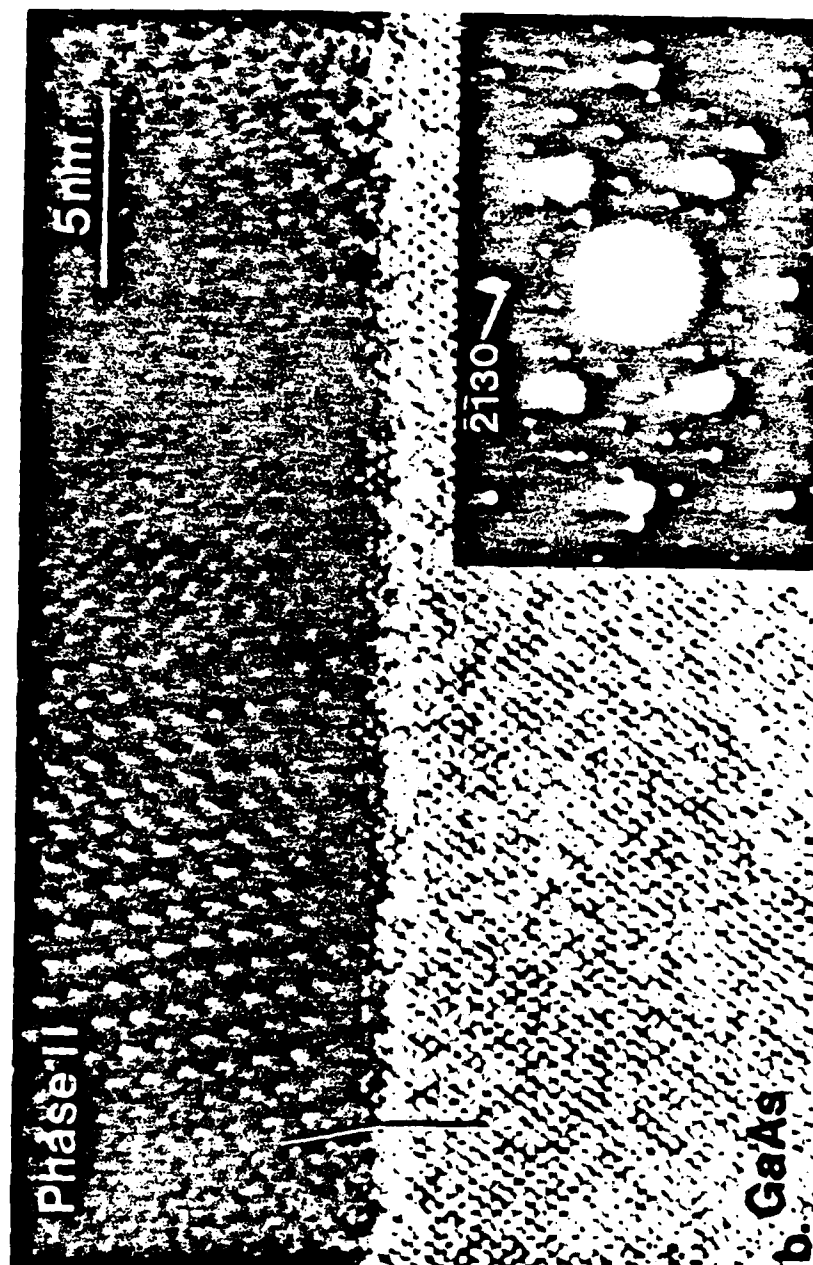


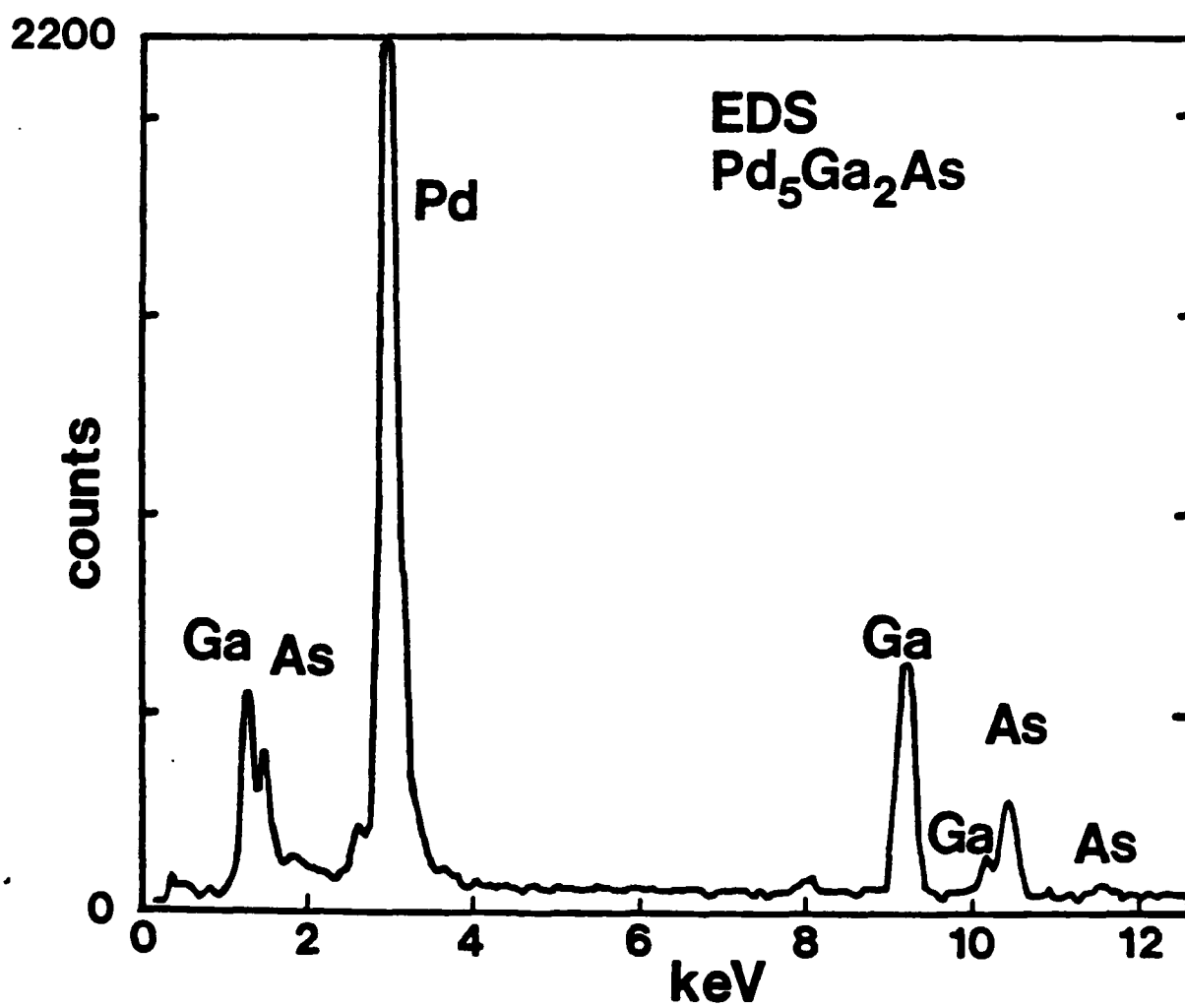
60 nm Pd/GaAs, 500°C, 10 min, SiO₂ cap

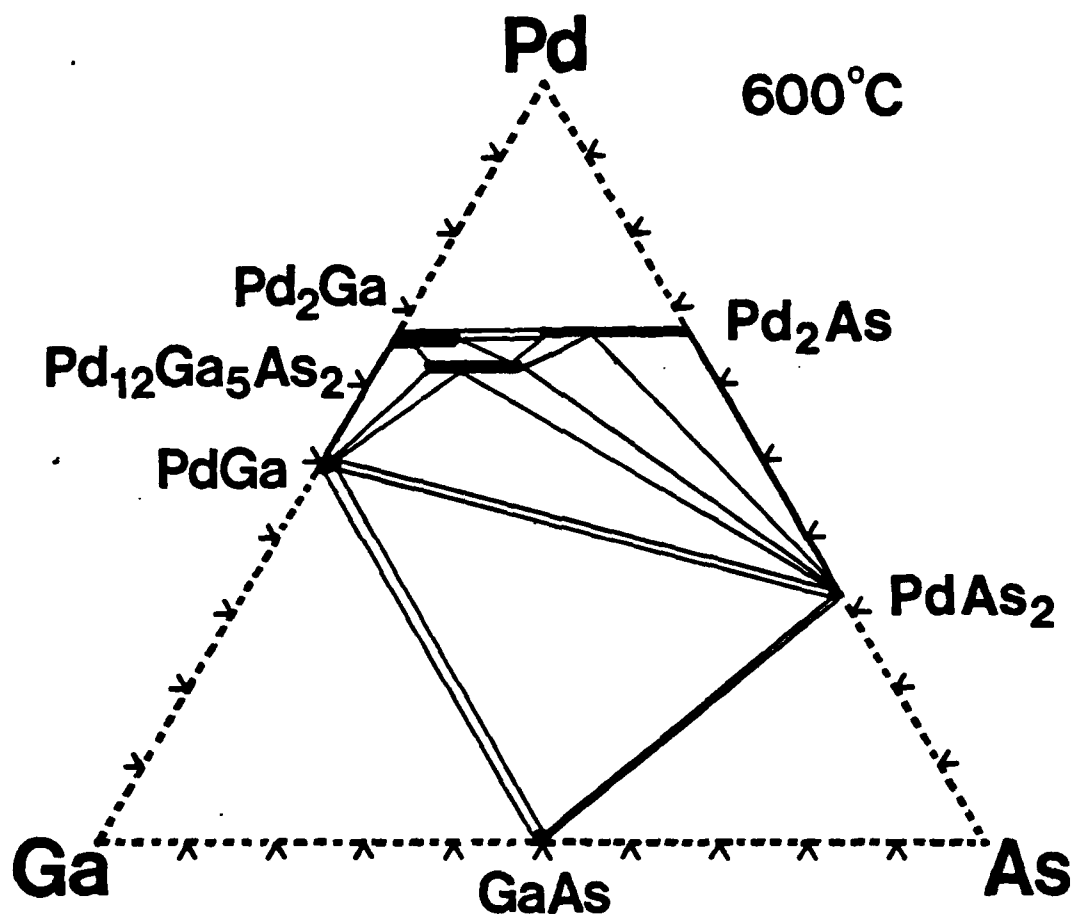




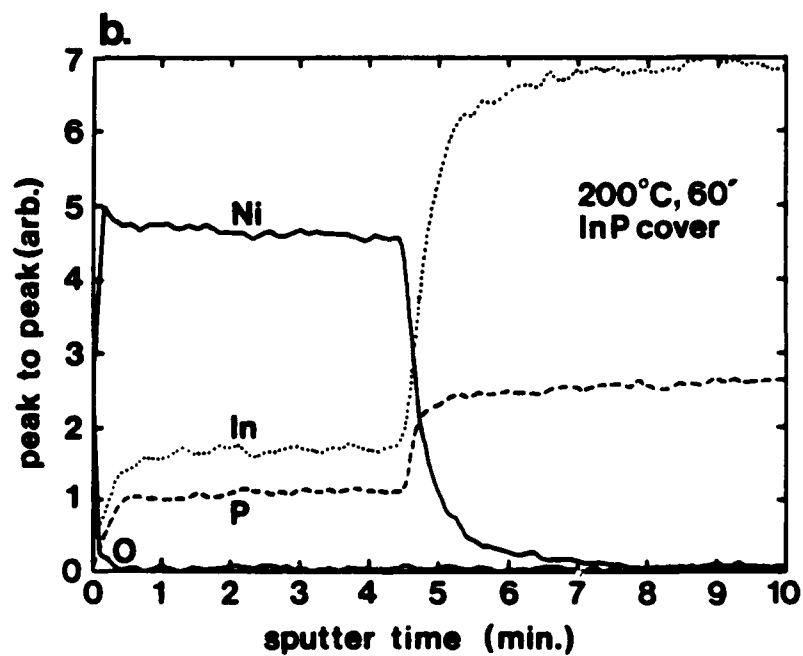
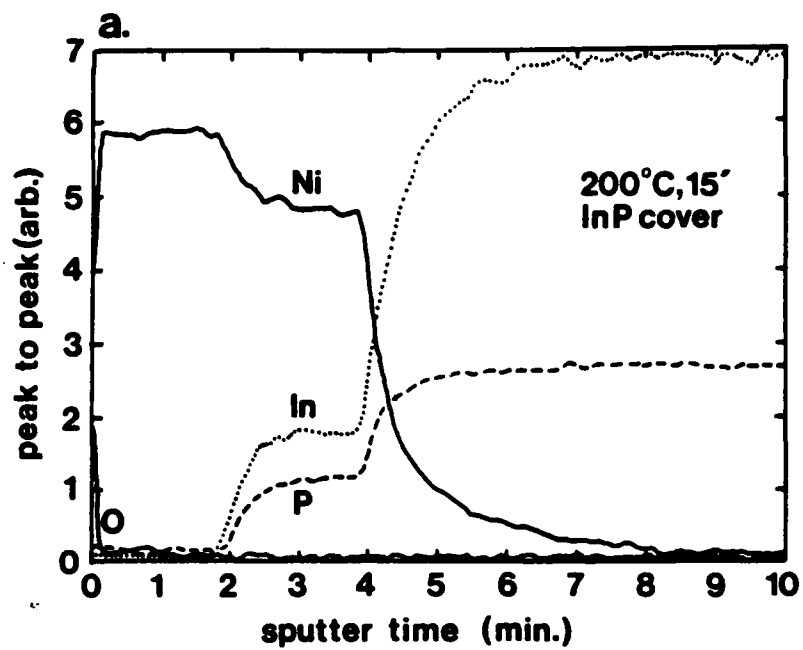




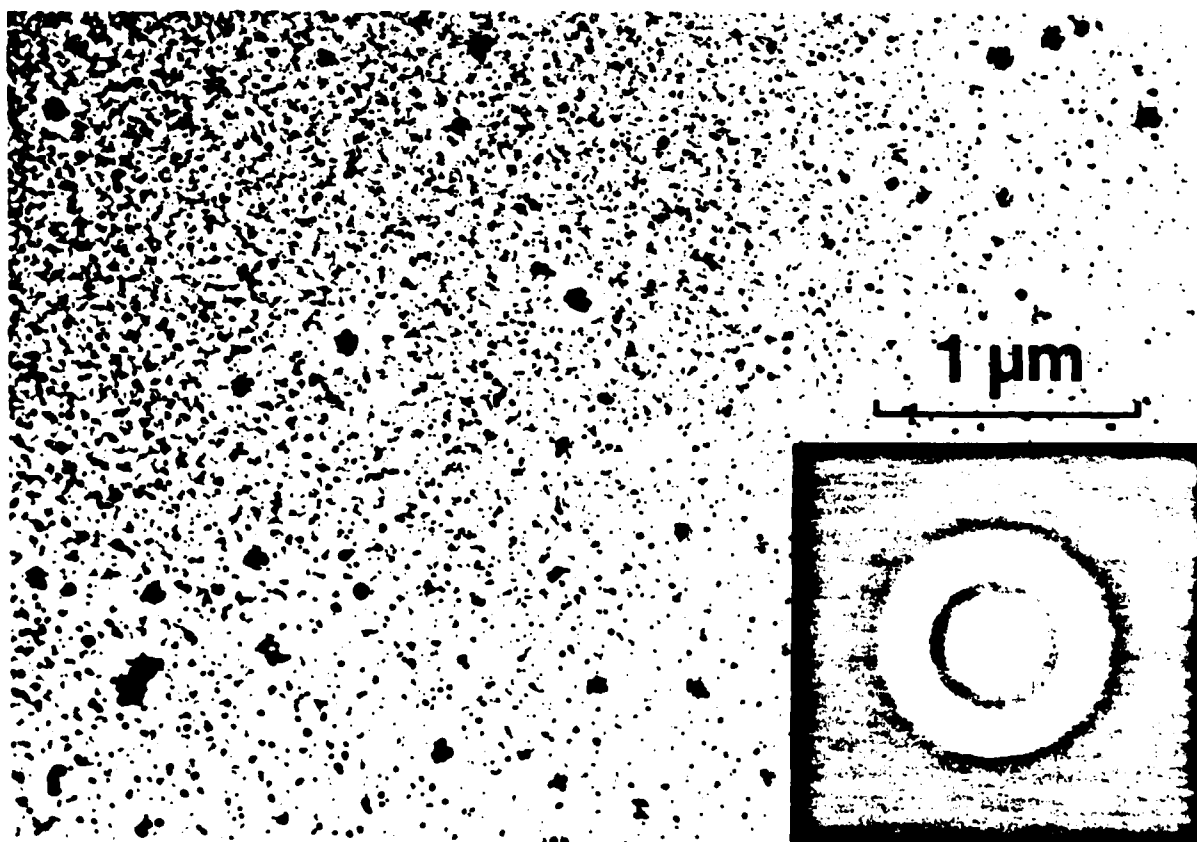
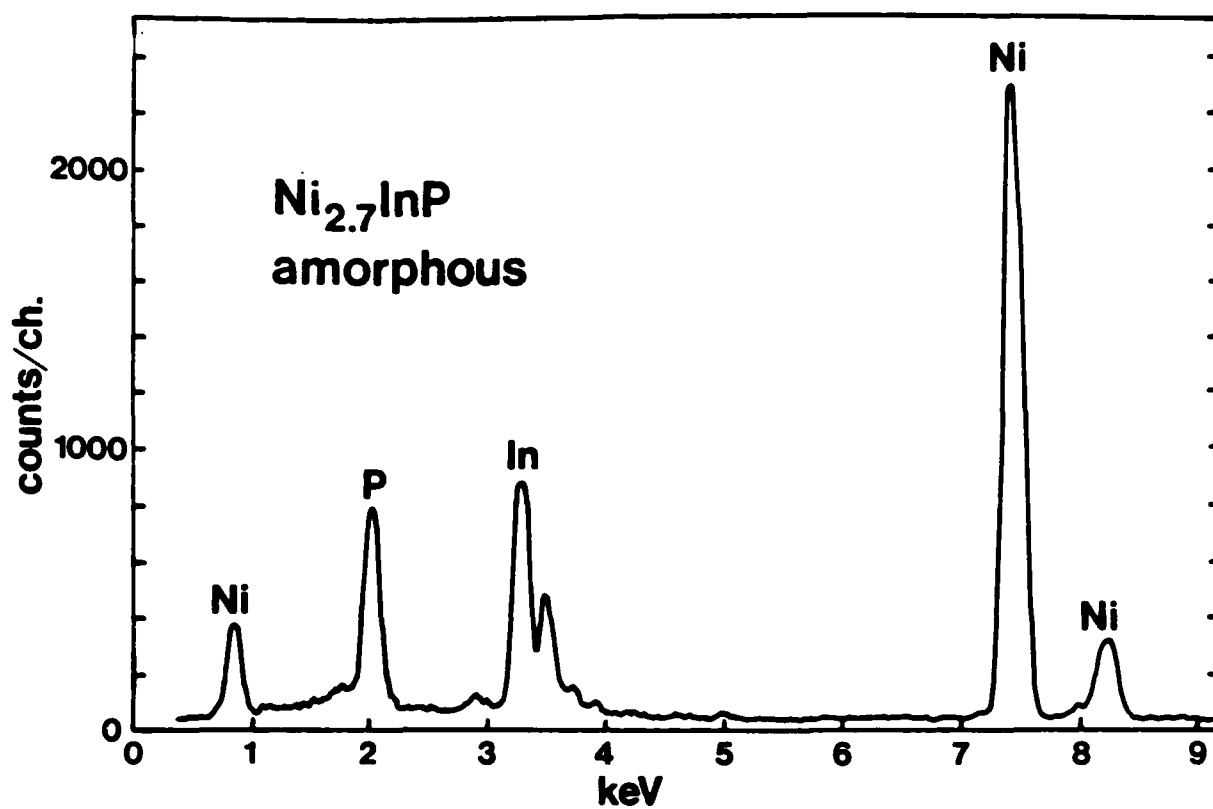


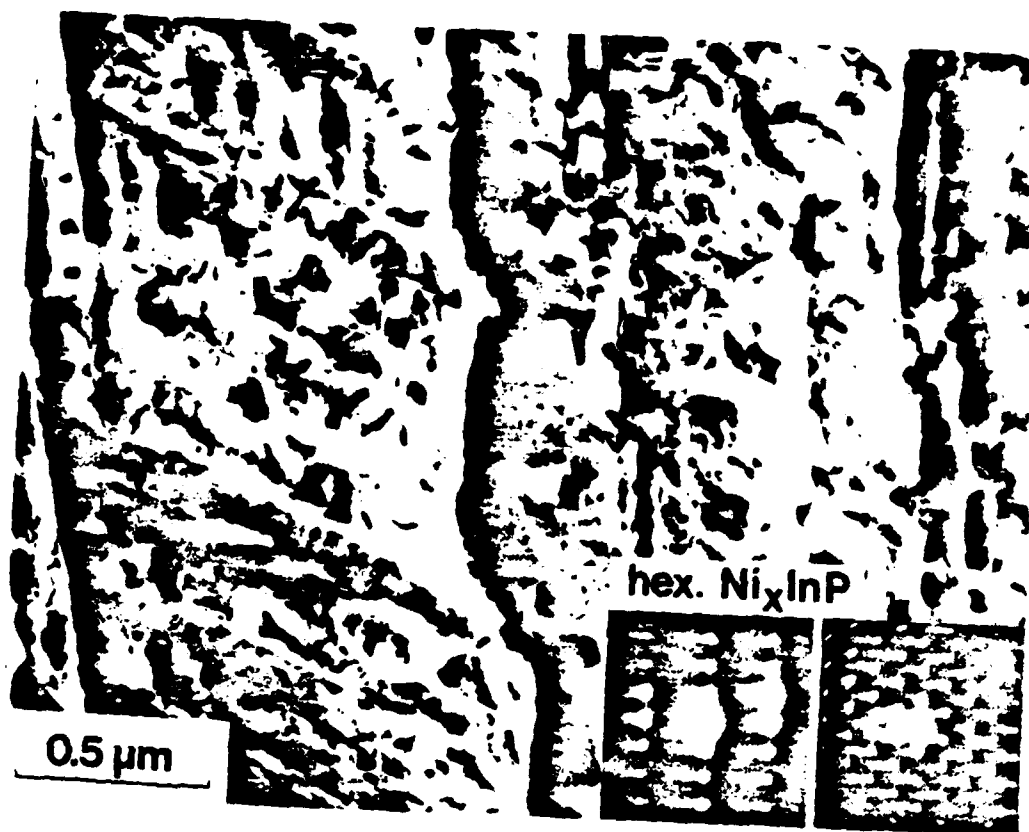


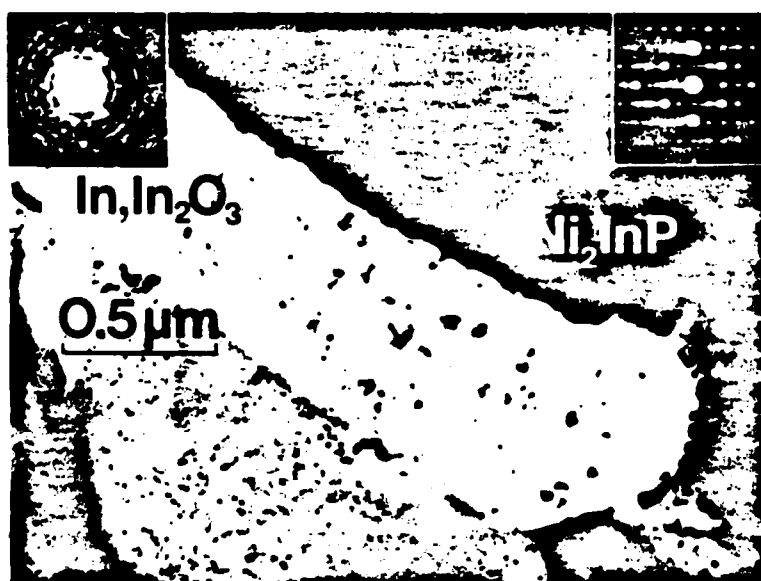
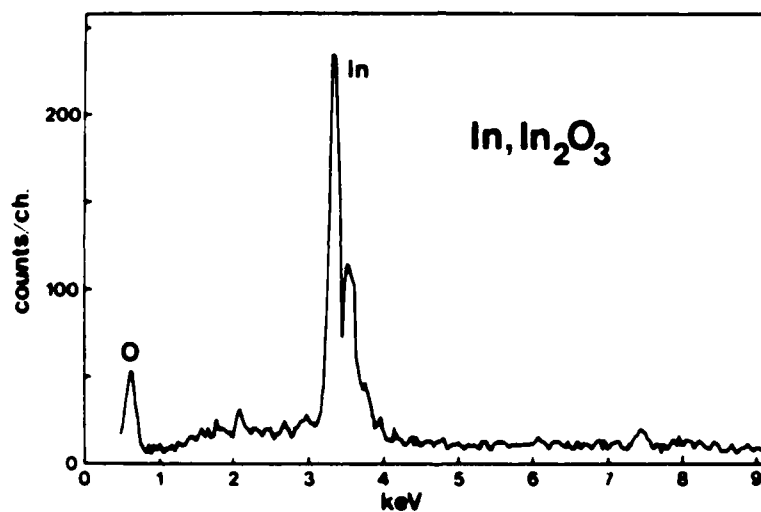
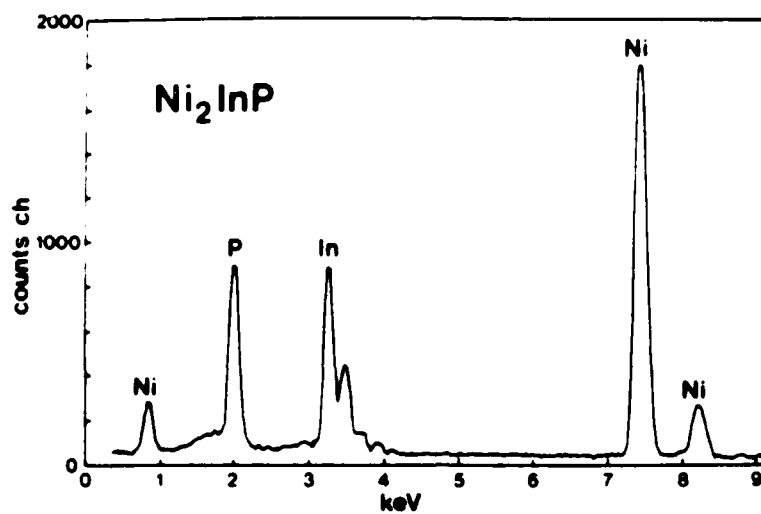
El-Boragy & Schubert, Z.Metall., 1981

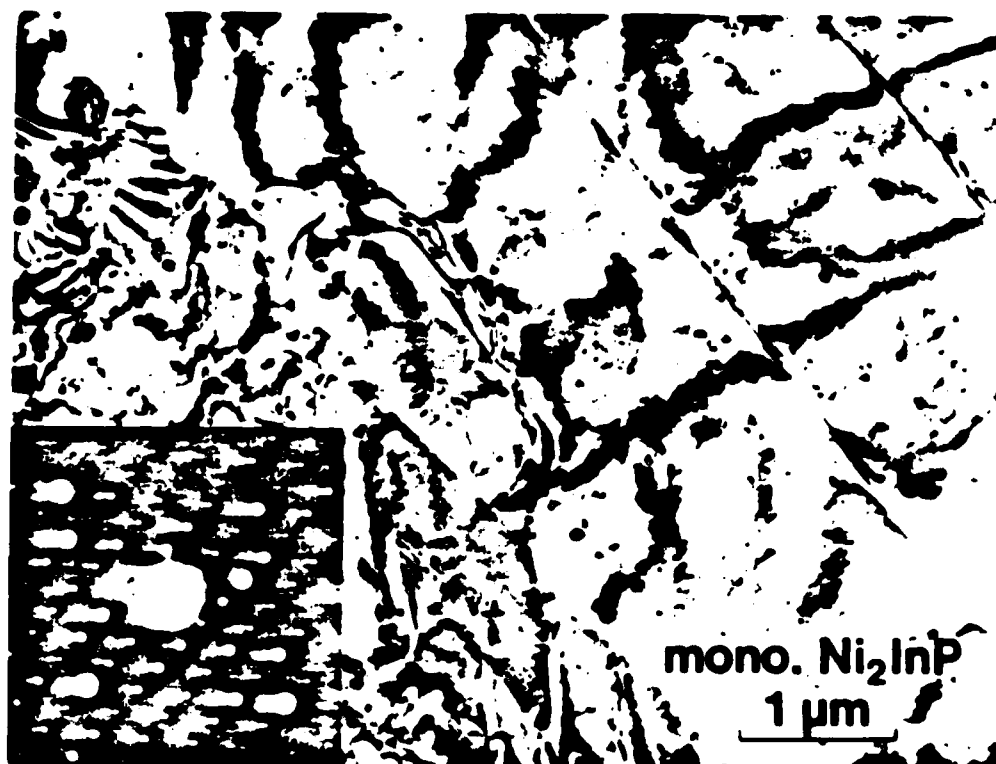


XBL 869-3271









Conclusion

- o **Bulk equilibrium M-A-B phase diagrams, if available, can be used to predict the stable phases resulting from an M/AB reaction with the following caveats:**
 - o **surface and interface contributions to the free energy may be significant (e.g. Pd/GaAs)**
 - o **An M/AB system cannot be assumed to be a closed system (e.g. Pd/GaAs, Ni/InP, ...)**
- o **Bulk equilibrium M-A-B phase diagrams are not available for most systems of interest**
 - > more experimental data is needed**

Intermediate and Stable Phases in Selected M/AB Systems

<u>System</u>	<u>Intermediate</u>	<u>Stable*</u>
Co/GaAs	Co ₂ GaAs ?	CoGa, CoAs
Rh/GaAs	RhAs	RhGa, RhAs ₂
Ir/GaAs	IrGa	Ir ₃ Ga ₅ , IrAs ₂
Ni/GaAs	Ni ₃ GaAs	NiGa, NiAs
Pd/GaAs (60nm)	Pd _x GaAs (I and II) Pd ₂ Ga, Pd ₂ As	PdGa, PdAs ₂
Pd/GaAs (12nm)	Pd _x GaAs (I)	Pd ₅ Ga ₂ As (II)
Pt/GaAs	Pt ₃ Ga	PtGa, PtAs ₂
Ni/InP	Ni ₂₋₇ InP (amor.) Ni _x InP (hex.)	Ni ₂ InP (mono.)

*e-gun deposited on (100) GaAs, capped with SiO₂. Stable phases are final product phases after annealing at 500°C < T < 700°C

Thermally Stable Ohmic Contacts to n-type GaAs

M. Murakami, N. Braslau, Y. C. Shih and W. H. Price

November 3, 1986

Outline

- I. Concern for AuNiGe Ohmic Contacts**
- II. Thermally Stable Ohmic Contacts**
 - MoGeW System**
 - MoGeInW System**
- III. Summary**

I. AuNiGe Ohmic Contacts

Advantages:

- (a) Low contact resistance
- (b) Extensive history (invented by N. Braslau in 1967)
- (c) Excellent run-to-run reproducibility
- (d) Prepared by standard evaporation and annealing techniques

Disadvantages:

- (a) Thermally unstable (process requirement— 400°C, 2 hrs)
- (b) Require a barrier layer between Al-Cu wiring and contact metal

Focus of the Present Research for AuNiGe Contact Metals:

- Explore the possibility to improve thermal stability

Approach:

- Identify compounds or phases which produce low R_c
- Investigate thermal stability of these compounds

AuNiGe Ohmic Contacts

typical as-deposited sample

Au	50 nm
Ni	30 nm
Au-Ge	100 nm
Ni	5 nm

/// GaAs ///

Si peak doping: $1 \times 10^{18} / \text{cm}^3$

- Annealed in Ar/H₂ atmosphere
- R_c measurement transmission line method
- Microstructural analysis X-ray diffraction, TEM, AES

"Correlate microstructures with low or high R_c "

"Low Contact Resistance"

"High Contact Resistance"

AD-A183 158

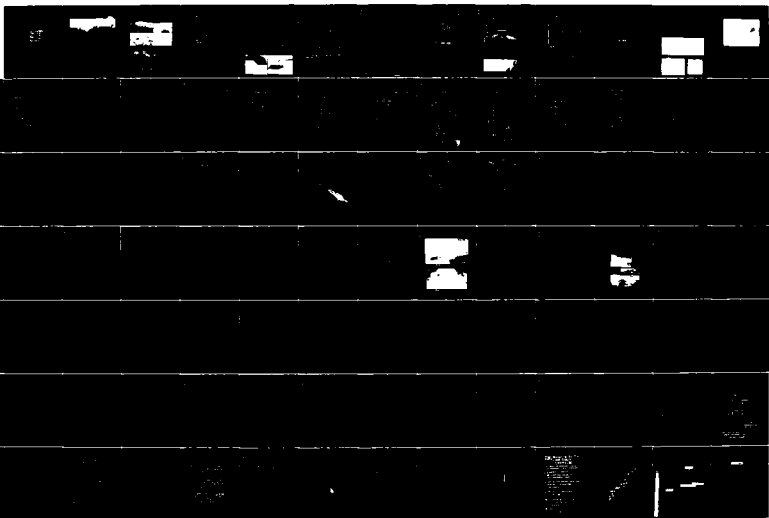
A WORKSHOP ON 3-5 SEMICONDUCTOR: METAL INTERFACIAL
CHEMISTRY AND ITS EFFECTS (U) STANFORD UNIV CA
W E SPICER ET AL. 05 NOV 86 N00014-87-G-0038

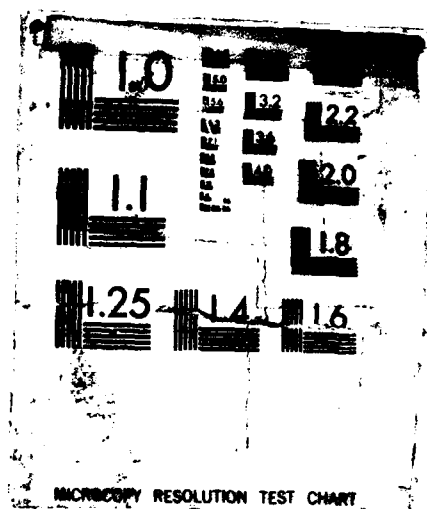
3/7

UNCLASSIFIED

F/G 20/12

NL

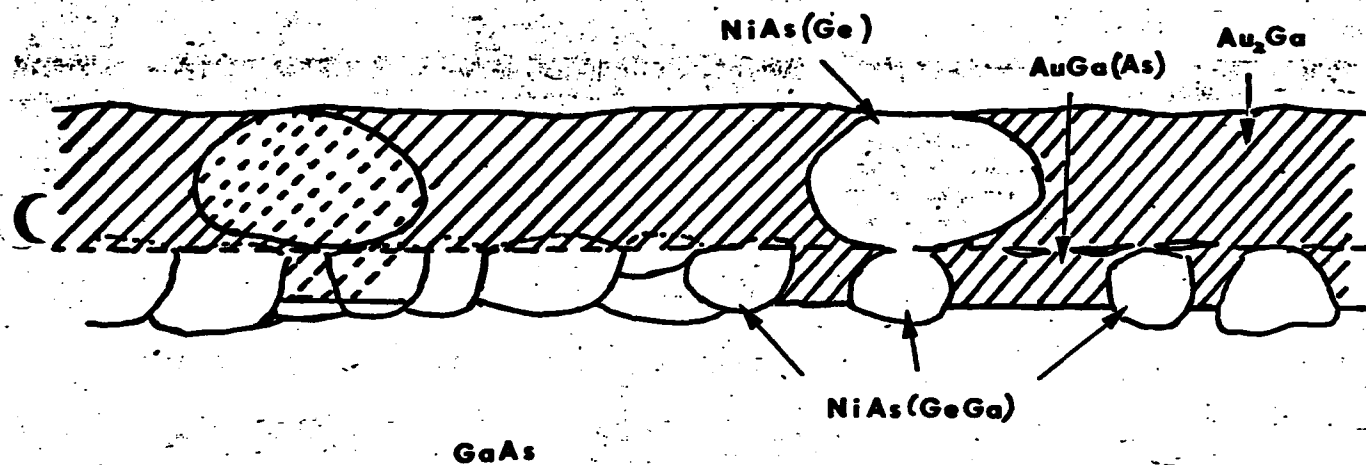




5 Ni 1st layer-contact after annealing at 440°C for 2 min.

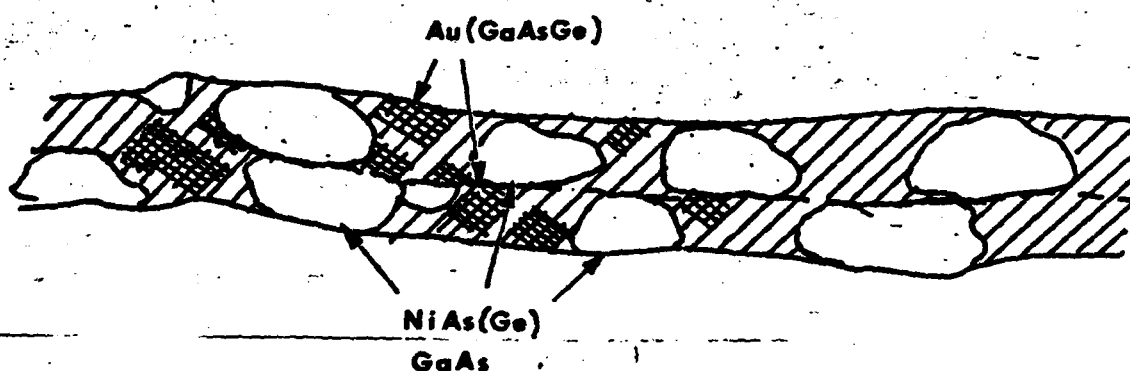


0.1μm



"Low Contact Resistance"

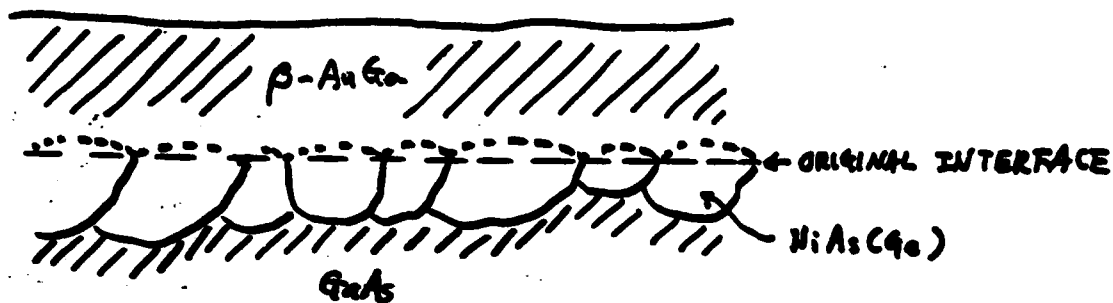
10 Ni 1st layer contact after annealing at 440°C for 2 min.



"High Contact Resistance"

Microstructure Which Produces Low Contact Resistance

—Cross-sectional TEM, X-ray Diffraction, AES



- NiAs(Ge) compounds in contact with the GaAs substrate
- $\beta\text{-AuGa}$ phase ($T_m = 360^\circ\text{C}$) close to the top surface

Concern for Device Application

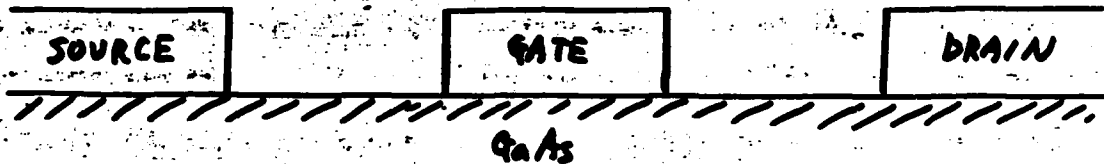
1. Profile at contact edges would deteriorate after contact formation
2. The microstructure would be unstable at 400°C annealing

Deterioration of Edge Profile After Formation of Contact

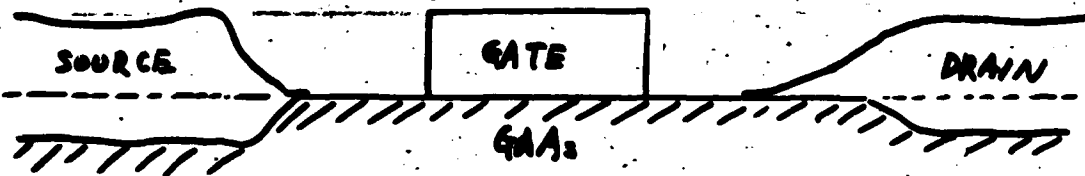
Melting point (360°C) of β -AuGa < Contact formation temp (440°C)

Deterioration of Edge Profile

Before annealing

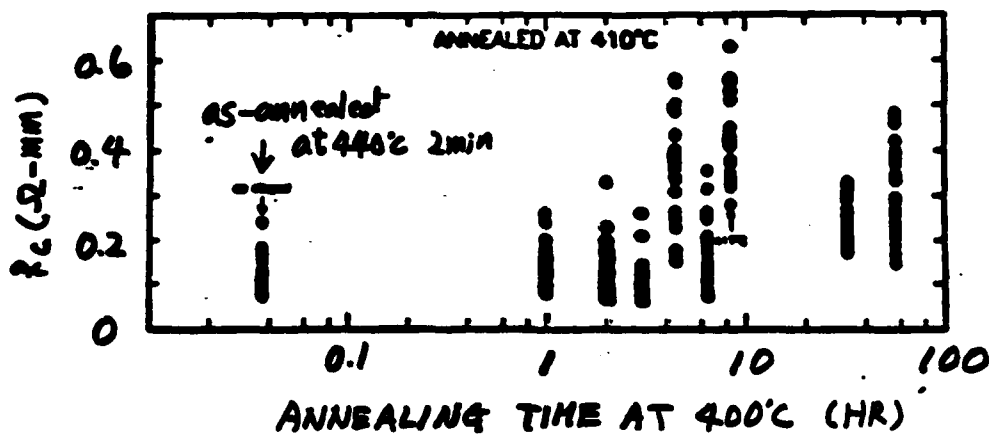


After 440°C 2min annealing



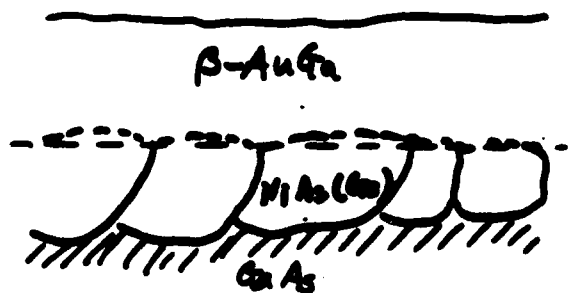
(b) Thermal stability at 400°C annealing

• Electrical resistance measurement

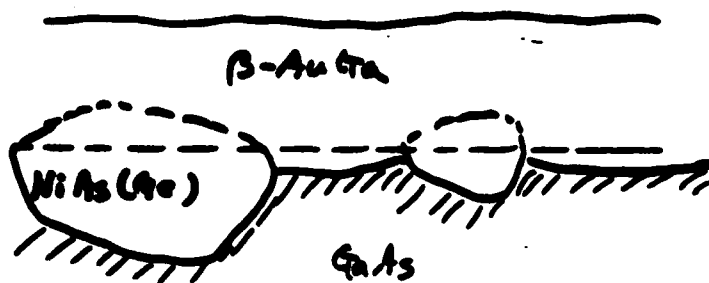


Grain growth and phase transformation of $\beta\text{-AuGa}$ at 400°C

BEFORE 400°C ANNEAL



AFTER 400°C ANNEAL



II. MoGeW Ohmic Contacts

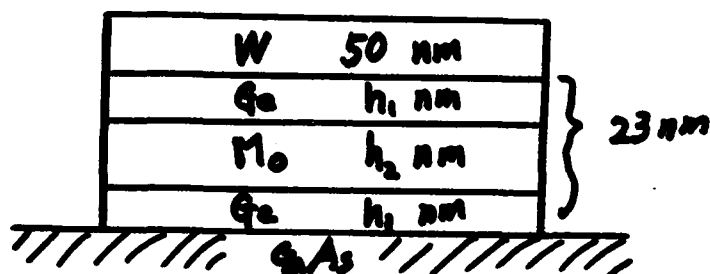
Why MoGeW Contact Metal?

- First ohmic contact to n-type GaAs formed using refractory metals (Tiwari, Kuan and Tierney, 1983)
- Formed by annealing at $\sim 800^{\circ}\text{C}$
- Expected to be thermally stable at 400°C after contact formation

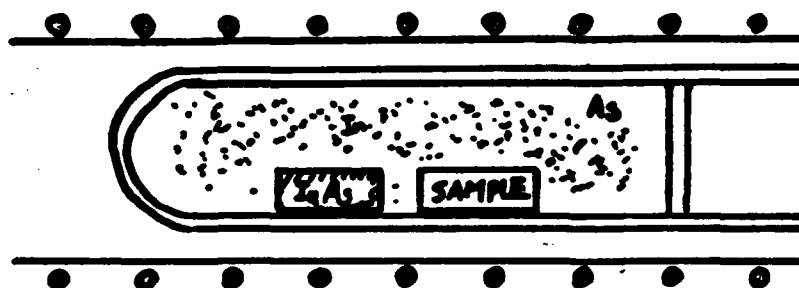
Focus of Present Research

- (a) Search process (composition-temperature) window to form $R_c < 0.5 \Omega\text{-mm}$
- (b) Investigate thermal stability at 400°C annealing
- (c) Further reduction of R_c — understand the carrier transport mechanism

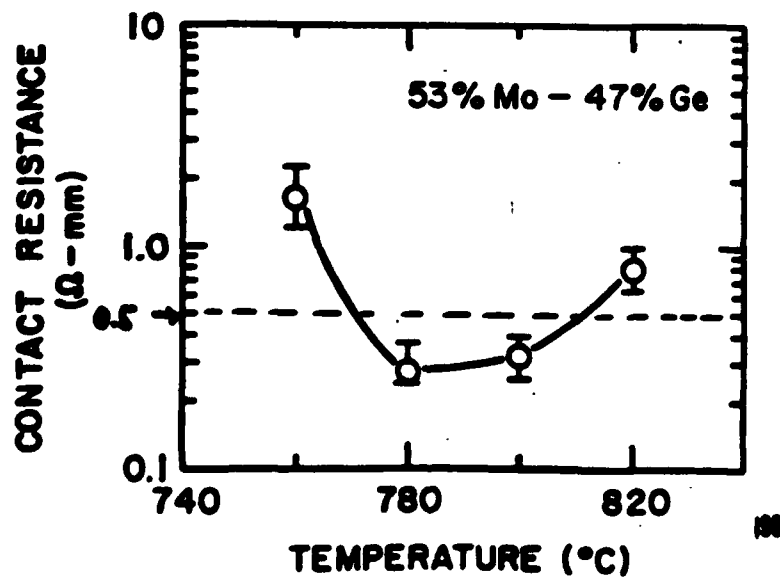
MoGeW Contacts Annealed in InAs Overpressure Atmosphere



- Annealed in InAs overpressure atmosphere



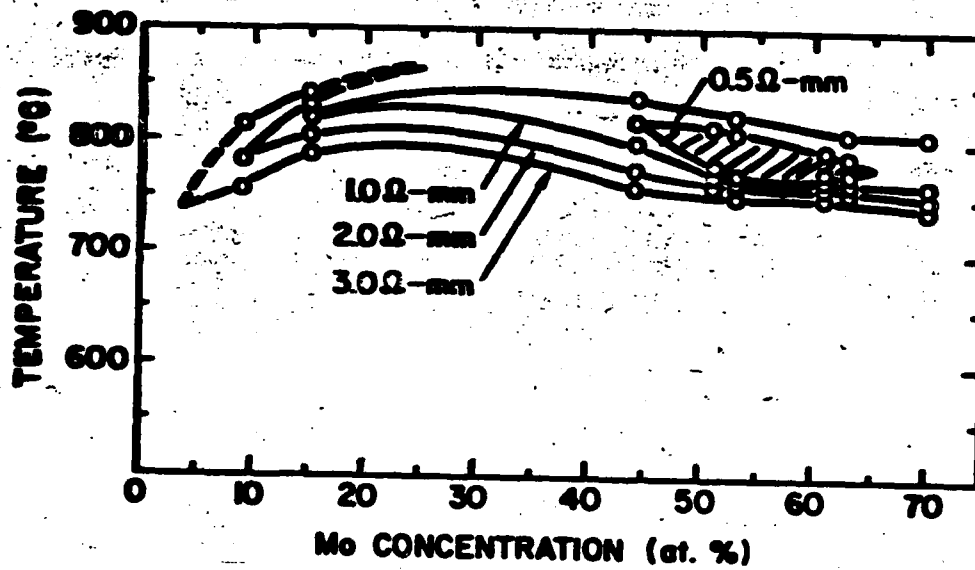
Contact Resistance



Search Process Window for $R_c < 0.5 \Omega\text{-mm}$

variables — • Mo/Ge composition ratio, • annealing temperature

Contact Resistance

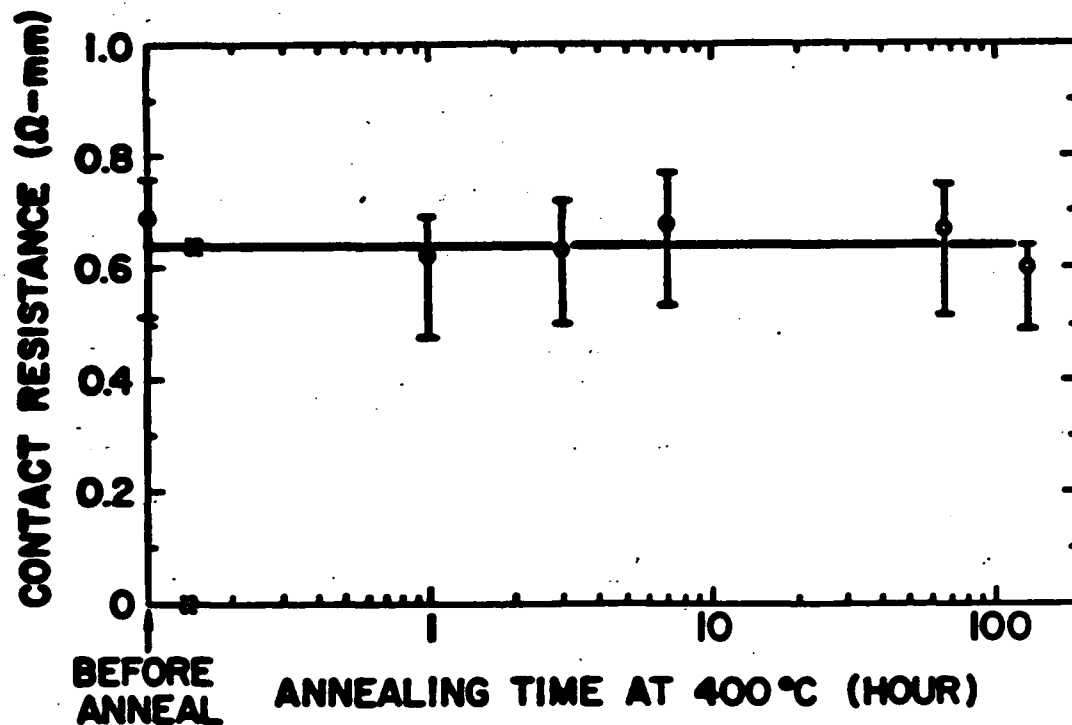


Morphology at Metal/GaAs Interface



Thermal Stability at 400°C After Formation of Ohmic Contact

Isothermal annealing at 400°C for ohmic contact formed at 800°C



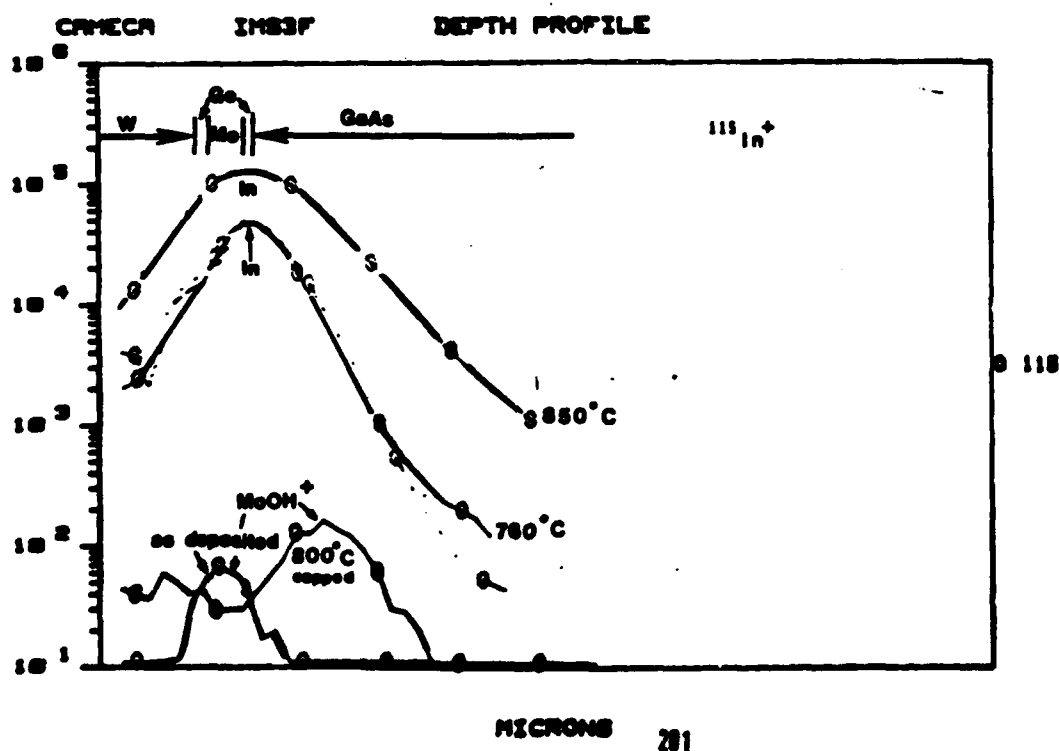
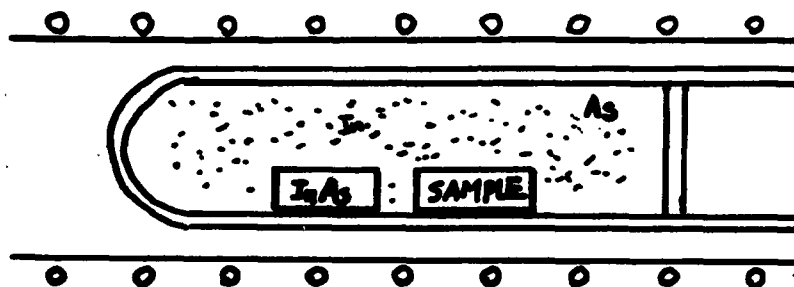
Concern for MoGeW Ohmic Contact

1. Narrow (composition-temperature) process window
2. Further reduction in the R_c values

Understand the carrier transport mechanism

13

- Annealed in InAs over pressure atmosphere



(1) Direct Deposition of Indium

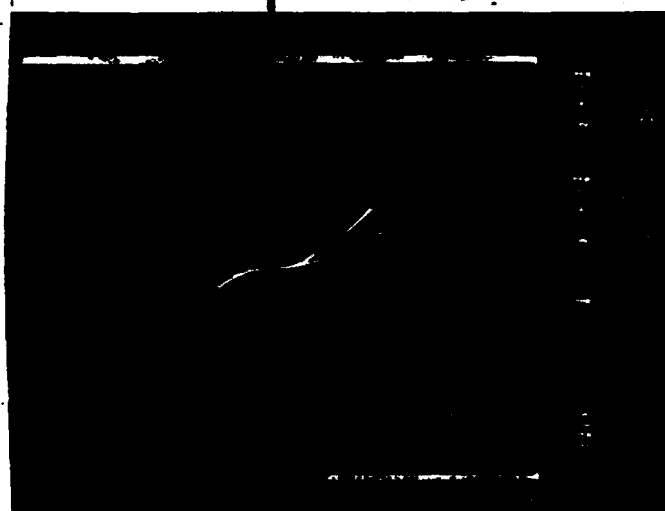
W	50 nm
Mo	13 nm
Ge	10 nm

/// GaAs ///

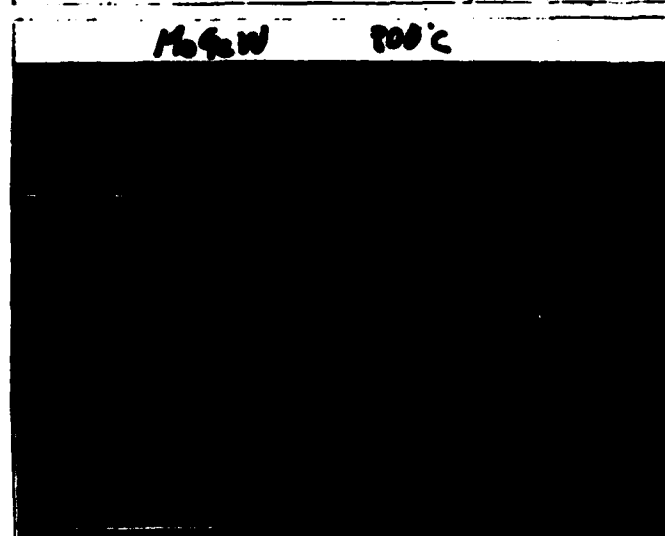
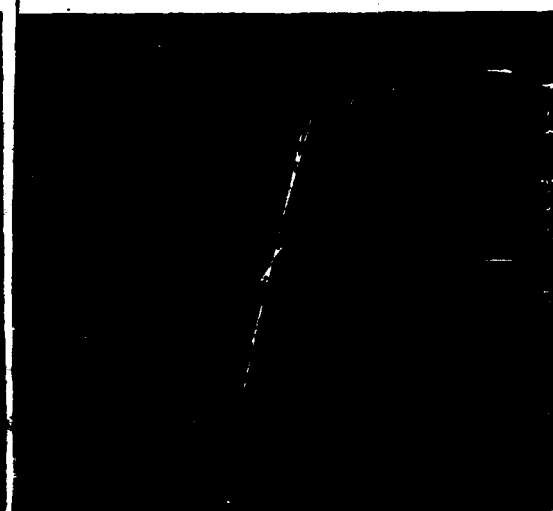
W	50 nm
Mo	13 nm
In	2-6 nm
Ge	10 nm

/// GaAs ///

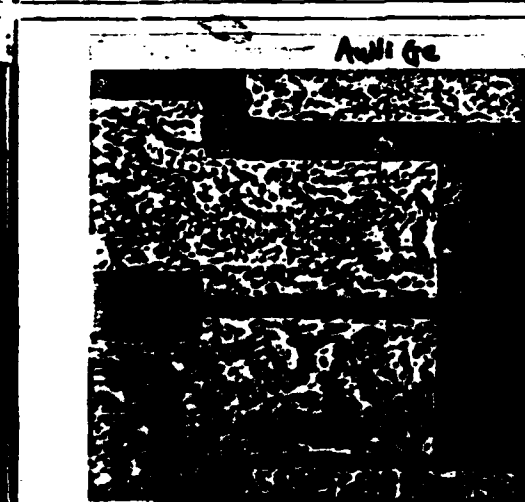
capped by 100nm thick Si_3N_4 layer
annealed at 800°C for 10 min in Ar/ H_2 gas



RL44 800°C 10 min Si_3N_4 capped



MoGeW 800°C



Anti Ge

Microstructure Which Produces Low Contact Resistance



Before Anneal

W	40 nm
Mo	12 nm
In	4 nm
Ge	10 nm
GaAs	

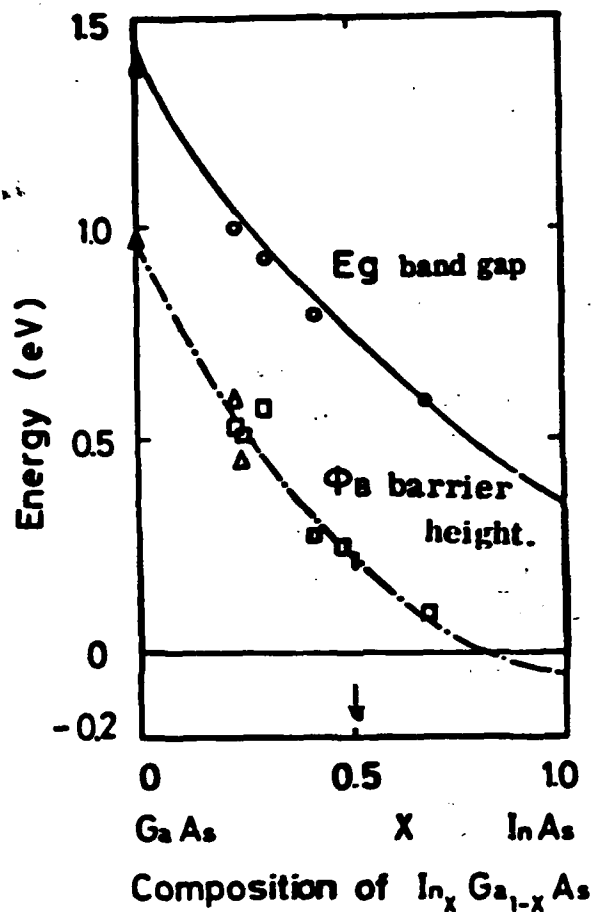


750°C Anneal

W, Ge	40 nm
Mo ₅ As ₄	25 nm
(Mo ₂ Ge ₃)	
In GaAs	10 nm
GaAs	

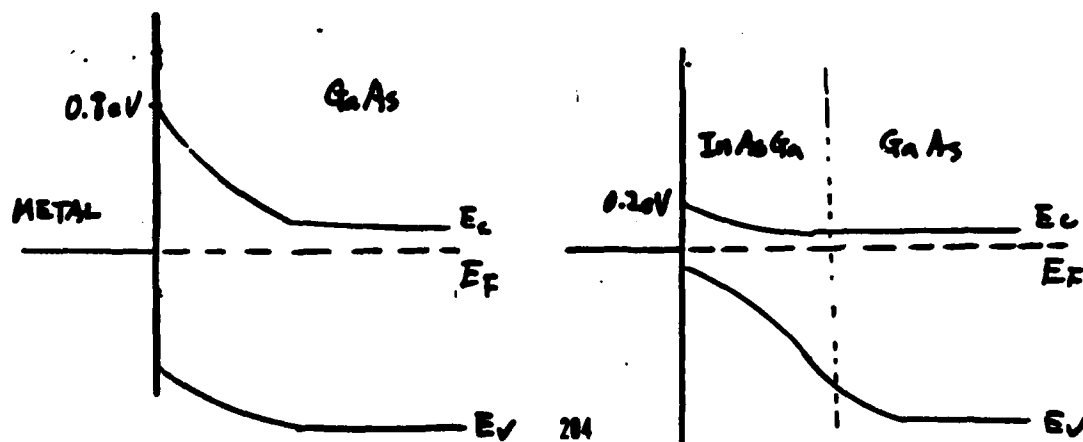
(c) Present Understanding

InGaAs layer could contribute the barrier height reduction



(Kajiyama, 1973)

$In_{0.5} Ga_{0.5} As$



Summary

I. AuNiGe ohmic contacts

- Low contact resistance ($\sim 0.2 \Omega\text{-mm}$)
- Deterioration of edge profiles
- Thermally unstable at 400°C

II. MoGeW ohmic contacts (InAs overpressure annealing)

- Thermally stable at 400°C
- $R_c \sim 0.3 \Omega\text{-mm}$
- Poor run-to-run reproducibility

III. MoGeInW ohmic contact

- Good reproducibility
- No visible morphological change
- Wide application (short diffusion distance)
- $R_c \sim 0.8 \Omega\text{-mm}$

Focus of Future Study for MoGeInW Ohmic Contacts:

"Reduction of $R_c < 0.2 \Omega\text{-mm}$ "

OHMIC CONTACTS

by

T.C. McGill + W.J. Boudville

California Institute

of

Technology

The LORD created so-called ohmic contacts to give solid-state types (especially theorists) an opportunity to make fools of themselves.

H. Kroemer (October 1984).

REQUIREMENTS

FOR

OHMIC CONTACTS

A. CONTACT RESISTANCE

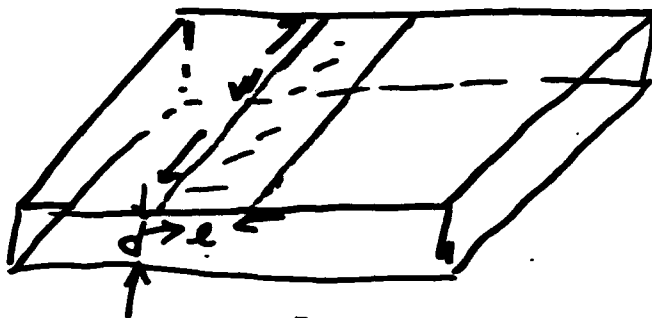
SMALL COMPARED TO

SOURCE-DRAIN RESISTANCE

B. FLUCTUATIONS IN CONTACT

RESISTANCE SMALL

SIMPLE CONSIDERATIONS FOR OHMIC CONTACT



ρ_c = specific contact resistance Ω -Area.

$$R_c \equiv \text{Contact Resistance} \approx \frac{\rho_c}{dw}$$

$R_{SD} \equiv$ Source-Drain Resistance

$$\approx \frac{l}{wd} \rho_{\text{Bulk-channel}}$$

Condition for neglecting

$$R_{SD} > R_c$$

or

$$\left\{ \rho_c < l \rho_{\text{Bulk-channel}} \right\} \quad 200$$

Numerical Considerations

$$\rho_{\text{Bulk}} \approx 4 \times 10^{-2} \Omega\text{-cm.}$$

$$l \sim 1 \mu\text{m.}$$

$$\rho_c < 4 \times 10^{-6} \Omega\text{-cm}^2$$

Future

$$\rho_c < 4 \times 10^{-6} \Omega\text{-cm}^2 \left(\frac{l}{1 \mu\text{m}} \right)$$

OUTLINE

- A. SIMPLE MODEL OF
OHMIC CONTACT
- B. FLUCTUATIONS IN
POTENTIAL $\Rightarrow$ FLUCTUATIONS
IN CONDUCTANCE
- C. POSSIBLE WAYS OF
SUPPRESSING FLUCTUATIONS
- D. SUMMARY
- E. FUTURE

SIMPLE CONTINUUM MODEL

I. FIRST THEORY CHANG, FANG, AND SEE, SSE (1971).

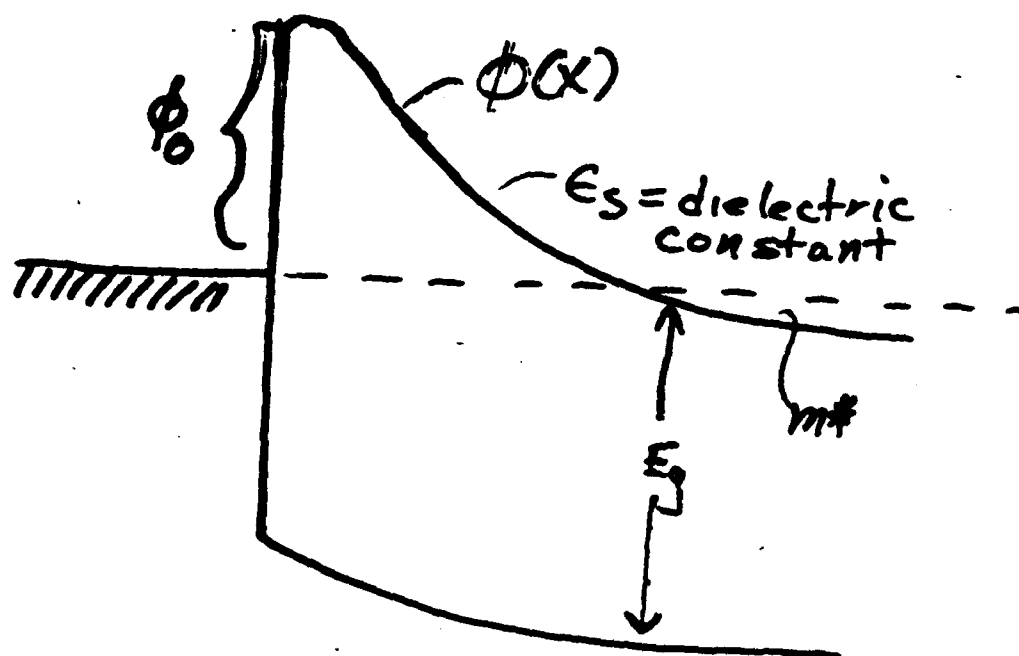
- VERY SIMPLE MODEL OF SCHOTTKY BARRIER

- $K_i(E) \sim \sqrt{\frac{2m_e^* E}{\hbar^2}}$

II. IMPROVED THEORY

- USE TWO BAND MODEL OF COMPLEX BAND STRUCTURE

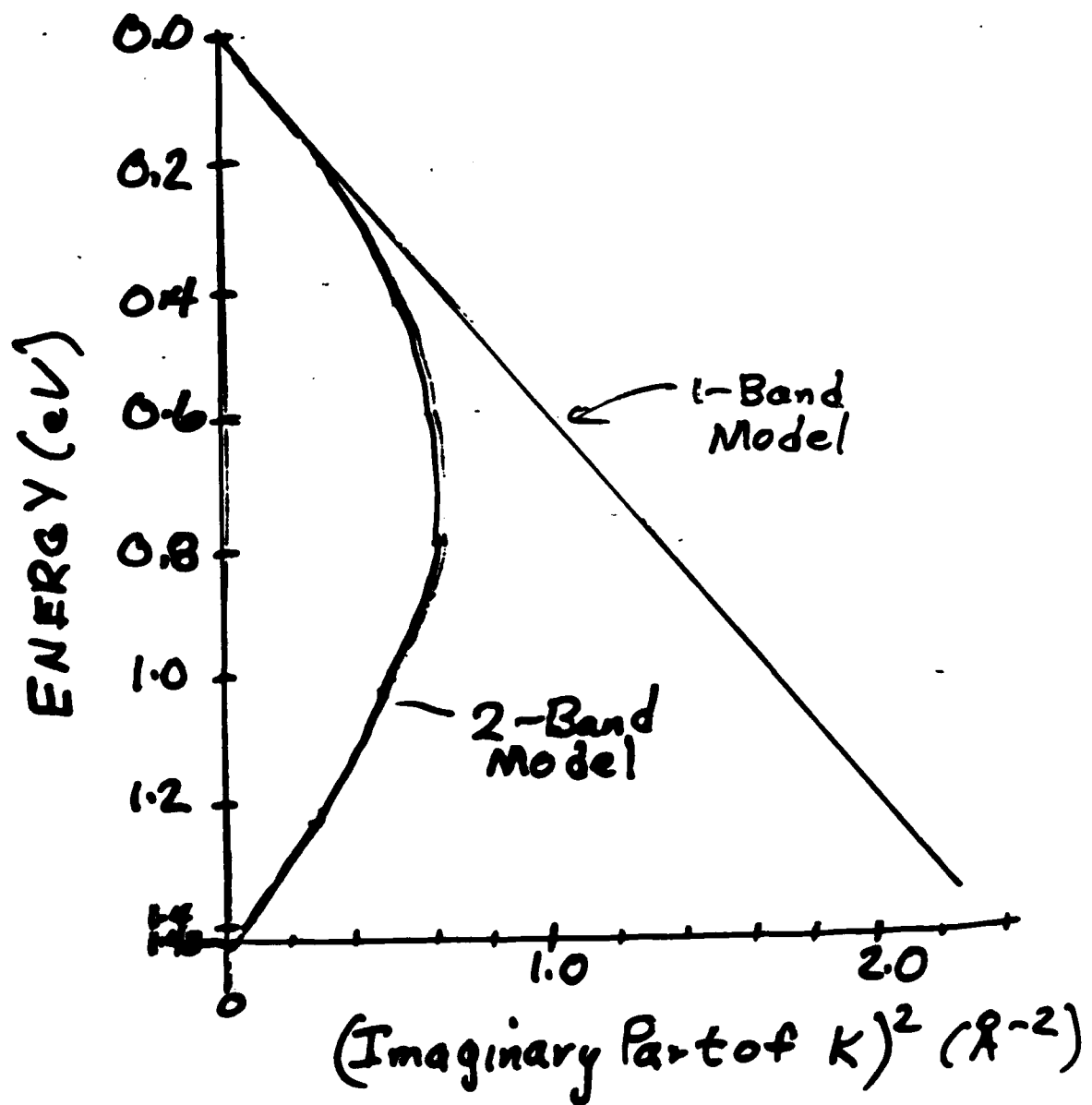
BARRIER MODEL



$$\phi(x) = \phi_0 + \frac{N_D e^2}{2\epsilon_0 \epsilon_s} (x^2 - 2x_0 x) - \frac{e^2}{8\pi\epsilon_0 \epsilon_s x} - \frac{N_A e^2 d}{\epsilon_0 \epsilon_s} e^{-x/d}$$

$$x_0 = \sqrt{\frac{2\epsilon_0 \epsilon_s}{N_D e^2} [\phi_0 + V_A - V_D]}$$

TWO BAND VS ONE BAND MODEL



CURRENT

$$J_{NET} = J_{L \rightarrow R} - J_{R \rightarrow L}$$

$$= 2e \int \frac{d^2 k_{||}}{(2\pi)^2} \int_0^{\infty} \frac{dk_{\perp}}{2\pi} \frac{\hbar k_{\perp}}{m^*} T(E_{\perp}) [f_L(E) - f_R(E)]$$

$T(E_{\perp})$ = Transmission coefficient

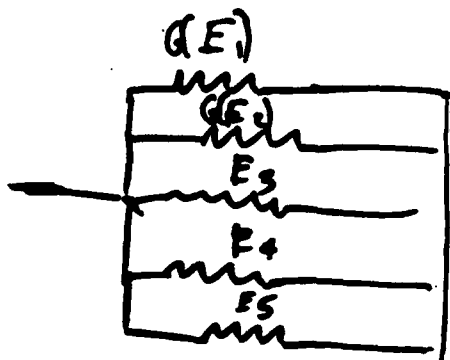
$$= \exp \left[-2.0 \int_{\text{over barrier}} k_{im}(x) dx \right]$$

$f_L(E), f_R(E)$ = Fermi functions.

CONDUCTANCE AND RESISTANCE.

$$G \text{ (S/m}^2\text{)} = \frac{1}{R \text{ (}\Omega\text{m}^2\text{)}} = \left(\frac{\partial J}{\partial V} \right)_{V=0}$$

$$G = \frac{1}{R} = \frac{m^* e^2}{2\pi^2 \hbar^3} \int dE_{\perp} \frac{T(E_{\perp})}{e^{(E_{\perp} - E_F)/kT} + 1}$$



$$G(E) = \frac{m^* e^2}{2\pi^2 \hbar^3} \frac{T(E_{\perp})}{e^{(E_{\perp} - E_F)/kT} + 1}$$

CALCULATIONS

$$\phi_0 = 0.80 \text{ eV}$$

$$E_{\text{gap}} = 1.43 \text{ eV}$$

$$\epsilon_s = 13.18$$

$$m_r^* = 0.065 m_e$$

$$T = 300^\circ \text{K}$$

$$E_{r \rightarrow L} = 0.28 \text{ eV}$$

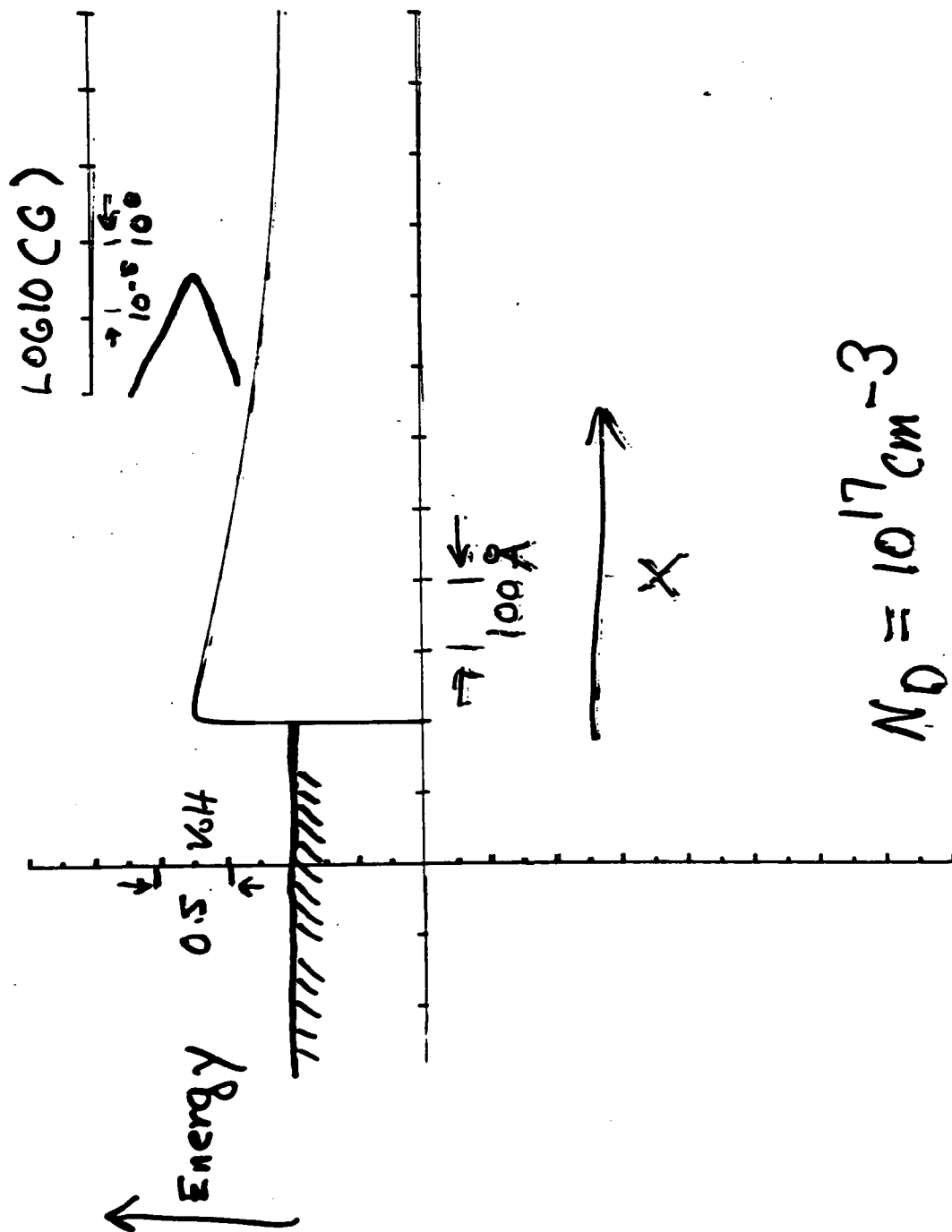
$$m_L^* = 0.55 m_e$$

$$N_s = 3 \times 10^{14} \text{ cm}^{-2}$$

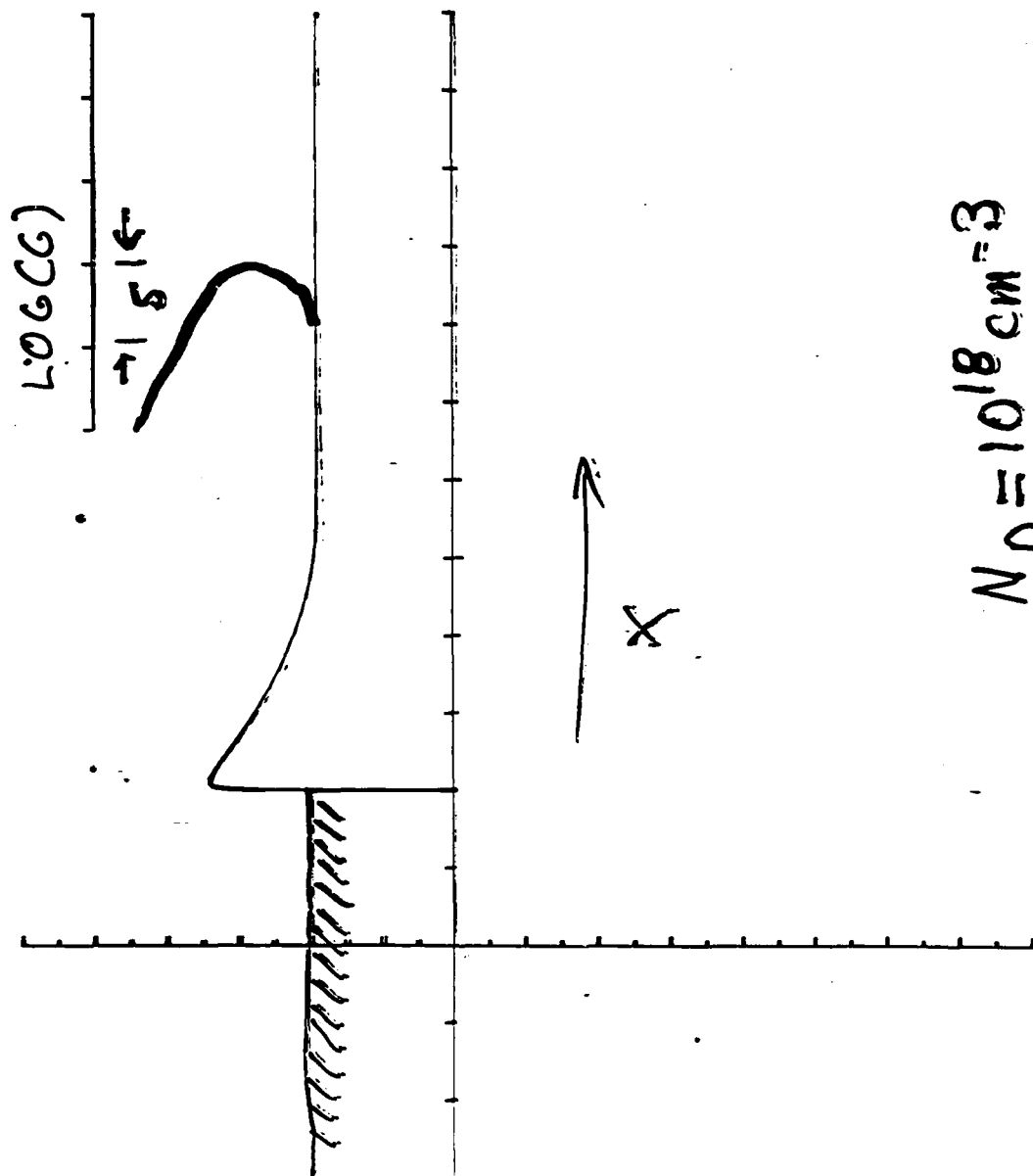
$$d = 5 \text{ \AA}$$

$$\text{DOPING} = ?$$

DISTRIBUTION OF CONDUCTANCE

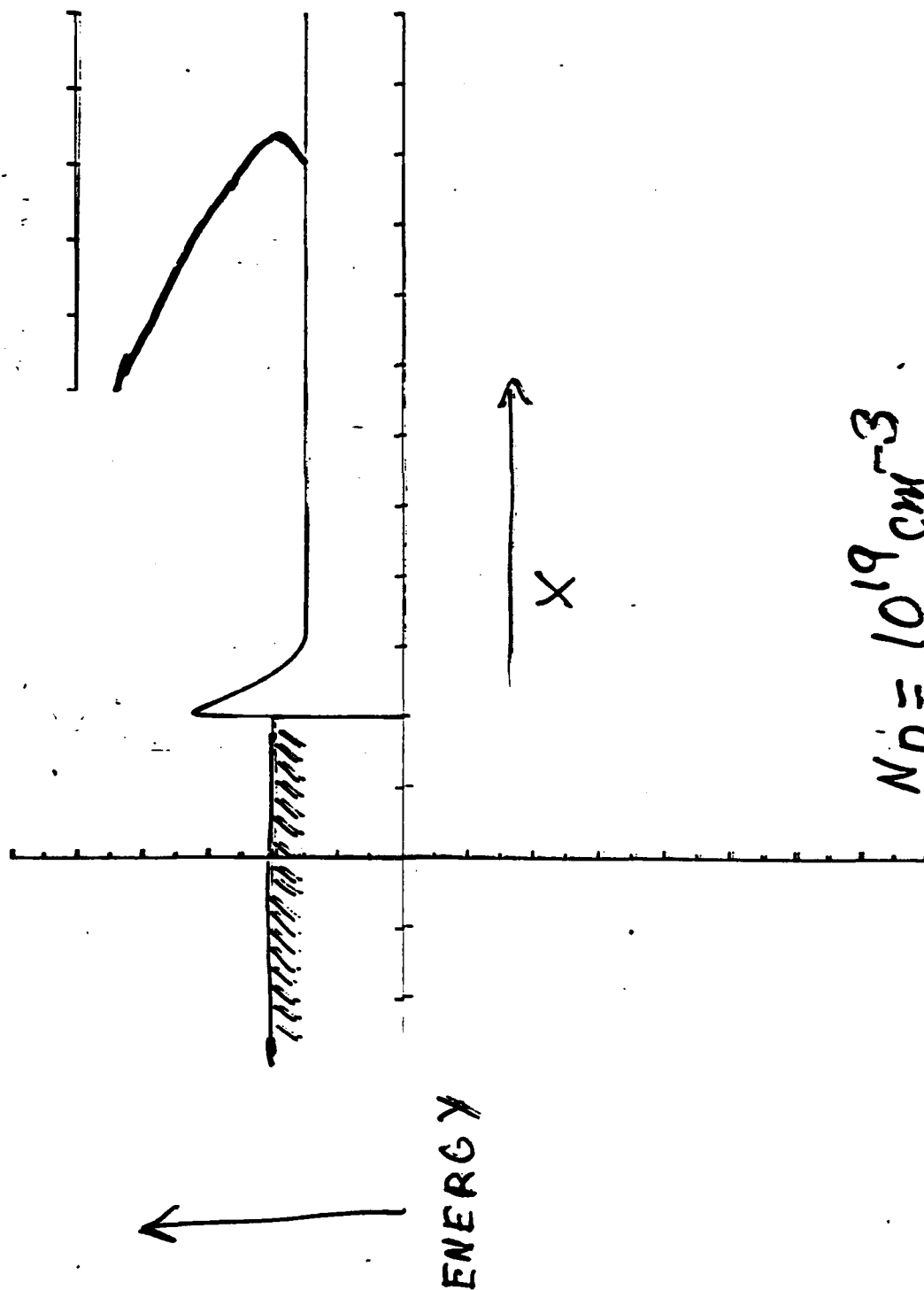


DISTRIBUTION OF CONDUCTANCE



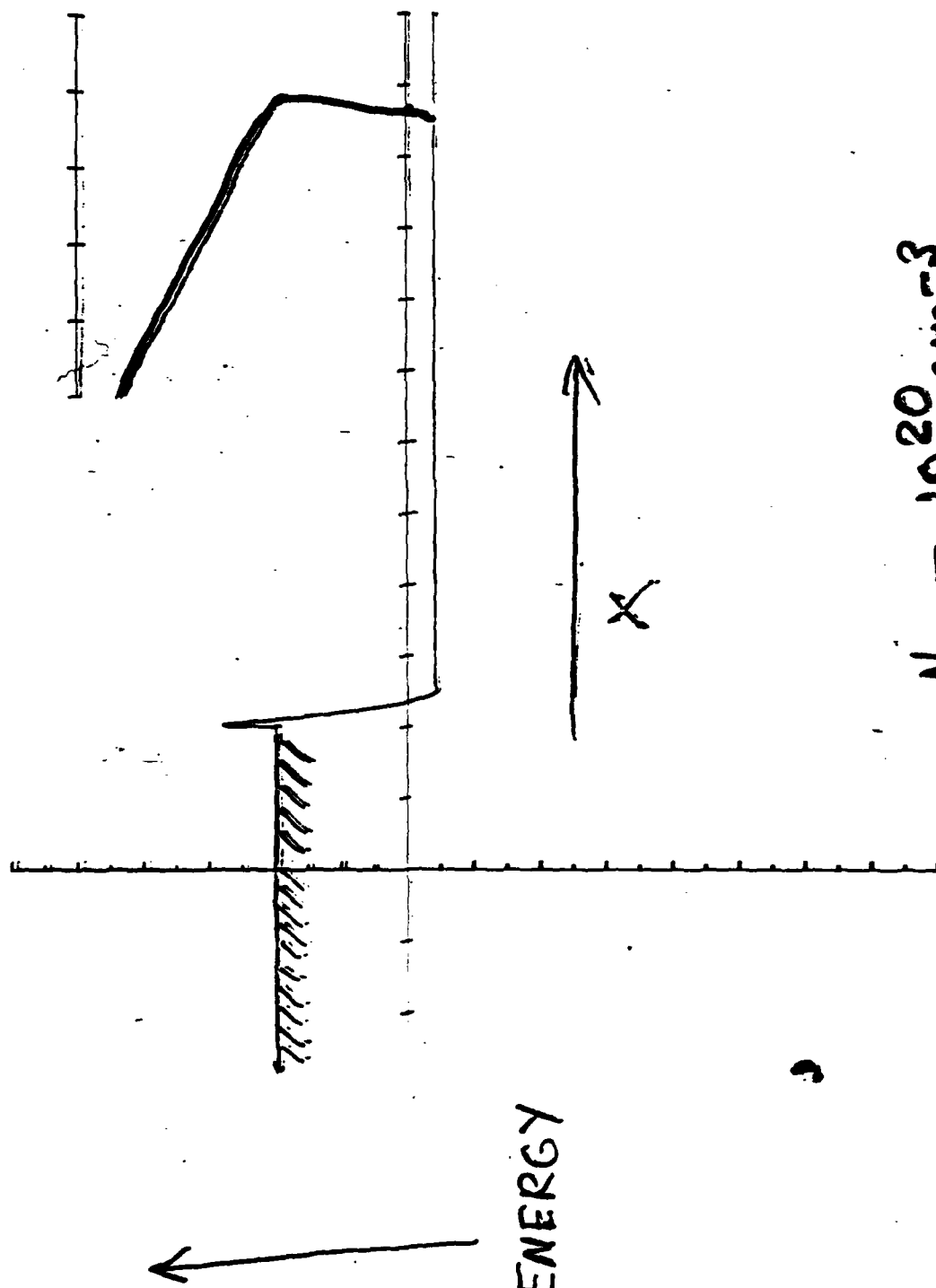
$$N_D = 10^{18} \text{ cm}^{-3}$$

DISTRIBUTION OF CONDUCTANCE



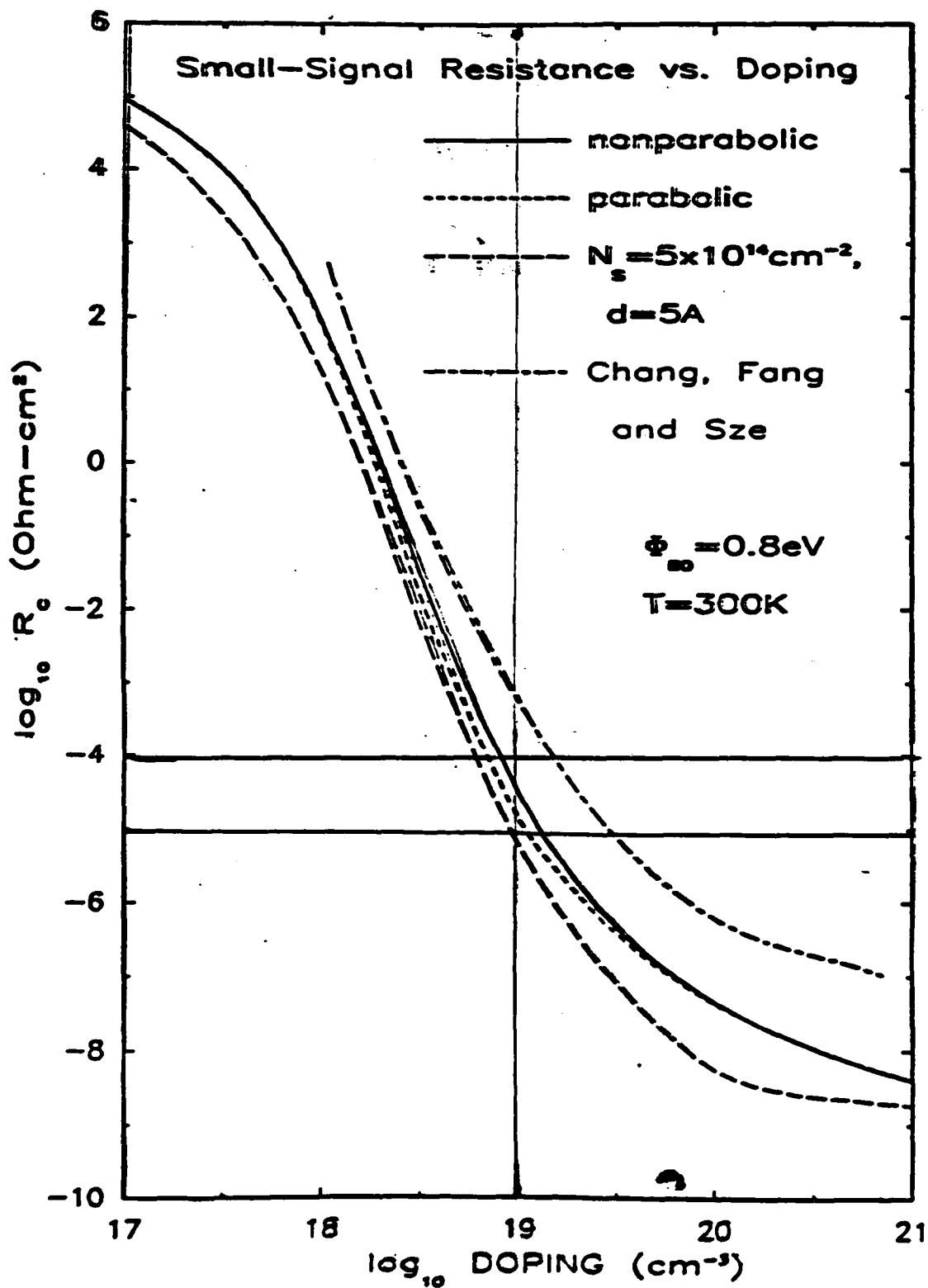
$$N_D = 10^{19} \text{ cm}^{-3}$$

DISTRIBUTION OF CONDUCTANCE

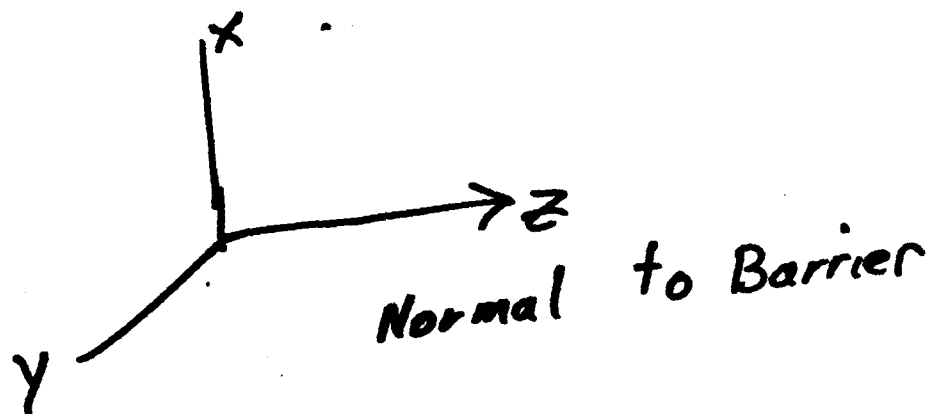


$$N_D = 10^{20} \text{ cm}^{-3}$$

ENERGY



INHOMOGENEOUS MODEL



$$G = \int G(x, y) dx dy = \langle g \rangle (\text{Area})$$

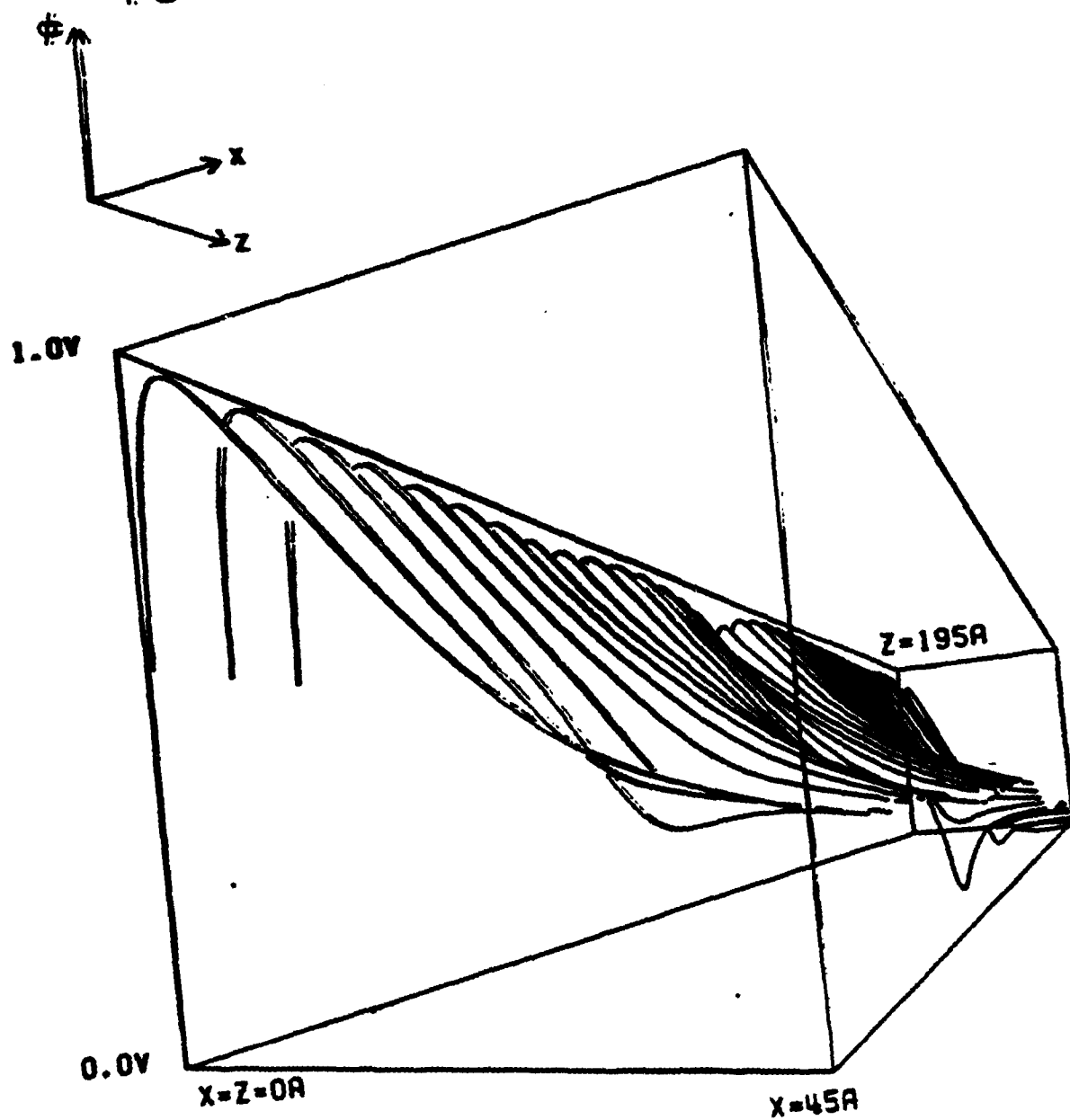
where $G(x, y)$ = conductance/area
at (x, y) .

- REGIONS OF HIGH G
DOMINATE

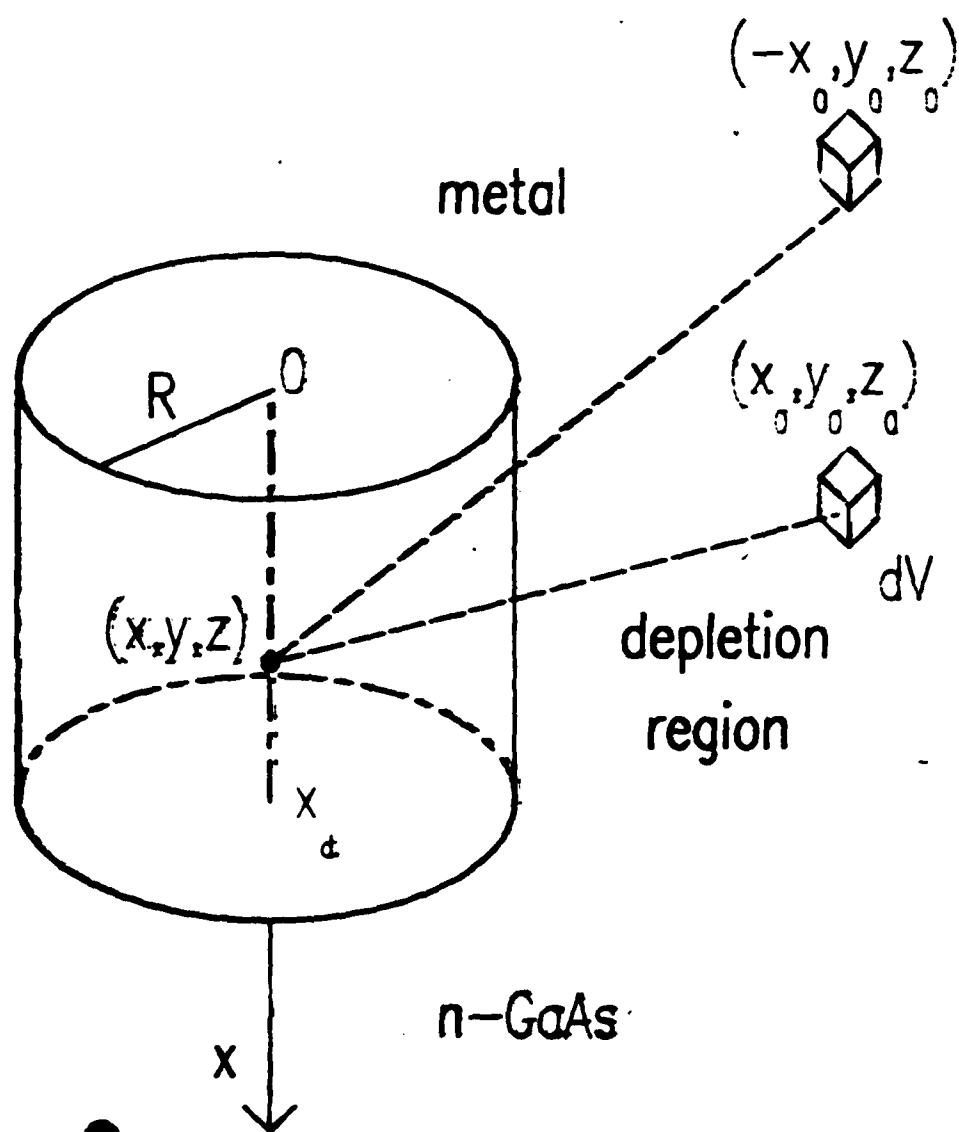
SPATIAL INHOMOGENEITY
DUE
TO DISCRETE DOPANTS.

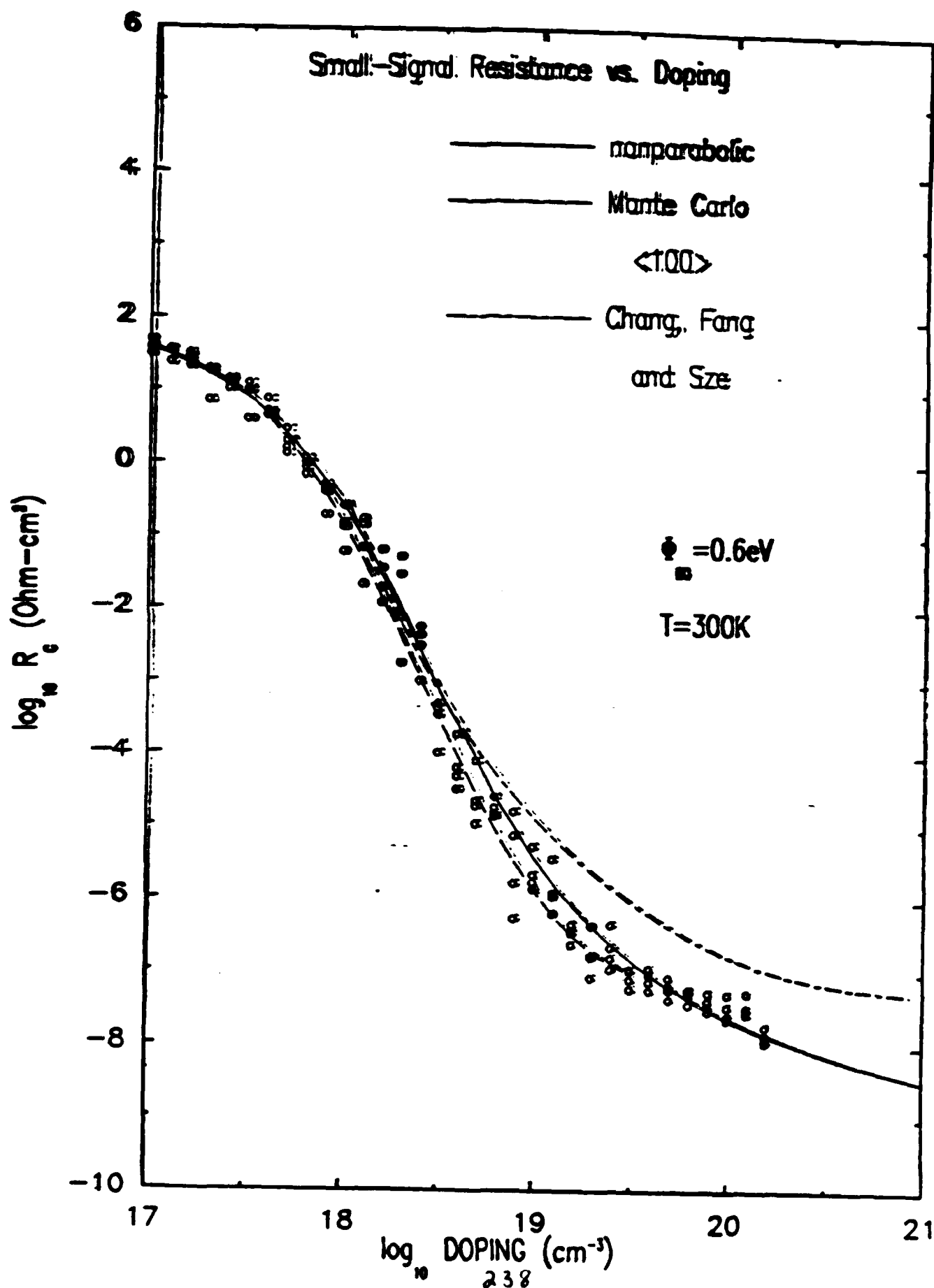
- DOPANT ATOMS DISCRETE.
⇒ POTENTIAL INHOMOGENEOUS
- USE "RENO" TECHNIQUES
TO SIMULATE EFFECT.

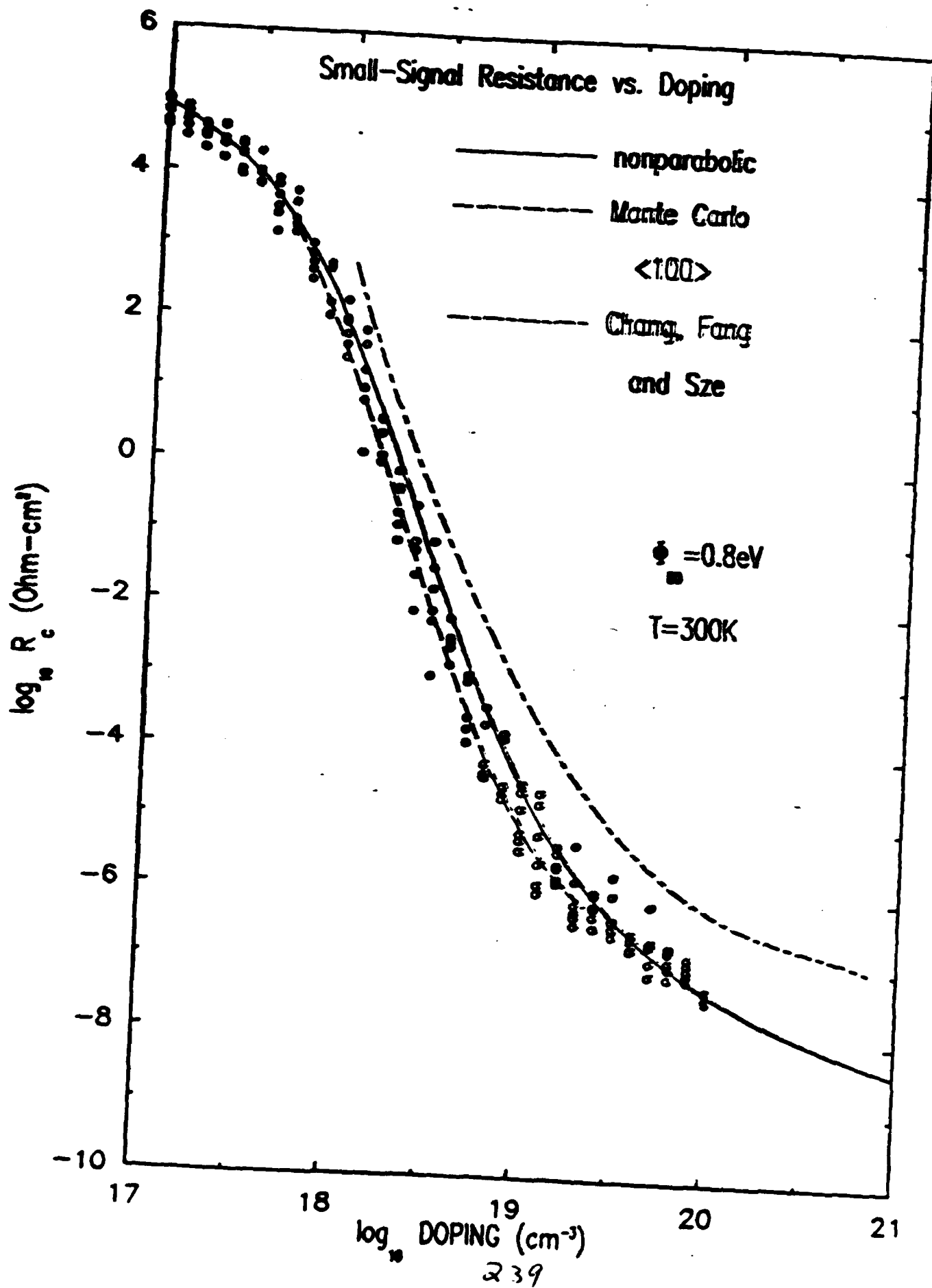
POTENTIAL IN DEPLETION REGION

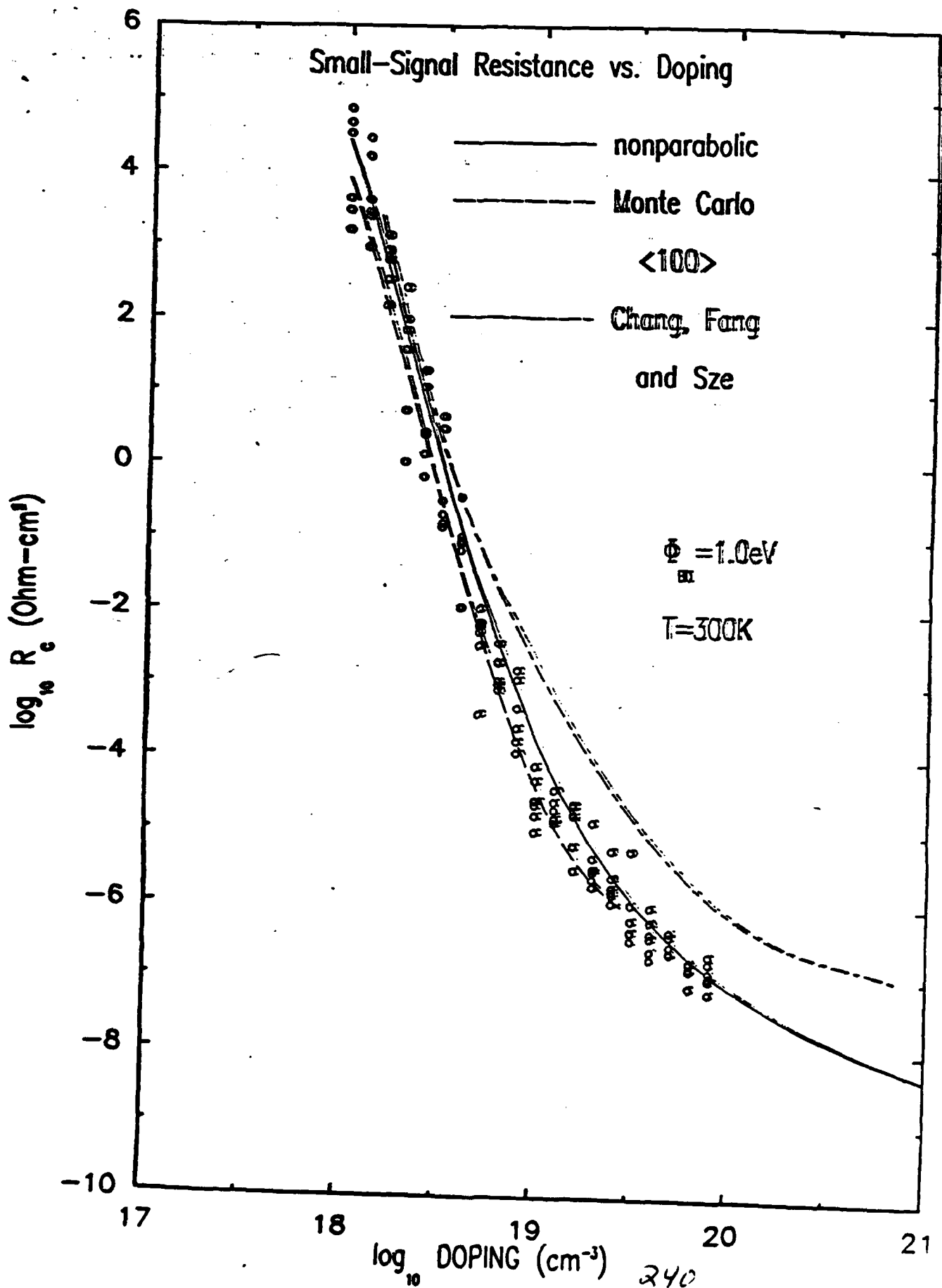


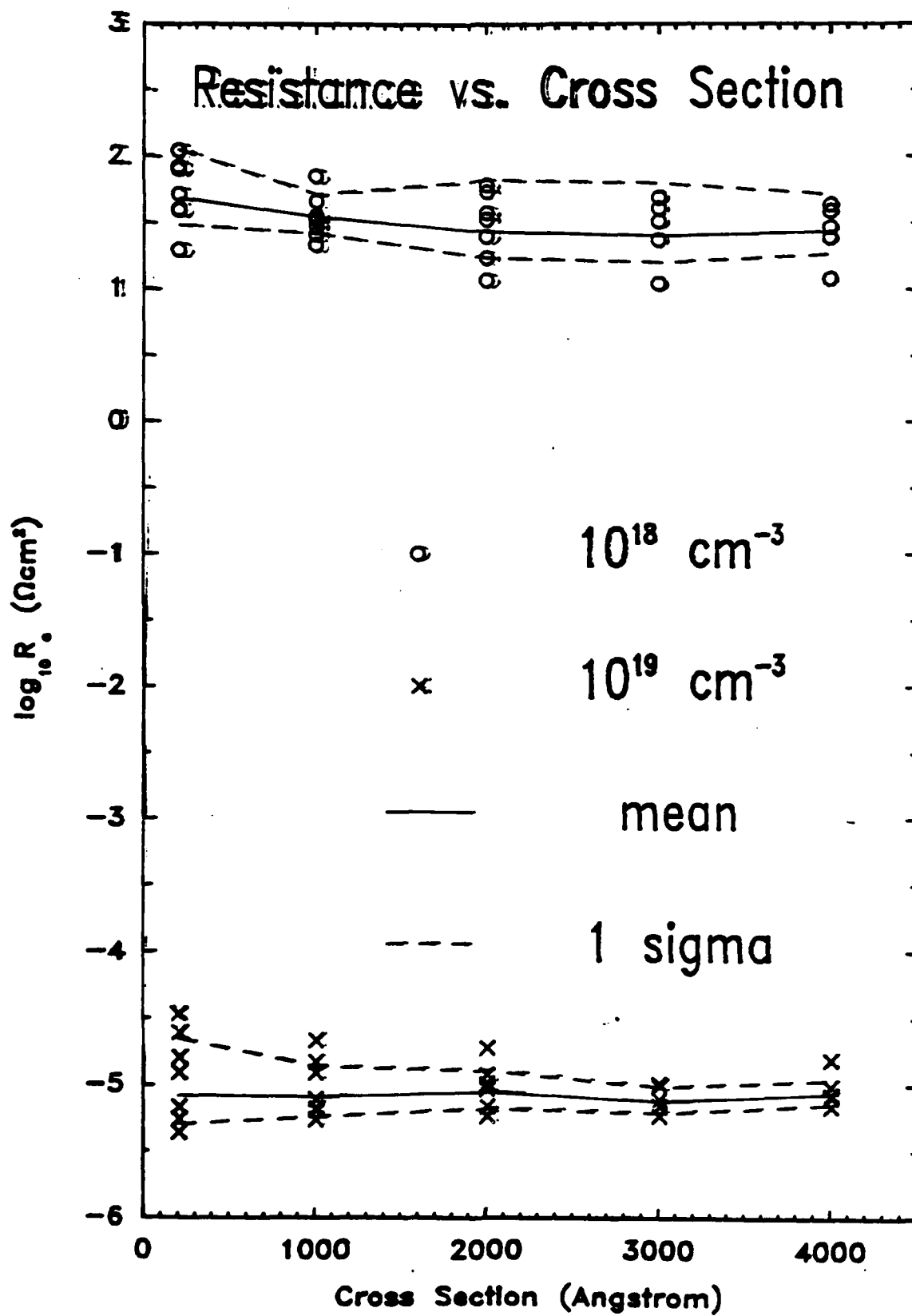
Contributions to the Potential

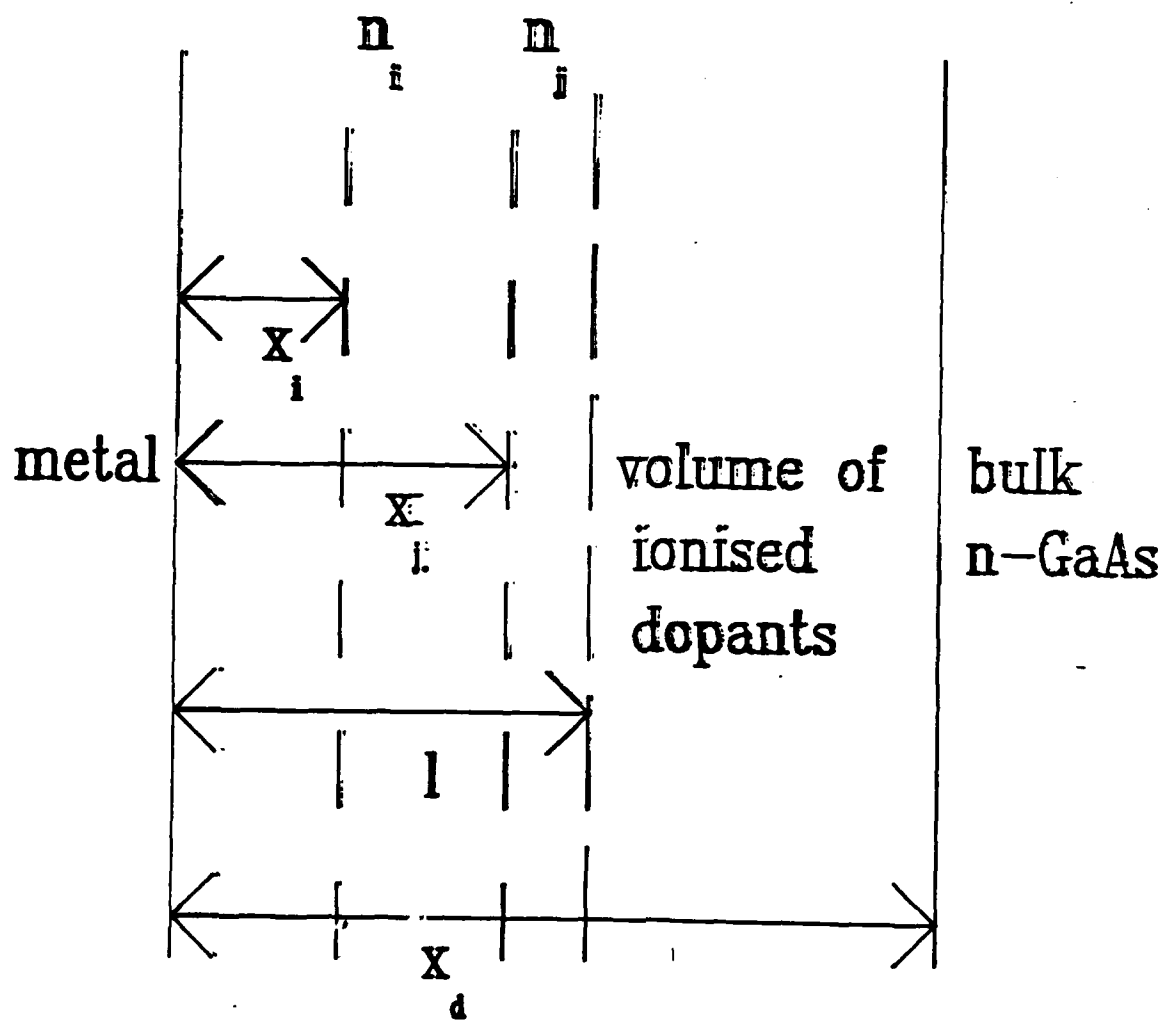


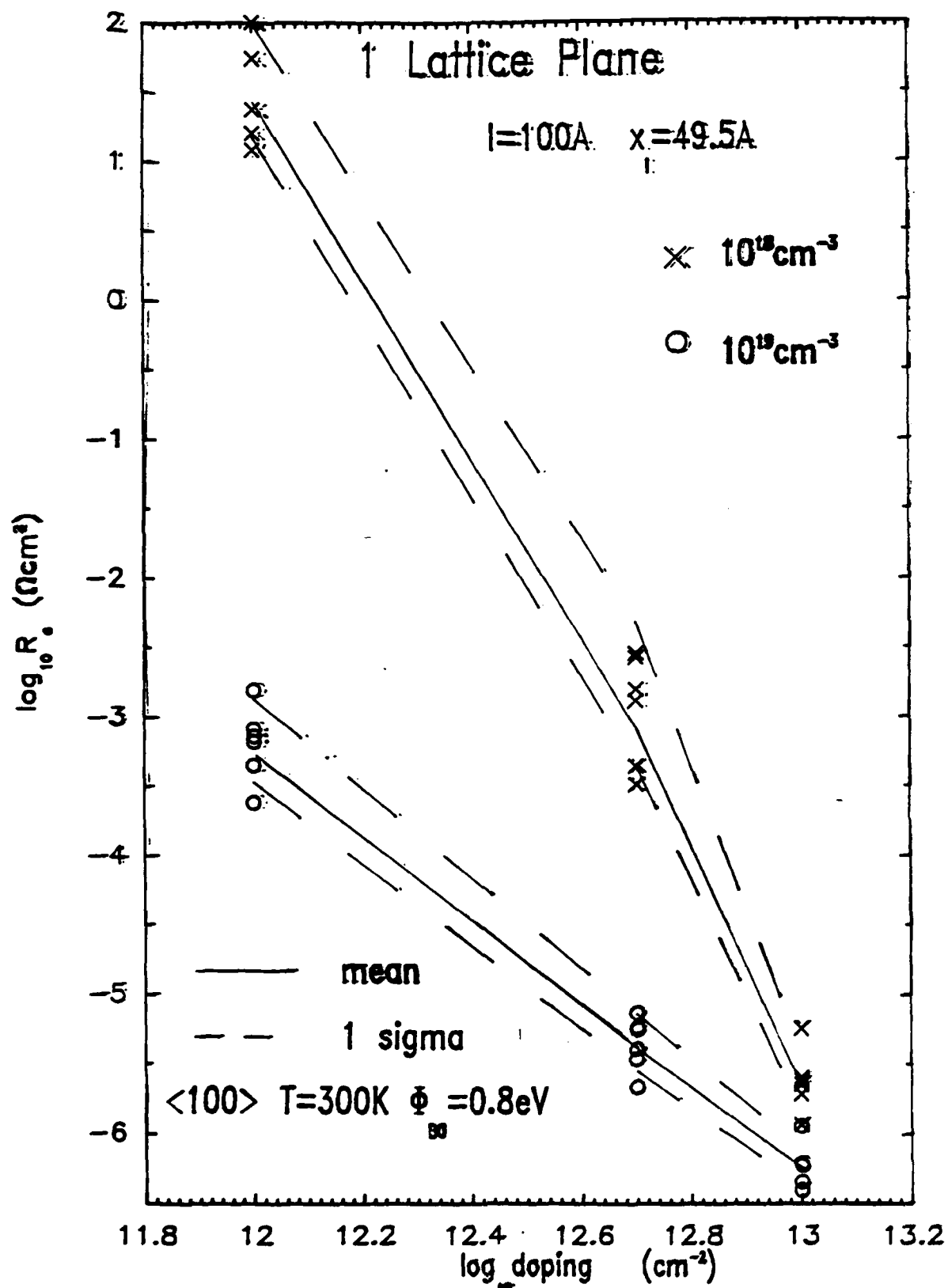


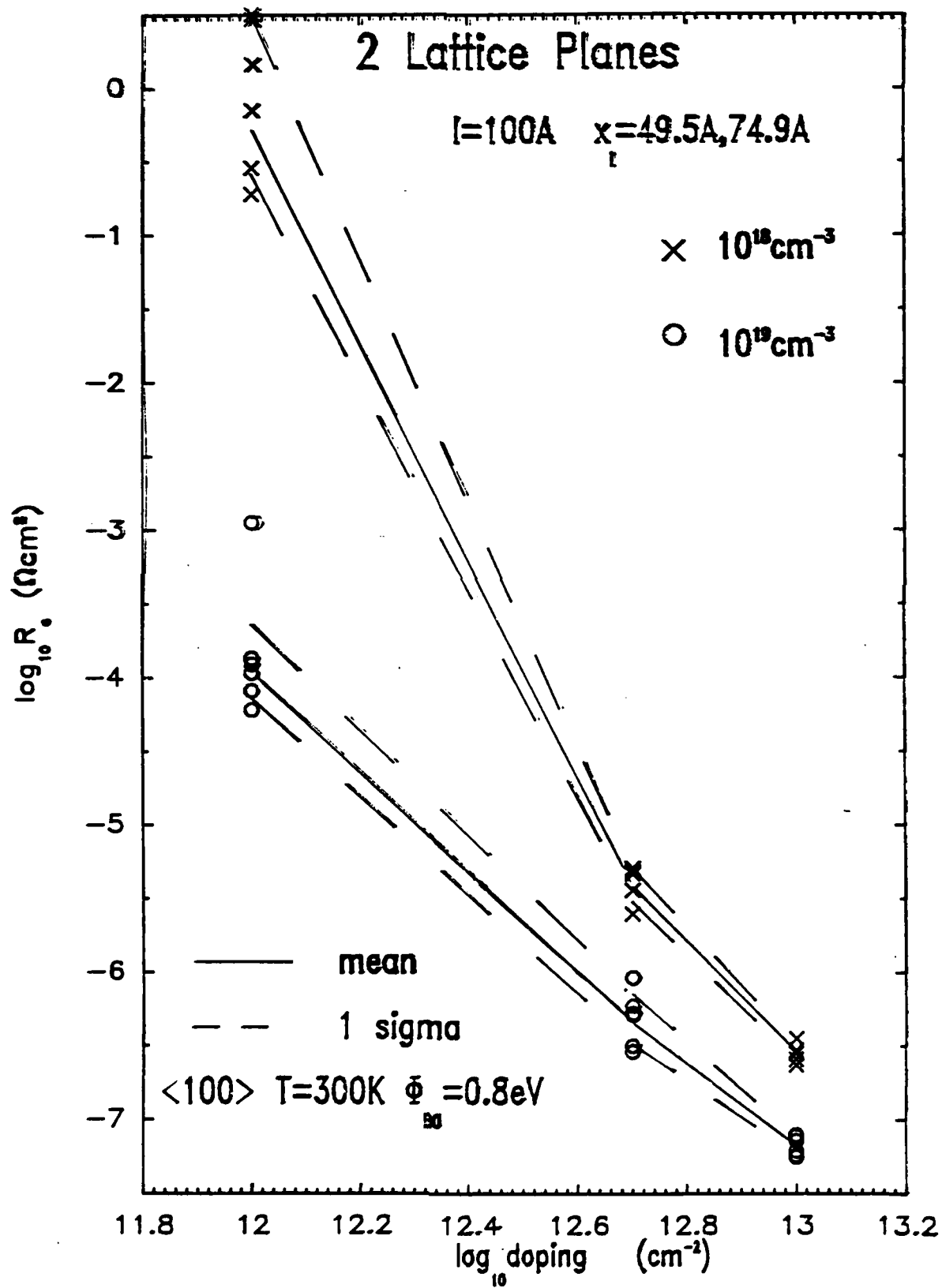












SUMMARY

- A. OHMIC CONTACTS COULD
LIMIT SMALL DEVICES
- B. FLUCTUATIONS ARE
INHERENT DUE TO
DISCRETE DOPING
- C. DELTA-DOPING ALLOWS
SUPPRESSION OF FLUCTUATIONS

FUTURE

- A. WHAT IS MINIMUM
VALUE OF ρ_c ?
- B. HOW DOES ρ_c DEPEND
ON METAL?
- C. CAN FLUCTUATIONS BE
SUPPRESSED?
- D. WHAT ARE THE NOISE
PROPERTIES OF OHMIC
CONTACTS?
- E. WHAT IS THE DISTRIBUTION
OF ELECTRONS EMITTED BY
"OHMIC" CONTACT UNDER LARGE
BIAS ?

S. S. Lau

**Non-alloyed ohmic contact by
Solid State Reactions**

U.C.S.D.

IBM

Cornell

Eric Marshall
Bei Zhang
L. C. Wang
S. S. Lau

T. F. Kuech

K. Kavanagh

We concentrate on:

Ge/Pd/n - GaAs

and

Si/Pd/n - GaAs

The use of Ge-Pd on n-GaAs is not new:

A. K. Sinha et al 1975

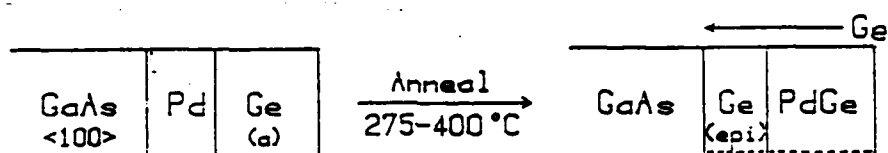
H. R. Grinolds and G. Y. Robinson 1980.

n-GaAs	Ge	Pd
1.2×10^{16}	500 Å	500 Å

500 - 600°C
 $3 - 4 \times 10^{-7} \Omega \text{cm}^2$
Surface very rough

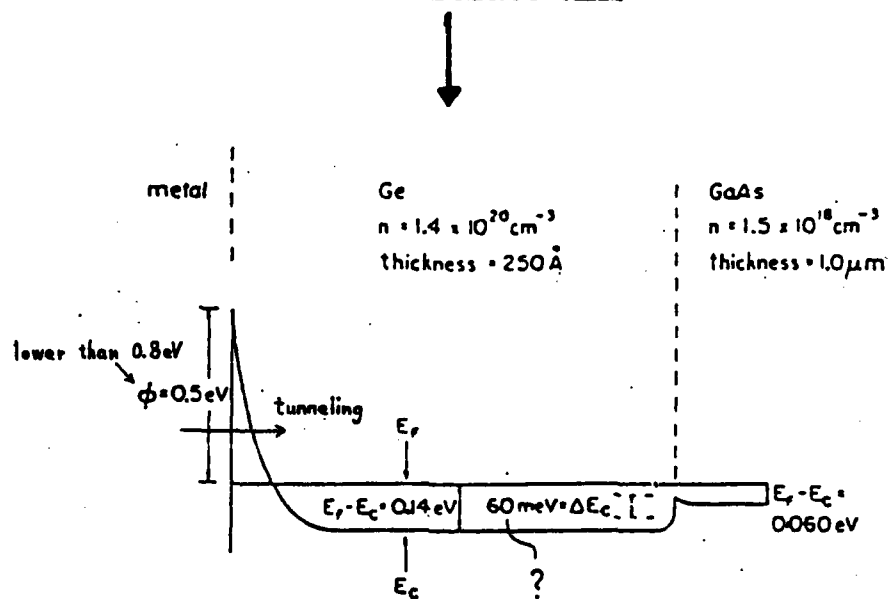
The contact deposition scheme is inverted in our case →
appears to make a big difference

Solid State Reactions:
Configuration(schematic):



Thickness: 500 Å 1150 Å
 Atomic Ratio: 1 : 1.5

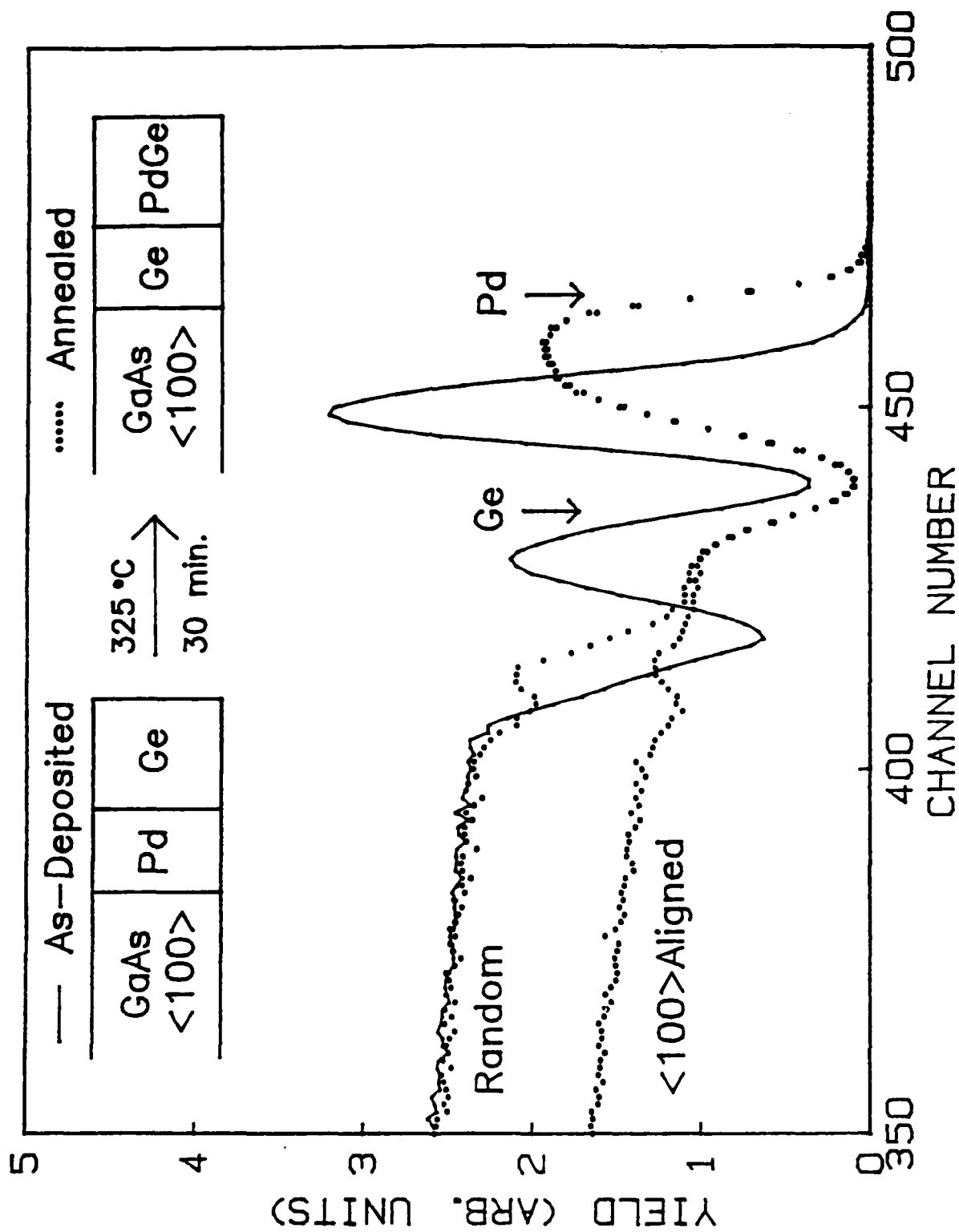
The idea is to simulate this

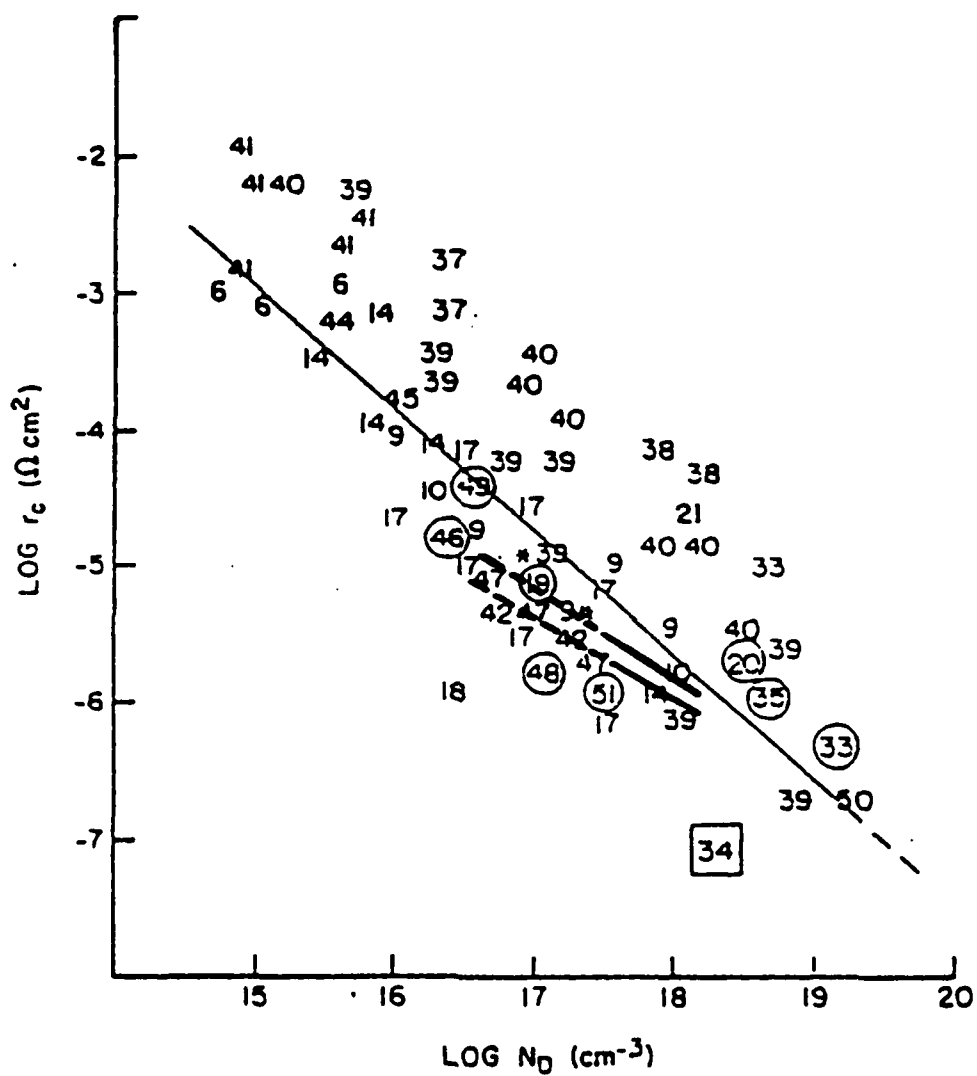


R. Stall, C.E.C. Yeod, K. Board, and L.F. Eesteen,
 Electronics Letters, 15, 888 (1979).

$$R_c \sim 10^{-7} \Omega \text{ cm}^2 \text{ or less}$$

249





Observed contact resistance a function of n-GaAs doping.



a) — 50nm



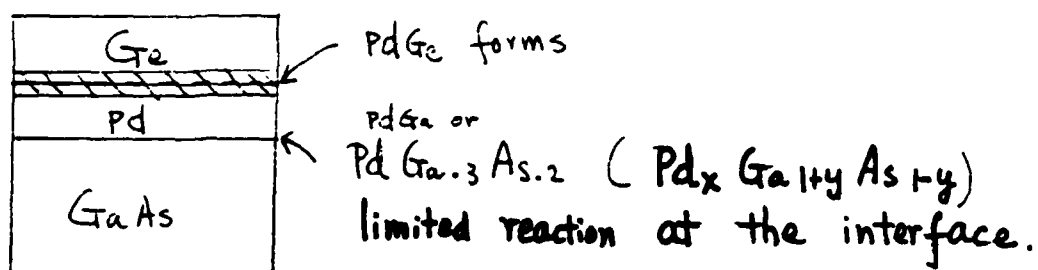
b) — 5nm

Conditions for ohmic behavior:

- (1) Pd must be in contact with GaAs initially
(Ge/Pd/GaAs $\rightarrow$ low ρ_c ; Pd/Ge/GaAs $\rightarrow$ high ρ_c)
- (2) Ge is necessary
(Pd/n-GaAs $\rightarrow$ high ρ_c or non- Ω .)
- (3) Complete transport of Ge generally leads to
lower ρ_c and better thermal stability.

How does the Ge/Pd system work?

It is proposed:



Formation of PdGa (or PdGa₃As₂) → Excess
Ga vacant sites → Ge occupies these sites, surface →
 n^+

If this replacement mechanism works for n type
GaAs, the same mechanism should not yield low ρ_c
for p type GaAs!

a) ——— 40nm

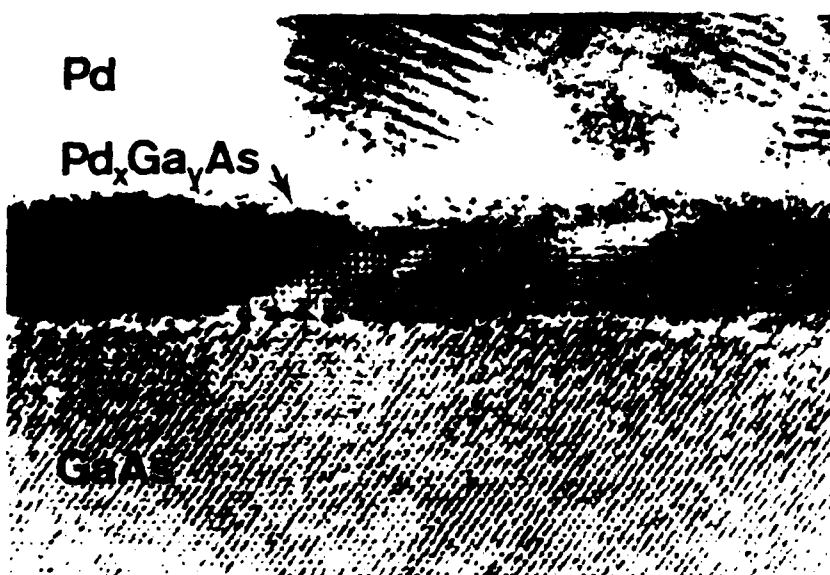
Ge



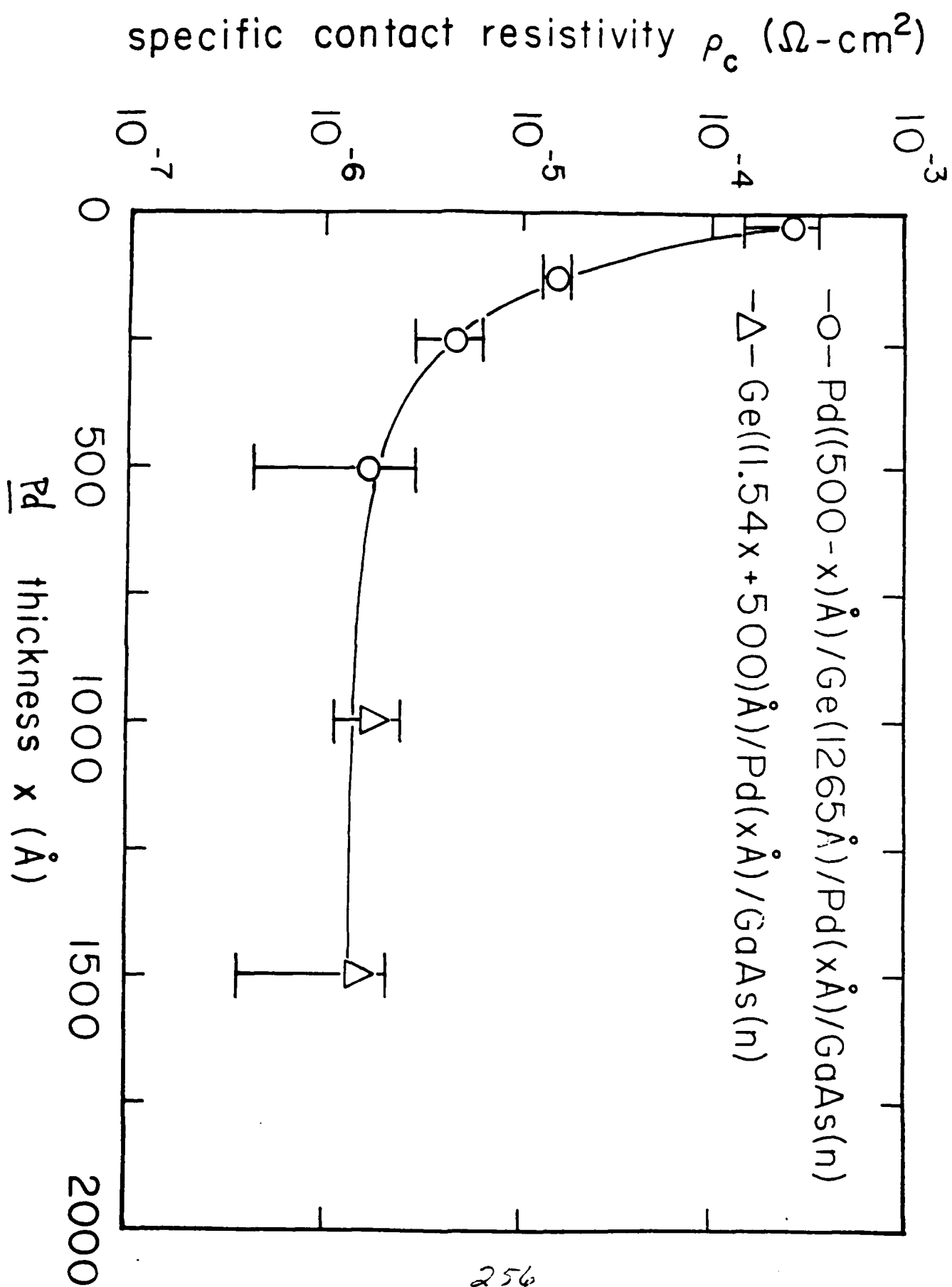
Pd

← Pd_xGa_yAs

GaAs



b) ——— 4nm



Experimentally:

(1) For n-type GaAs.

Ge/Pd yields low ρ_c from 4×10^{16} to $2 \times 10^{18}/\text{cm}^3$

($N_c = 4.7 \times 10^{17}$)

Pd alone does not work well.

(2) For p-type GaAs,

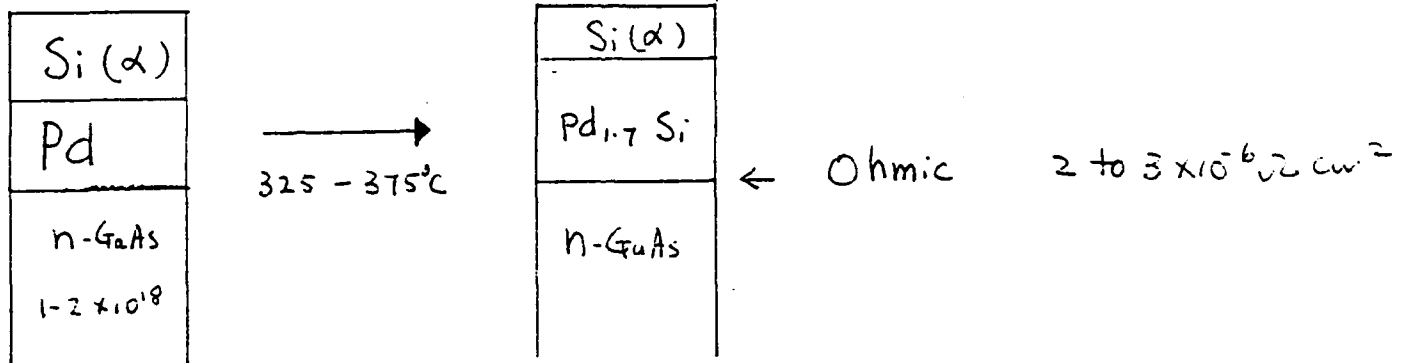
Ge/Pd yields low ρ_c from $> 1 \times 10^{19}/\text{cm}^3$

($N_v = 7 \times 10^{18}/\text{cm}^3$. For lower concentrations, Pd

alone works better. To dope p type surface selectively, a metal which form mAs should be used.

Is the Ge/GaAs heterojunction important in this Ohmic contact scheme?

The evidence we have so far seems to say no.



Note:

- (1) the temperature is low – no macroscopic Si transport (from Backscattering measurement)
- (2) even if there is some microscopic Si transport – the lattice match is poor - should not result in good epitaxy.

Heterojunction does seem to play an important role in ohmic contact formation.

SUMMARY

- (1) For this ohmic contact scheme to work:
 - (i) Pd must be in contact with GaAs initially.
 - (ii) Ge is necessary.
- (2) The replacement mechanism seems to be applicable.
- (3) The interface is structurally abrupt to atomic dimensions.
- (4) Thermal stability - good at $\sim 400^{\circ}\text{C}$ for hours (still in the 10^{-6} range) - appear to be related to the uniformity of the transport.
- (5) Applicable to n, p GaAs, n, p InGaAs n, p InGaAsP and n - InP.

Large Variations of GaAs Schottky Barrier Height by Interface Layers

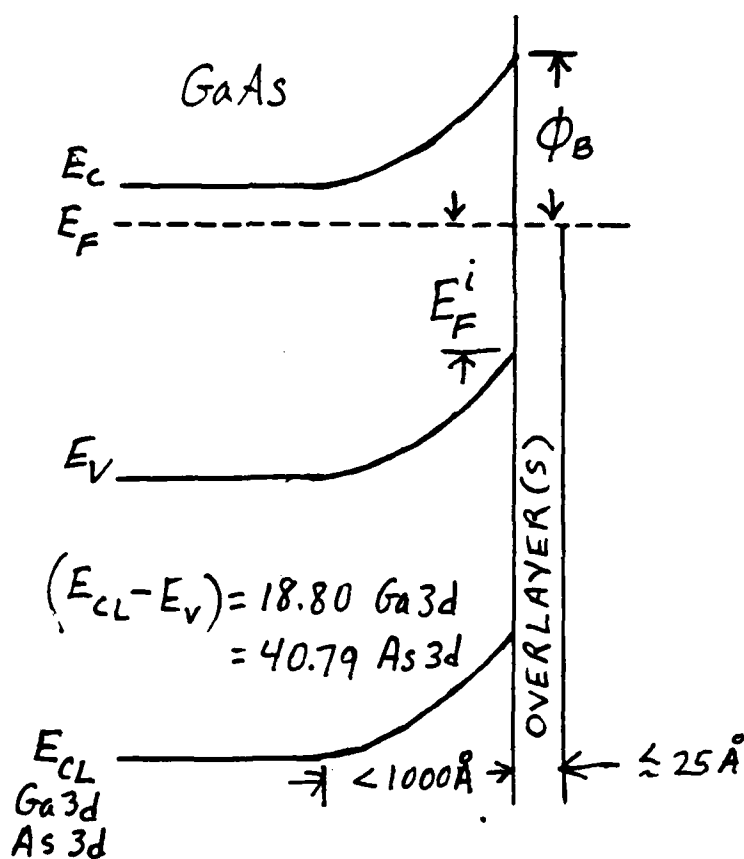
J. R. Waldrop
Rockwell International

Three examples of interface Fermi energy E_F^i varying by
more than 0.6 eV at n-type GaAs (100) interfaces

- a) oxides + Au
- b) metals + chalcogens (S, Se, Te)
- c) model AuGeNi contacts for ohmic contact
applications

EXPERIMENTAL TECHNIQUES:

- XPS FOR INTERFACE FERMİ ENERGY E_F^i AND CHEMISTRY
- I-V AND C-V ELECTRICAL MEASUREMENTS FOR ϕ_B



E_{CL} MEASURED AT INTERFACE

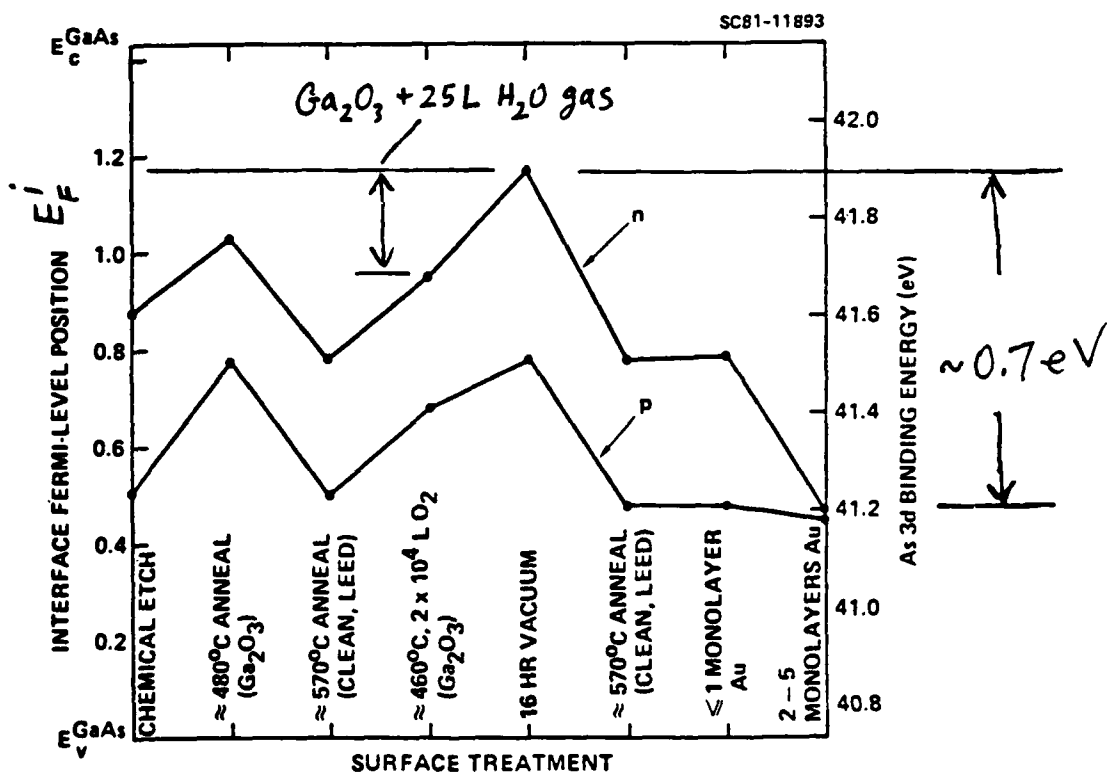
$$E_F^i = E_{CL} - (E_{CL} - E_V) \text{ eV}$$

$$\Delta E_F^i = \Delta E_{CL} \quad 262$$

$$\phi_B = 1.43 - E_F^i \text{ eV}$$

CHANGE IN E_F^i FOR OXIDE AND METAL SURFACE TREATMENTS (GRANT et al JVST 19, 477 (1981))

GaAs (100)

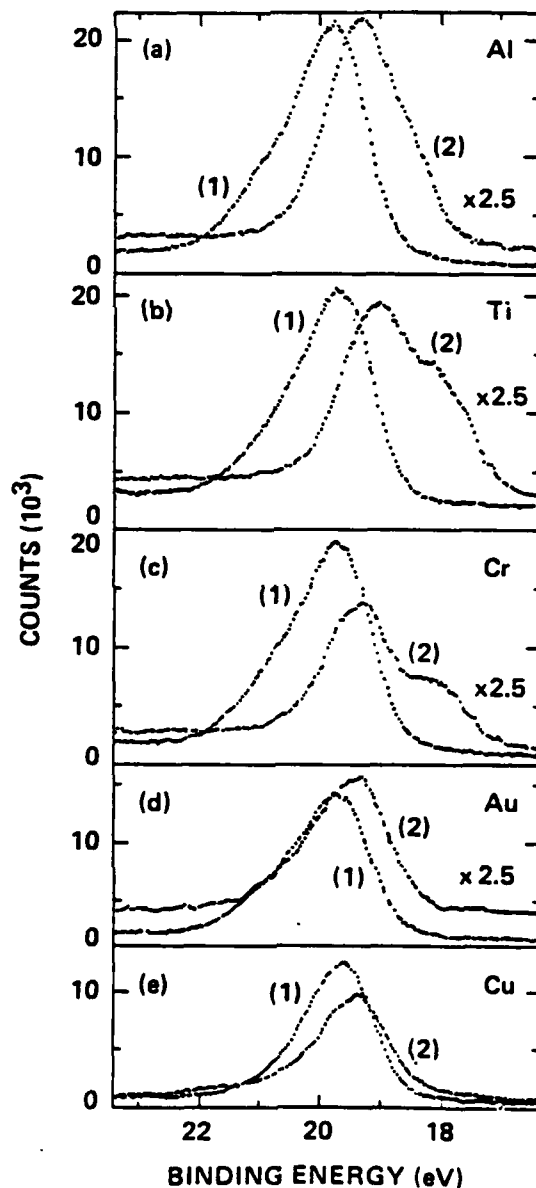


(SAME BASIC BEHAVIOR ON 110 SURFACE)

DEPOSITION OF METALS ON Ga_2O_3 SURFACE

$$\Delta E_{\text{Ga}3d} = \Delta E_F^i$$


KOWALCZYK, et al
Appl Phys Lett 38, 167 (1981)



Ga 3d core level

(1) INITIAL Ga_2O_3 SURFACE (LOW BAND BENDING)

(2) AFTER DEPOSITION OF SEVERAL MONOLAYERS METAL

INCREASE IN $\text{Ga}3d$ B.E. IN EACH CASE INDICATES
INCREASE OF E_F^i WITH METAL DEPOSITION

- low band bending, $E_F^i \sim 1.2$ eV, observed for Ga_2O_3 (H_2O) covered 100 surfaces
- results of Offsey et al (Appl Phys Lett 48, 475 (1986)) indicate low band bending on oxide surfaces after treatment with water and laser irradiation
- low band bending condition eliminated after metal deposition onto Ga_2O_3
- up to ~ 0.7 eV shift in E_F^i occurs with sequential oxide and metal surface treatments

metal-chalcogen (S, Se, Te)-GaAs interfaces

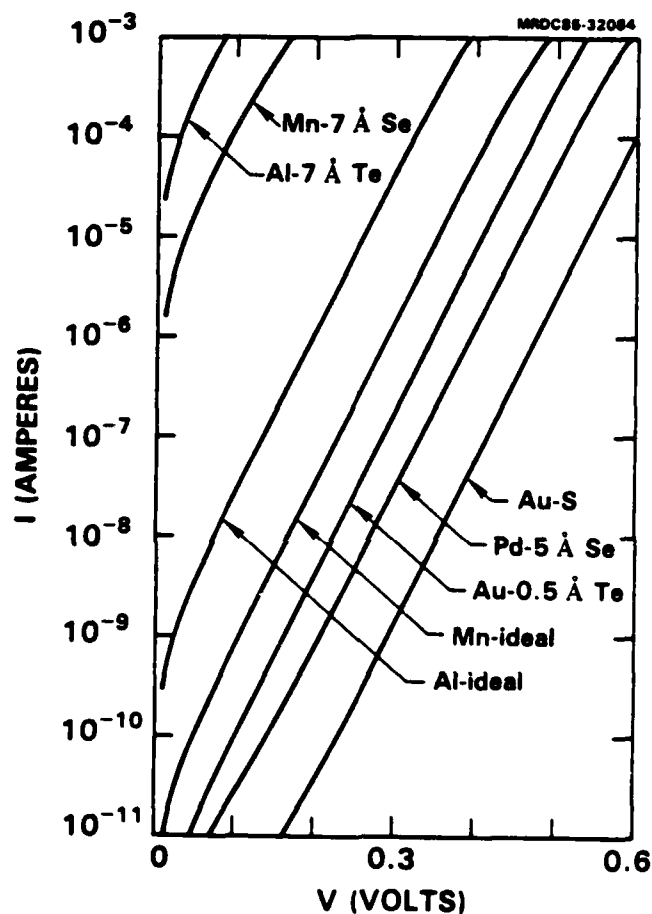
Waldrop, JVST B3, 1197 (1985)

APL 47, 1301 (1985)

- H₂S exposure (~425°C) of clean GaAs prior to R.T. Al deposition gives I-V measured ϕ_B of ~0.4 eV (Massies, et al, APL 38, 693 (1981))

Summary of XPS results

- exposure of clean R.T (100) surfaces to elemental S, Se, or Te increases E_F^i ~0.15 eV to $E_F(\text{chalcogen}) = \sim 0.85$ eV. Chalcogen exposure alone does not account for low ϕ_B
- S and Se form ~5Å reacted region, Te is nonreactive
- Additional E_F^i shift occurs with metal deposition onto chalcogenide surface
- reactive metals (Al, Mn) increase E_F^i upon metal-chalcogen reaction; nonreactive metals (Au, Ag, Pd) decrease E_F^i
- Final E_F^i is after metal deposition
- XPS observed range in E_F^i is >0.5 eV



REPRESENTATIVE I-V DATA FOR A SELECTION
OF GaAs SCHOTTKY BARRIER CONTACTS
AREA = $5.07 \times 10^{-4} \text{ cm}^2$

I-V DATA CONSISTENT WITH XPS E_F^i OBSERVATIONS
NONREACTIVE METAL-CHALCOGEN CONTACTS HAVE
HIGHER ϕ_b THAN REACTIVE METAL-CHALCOGEN
CONTACTS 267

Table I
Influence of Interface S, Se and Te on the Schottky Barrier
Height of Various Metal Contacts to GaAs

Metal	Interface	n	ϕ_B^{IV} (eV)	ϕ_B^{CV} (eV)
Al	S	1.05	0.52	0.45
	1.5 Å Se	1.03	0.53	0.52
	4 Å Se	--	~ 0.35	--
	21 Å Se	1.19	0.48	0.39
	3 Å Te	1.04	0.51	0.53
	7 Å Te	1.06	0.44	0.40
	22 Å Te	1.06	0.52	0.50
	ideal	1.04	0.74	0.75
	ideal ^a	1.07	0.85	0.84
Mn	7 Å Se	1.08	0.51	0.61
	ideal	1.03	0.82	0.82
Ti	11 Å Te	1.02	0.72	0.72
	ideal ^a	1.03	0.83	0.83
Au	S ^b	1.03	1.00	1.02
	20 Å Se ^b	1.08	0.97	0.96
	0.5 Å Te	1.03	0.89	0.87
	10 Å Te	1.03	0.83	0.81
	~ 100 Å Te	1.02	0.79	0.78
	ideal ^{a,b}	1.03	0.89	0.89
Ag	S ^b	1.05	0.96	0.99
	3 Å Te	1.04	0.84	0.84
	ideal, ^{a,b}	1.03	0.90	0.89
Pd	5 Å Se	1.04	0.93	0.94
	ideal ^a	1.03	0.91	0.93

I-V C-V

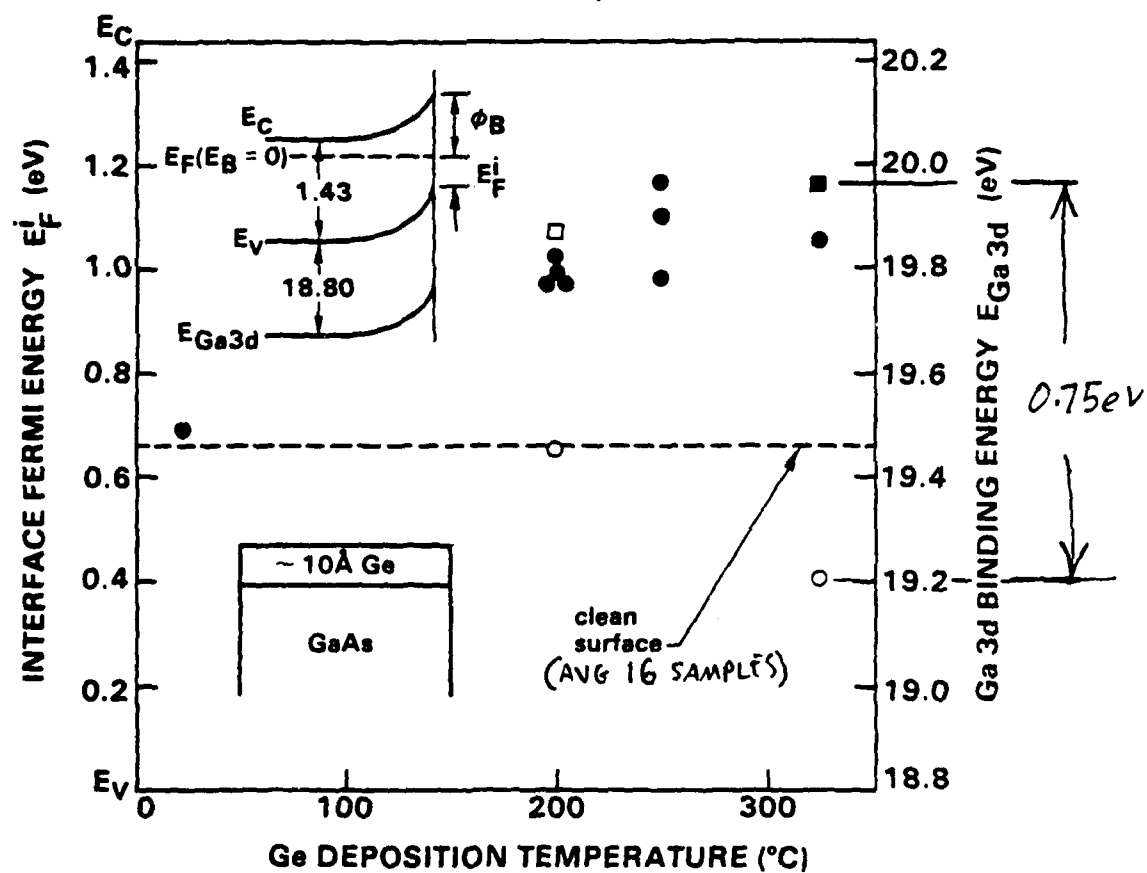
ϕ_B RANGE IS ~0.35 eV TO 1.0 eV
268 (~0.65 eV VARIATION)

Model AuGeNi contacts to GaAs

Waldrop and Grant, submitted to APL

- nonalloyed contacts consisting of Au, Ni, Ge, NiAs, and Te layers
- correlation of interface composition and ϕ_B
- XPS for E_F^i measurement and composition analysis
- ϕ_B measured on thick contacts by I-V (XPS characterized interfaces)
- high temperature nonalloyed ohmic contact applications

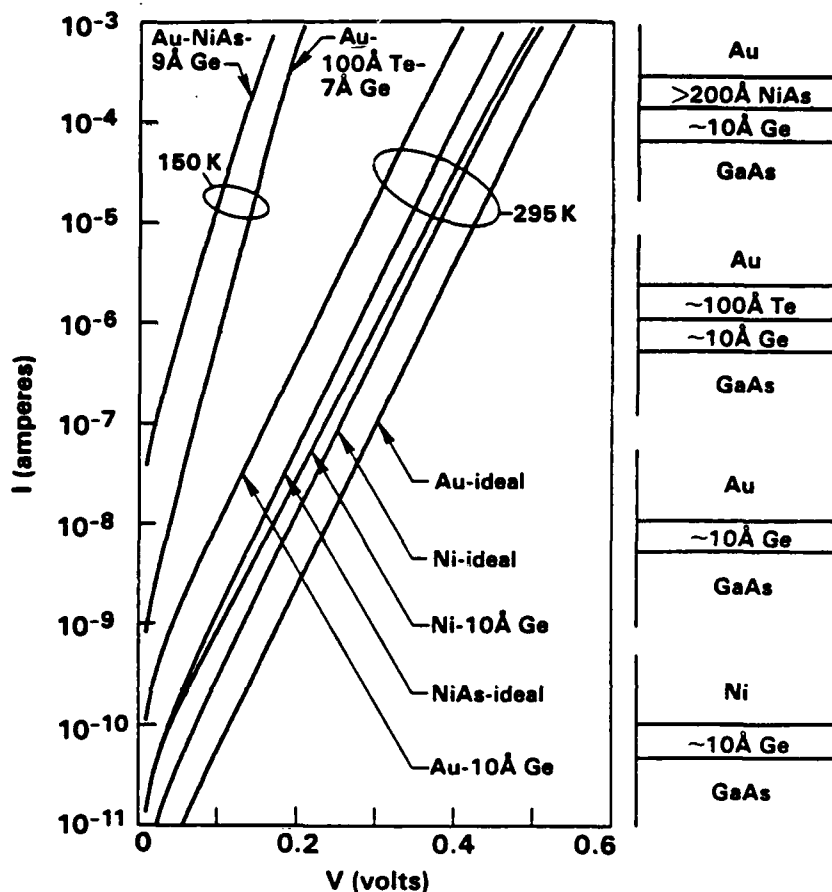
- 10^{-7} Torr As DURING Ge DEPOSITION
- 10^{-6} Torr As " "
- VACUUM CLEANED / VACUUM Ge DEPOSITION
- CLEANED IN 10^{-6} Torr As / VACUUM Ge DEPOSITION



E_F^i FOR THIN ($\sim 10\text{\AA}$) Ge OVERLAYER ON
CLEAN GaAs (100)

MAX E_F^i VARIATION IS 0.75 eV

MAXIMUM E_F^i IS ~ 1.2 eV
270



Representative I-V data for a selection of contacts that have a variety of structures (area = $5.07 \times 10^{-4} \text{ cm}^2$)

Multilayered contacts are shown on right

For contacts with Ge interlayer, $E_F^i = 1.0 - 1.2 \text{ eV}$ before subsequent depositions

XPS E_F^i measurements for deposition on Ge overlayer consistent with I-V measurements

- low ϕ_B obtained when Ge layers are deposited under certain conditions and Ge-GaAs interface is separated from metal by intervening layer
- intervening layer was NiAs or Te
- for all contact structures ϕ_B ranged from 0.23 to 0.89 eV (~0.65 eV range)

Summary

- E_F^i of $\sim 1.0 - 1.2$ eV can be obtained with $\text{Ga}_2\text{O}_3(\text{H}_2\text{O})$ overlayers, $\text{Ge}(\text{As})$ overlayers, and metal-chalcogen reactions
- ϕ_B (E_F^i) variations > 0.6 eV can occur with interfaces that have a wide variety of compositions
- E_F^i is not restricted to a narrow range for all GaAs interfaces

Effects on Schottky Barriers of
Metal Substitution in Semiconductors*

E. A. Kraut and W. A. Harrison**

Rockwell International Science Center
Thousand Oaks, California 91360

ABSTRACT

The question of what effects transport of metal atoms into the semiconductor at a Schottky barrier may have on the barrier properties is examined using tight-binding theory based on universal parameters. For example, the total change in energy associated with an interchange of aluminum and gallium atoms across an interface between metallic aluminum and gallium arsenide is calculated and is found to favor the interchange in agreement with the experimental results of Bachrach and others. Since aluminum and gallium have the same valence this interchange does not transfer charge nor generate appreciable dipoles. However, we take the Schottky barrier height to be determined by the position of the bands relative to the average hybrid energy of the compound, which is expected to match the Fermi-energy of the metal, as suggested by Harrison and Tersoff (PCSI, 1986), who find the energy to the valence band maximum (relative to the average hybrid energy) differs by 0.12 eV between GaAs and AlAs, the latter lying lower. Thus, for example, if 25% of the first layer of Ga atoms are replaced by Al, the Schottky barrier for holes in a junction with p-type material would be increased by 0.03 eV. The shift for n-type barriers can be similarly estimated using the experimental band gaps and is larger. The corresponding calculation for any other system is just as easily obtained using our recent tables of energies of substitution to determine if substitution is expected and the tables of band-lineups to estimate the sign and magnitude of the effect.

*Supported, in part, by ONR Contract No. N00014-85-C-0135

** Permanent address: Applied Physics Department, Stanford University, Stanford California 94305.

Effects on Schottky Barriers
of Metal Substitution in
Semiconductors

E. A. Kraut¹ and W. A. Harrison²

Rockwell International
Science Center ¹

Thousand Oaks, CA 91360
and

Applied Physics Department
Stanford University²
Stanford, CA 94305

Work supported, in part, by ONR
Contract # N00014-85-C-0135

When a metal/semiconductor junction is formed some of the metal atoms may become incorporated into the semiconductor lattice.

A good example is the incorporation of Al atoms into the GaAs lattice at an Al/GaAs interface.

We have used Harrison's tight-binding theory with universal parameters to:

- 1.) calculate the energetics of this interchange and to
- 2.) determine the resulting shift in Schottky barrier height

INTERFACE BETWEEN METALLIC ALUMINUM & GALLIUM ARSENIDE

Total Change in Energy To
Substitute an Al atom for a bulk
Ga atom in GaAs:

- 1.) Energy to remove an Al atom
from bulk Al (cohesive energy)
3.39 eV/atom (exp val from Kittel)
- 2.) Energy gained by replacing a Ga
atom in GaAs by an Al atom
-1.03 eV (Our calculations)
- 3.) Energy to add the released Ga
atom to a clump of metallic Ga
-2.81 eV/atom (coh.energy-Kittel)
- 4.) Net energy gain by replacement:
 $3.39 - 1.03 - 2.81 = -0.45$ eV/atom

Conclusion: Substitution will occur
for high enough temperature given
long enough time 278

Effect on Schottky Barrier Height

1.) Al and Ga have the same valence so, to first order, there is no charge transfer nor appreciable dipole generation.

2.) The Schottky barrier height is determined by the position of the bands relative to the average hybrid energy of the compound which is expected to match the Fermi energy of the metal (Harrison and Tersoff, 1986).

3.) Relative to the average hybrid energy, the valence-band maximum of AlAs is 0.12 eV lower than the VBM in GaAs. Thus if 25% of the first layer of Ga atoms are replaced by Al atoms, the Schottky barrier for holes in a junction with p-type GaAs would be increased by 0.03 eV. ²⁷⁹

Tin on Germanium : Also Homopolar
Energy cost to remove a tin atom
from the metal = 3.14 eV/atom

Energy cost to replace a Ge atom
in bulk Ge by a tin atom = 1.12 eV

Energy gained by returning the Ge
atom to bulk Ge = 3.85 eV

There is now a net energy cost for
the exchange: $3.14 + 1.12 - 3.85 = 0.41$
The two are not very soluble
largely because of the misfit
energy which dominates the 1.12
 eV/atom it costs to substitute tin
in Ge. So little mixing is expected
and the effect of what little
mixing occurs is readily estimated.

Aluminum on Germanium

Heterovalent Substitution

Energy cost to remove an Al atom from the metal = 3.39 eV/atom

Energy cost to replace a Ge atom in bulk Ge by an Al atom = 2.34 eV

Energy gained by returning the Ge atom to bulk Ge = 3.85 eV

Net energy cost = $3.39 + 2.34 - 3.85 = 1.88$ eV/atom

Because the Al only brings 3 valence electrons with it, we supply the missing electron from the Ge valence band, leaving a hole.

If we started with intrinsic Ge the Al substitution dopes Ge p-type

If the starting Ge is n-type, an electron at the Fermi energy near the CB edge could drop to the hole, gaining a few tenths of an eV and reducing the substitution energy by this amount.

In any case, the actual energy cost to substitute Al for Ge is large. Doping in general is energetically expensive. The energy cost is primarily associated with the rearrangement of bond polarity. We conclude that doping effects, charge shifts, and Schottky barrier variations associated with heterovalent metal substitution into a semiconductor must be associated primarily with nonequilibrium processes i.e. they will not be observed even at high temperatures over long time intervals. These observations may have a bearing on the stability of various types of metal/semiconductor contacts.

Summary

- Appreciable atomic transfer can occur in special cases-homopolar substitution or compensating doping
- Where large effects can occur-the heteropolar case-the amount of substitution in equilibrium is too small to allow appreciable effects.
- These calculations for other systems are just as easily done using our recent tables of energies of substitution¹⁻³ and the recent Harrison-Tersoff tables of band lineups.⁴

1.) E.A. Kraut and W. A. Harrison, J. Vac. Sci. Technol. B 3(4), 1267(1985)

2.) E. A. Kraut and W.A. Harrison, J. Vac. Sci. Technol. B 2(3), 409 (1984) 3.) E. A. Kraut

and W. A. Harrison, to be published

4.) W. A. Harrison and J. Tersoff, J. Vac. Sci. Technol. B 4(4), 1058(1986)

III-V Interfaces: Schottky Barriers vs.
Heterojunctions

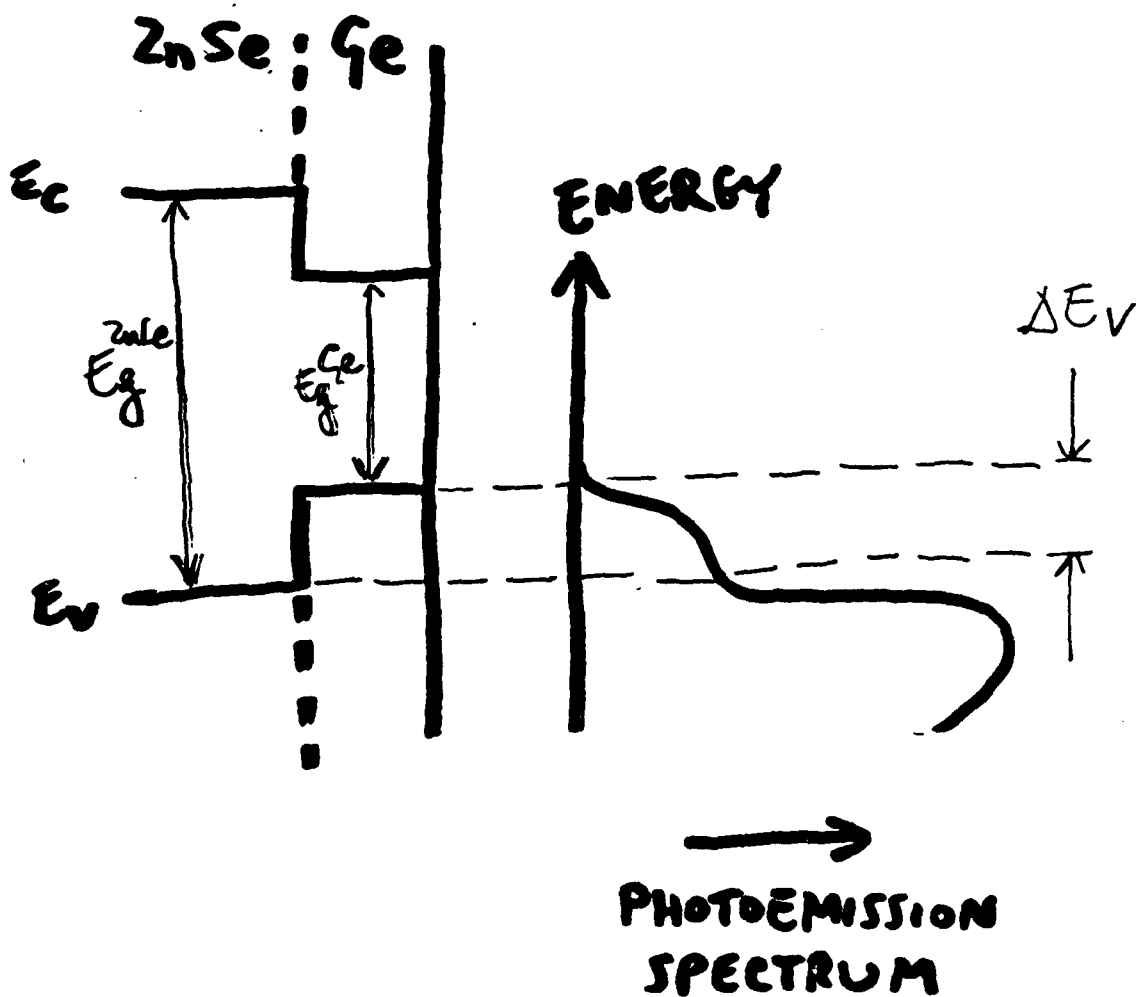
Giorgio Margaritondo

University of Wisconsin

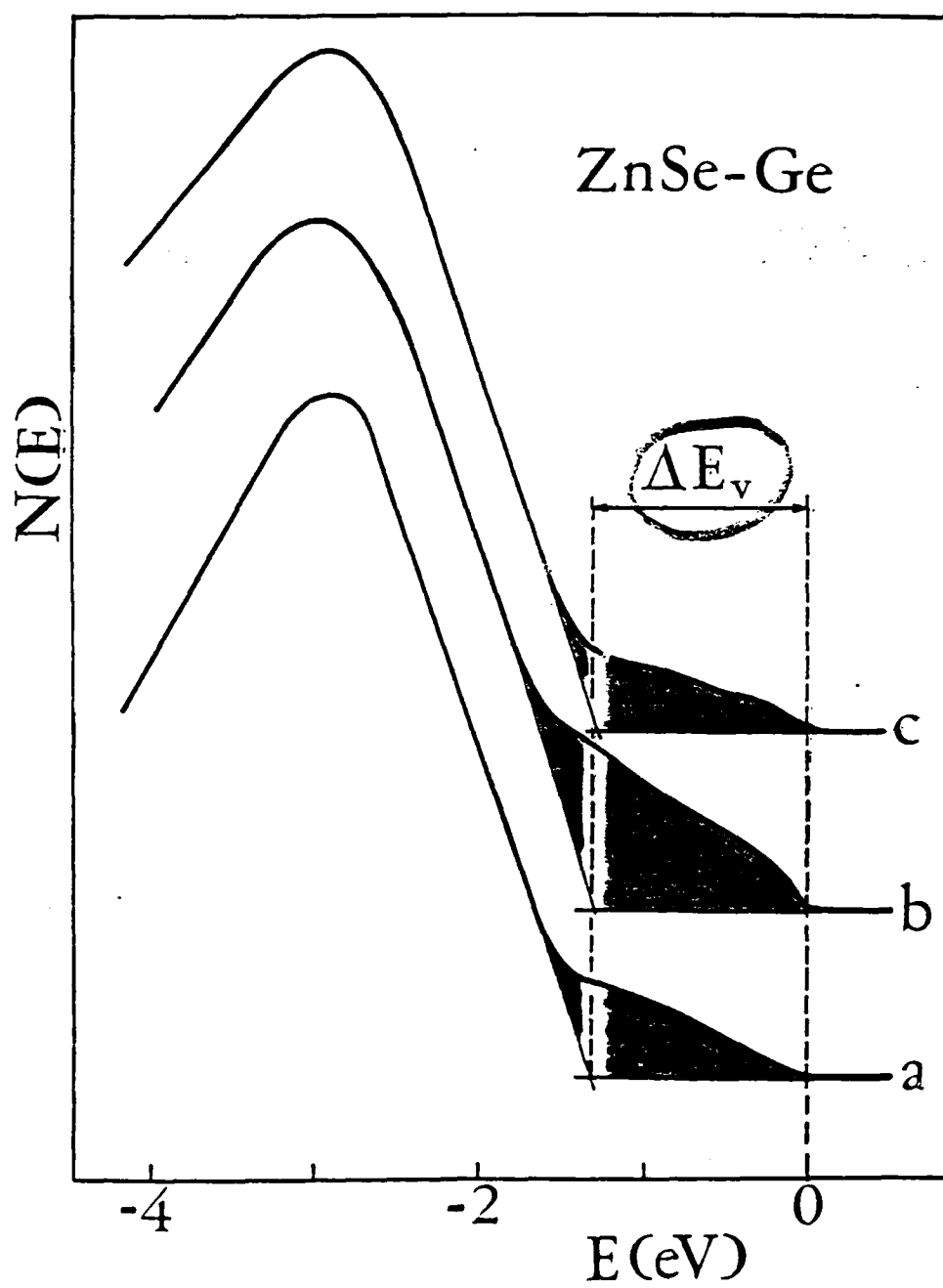
MARGARITON

HETEROJUNCTION BAND LINEUPS
VS.
SCHOTTKY BARRIER HEIGHTS

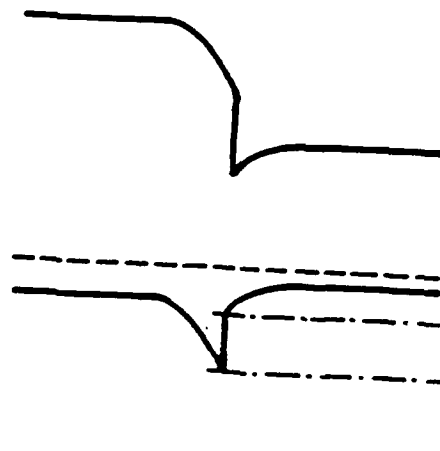
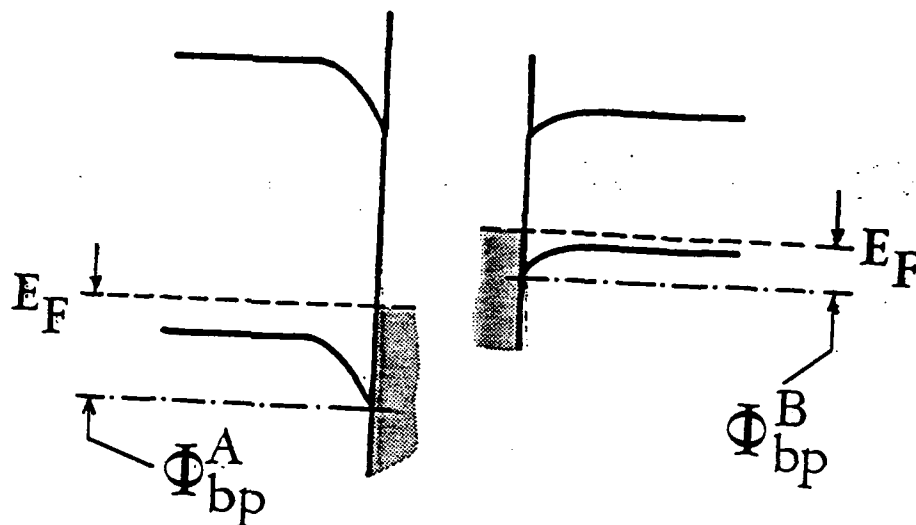
What can we learn from their
correlation?



**PHOTODEMISSION
MEASUREMENTS OF
BAND LINEUPS**



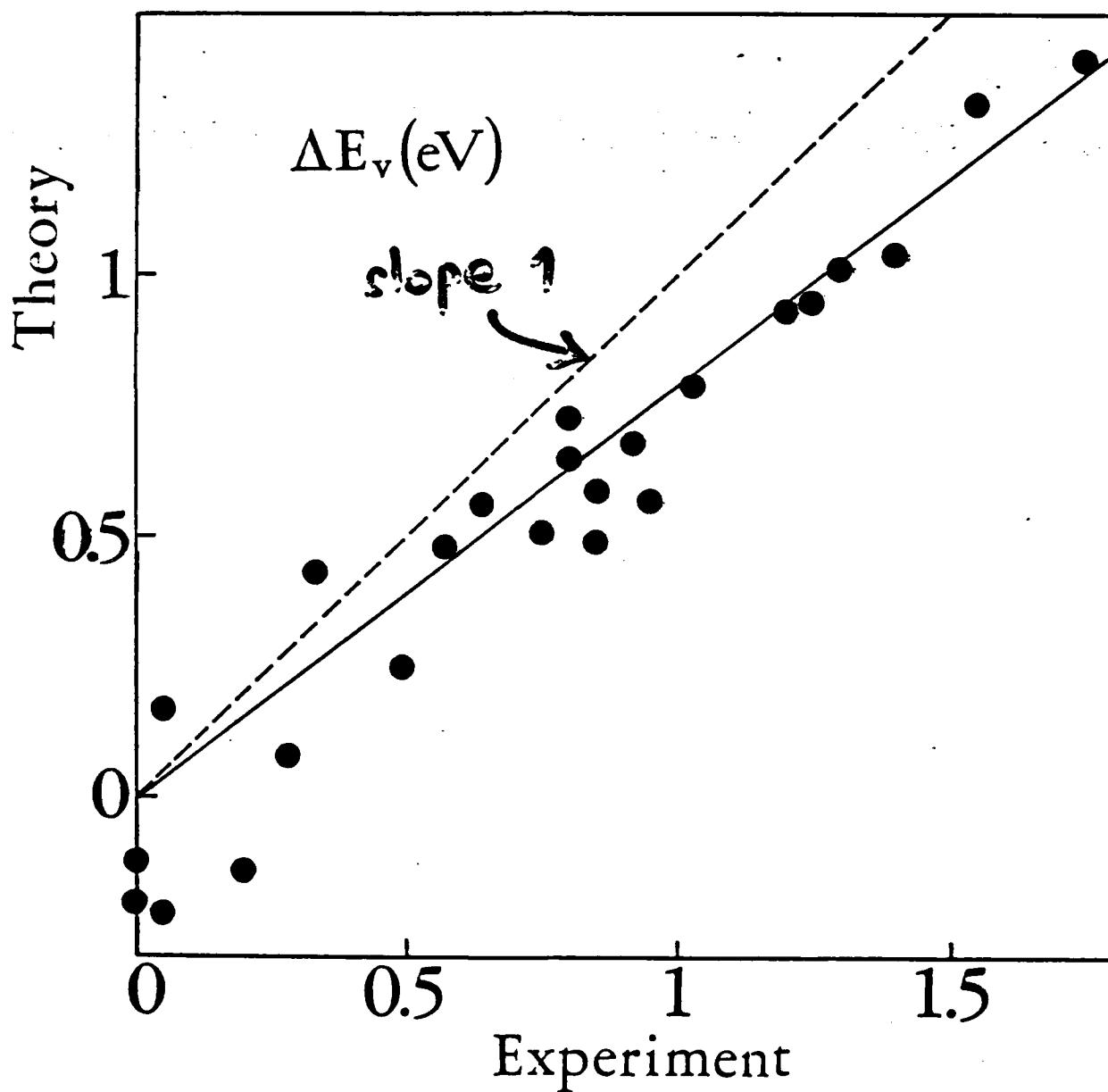
CORRELATION BETWEEN SCHOTTKY BARRIERS AND HETEROJUNCTION BAND DISCONTINUITIES



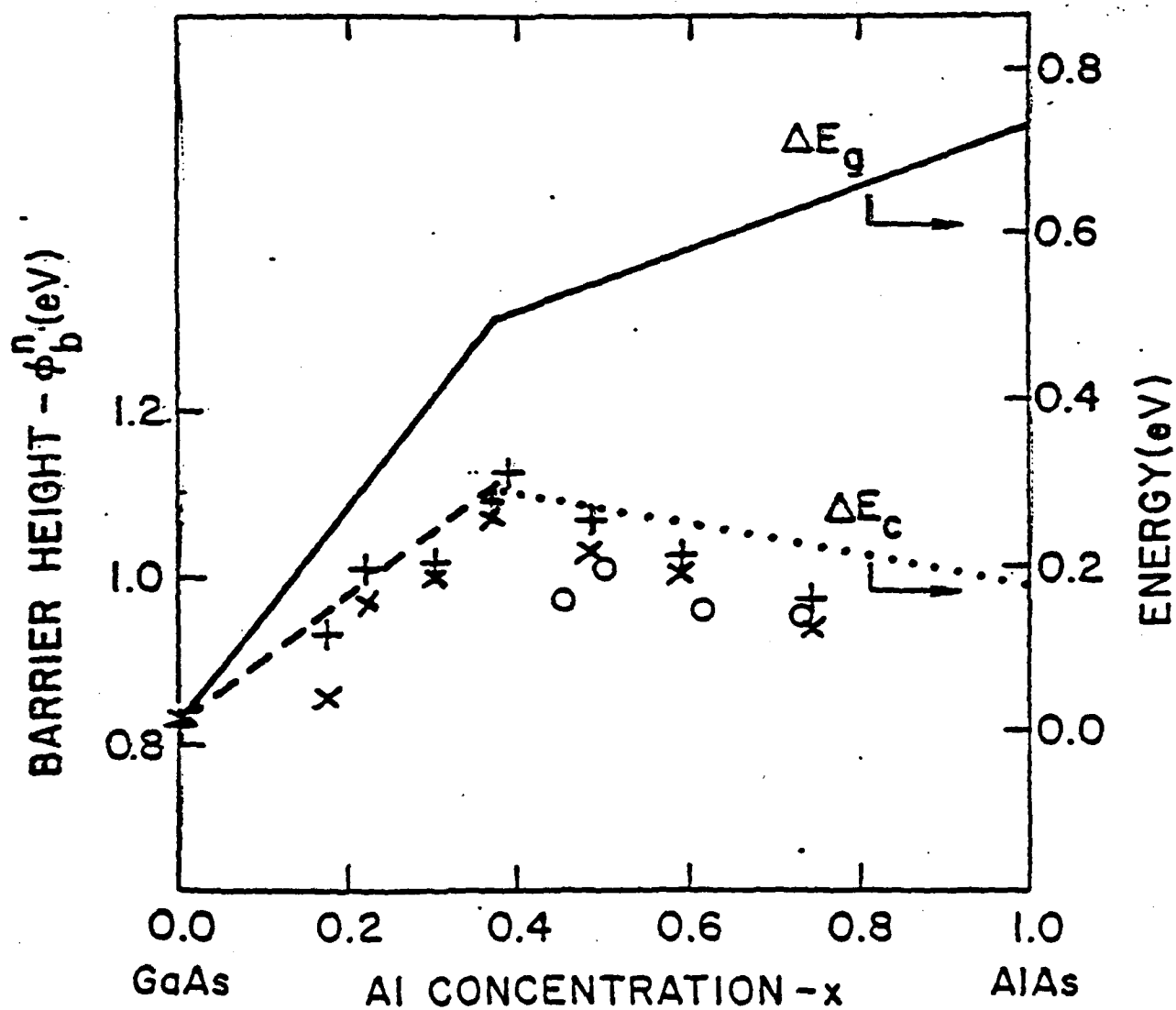
$$\Delta E_v = \Phi_{bp}^A - \Phi_{bp}^B = \Delta \Phi_{bp}$$

(A NAÏVE PICTURE !!!)

* CORRELATION BETWEEN SCHOTTKY BARRIERS & HETEROJUNCTION BAND DISCONTINUITIES



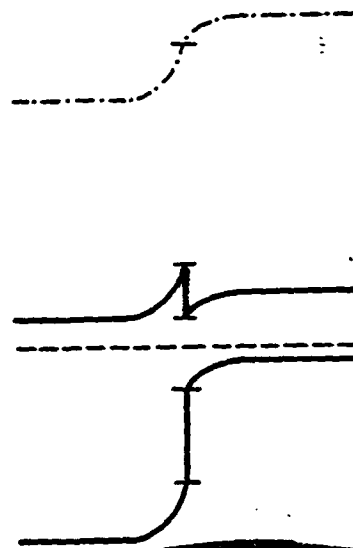
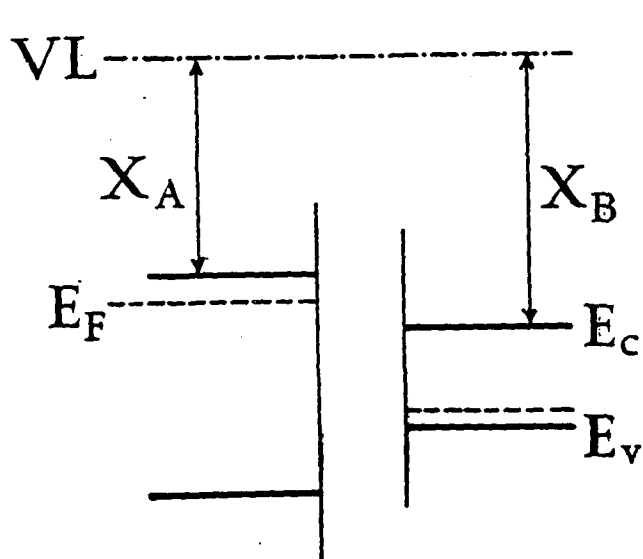
CORRELATION BETWEEN
HETEROJUNCTION BAND LINEUPS
& SCHOTTKY BARRIER HEIGHTS
(EIZENBERG, HEIBLUM, NATHAN & BRESLAU)



THE CORRELATION BETWEEN
SCHOTTKY BARRIER HEIGHTS
AND HETEROJUNCTION BAND
DISCONTINUITIES IS
PREDICTED BY:

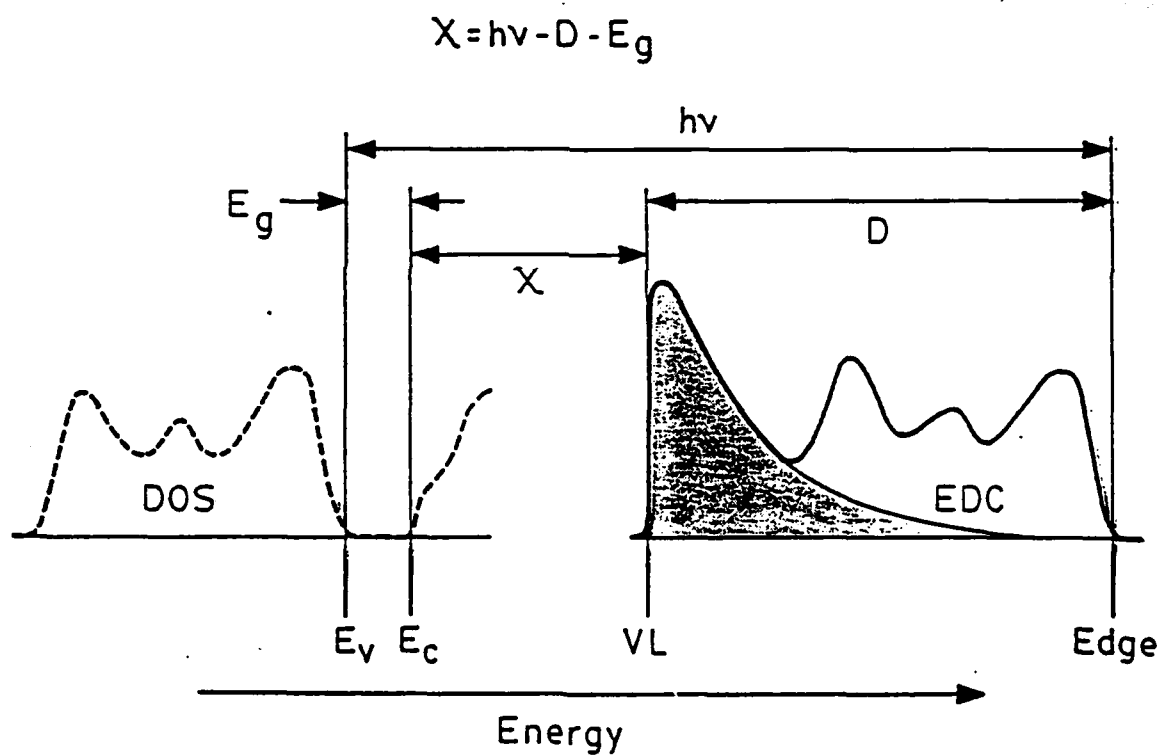
1. Schottky Model for M-S
Interfaces, plus Electron
Affinity Rule for S-S
Interfaces
2. Midgap-Energy (or Charge-
Neutrality-Point) Theory
for both M-S and S-S
Interfaces (Tersoff,
Flores and coworkers)

* ELECTRON AFFINITY RULE



$$\Delta E_C = X_B - X_A$$

* PHOTOEMISSION TEST OF THE ELECTRON AFFINITY RULE



**BREAKDOWN OF THE
ELECTRON AFFINITY
RULE**

The Rule Predicts:

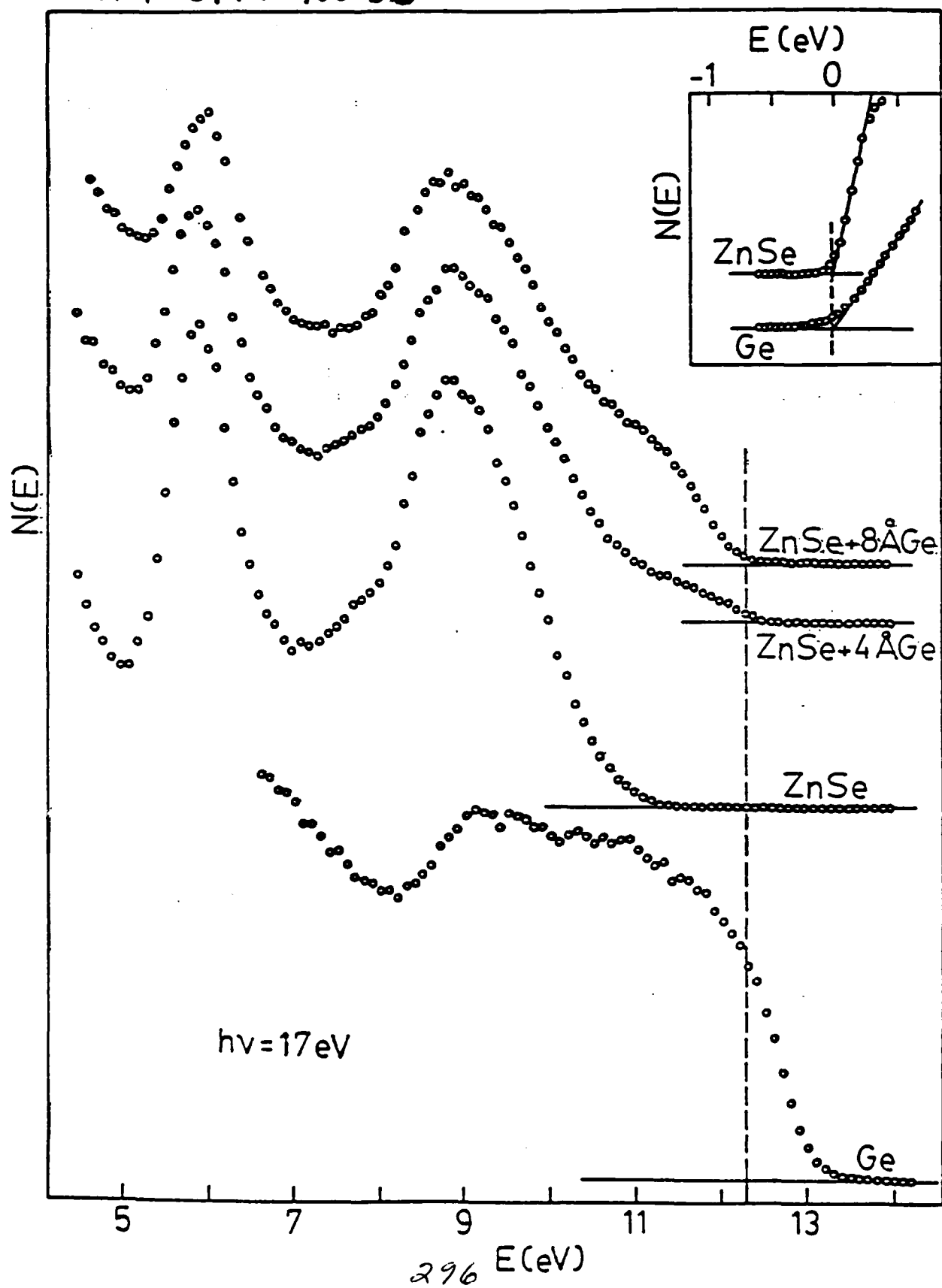
$$\Delta E_v = D_1 - D_2$$

**Experimental Reality
(ZnSe-Ge):**

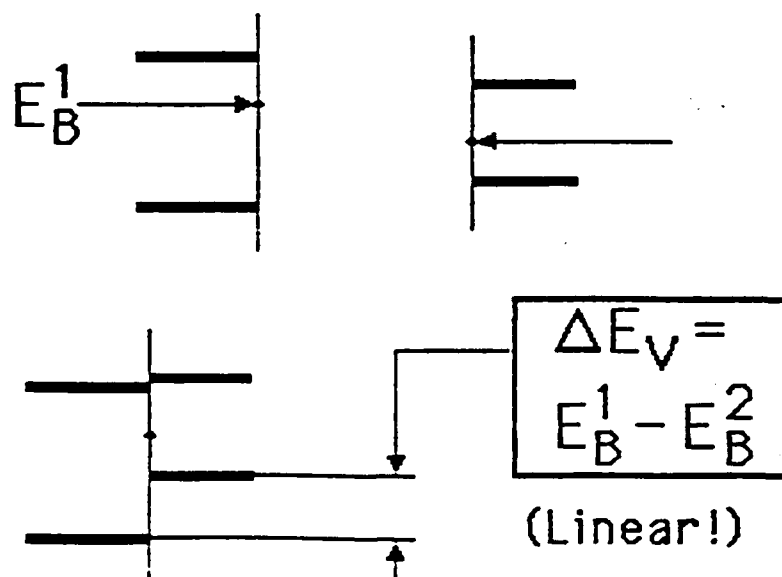
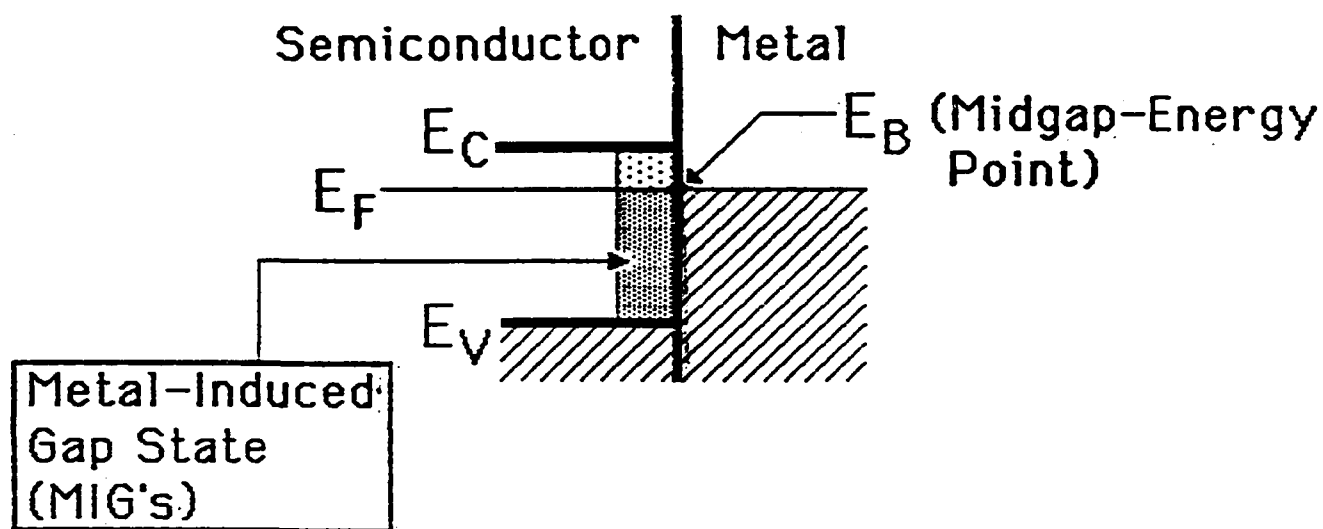
$$D_1 - D_2 = 2.21 \pm 0.46 \text{ eV}$$

$$\Delta E_v = 1.44^{+0.08}_{-0.15} \text{ eV}$$

* STANDARD OF THE ELECTRON AFFINITY RULE



* Midgap-Energy Approach (J. Tersoff)



HIGH-RESOLUTION ELECTRON ENERGY LOSS RESULTS:

Si(111)7x7 - Al

(M. KELLY, G. MARGARITONAS,
J. FRANKEL, G.J. LAPEYRÉ)

→ Si(111)7x7 is metallic; first
Al adatoms make it
non-metallic (GAP WIDENS)

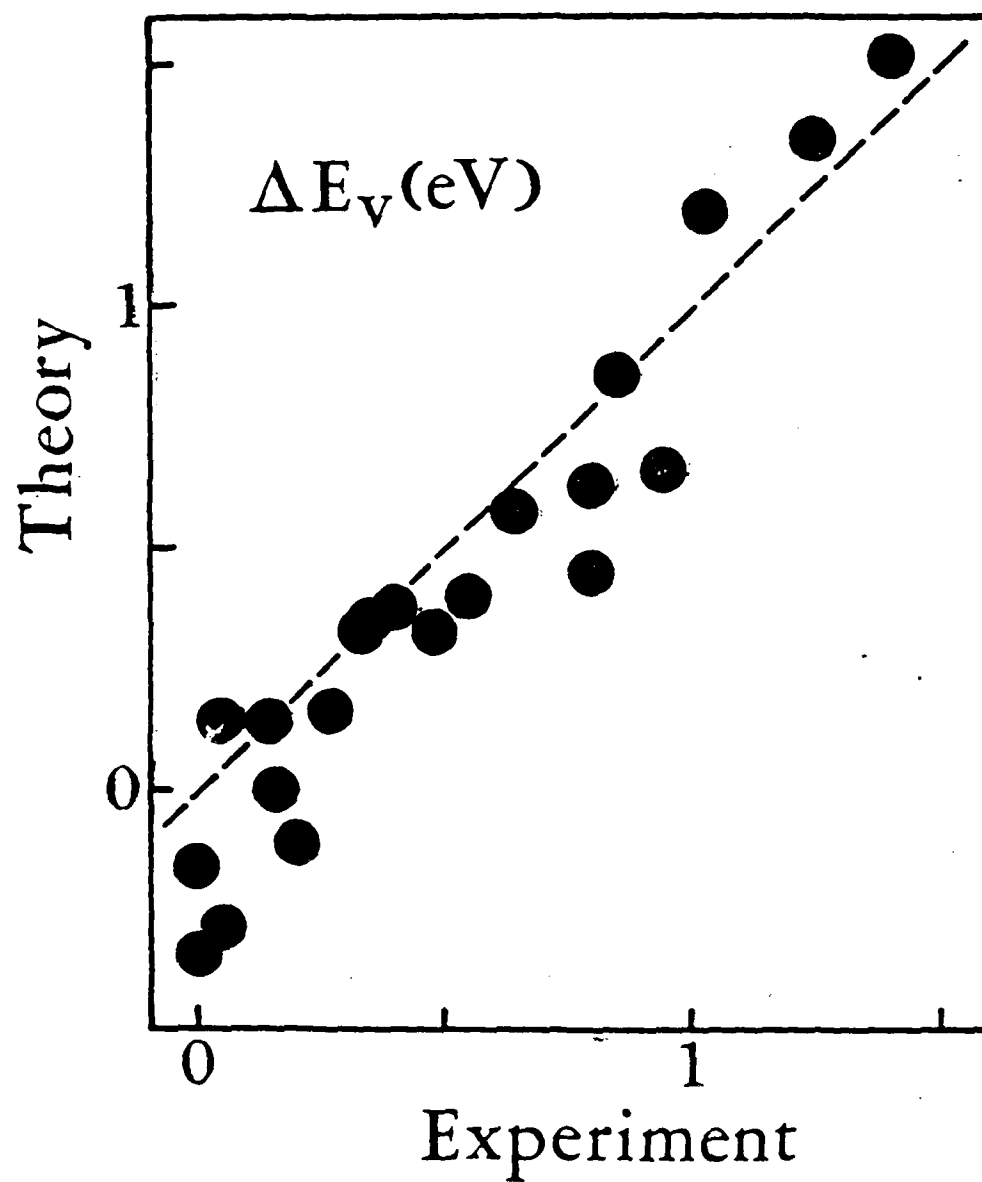
→ At $\approx$ monolayer coverage,
metallic character
reappears

→ At $\approx$ 1.5 monolayer
coverage:

* E_F movement saturates
(Schottky Barrier is
formed)

* Metallic character
is strong

~~X~~ MIDGAP - ENERGY - THEORY VS. EXPERIMENT (ΔE_v)



DEFINITION OF "LINEAR" MODELS:

Band Discontinuity = $T_1 - T_2$

T_i depends on semiconductor i

Examples:

- o ELECTRON AFFINITY RULE
(Anderson, Duke-Mailhiot, Flores et al., etc.)
- o MIDGAP-ENERGY APPROACH
()
- o TIGHT-BINDING
(Harrison)
- o PSEUDOPOTENTIAL
(Frensley-Kroemer)
- o DEEP-IMPURITY APPROACH
(Zunger et al., Langer-Heinrich)

General Optimization: Katnani-Margaritond

ALL THE GENERAL-PURPOSE HETEROJUNCTION DISCONTINUITY MODELS ARE

LINEAR MODELS:

$$\Delta E_v^{1,2} = T_1 - T_2$$

(WHERE THE TERMS T_1 , T_2 ARE DETERMINED BY THE TWO COMPONENTS OF THE HETEROJUNCTION)

(EXAMPLES: HARRISON, FRENSLEY-KROEMER, TERSOFF, ANDERSON ETC.)

CONSEQUENCES OF THE LINEARITY THAT CAN BE TESTED WITH OUR DATA BASE:

1. TRANSITIVITY: $\Delta E_v^{1,2} + \Delta E_v^{2,3} + \Delta E_v^{3,1} =$
2. THE DISCONTINUITIES ARE INDEPENDENT OF THE MICROSCOPIC INTERFACE PROPERTIES

GENERAL RESULT OF TESTS:

ALL LINEAR MODELS HAVE AN UNDERLYING ACCURACY LIMIT. THEIR AVERAGE ACCURACY IN PREDICTING THE BAND DISCONTINUITIES CANNOT EXCEED 0.15 eV.

AD-A183 158

A WORKSHOP ON 3-5 SEMICONDUCTOR: METAL INTERFACIAL
CHEMISTRY AND ITS EFFECTS (U) STANFORD UNIV CA
W E SPICER ET AL. 05 NOV 86 N00014-87-G-0038

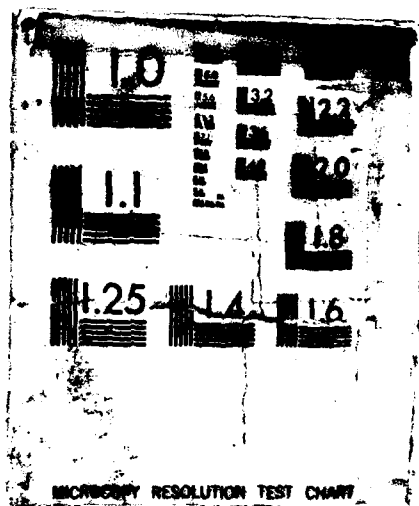
4/7

UNCLASSIFIED

F/G 20/12

NL

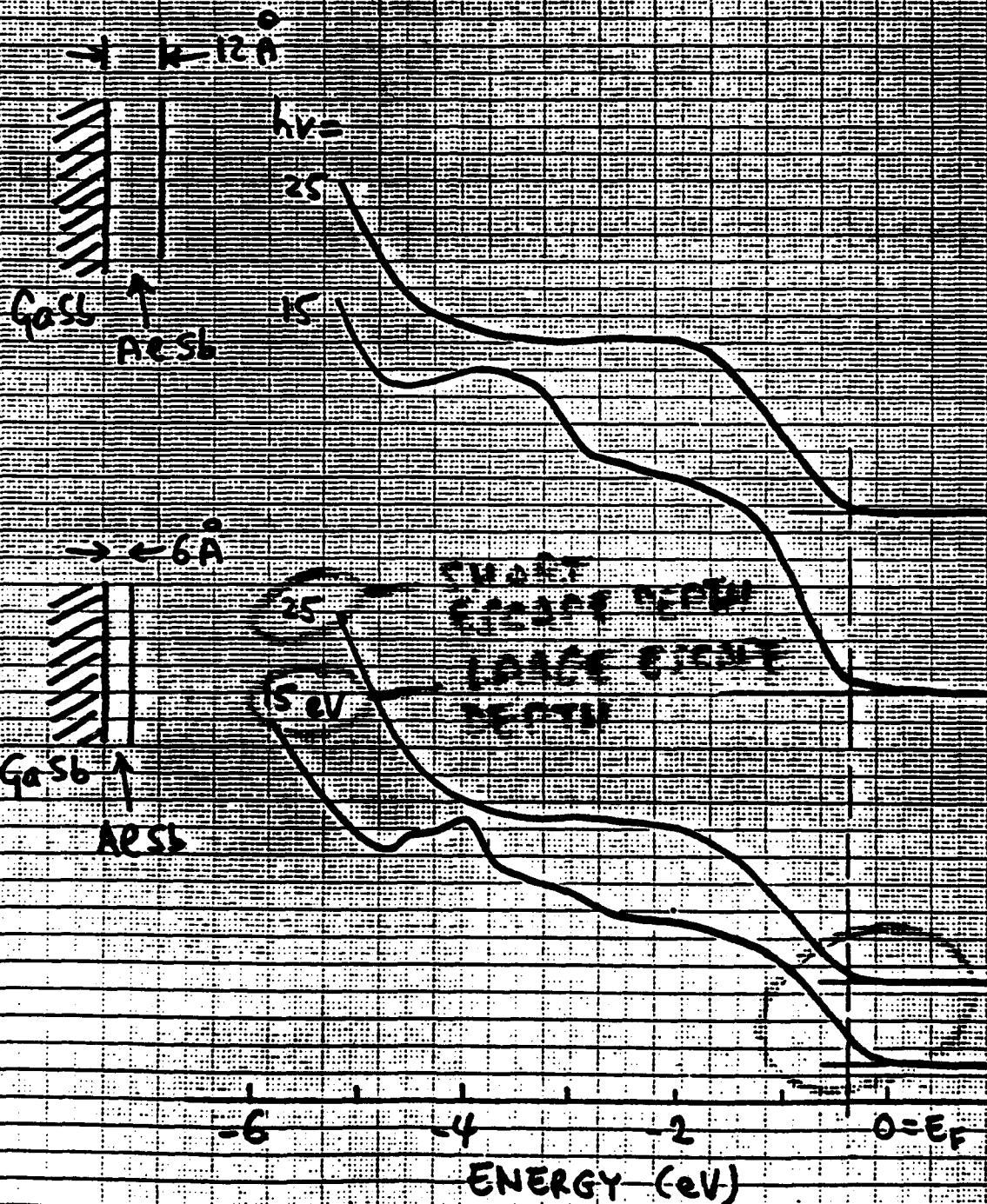




(INTERFACES -
PHOTODEMISSION

G. GUALTIERI, G. P. SCHWARTZ,
R. G. NUZZO, W. A. SUNDER

D. NILES, BARRY LAI, G. WEUS,
J. MCKINLEY, F. GERHARD,
G. HARRINGTON]



*** LOCAL FACTORS WHICH CAN**
POTENTIALLY INFLUENCE THE
HETEROJUNCTION BAND LINEUP:

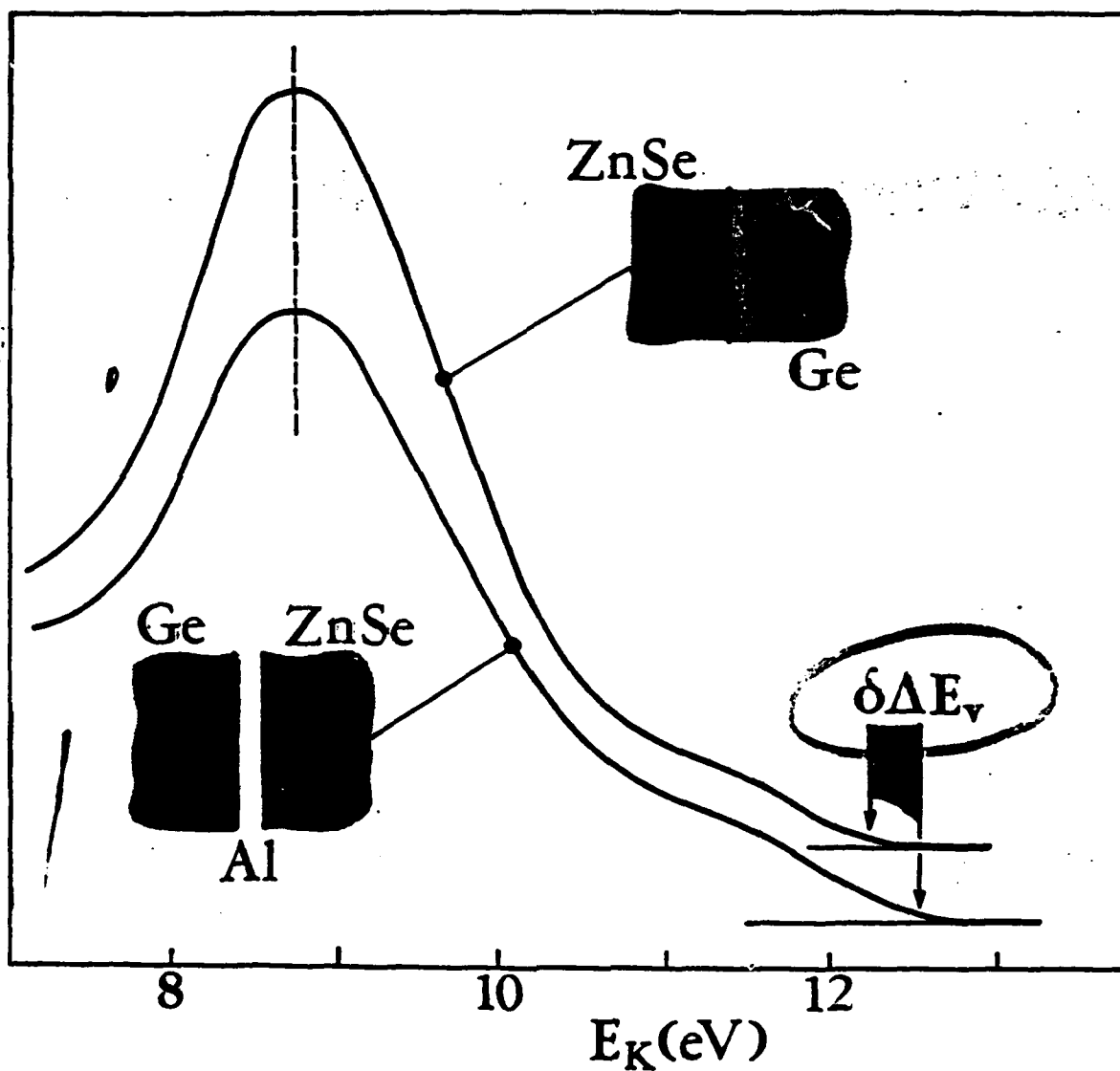
- * 1. Substrate Orientation**
- * 2. Local Morphology**
- * 3. Microdiffusion**
- * 4. Interface Bonds**
- * 5. Interface Defects**
- ... etc.**

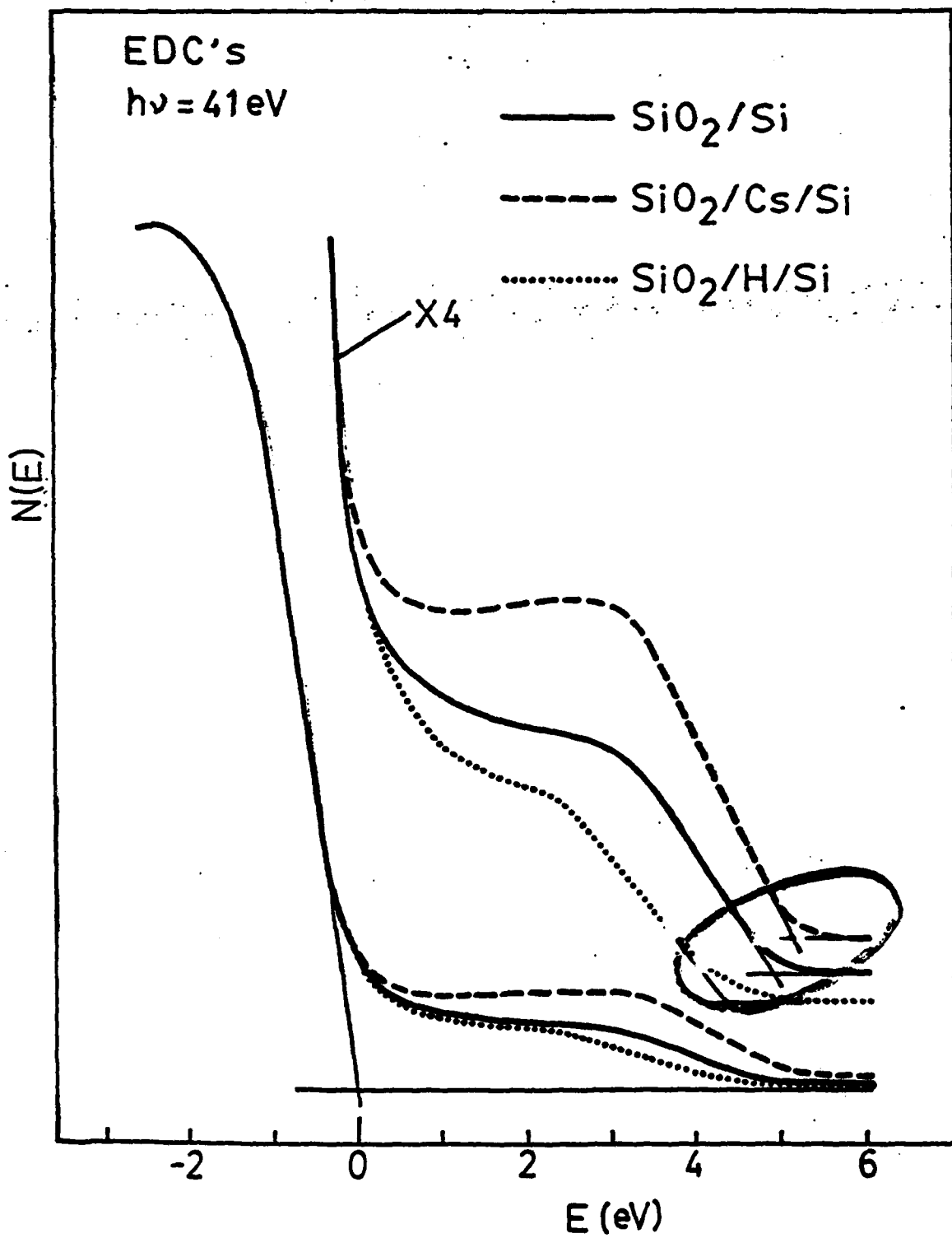
● **CAN WE CONTROL THE
HETEROJUNCTION BAND
LINEUP?**

YES -- BY USING:

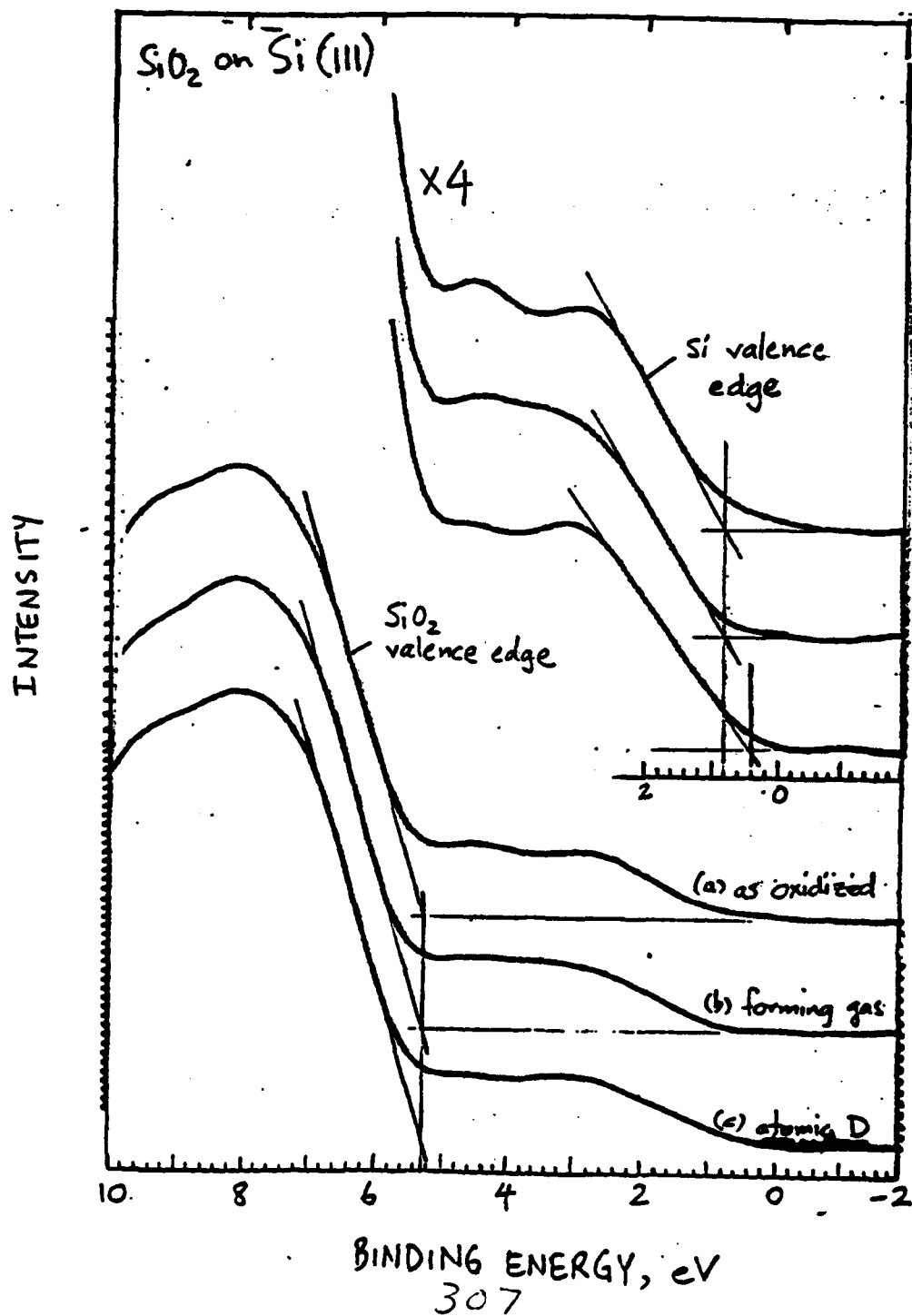
- **1. ULTRATHIN INTRALAYERS**
(Perfetti et al.,
Margaritondo et al.,
Grunthaner et al.)
- **2. DOPING PROFILES**
(Capasso et al.)

ON





[GRUNTHANER, P. & F.J.,
et al.]



A theoretical calculation for a ZnSe-Ge(110) heterojunction with an ultrathin intralayer

by

J.C. Durán*, A. Muñoz and F. Flores

Departamento de Física del Estado Sólido

Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain.

Abstract

We present a consistent tight-binding calculation of the ZnSe-Ge(110) heterojunction with an Al-monolayer between the two semiconductors. Our results are in reasonable agreement with the experimental evidence found by Niles et al, showing that an ideal interface is an adequate model to explain the interface behaviour. The shift in the valence band offset due to the Al-intralayer is interpreted as a shift in the difference between the charge neutrality levels of both semiconductors, induced by the deposited intralayer.

PACS numbers: 73.40.-c , 73.40.-Lq , 73.40.-Vz .

A comparison between conventional and in-situ
UHV processing for Co/GaAs structures

C.J.Palmstrøm, E.W. Chase,

**Bell Communications Research
Serin Physics Lab
Rutgers University
Box 849
Piscataway
N.J. 08854**

J.P. Harbison, C.C. Chang, A.S. Kaplan, D.-M. Hwang,

**Bell Communications Research
Navesink Research and Engineering Center
Box 7020
331 Newman Springs Rd.
Red Bank
N.J. 07701**

A.Yu, G.J. Galvin and J.W. Mayer

**Materials Science and Engineering
Bard Hall
Cornell University
Ithaca
N.Y. 14850**

K.-N. Tu and J. Cuomo

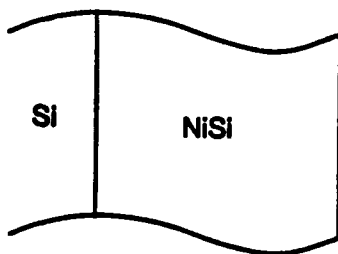
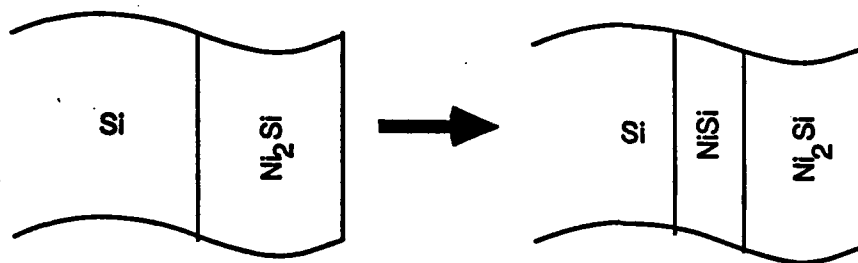
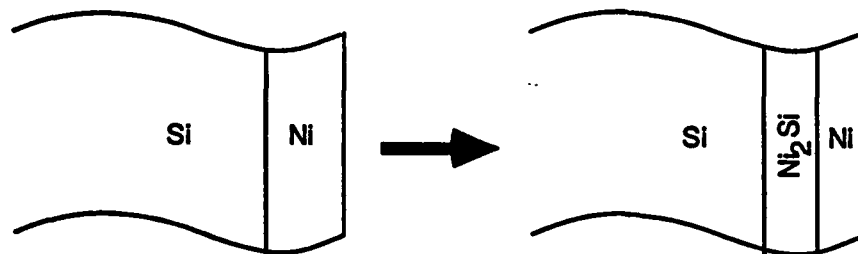
IBM YORKTOWN

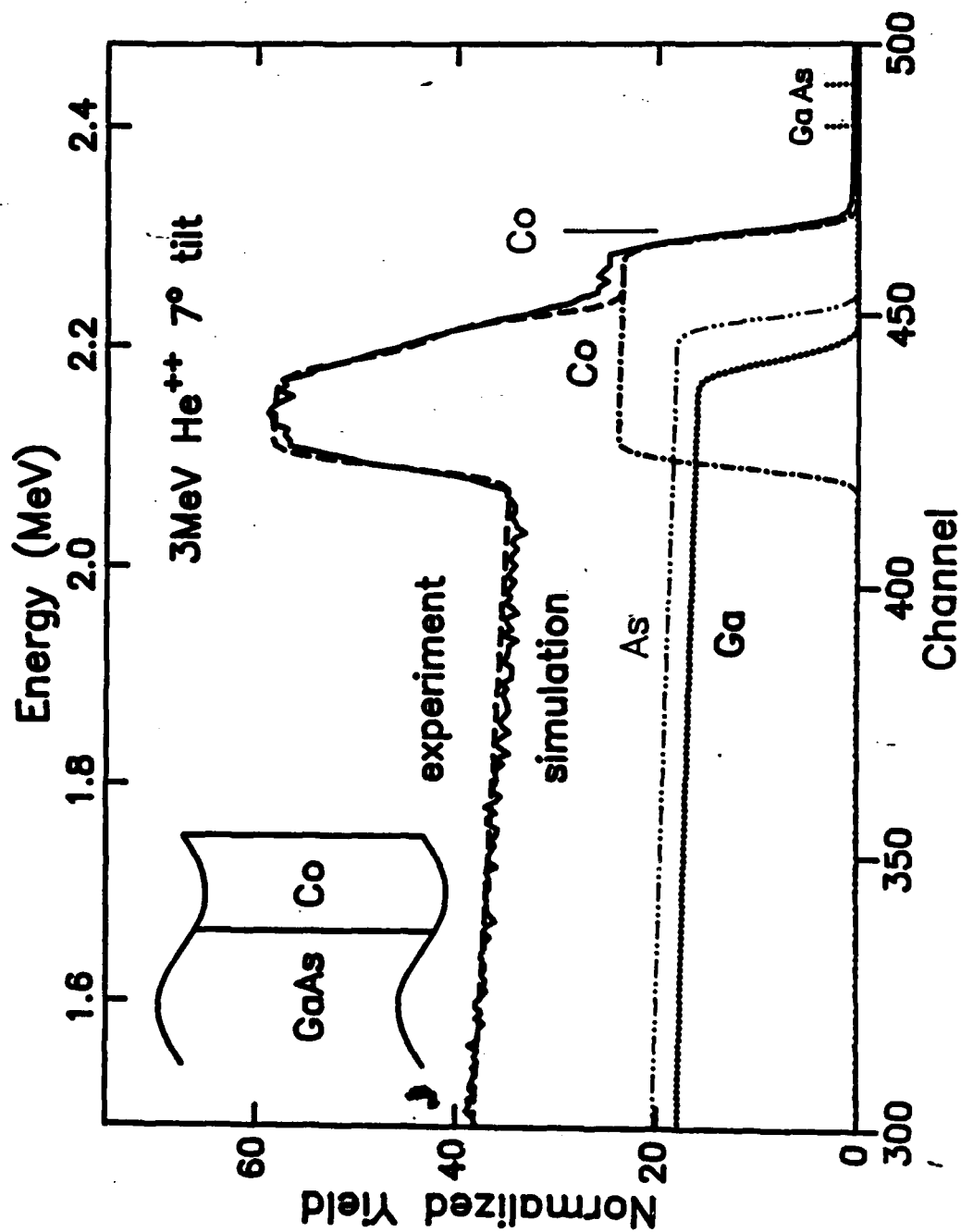
} Thick samples

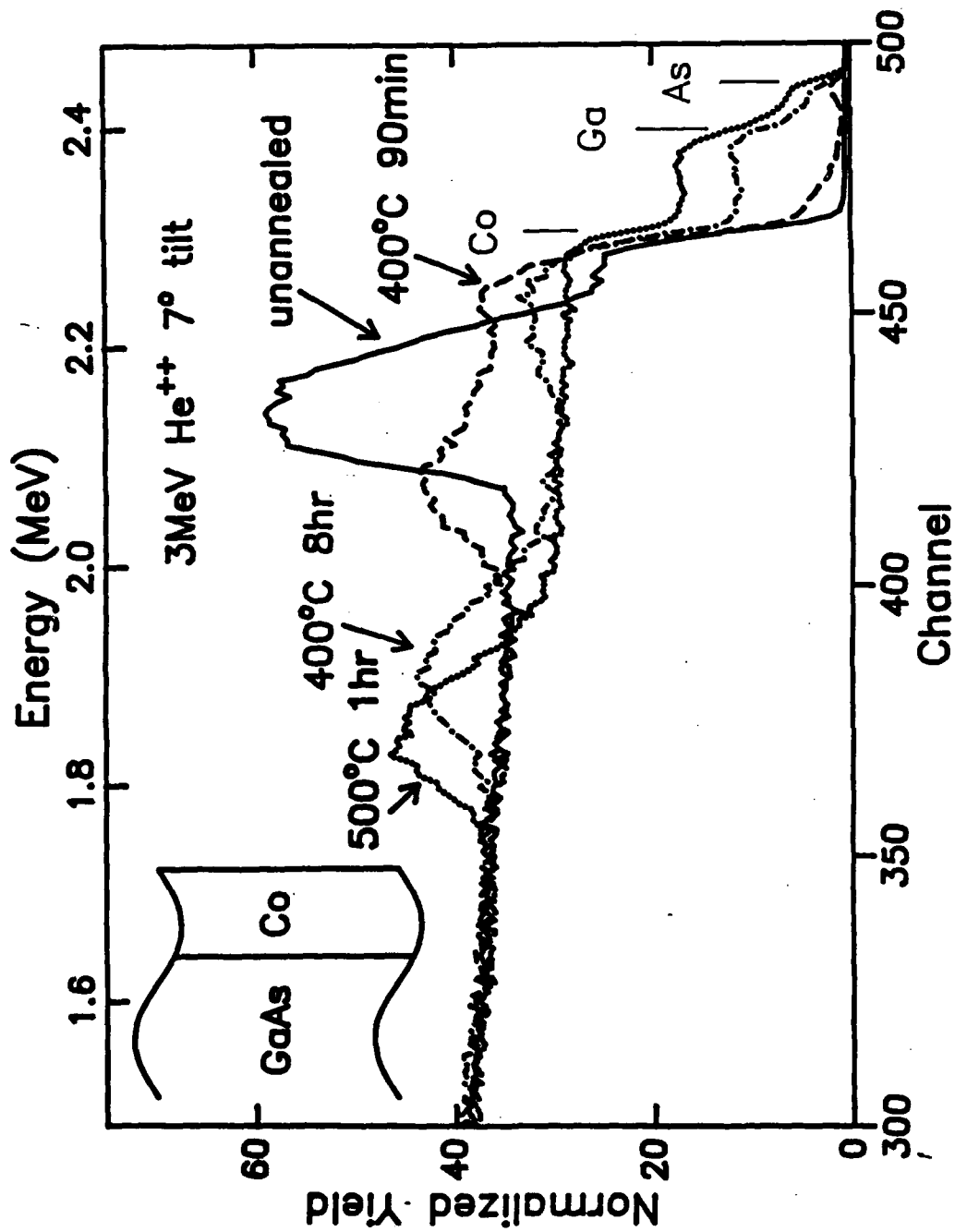
L. Doolittle & M. Thompson
Cornell.

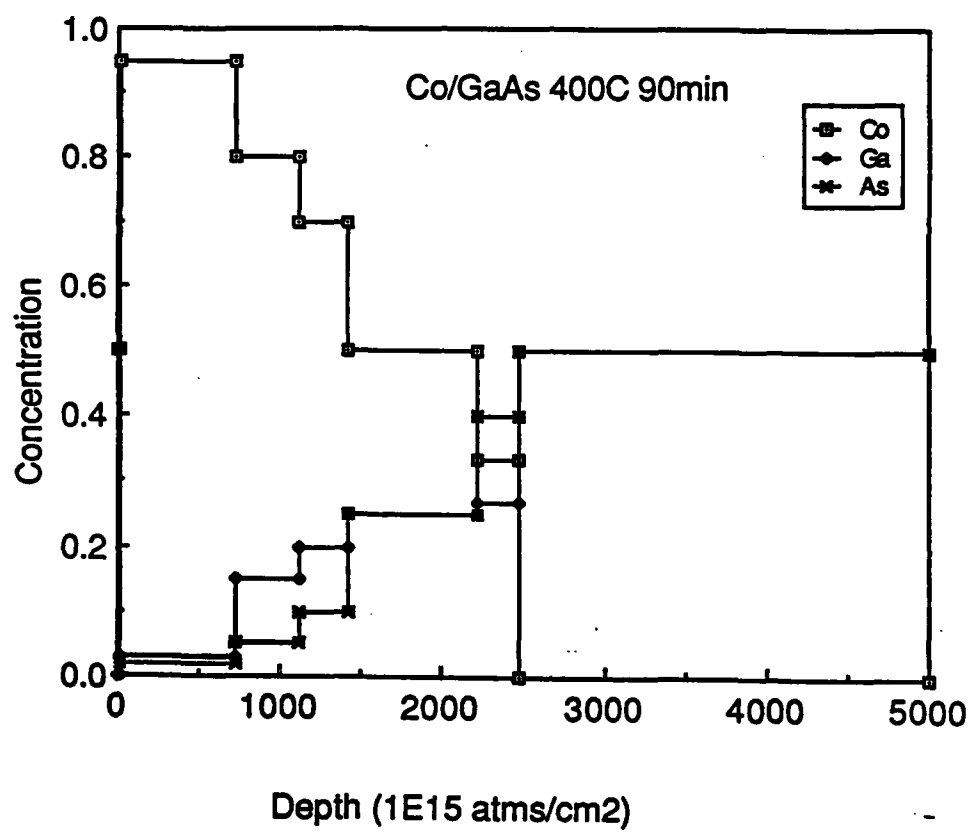
'RUMP' RBS
analysis program

Metal/Si reactions

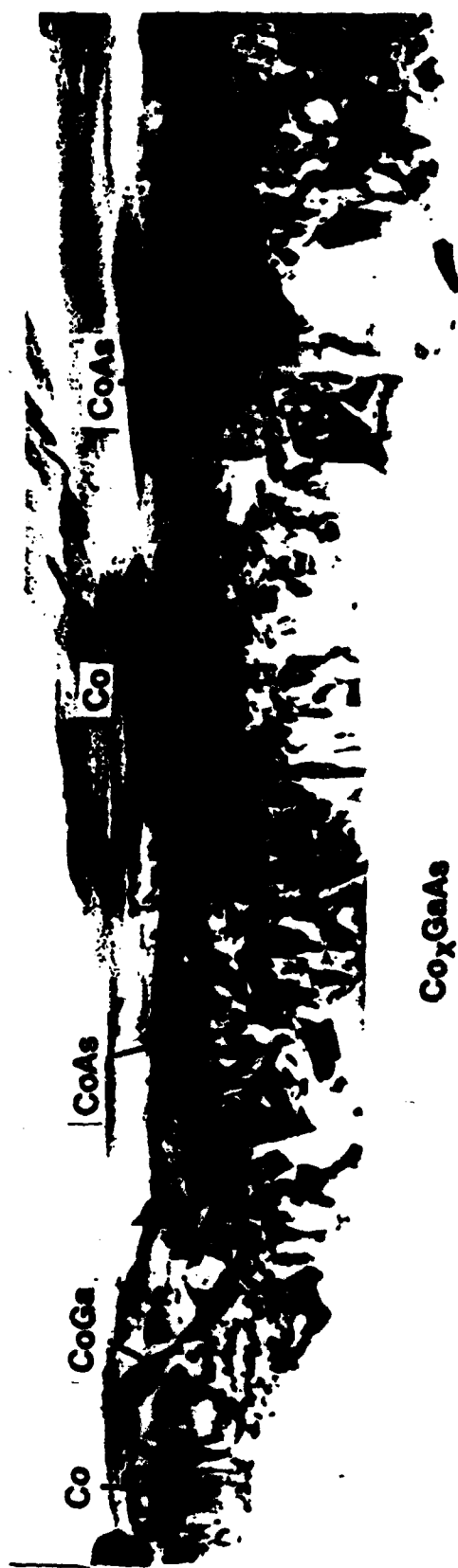








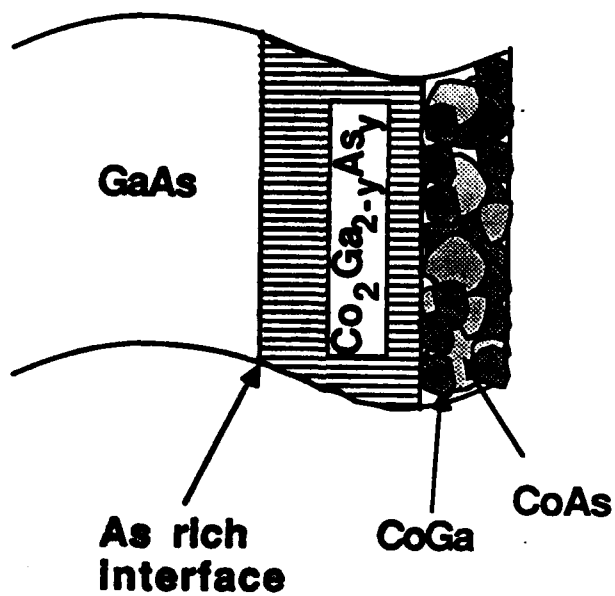
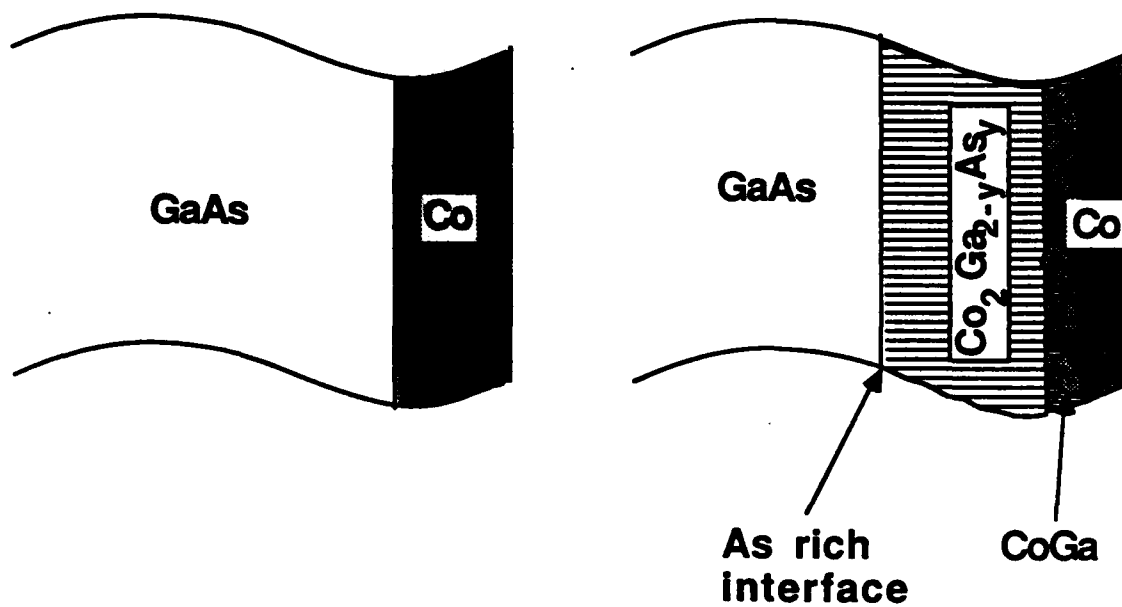




Co_xGaAs

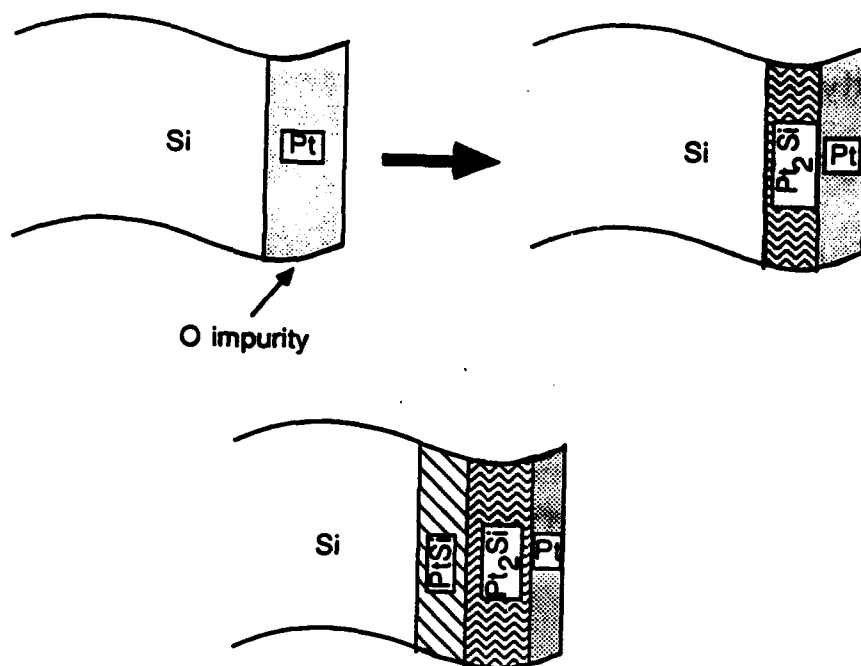
100nm

317

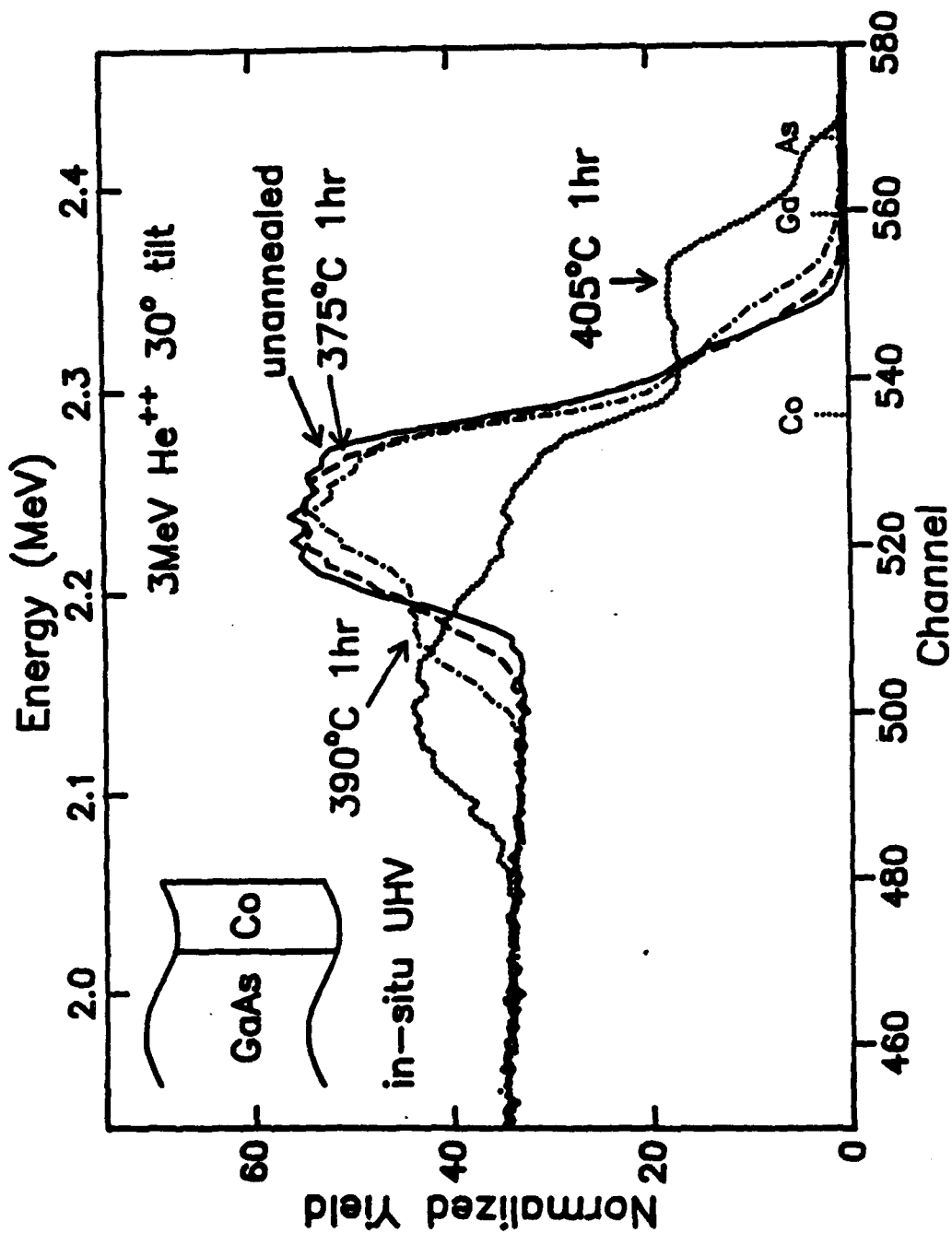


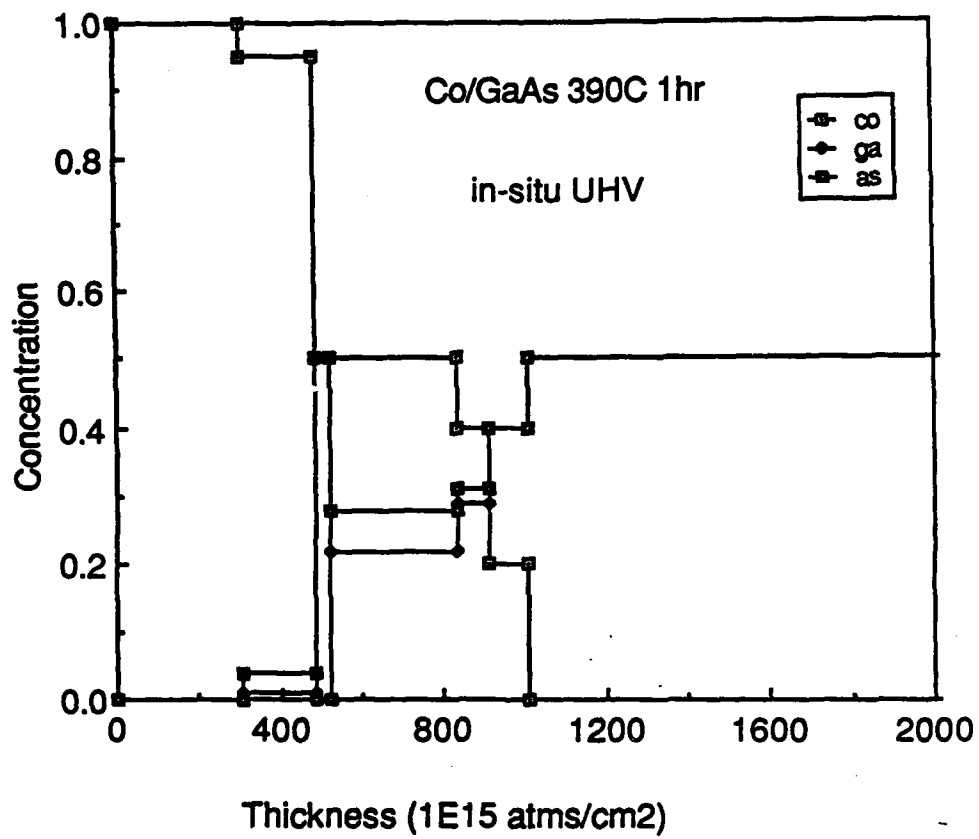
Why are there two distinct regions

- 1) Impurity effect**
- 2) Competing reactions**
 - a) Ternary phase formation ($\text{Co}_x\text{Ga}_{2-y}\text{As}_y$)**
 - b) Ternary phase decomposition (Metastable)**
 - c) Binary phase formation ($\text{CoGa} + \text{CoAs}$)**
 - d) Evaporation of arsenic**

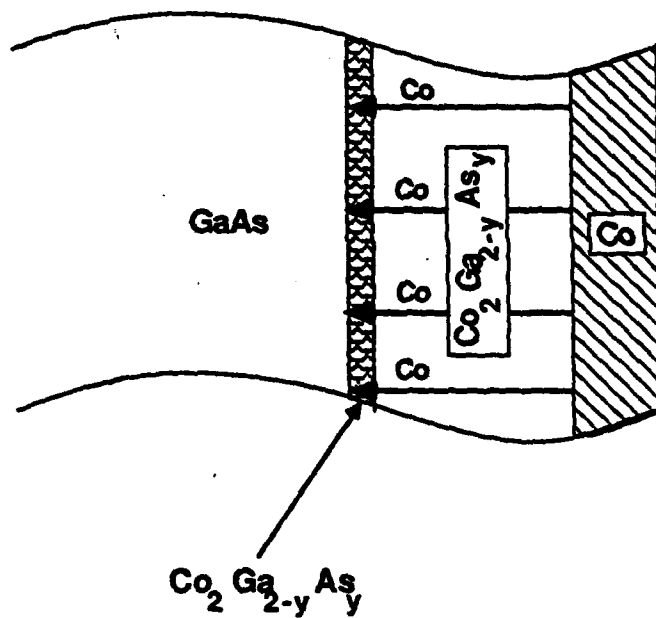


C.A. Crider et. al. JAP (1981)

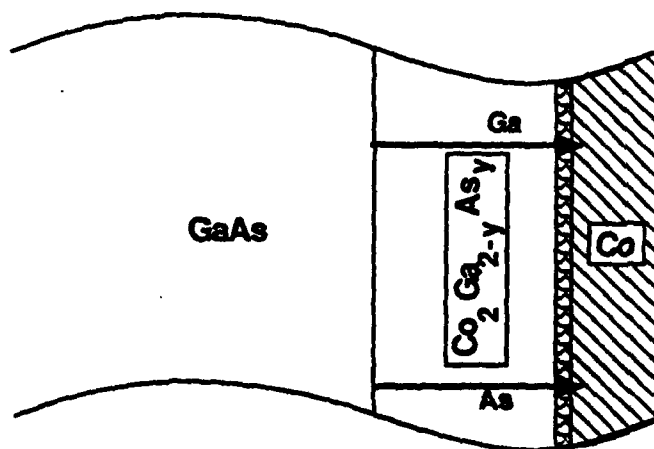


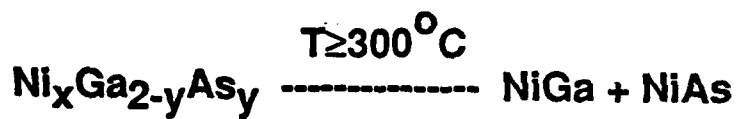
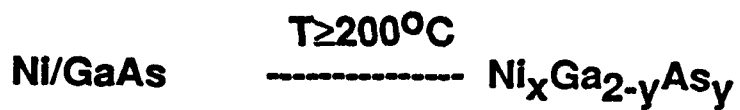


Co dominant diffusing species



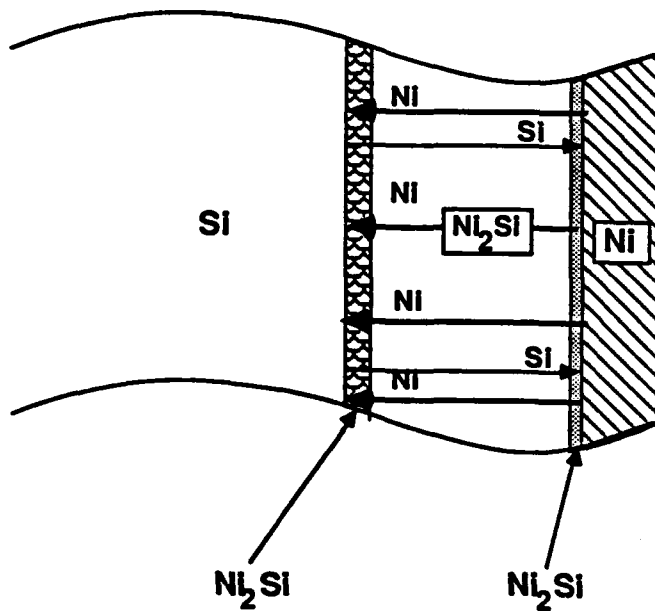
Ga and As dominant diffusing species

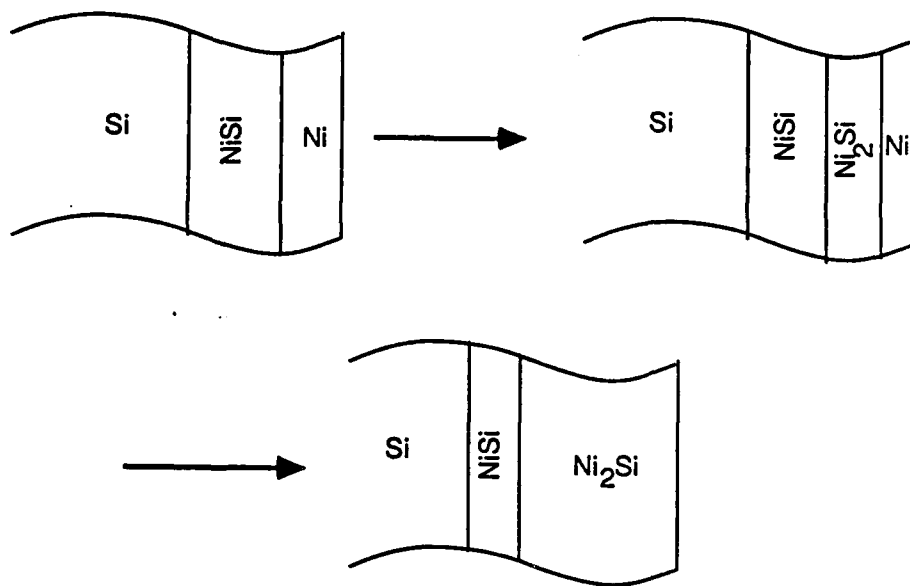


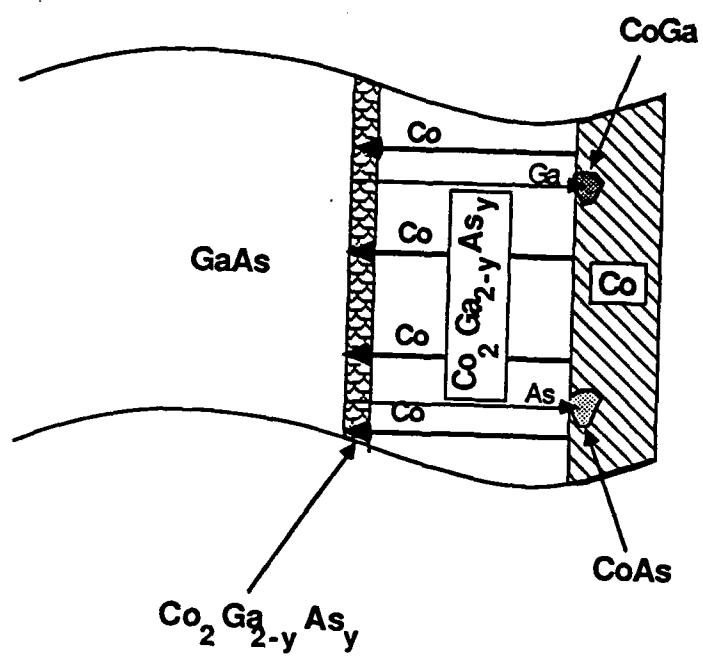


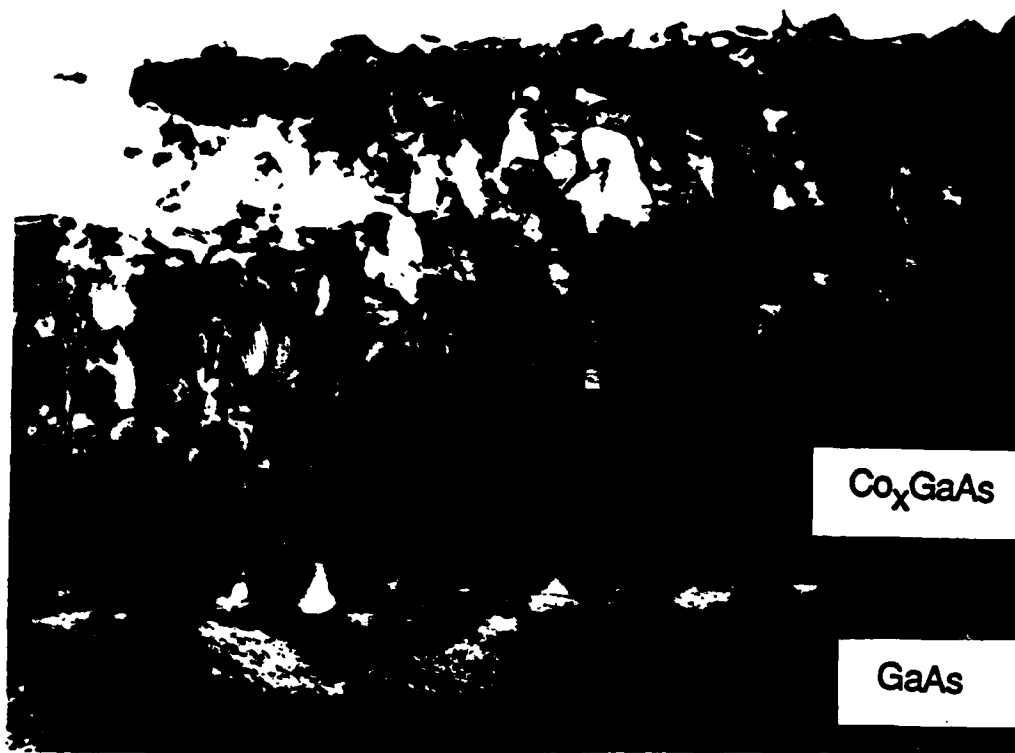
$$y \approx 1$$

Lahav et al (1984, 85, 86)
 Chen et al (1985)
 T. Sands (1986)





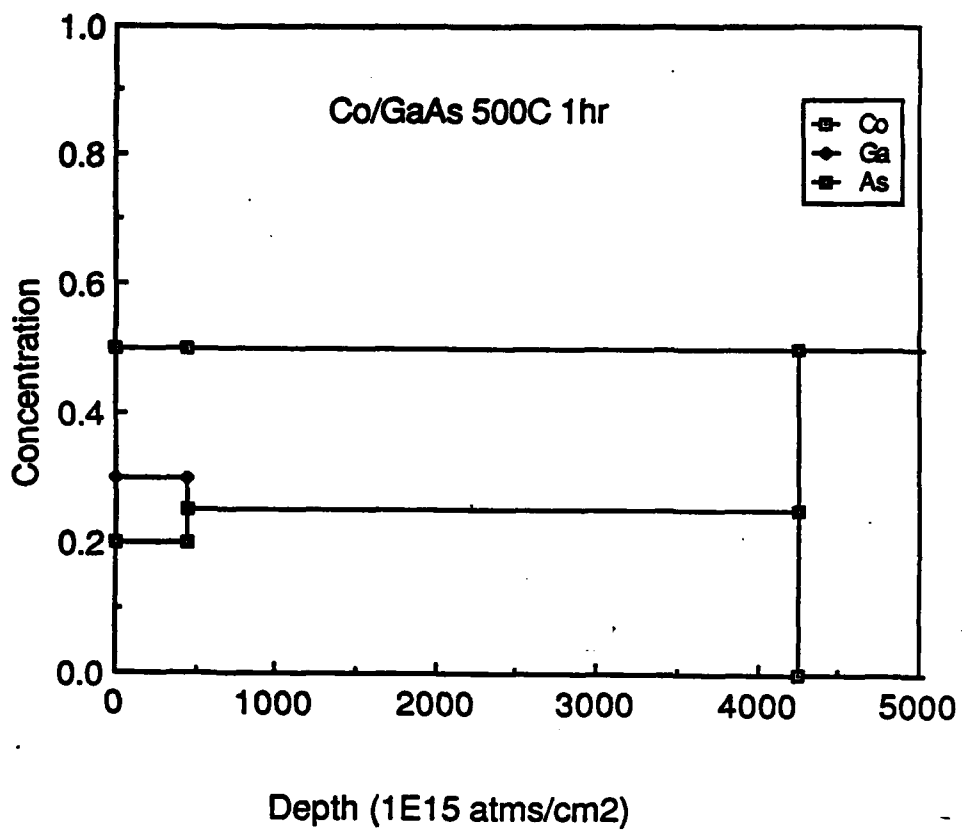




100nm

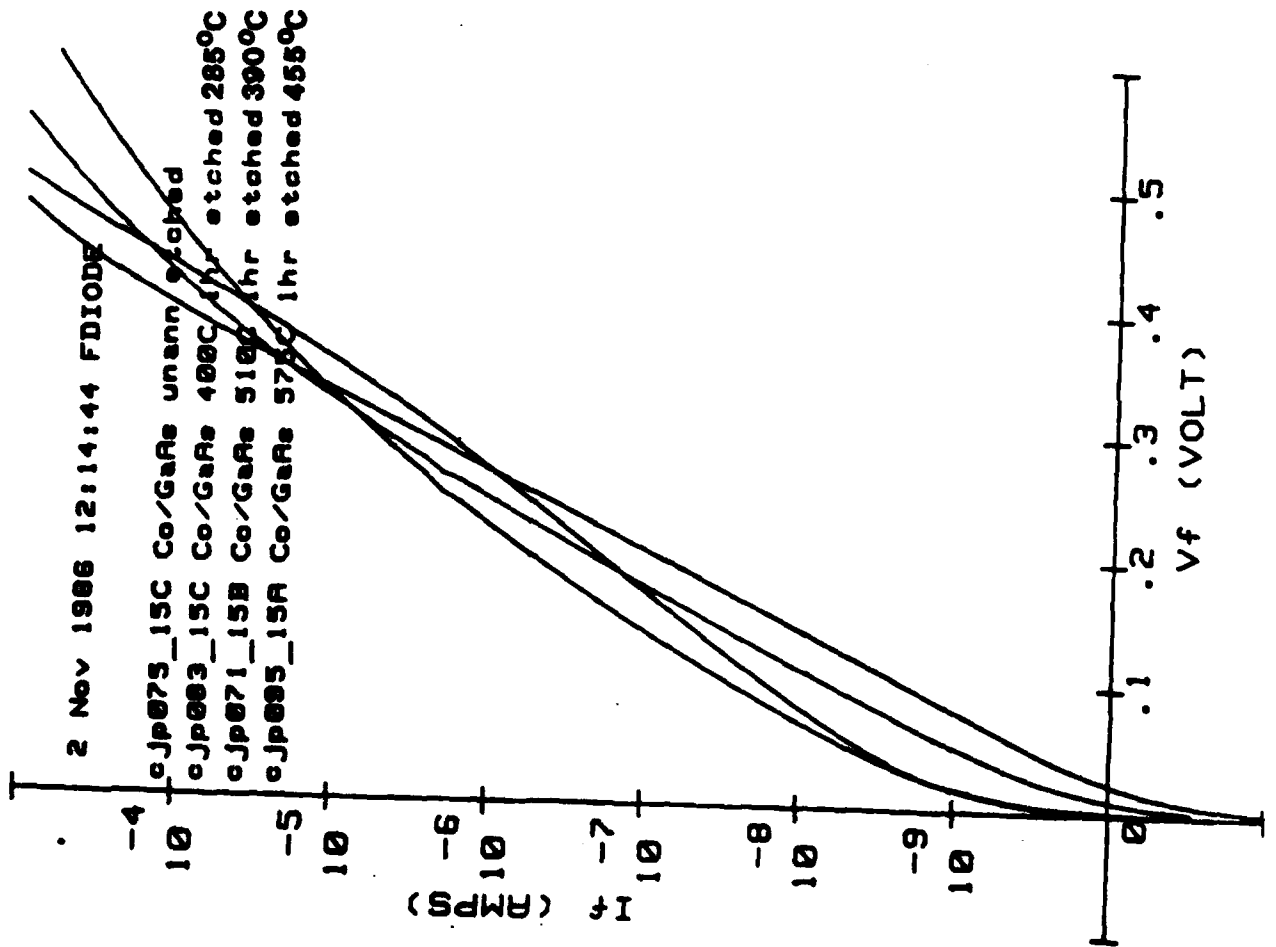


329





331



$\phi_{bn} \sim 0.79\text{eV}$ $n \sim 1.04$

332

Electrical study of Schottky diodes formed on clean cleaved III-V surfaces:

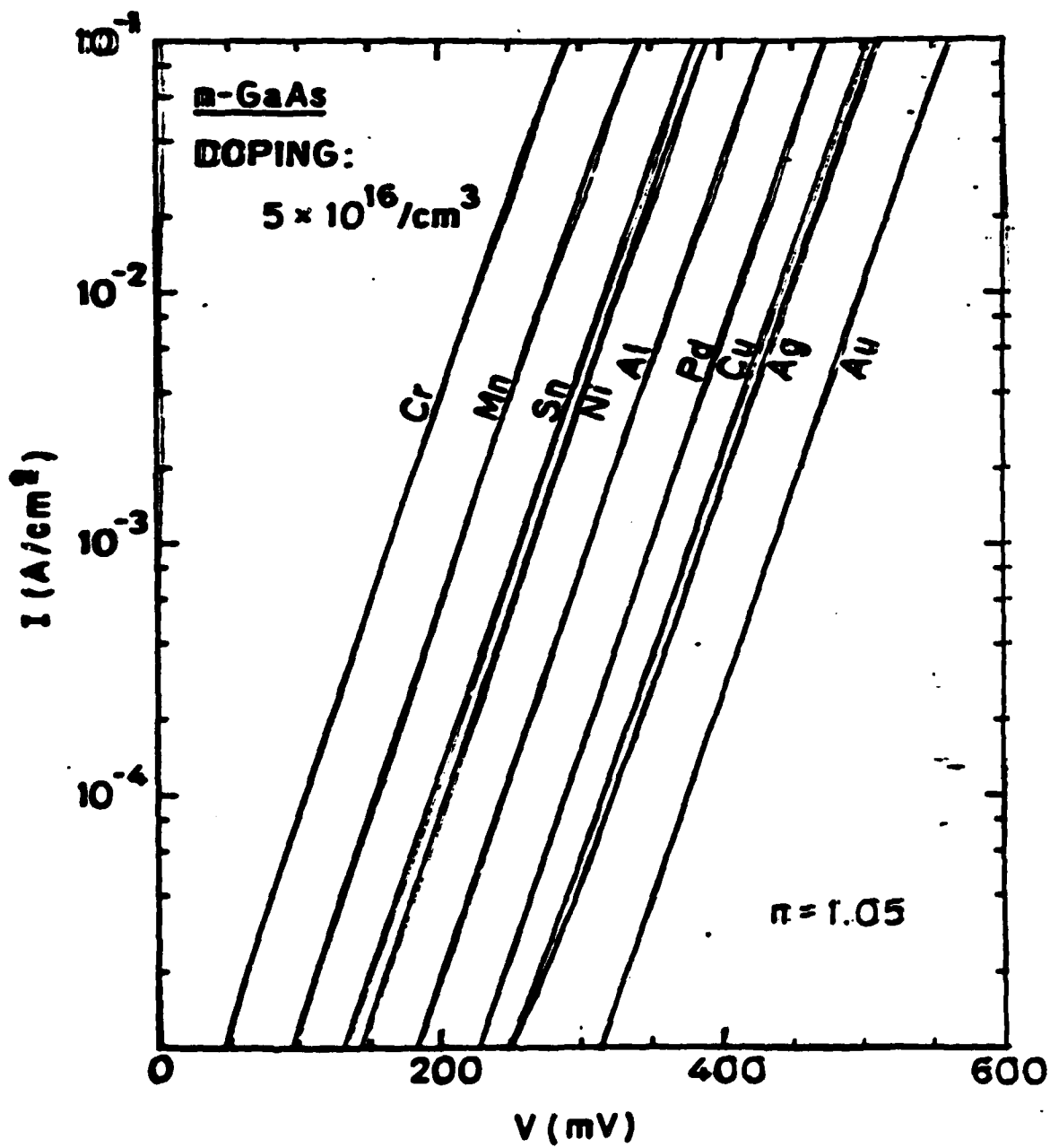
Implications to Theoretical Models

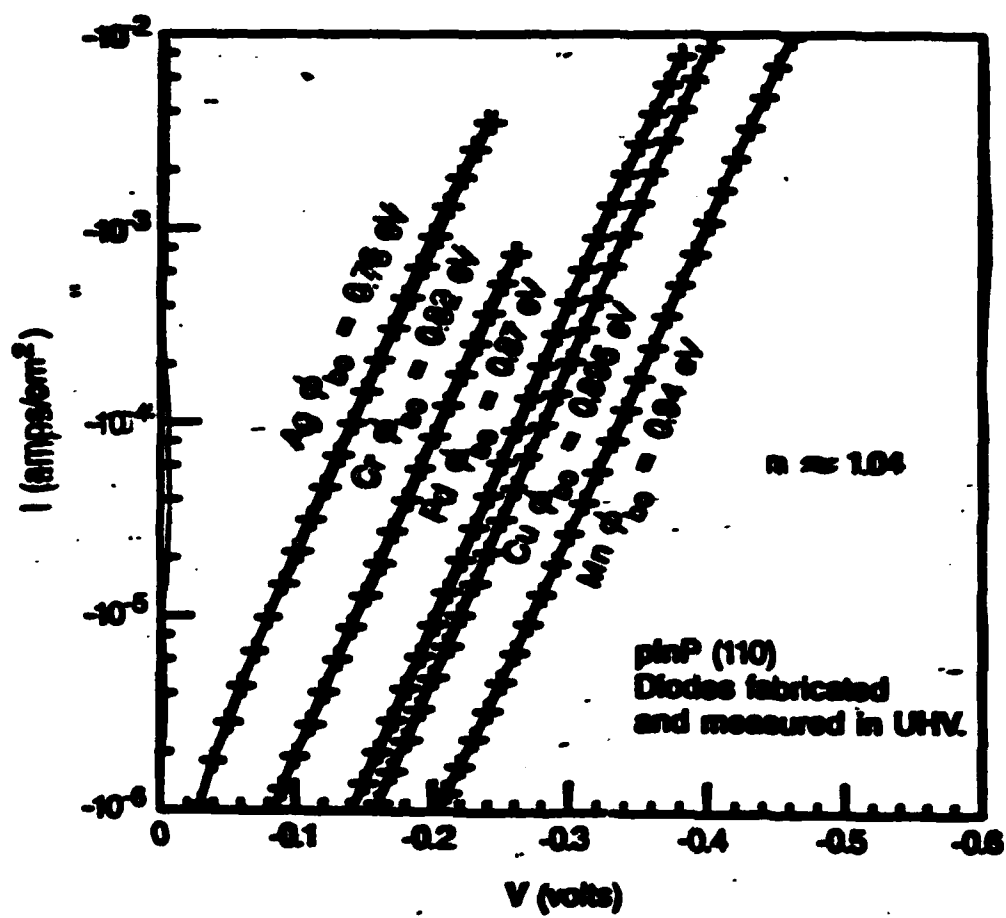
N. Newman, M. van Schilfegaarde, and W. E. Spicer

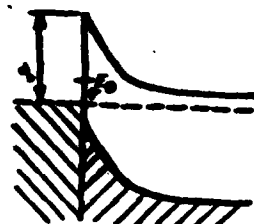
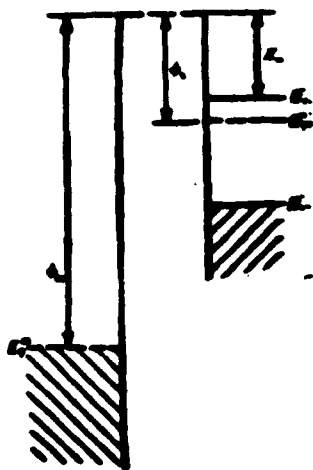
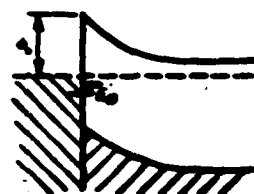
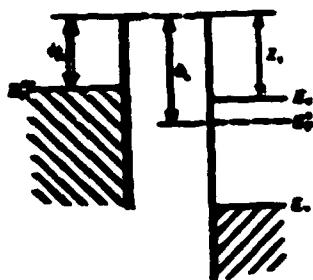
Stanford University

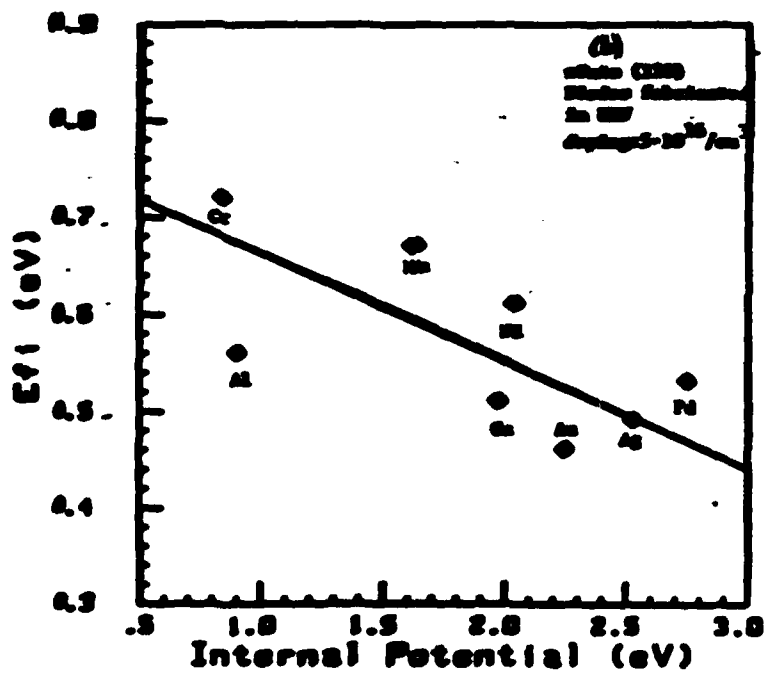
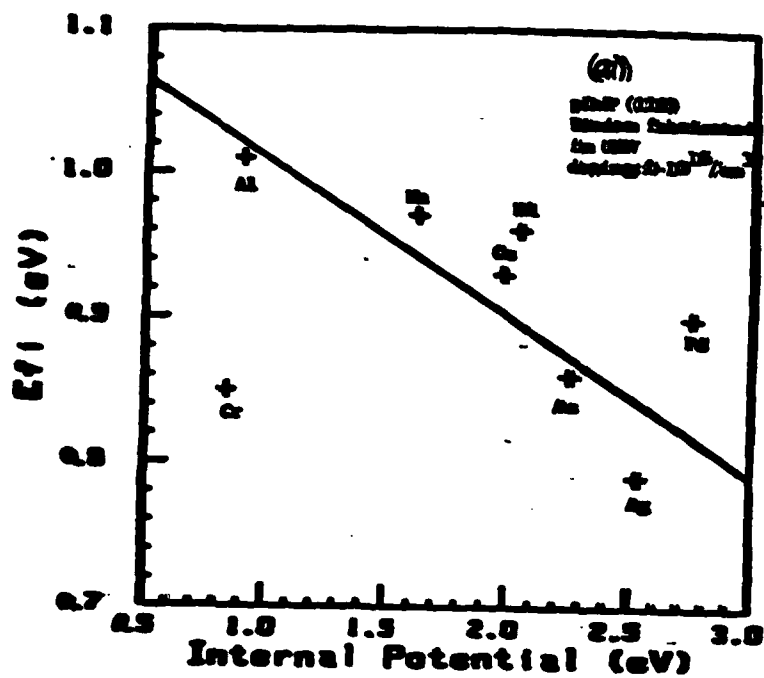
Z. Liliental-Weber and E. R. Weber

U.C. Berkeley



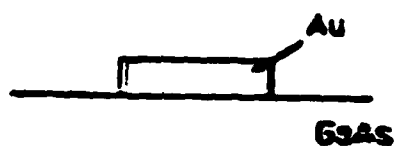






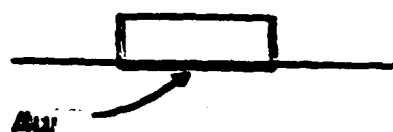
20

Room Temp.



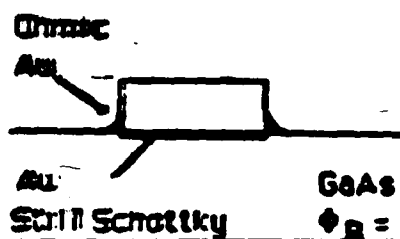
AuGaAs
 $\Phi_B = 0.91 \text{ eV}$

Anneal to 290°C



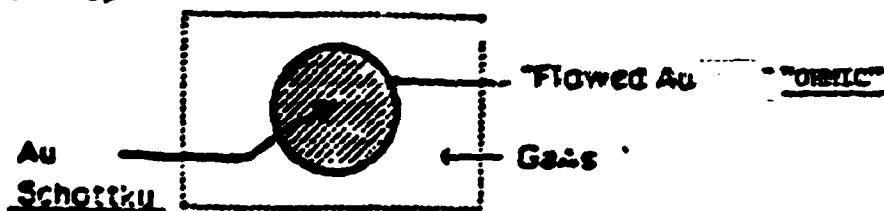
AuGa₂G₂As
 $\Phi_B = 0.8 \text{ eV}$

Anneal to >360°C (Au-Ga eutectic temperature)

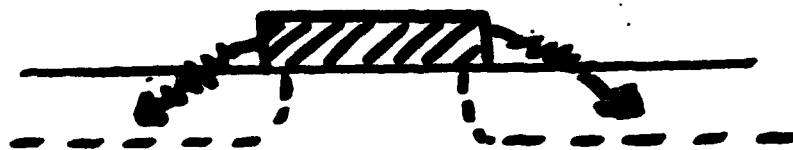
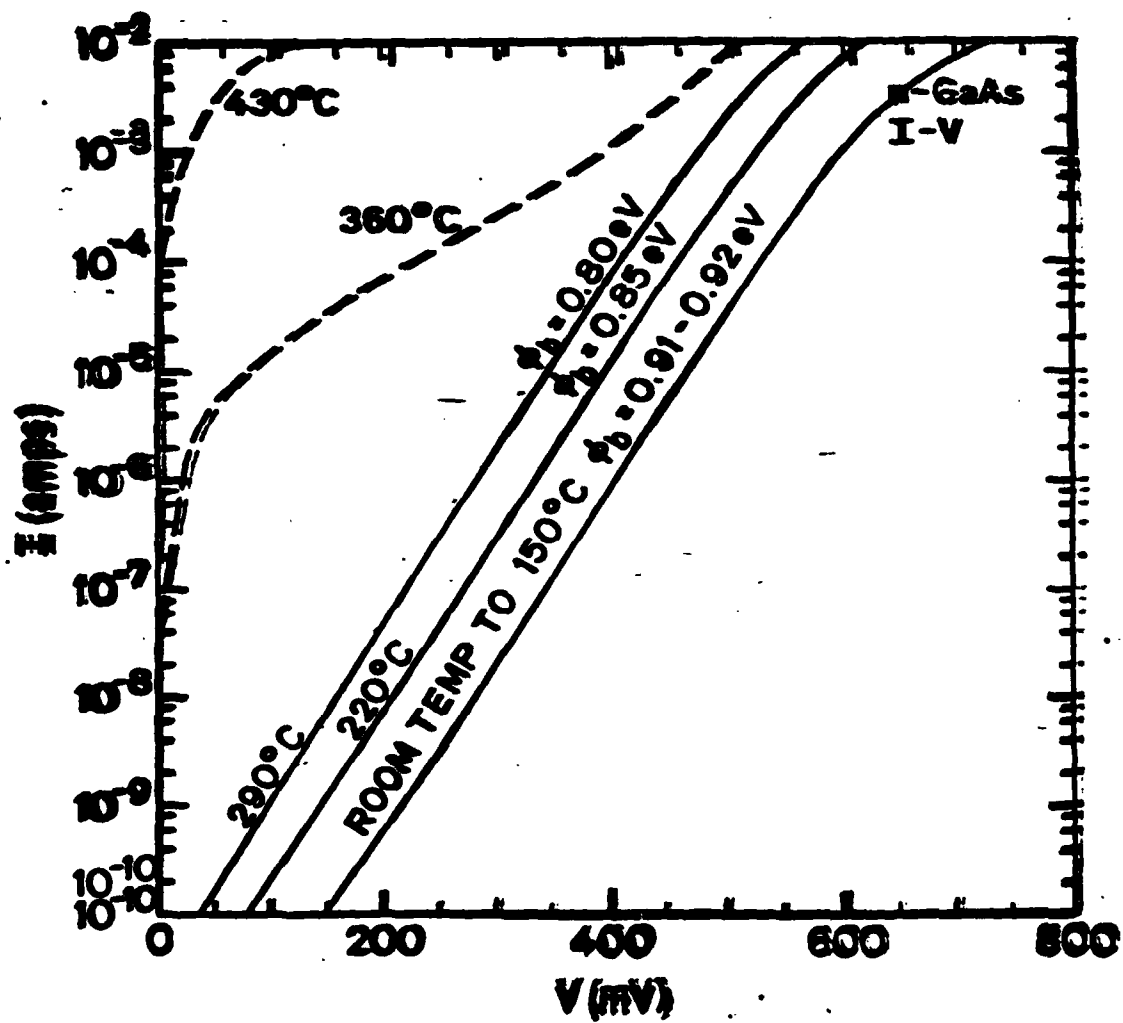


$\Phi_B = 0.8 \text{ eV}$

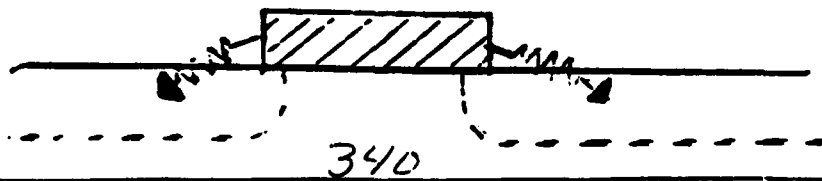
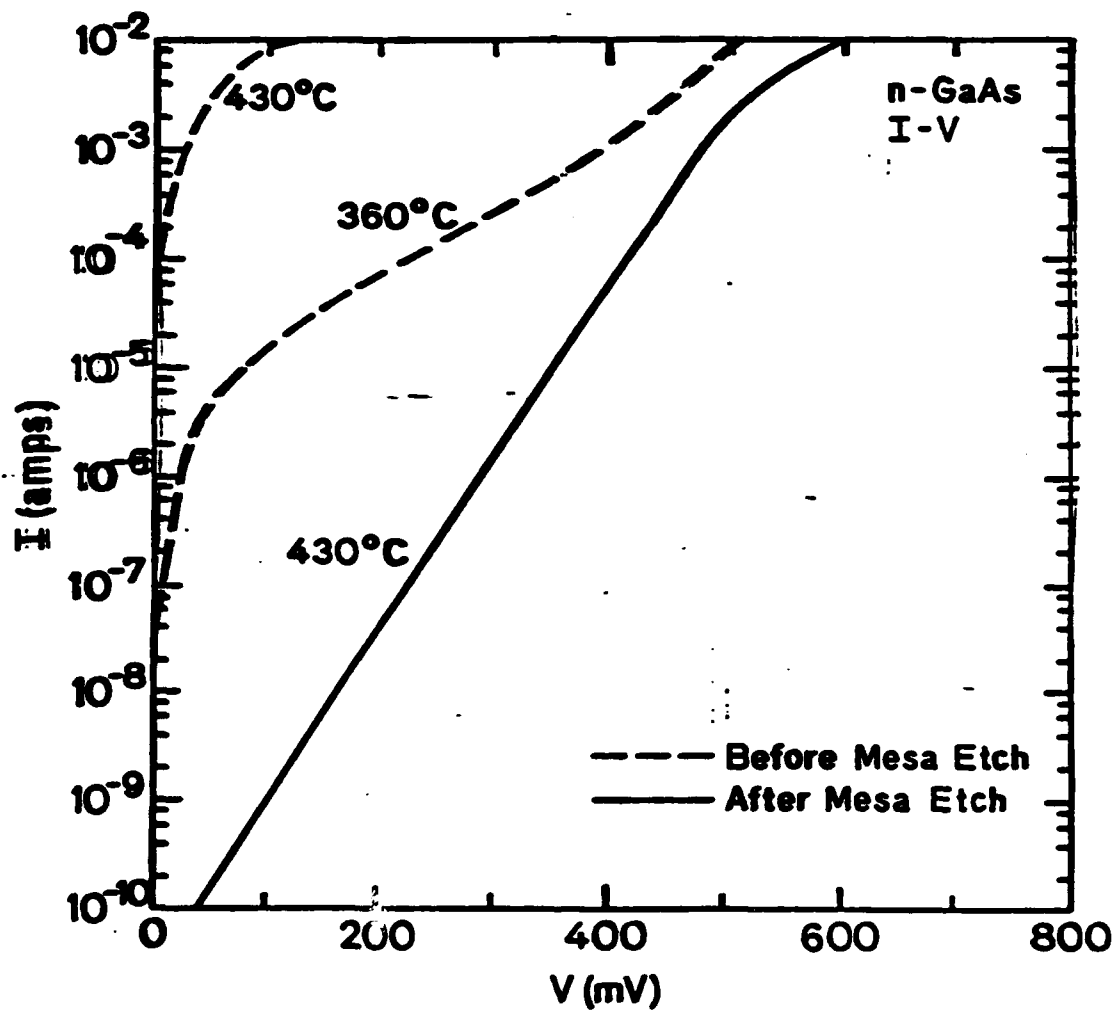
From Top

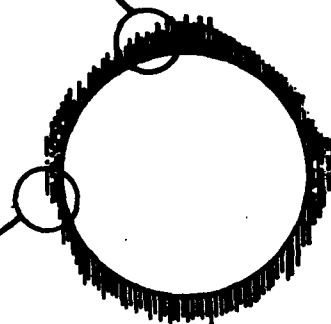
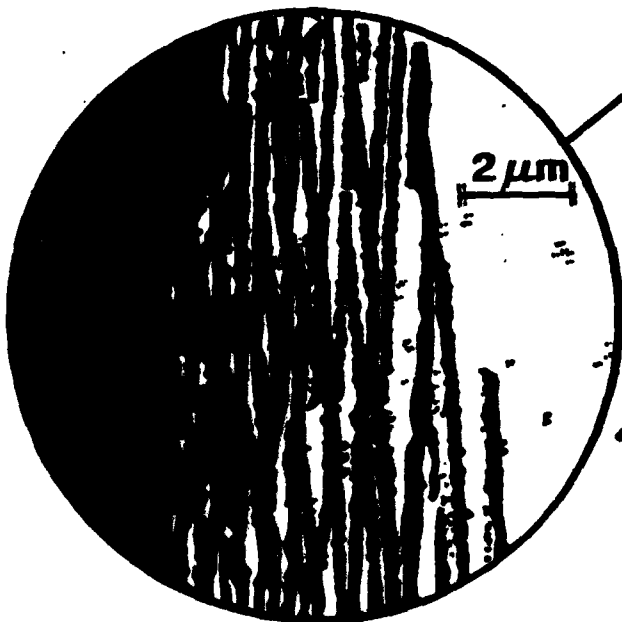
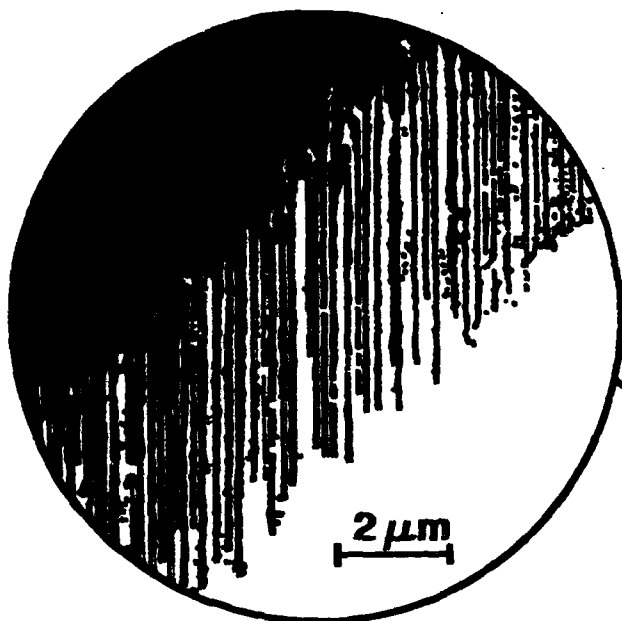


AU-GAAS HEAT TREATMENT

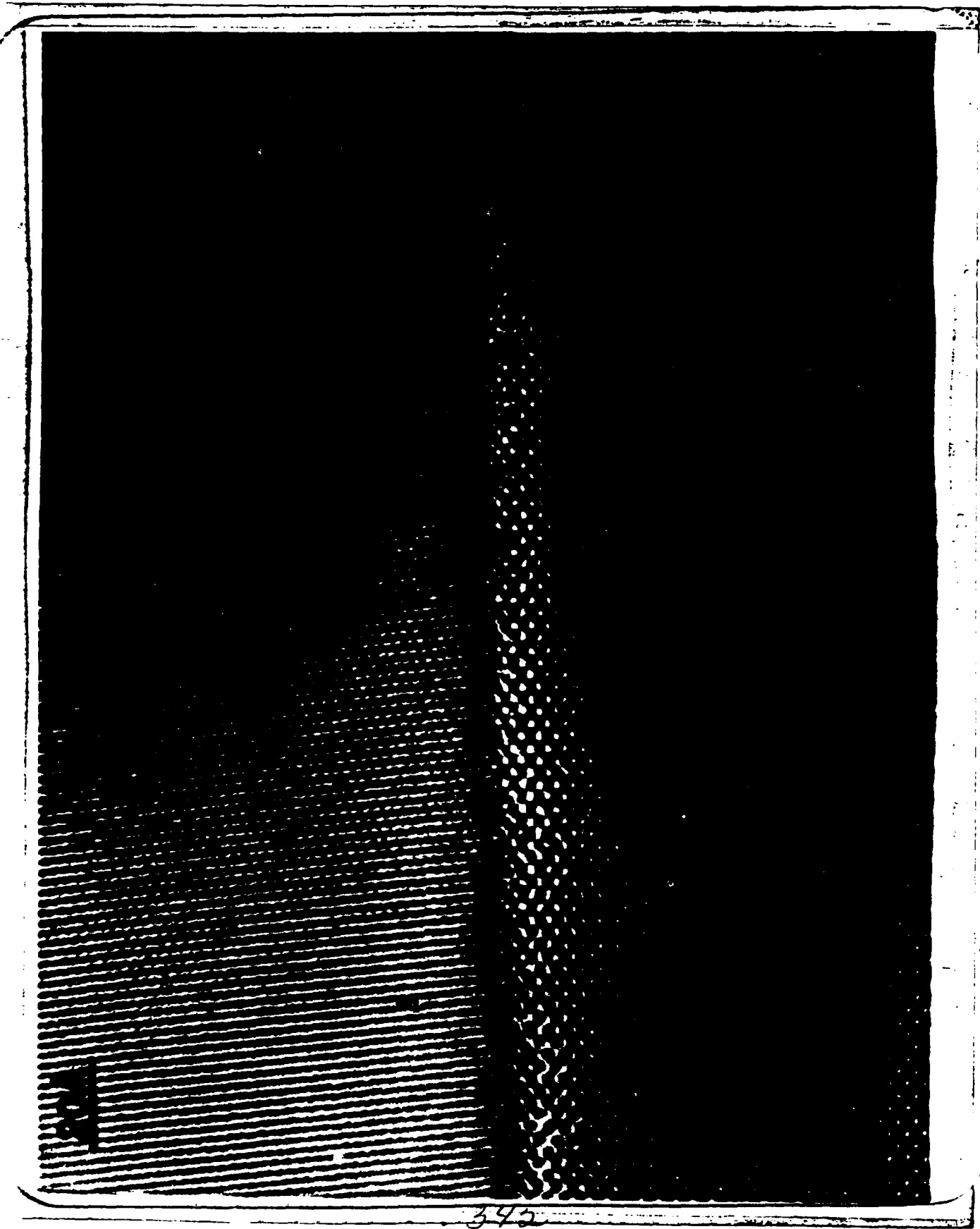


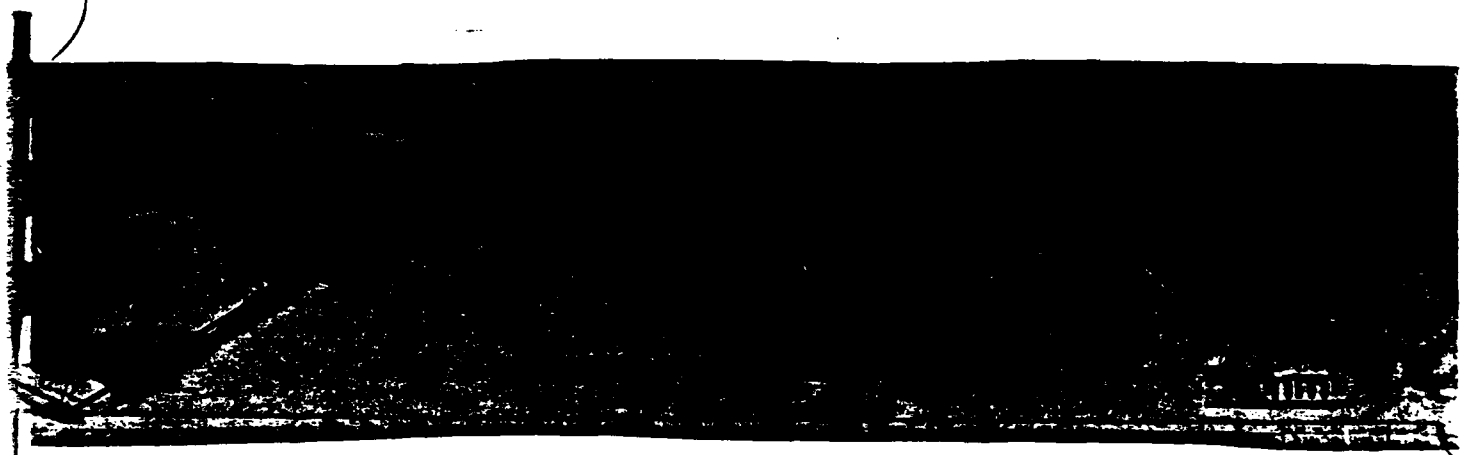
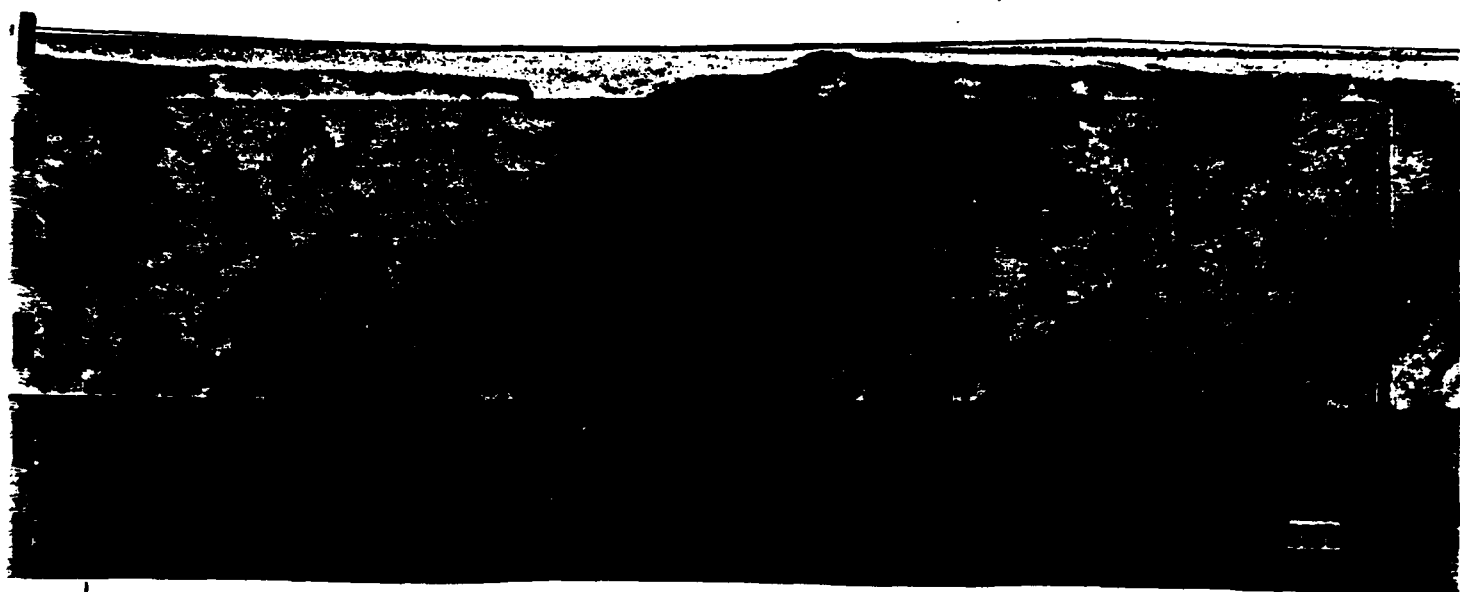
Au - n GaAs ANNEALING STUDY



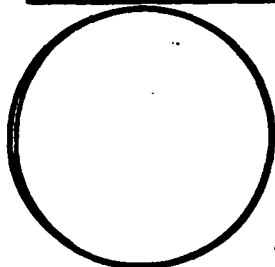


GaAs $\langle 110 \rangle$

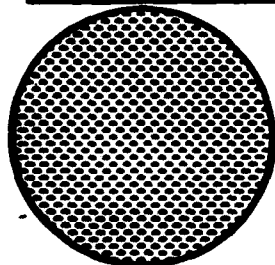




100 Å of Au deposited - unannealed

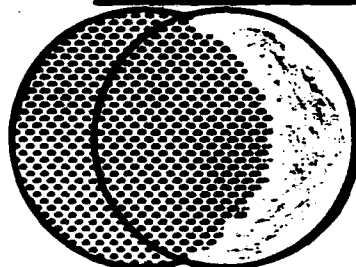


100 Å of Au Annealed at 325°C

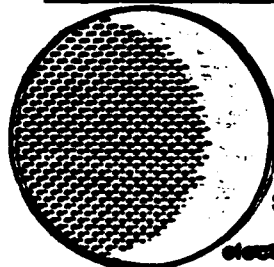


Forms separated islands
of Au-Sn alloy

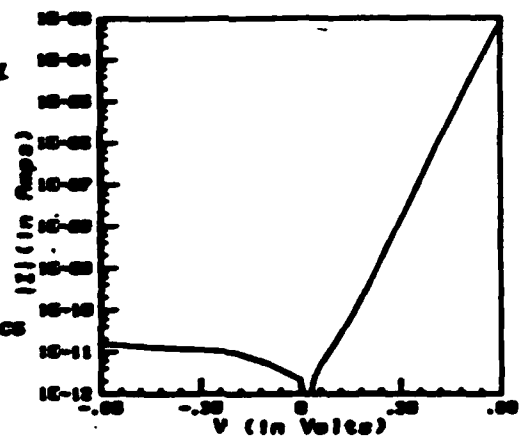
200 Å of Au deposited on top

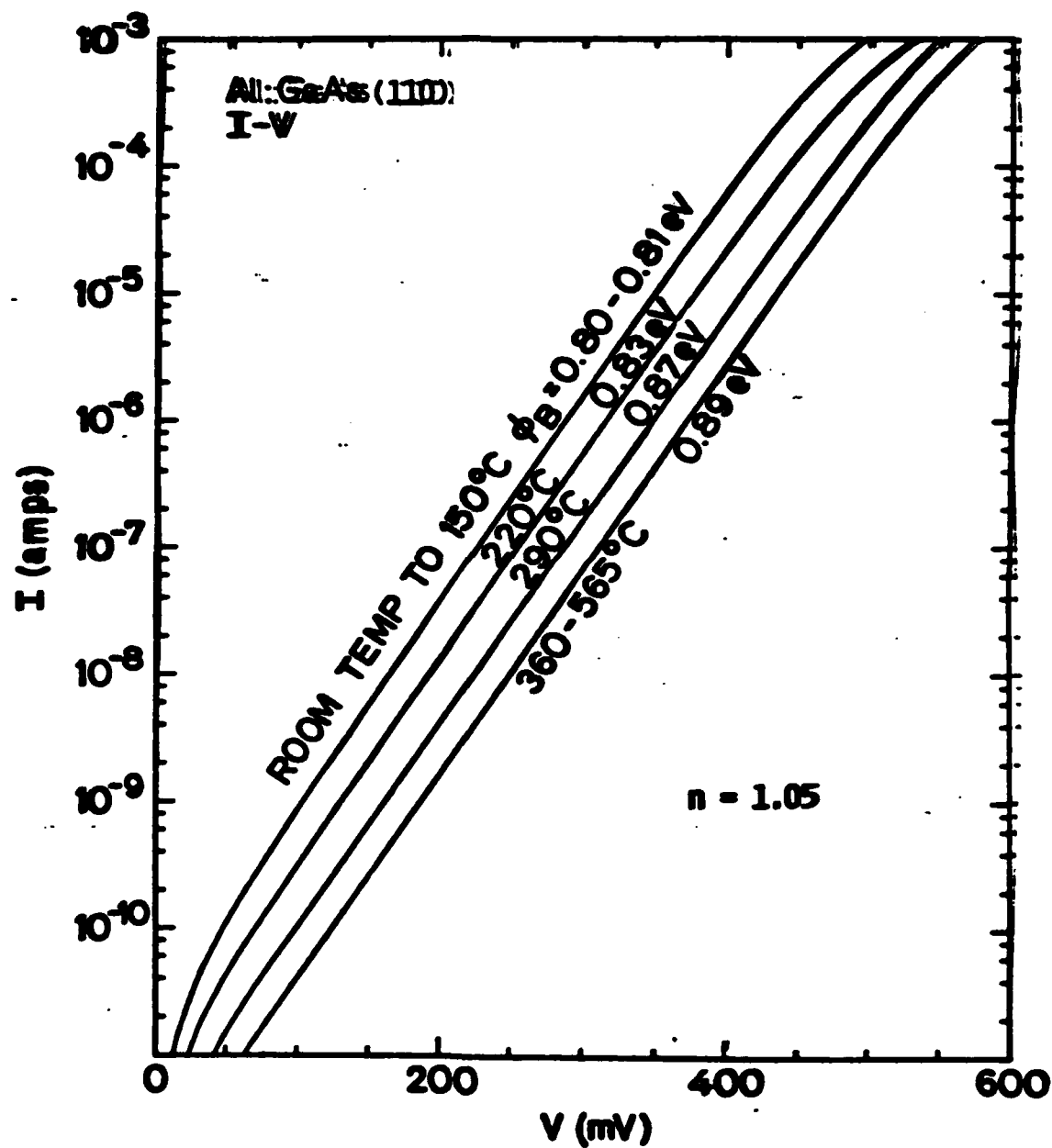


Mass shift to surface effect of majority

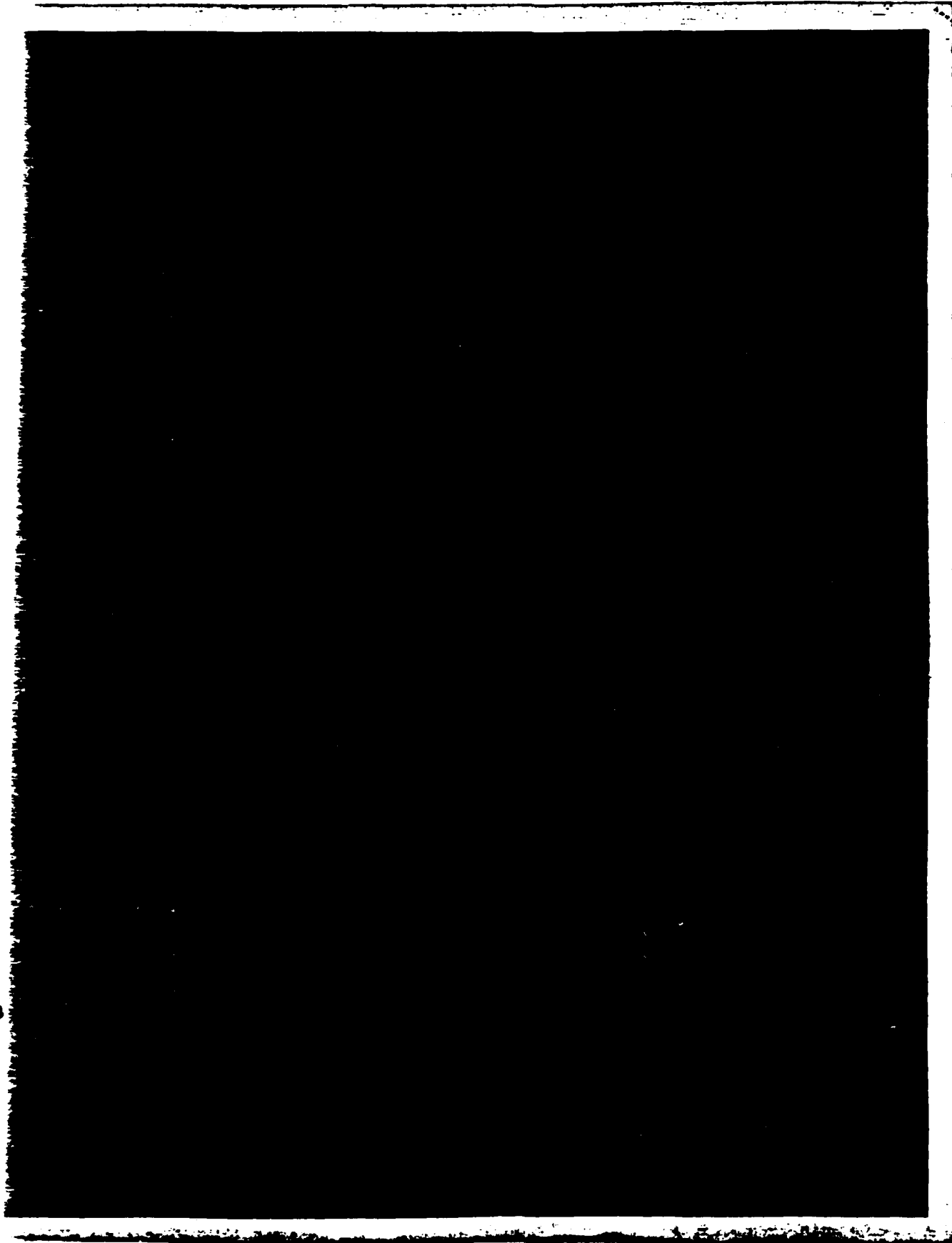


Strong rectifying
electrical characteristics





345



346

**THE STRUCTURE OF Au/GaAs AND Al/GaAs
INTERFACES**

Zuzanna Liliental-Weber

**Materials and Molecular Research Division
Lawrence Berkeley Laboratory
Berkeley, CA 94720**

THE STRUCTURE OF Au/GaAs AND Al/GaAs INTERFACES

- **INTRODUCTION**
- **Au AND Al CONTACTS ON CLEAVED GaAs (110)**
 - UHV-deposited structures
 - annealed structures (UHV-deposited)
 - annealed structures (air-exposed)
- **Au CONTACTS ON CHEMICALLY PREPARED GaAs (100)**
 - annealed structures
- **Al CONTACTS DEPOSITED BY MBE ON GaAs (100)**
 - as-deposited structures
- **CONCLUSIONS**

This work was done in cooperation with:

Nathan Newman, W.E. Spicer (cleaved structures)

R. Ludeke (MBE-deposited structures)

T. Sands (chemically prepared structures)

Funding was provided by:

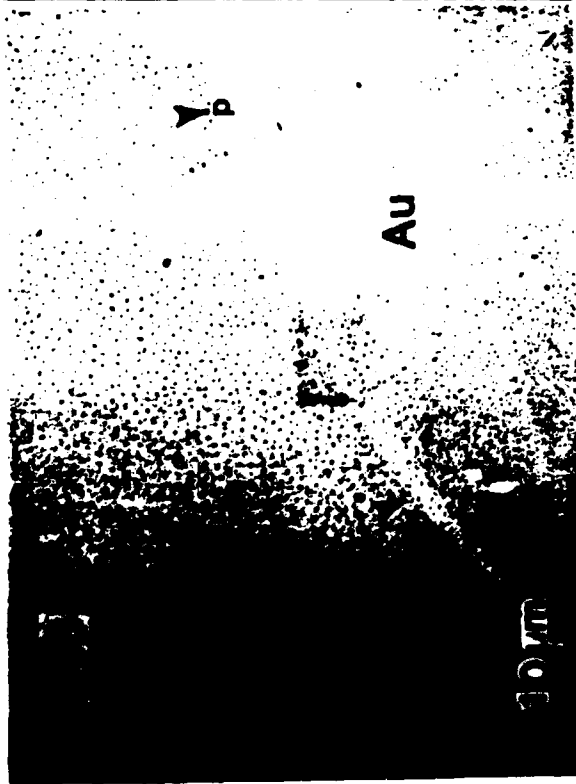
Department of Energy

Office of Naval Research/IST

Electron microscopy was carried out at the

National Center for Electron Microscopy, LBL, Berkeley

as-deposited



annealed at 400°C



part
control
sample

350

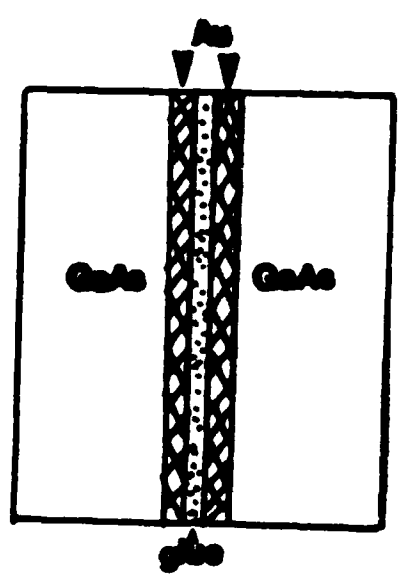
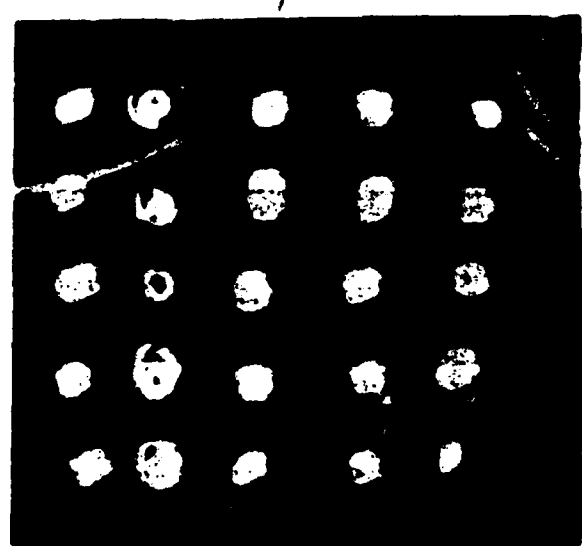


after mesa etching



after mesa etching
preferential etching
beneath the
crystallites

Au dots



cross-section
sample



plan view sample

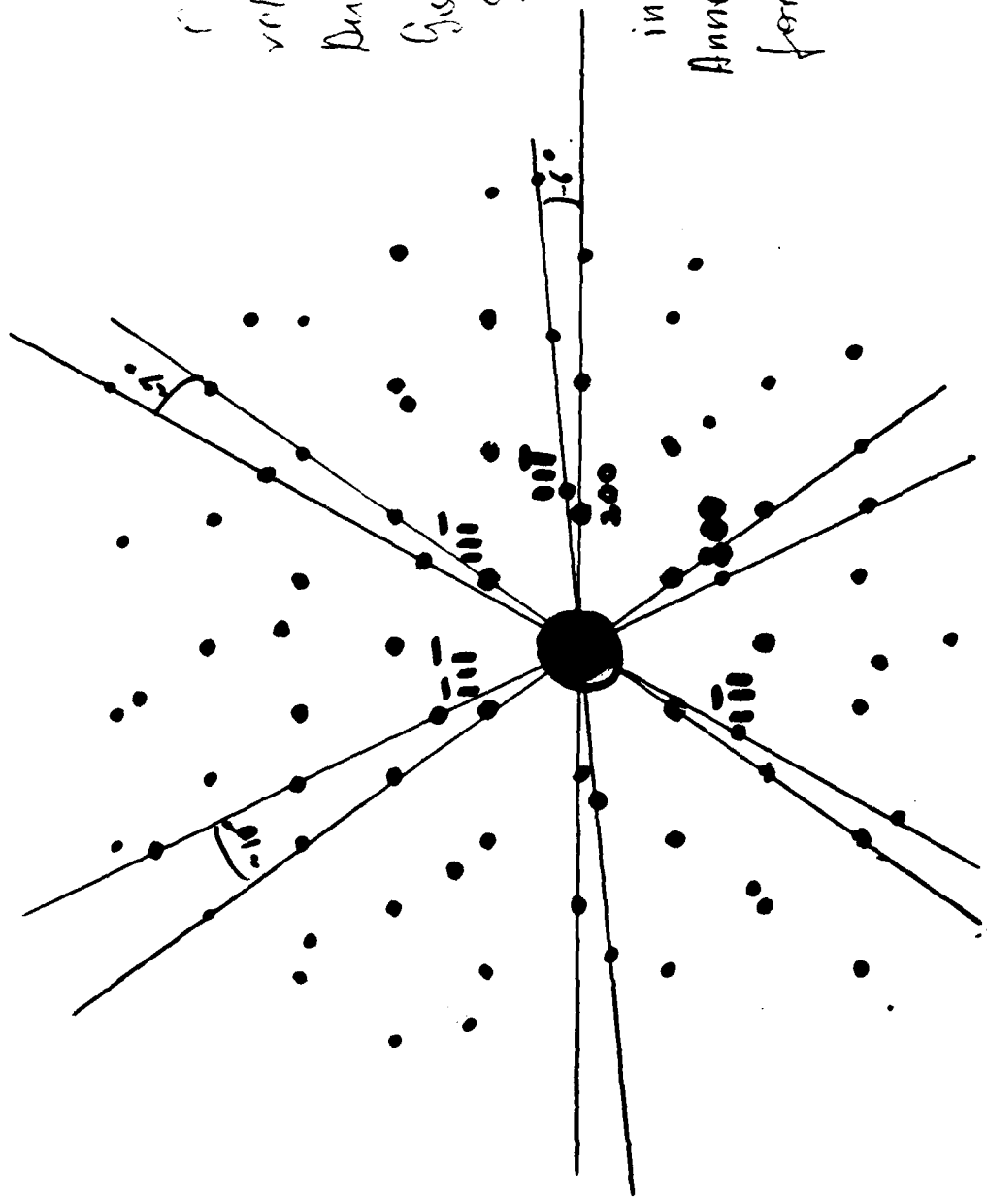
UHV cleaved
40°C annealing

20A

40A

35A

50As



Preparation
 relationship of
 Au planes with
 GaAs planes.
 Sample cleaved
 in UHV with
 in situ Au deposition.
 Annealing in N_2
 for 10 min at 400°C

353

$$\begin{aligned}
 (111)_{GaAs} &= 3.26 \text{ \AA} \\
 (111)_{Au} &= 2.355 \text{ \AA}
 \end{aligned}$$

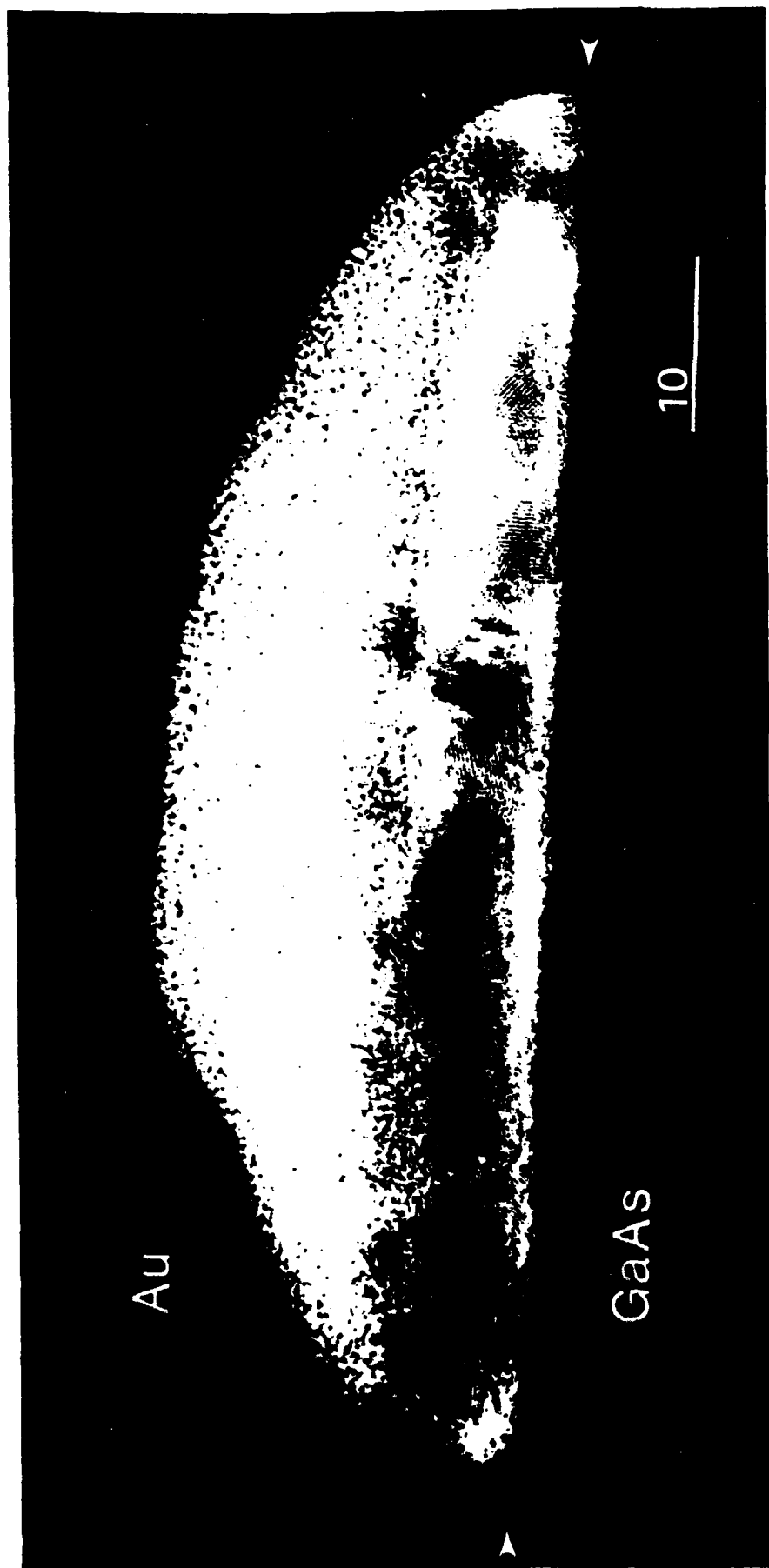
$$(200)_{GaAs} = 2.826 \text{ \AA}$$

$$(111)_{Au} = 2.355^\circ$$

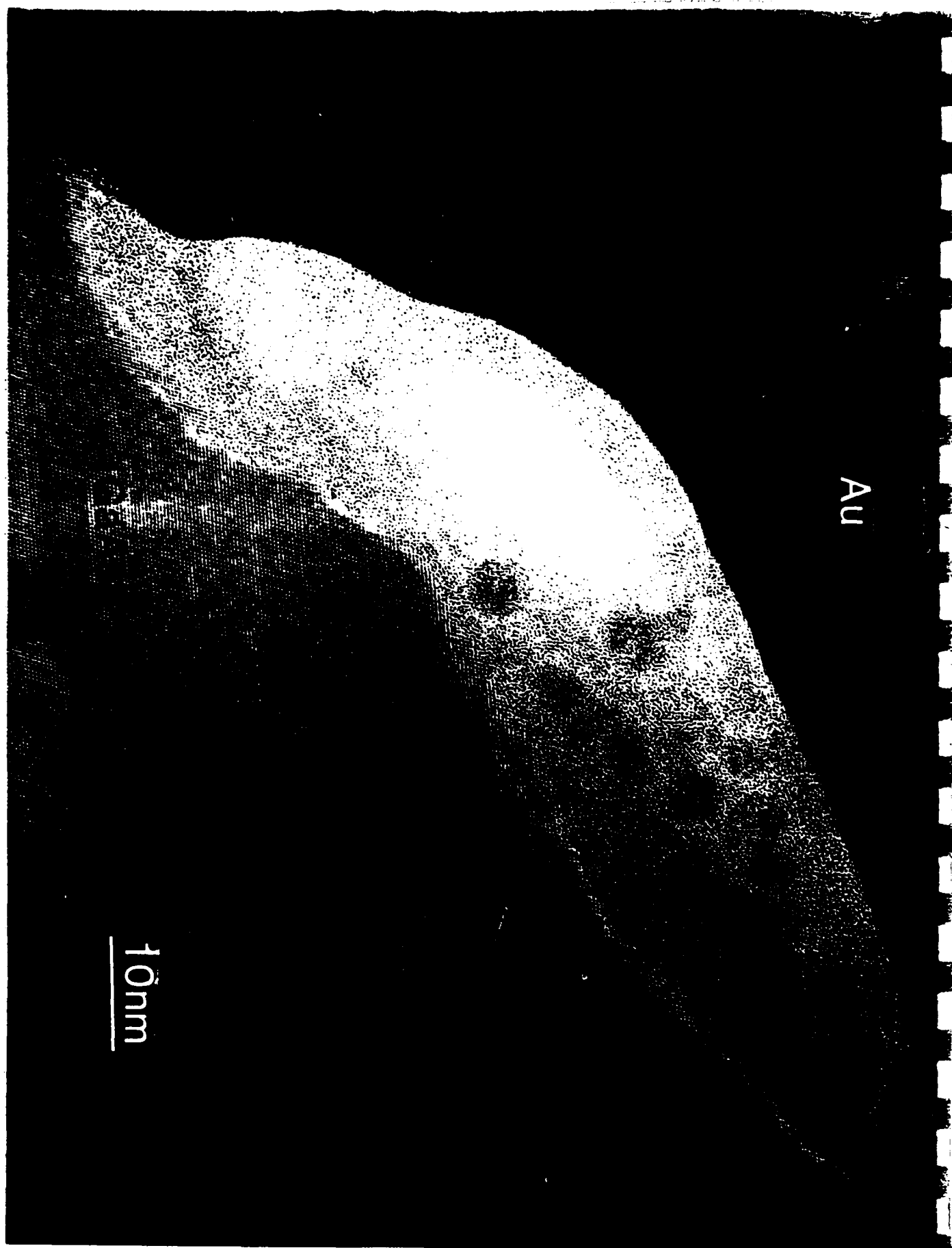
$$5 \times 2.826 = 6 \times 2.355 = 14.13^\circ$$



Trington formed in the Bu layer after
consolidating at 4050p



355 Polycrystalline Au particles present inside triangular formed
in Au after annealing at 400°C.



356
Treated - mixed in the Au layer on the surface of
- Gold. Polymers on particles are imbedded in surface

U-AUUHV2

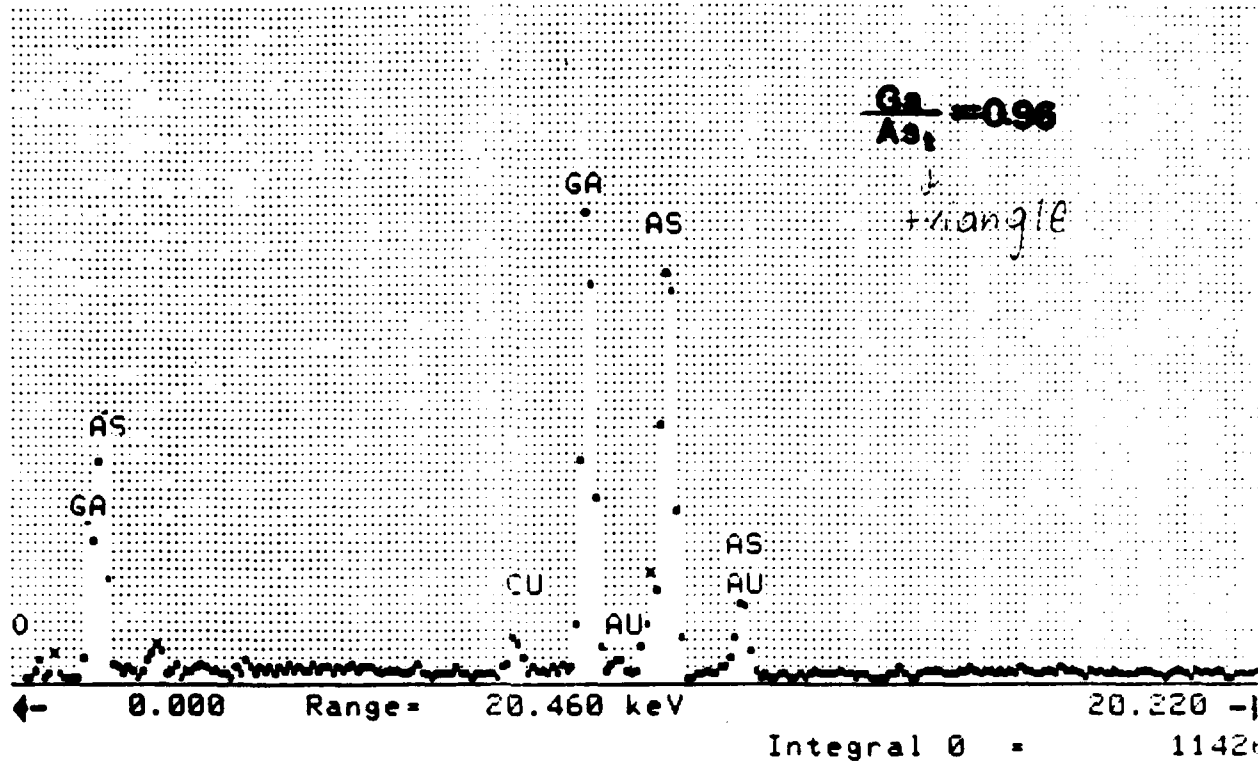
Vert = 500 counts Disp = 1

Preset =

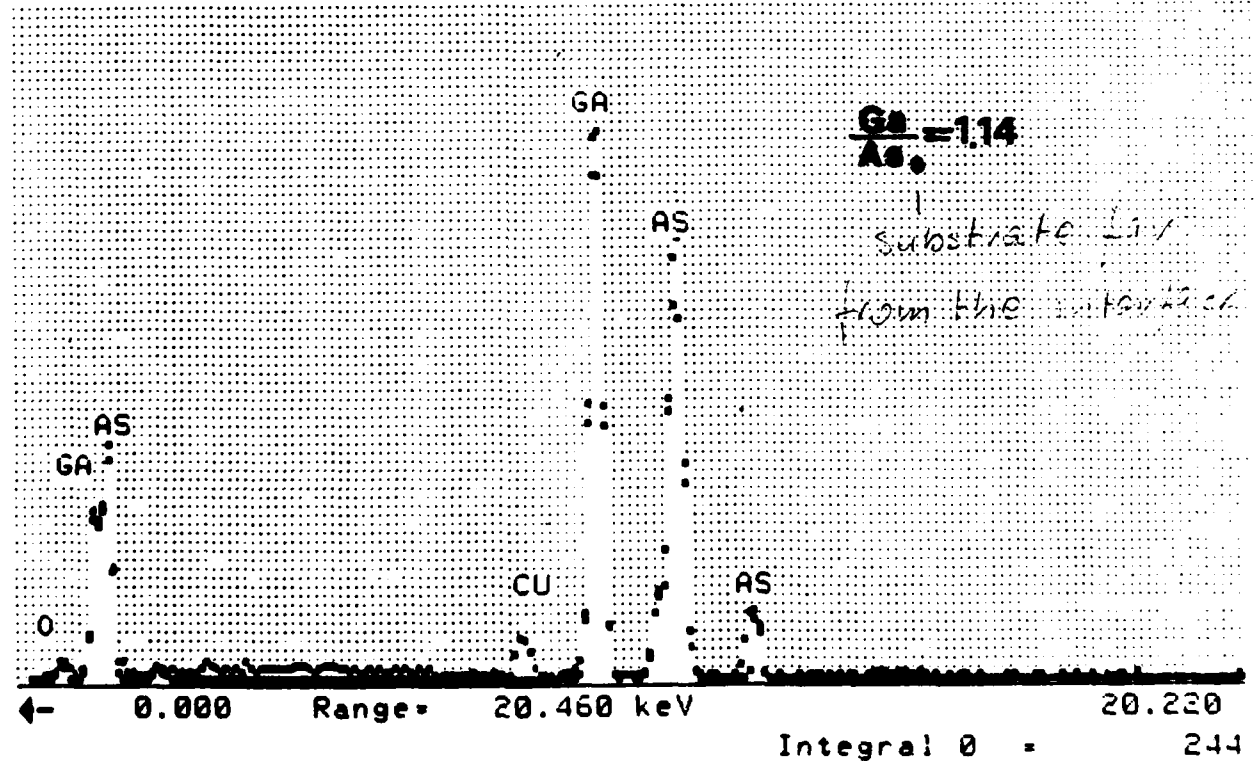
300 sec

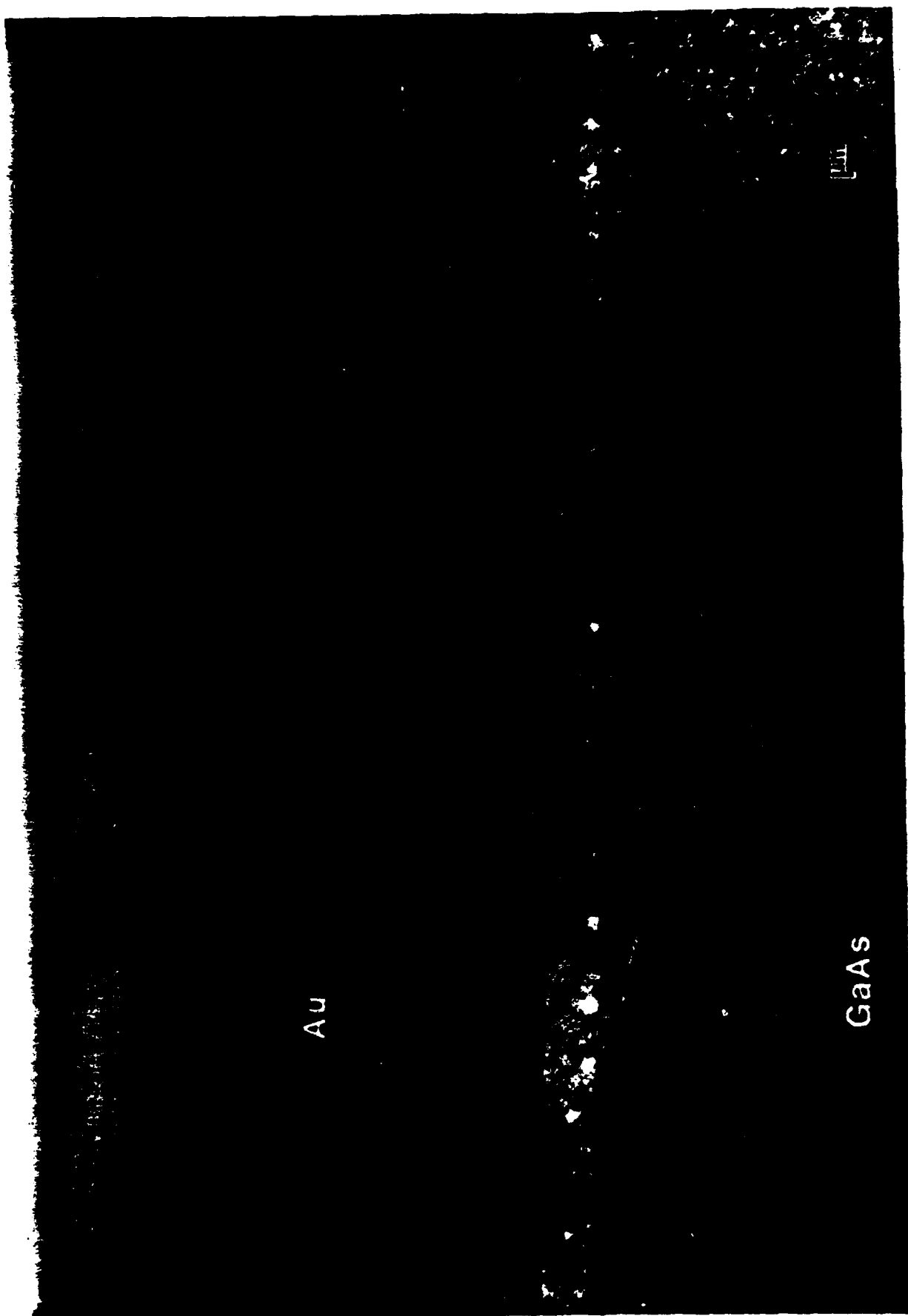
Elapsed =

500 sec



Vert = 1000 counts Disp = 1 Comp = 3 Preset = 300 se
Elapsed = 500 se





Au

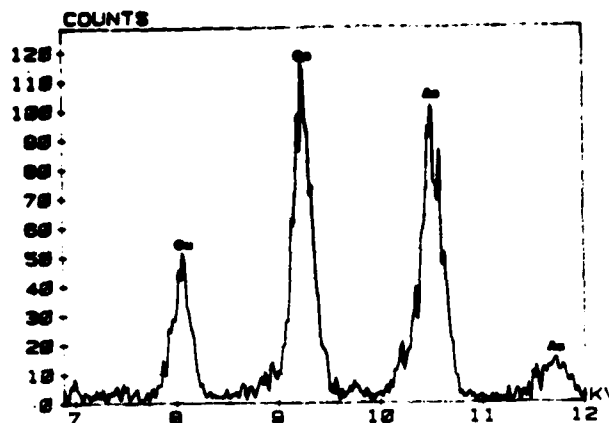
GaAs

Clusters of As distributed below the Au/GaAs interface

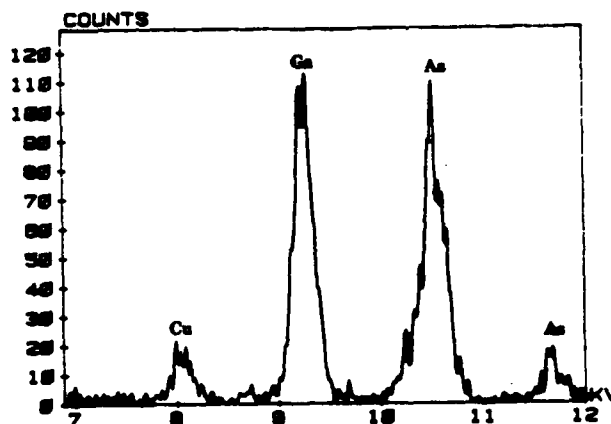
00857-5115A

Voids formed on the interface on the cleavage
steps

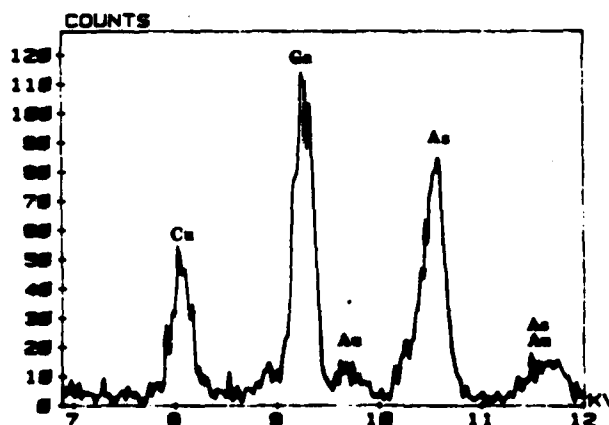
XAB857-5111



on Se
1.50 A
1.50 A



on Se
1.50 A
1.50 A



As
1.50 A
1.50 A

XBL 8510-4315

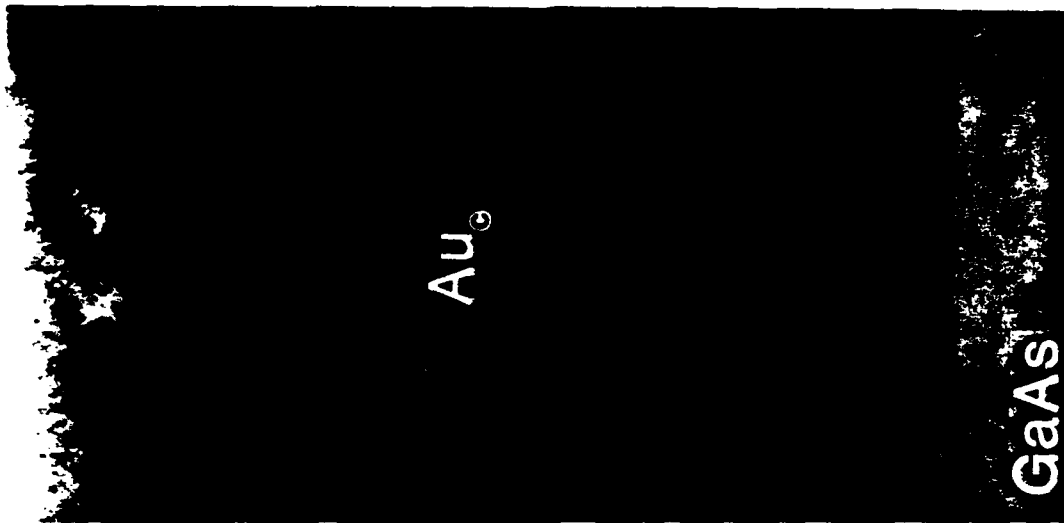
Line for H₂O₂ analysis
- 1.50 A for

e beam parallel to (100)

cross-section of Au/GaAs
interface on the periphery
of Au dot



cross section
of the Au/GaAs
interface
from the central
part of the Au
dot

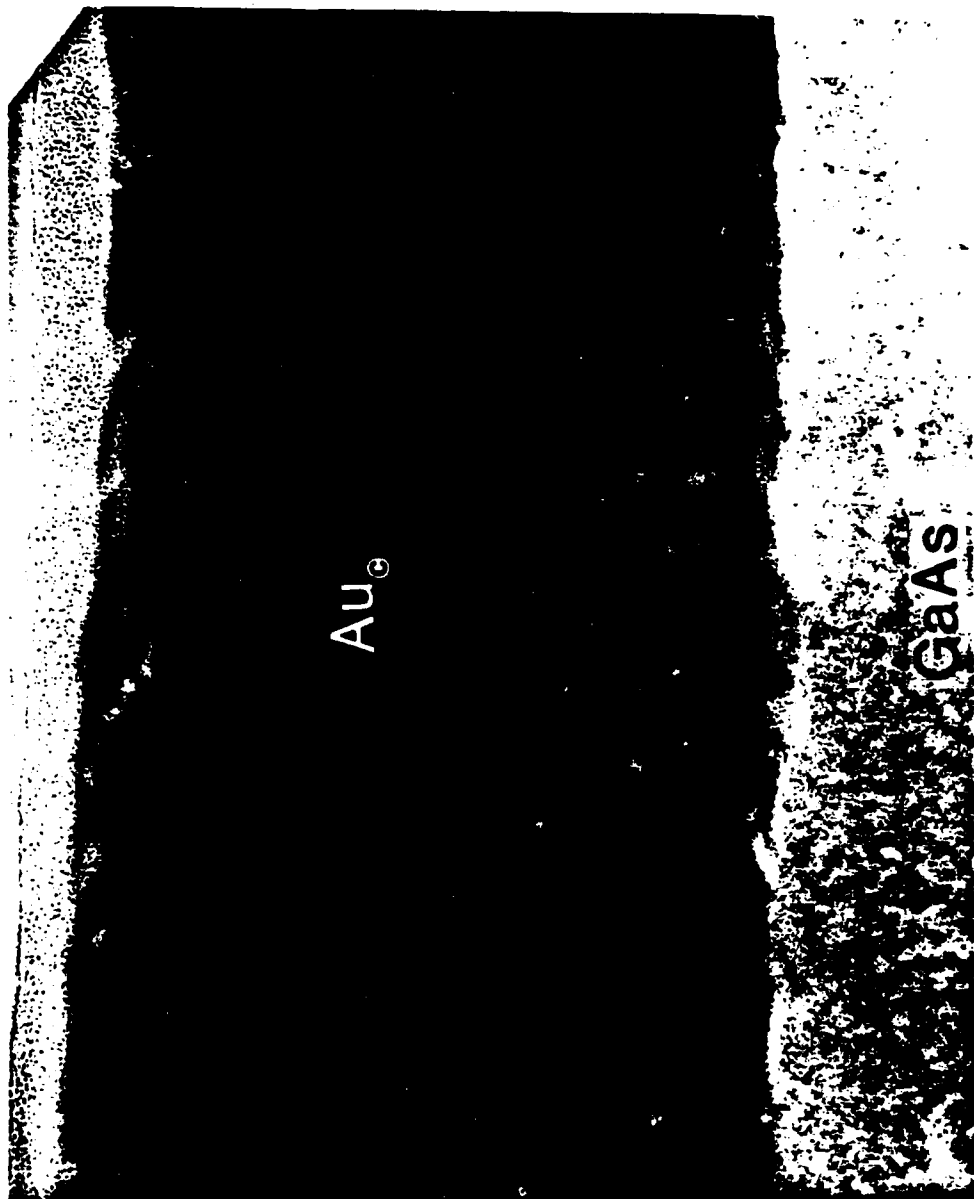
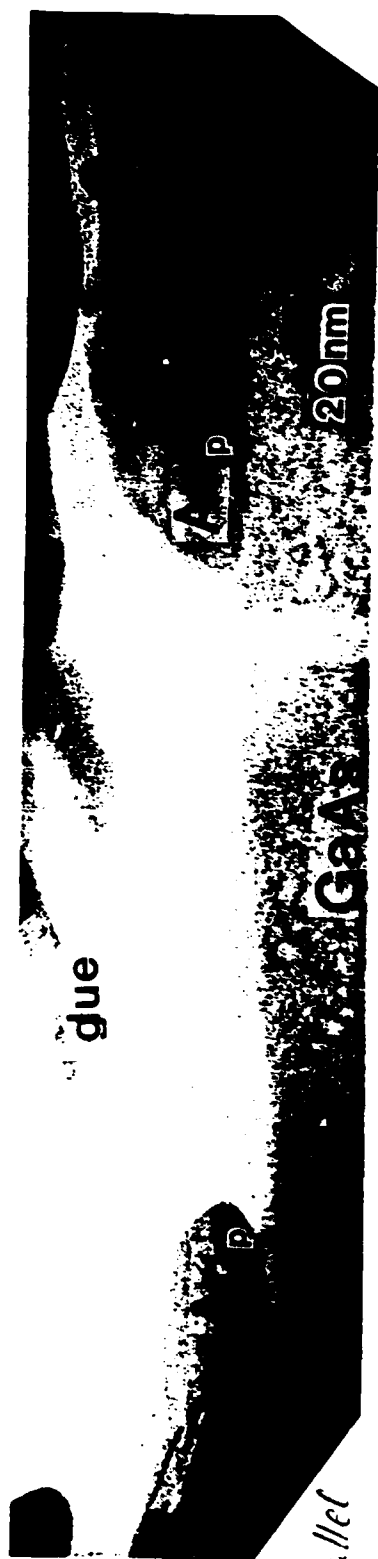


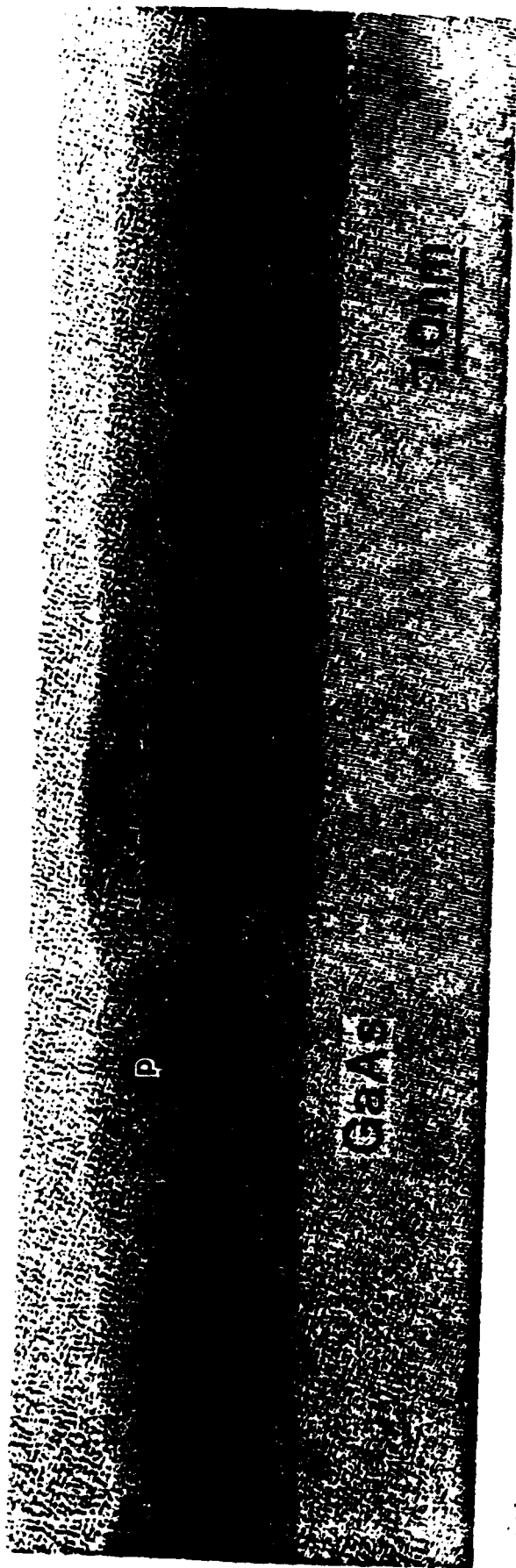
cross section
of the area
between two
crystallites on
the periphery
of annealed
Au dot
(beam parallel
to (011))



cross-section
of the interface
in the central
part of Au dot

362





$$(200)_{\text{GaAs}} = 2.826 \text{ \AA}$$

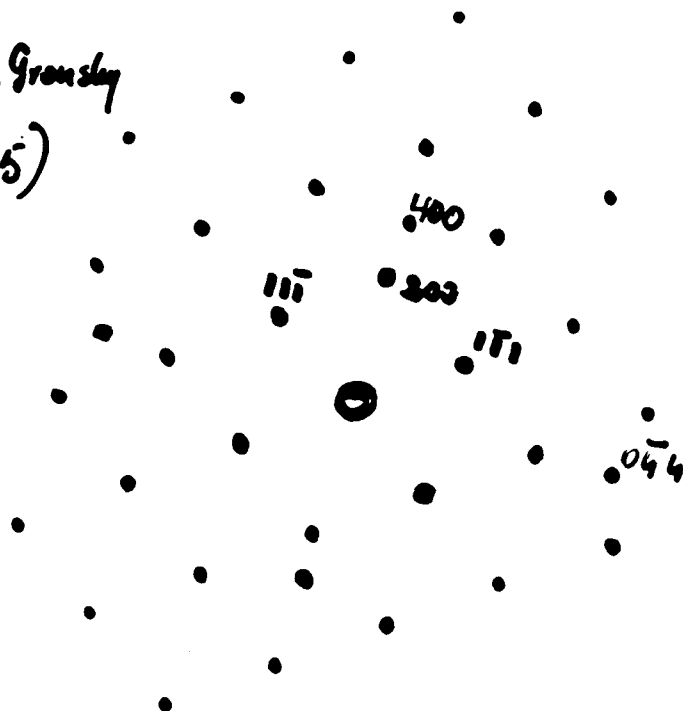
$$\{011\} \parallel \{011\}_{\gamma\text{Ga}_2\text{O}_3} \quad 17$$

$$400_{\gamma\text{Ga}_2\text{O}_3} = 2.05 \text{ \AA} \approx (200)_{\text{Au}} = 2.039 \text{ \AA}$$

$$\text{Al} = 2.024 \text{ \AA}$$

$$\text{Ag} = 2.044 \text{ \AA}$$

T. Sands, J. Washburn and R. Gronsky
Nat. Lett. vol 3, p. 247 (1985)



$$(220)_{\text{GaAs}} = 1.998 \text{ \AA}$$

$$\Rightarrow \frac{2}{3} \times 1.998 \text{ \AA} = 5.99 \text{ \AA}$$

$$(044)_{\gamma\text{Ga}_2\text{O}_3} = 1.45 \text{ \AA} \approx (022)_{\text{Au}} = 1.442 \text{ \AA} \quad 4 \times 1.45 \text{ \AA} = 5.8 \text{ \AA}$$

$$\sim 3\%$$

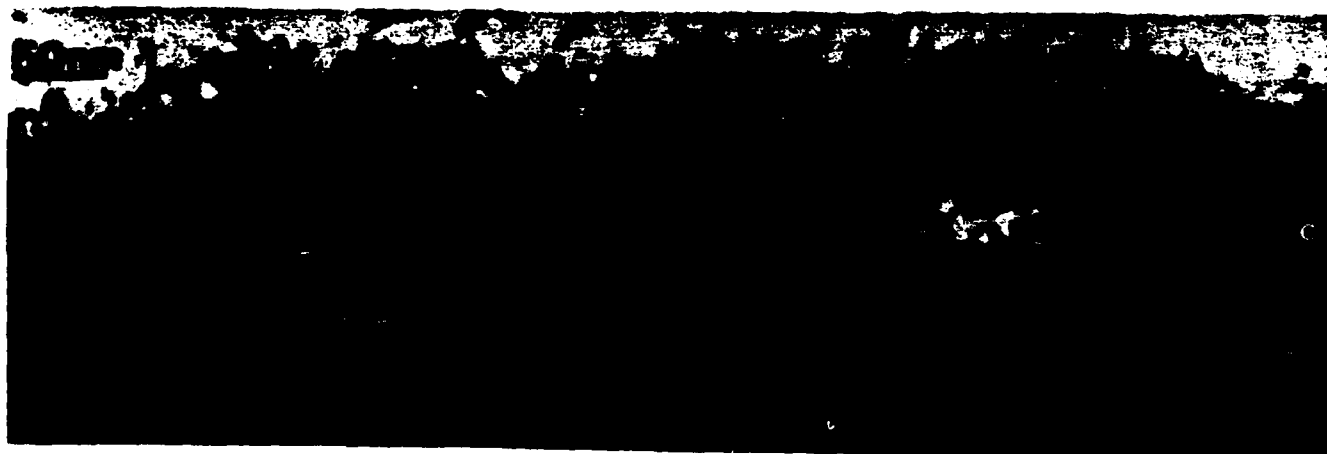
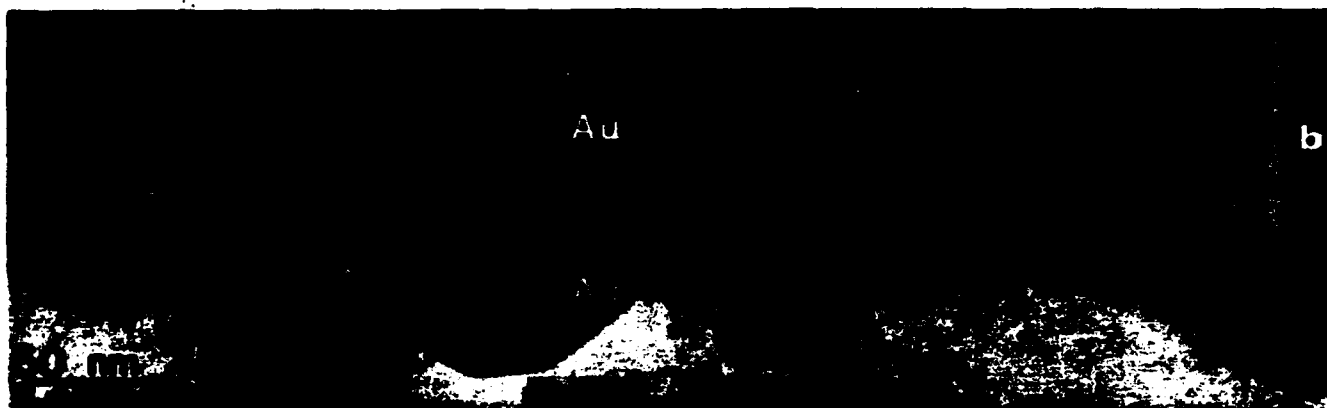
$$\text{Al} = 1.431$$

$$\text{Ag} = 1.445$$

J.W. Evans and O.R. Monteiro

GaAs exposed at 500°C to 30 Torr of oxygen

GaAs $\rightarrow$ epitaxial $\gamma\text{Ga}_2\text{O}_3 \rightarrow$ polycryst $\gamma\text{Ga}_2\text{O}_3 \rightarrow$ polycryst $\beta\text{Ga}_2\text{O}_3$



0X3882-1034

365

13-Jan-1966 20:12:56

U-AUTS7

Vert.

200 counts

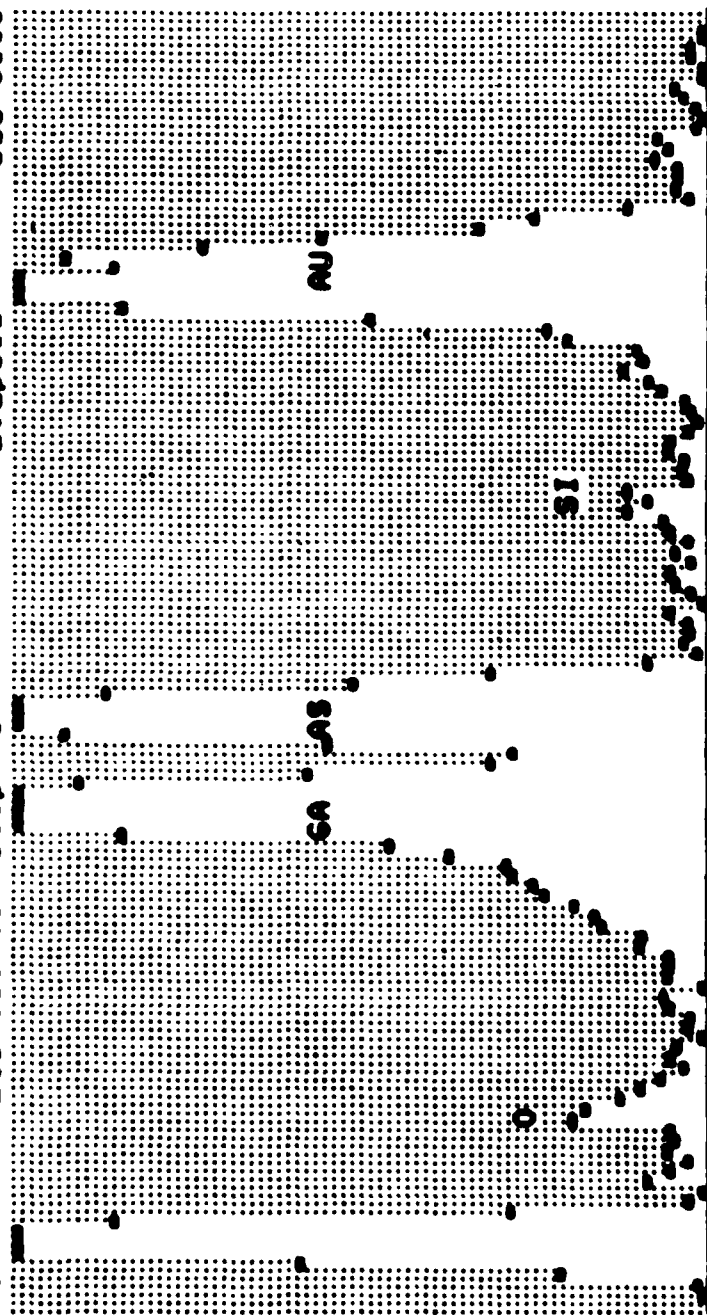
Disp. 1

Preset-

300 secs

Elapsed-

300 secs



0.160

Range= 20.460 keV

2.600 →

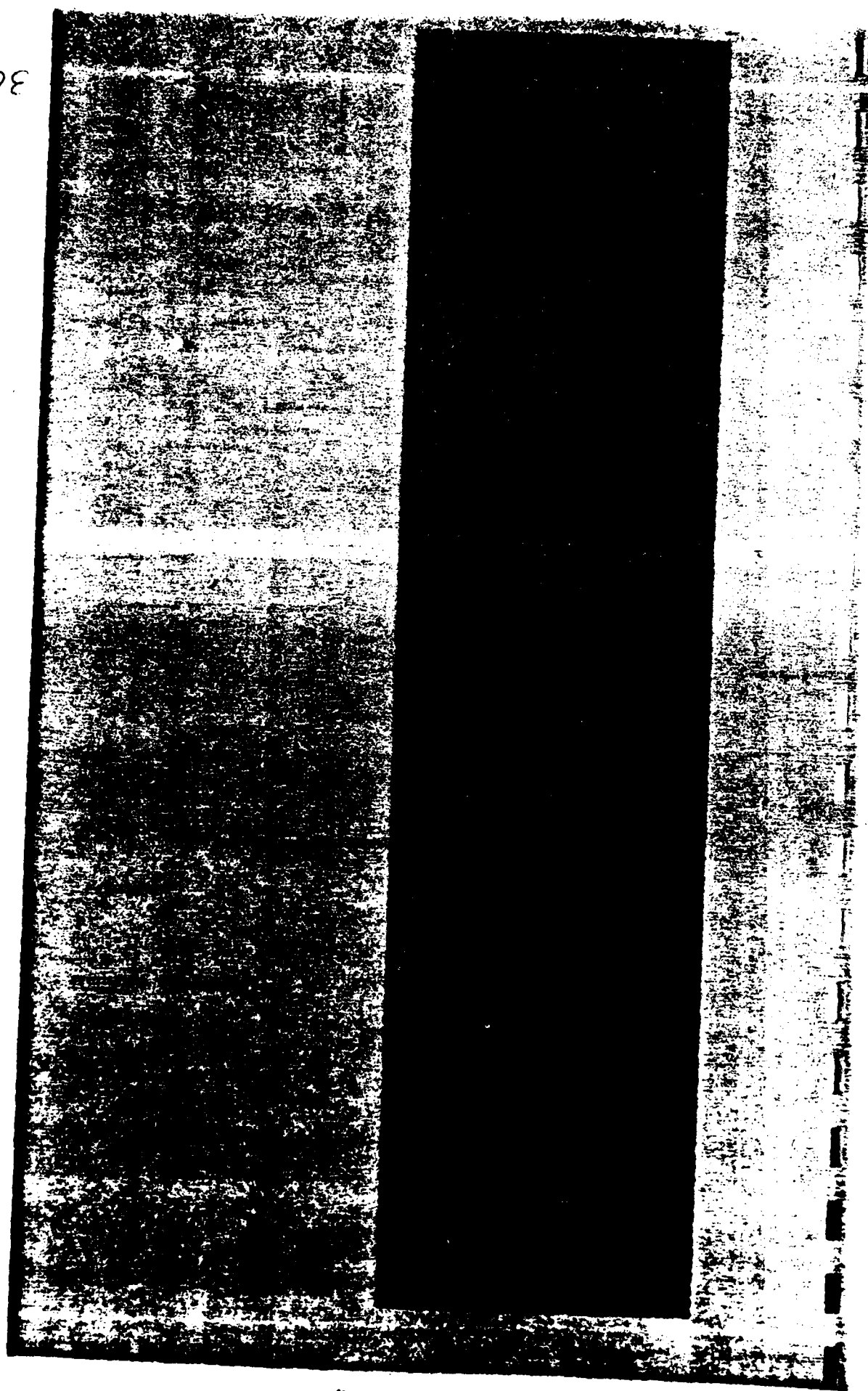
10770

Integral 0 -

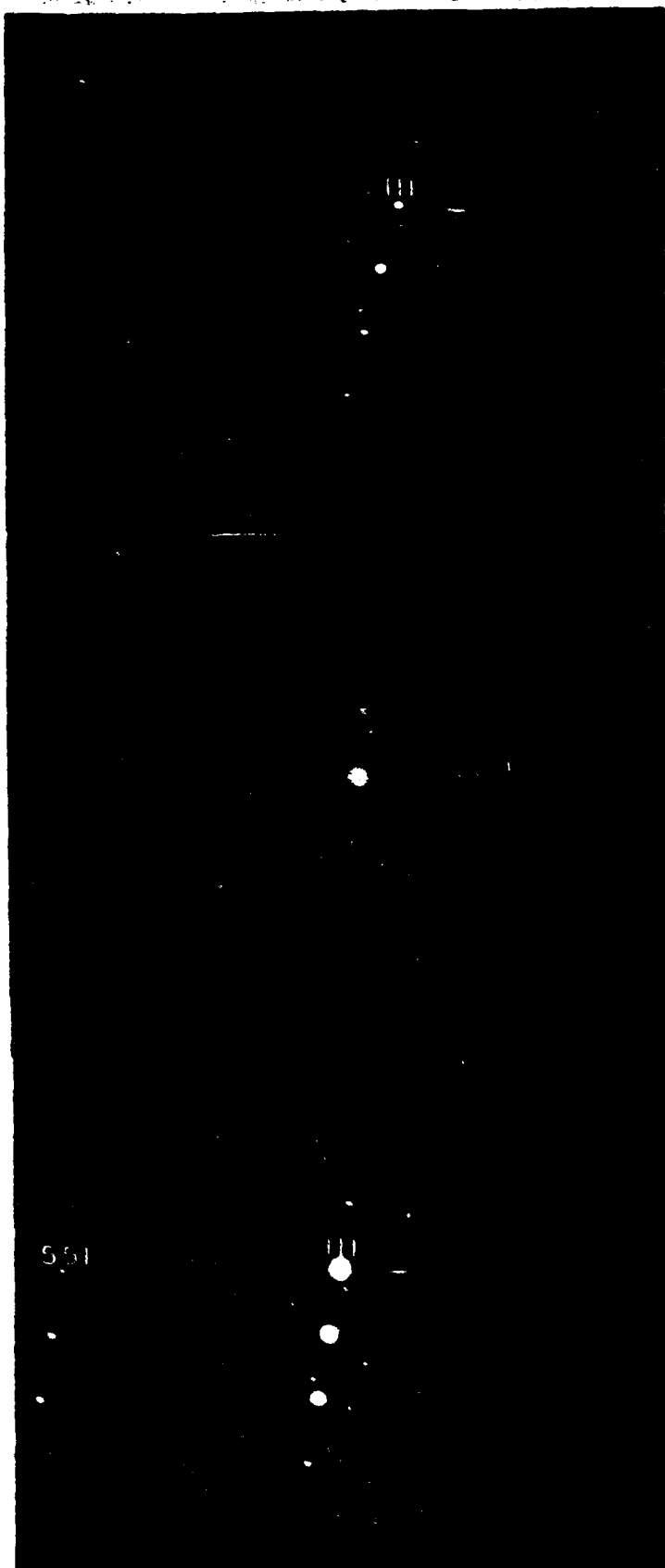
XBL 861-165 A

366

367



21



{112}

551

{2}

368

•XBB 686-6220

TO THE

9219-89898X

CONCLUSIONS

- **SURFACE PREPARATION (PRESENCE OF OXYGEN) DETERM**

- interface morphology
- metal grain orientation-relationship with GaAs
- formation of new phases

- **CONTACT FORMATION MECHANISM:**

- **Schottky contacts:**
 - * Au, Al and TiSi_2 Schottky contacts show increased As/Ga ratios in GaAs near the metal/semiconductor interface
 - * evidence for interfacial defects
 - * results support defect models of "Schottky" barrier formation
- **Ohmic contacts:**
 - * elongated crystallites at the periphery of annealed Au contacts protrude into the GaAs and provide low-barrier current paths
 - * protrusions at air-exposed interfaces do not provide current paths
 - * results support field-enhanced tunneling as dominant Ohmic contact mechanism

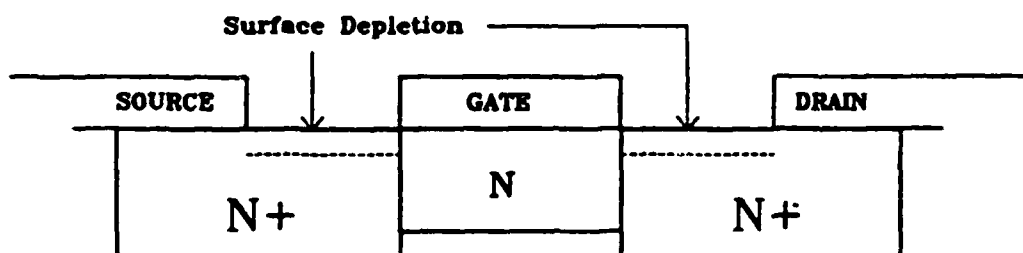
Refractory Silicide Contacts for Self-Aligned GaAs MESFETs

**T. Jackson
J. DeGelormo
G. Pepper
D. Basile (CMU)**

IBM

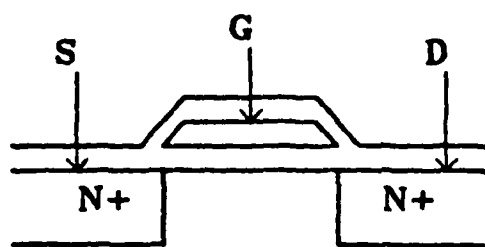
371

SELF-ALIGNED ENHANCEMENT MODE GaAs MESFET



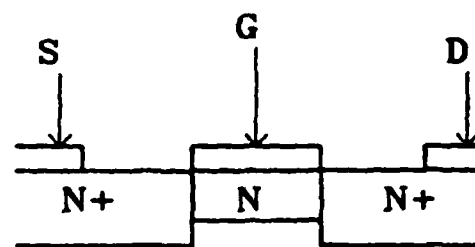
SI GaAs

SILICON GATE NMOS



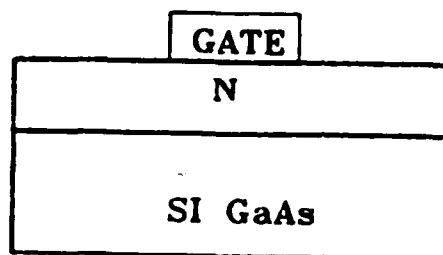
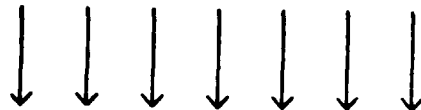
P-SILICON

SELF-ALIGNED GaAs MESFET



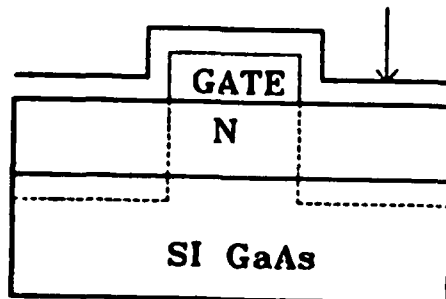
SI GaAs

N+ IMPLANT

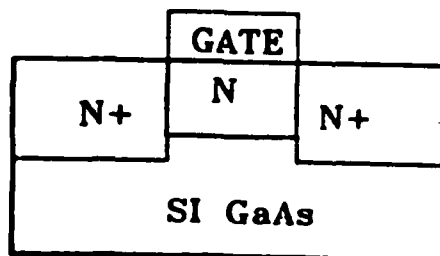


IMPLANT

ANNEAL CAP

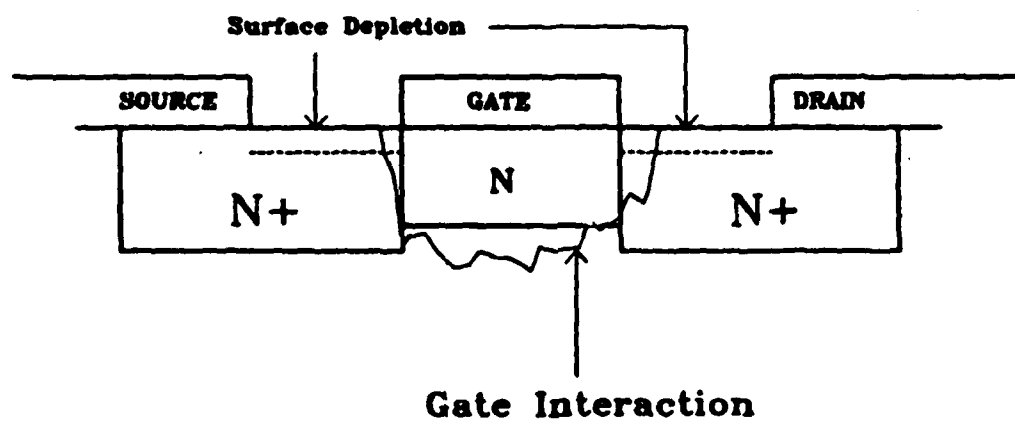


ANNEAL



SELF-ALIGNED

SELF-ALIGNED ENHANCEMENT MODE GaAs MESFET



SI GaAs

Refractory Gate Self-Aligned MESFET

Need a gate material that:

- **Can be patterned to small dimensions ($< 1 \mu\text{m}$).**
- **Can serve as a mask for the N⁺ self-aligning implant.**
- **Can survive the N⁺ implant activation anneal (800 - 1000° C, 1 sec. - 1 hr.) with stable barrier height, ideality and carrier concentration under the gate.**
- **Can survive As-rich anneal environment.**

Candidate Materials

- **Refractory Metals**
- **Silicides**
- **Nitrides**
- **Borides**
- **Carbides**
- **Et Ceterides**

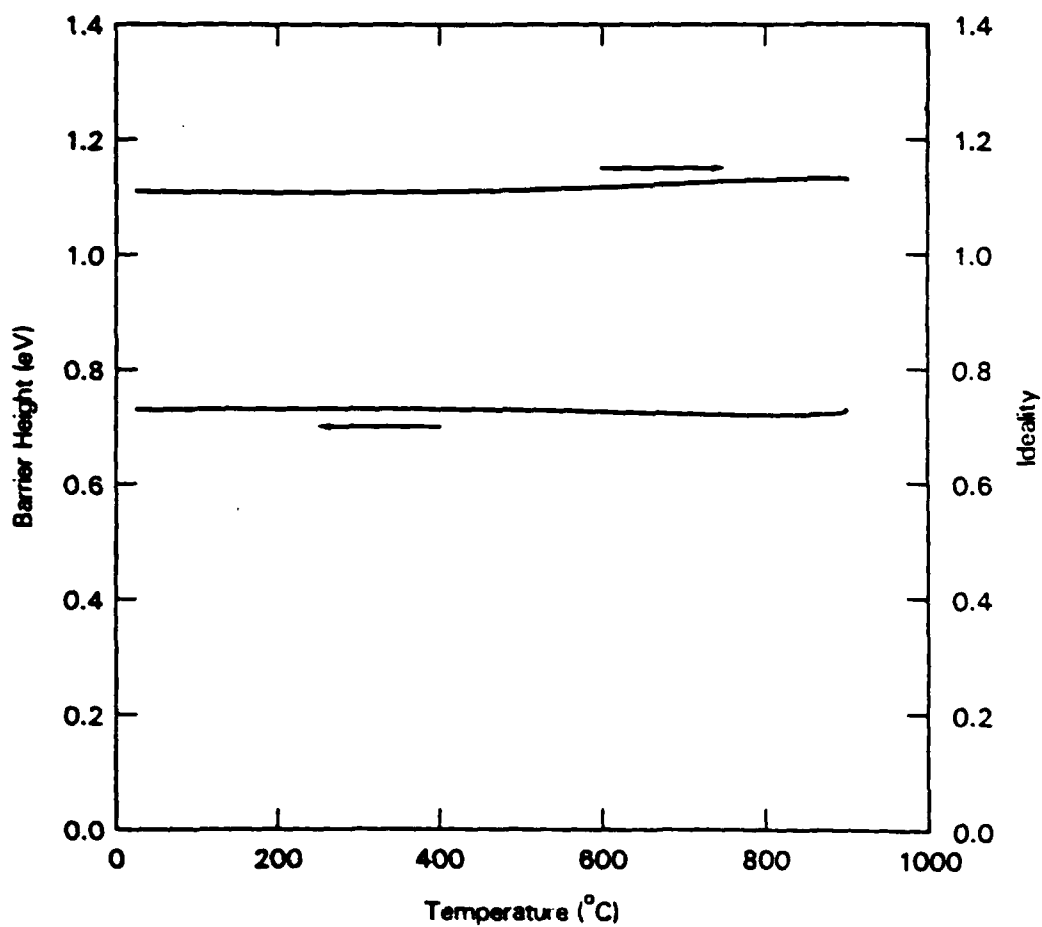
W/Si

- Pure W has large, columnar grain structure either as deposited or after moderate anneal (grains size $\sim$ film thickness). Interacts strongly with GaAs above $\sim 600^{\circ}$ C although FETs can be made by RTA.
- Many intentional or unintentional impurities (e.g. Al, O₂, N, Si). give drastically reduced grain size and reduce interaction between such films and GaAs.
- Use of Si as grain refiner also allows formation of stable refractory phases: W₅Si₃, W₃Si.

W/Si

- Easily etched to submicron dimensions (RIE).
- Dense film. Thin films useful as ion implant mask.
- "Good" films show amazing thermal stability on GaAs.
- Relatively stable in As-rich annealing environment (arsine atmosphere anneals okay).
- Acceptable film resistivity.

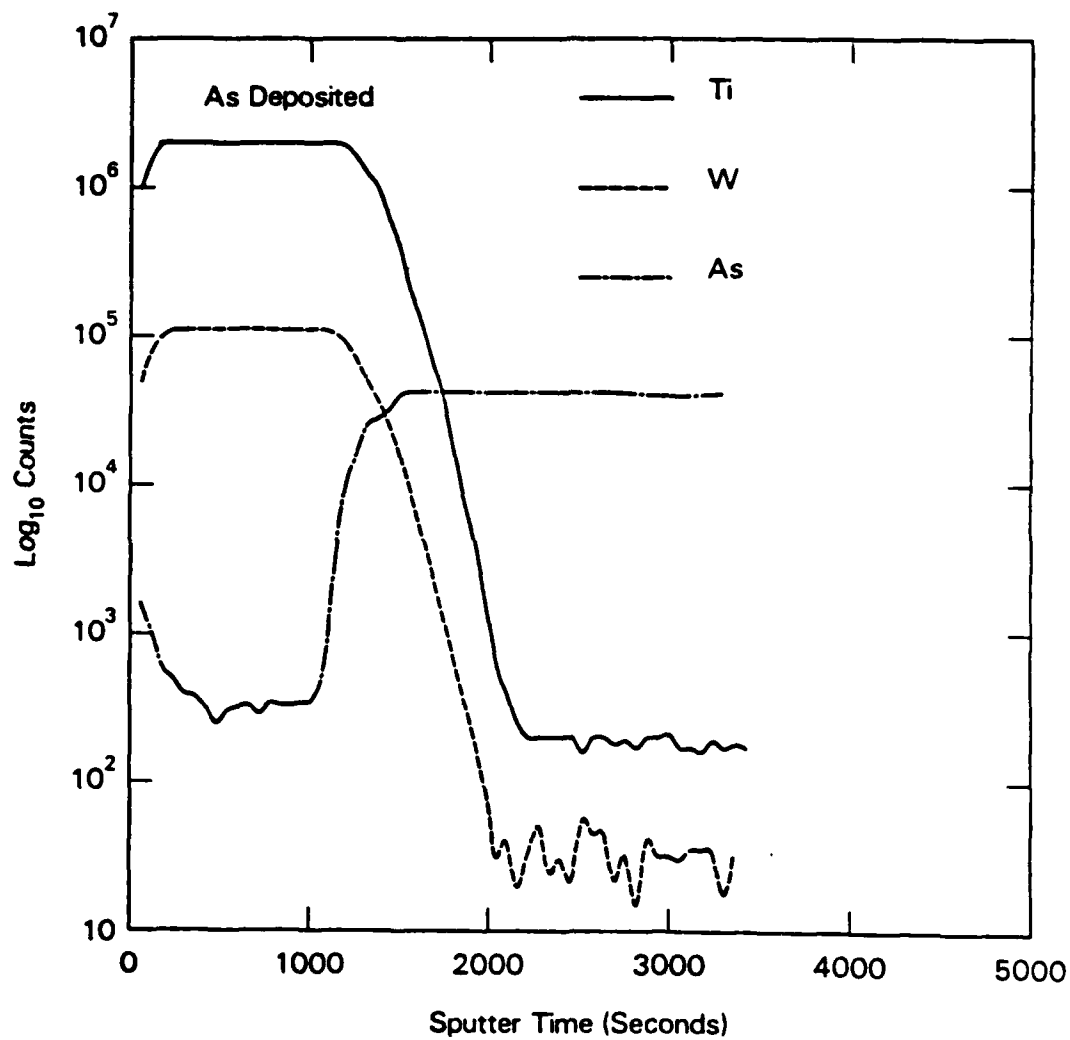
I-V: Ti/W



380

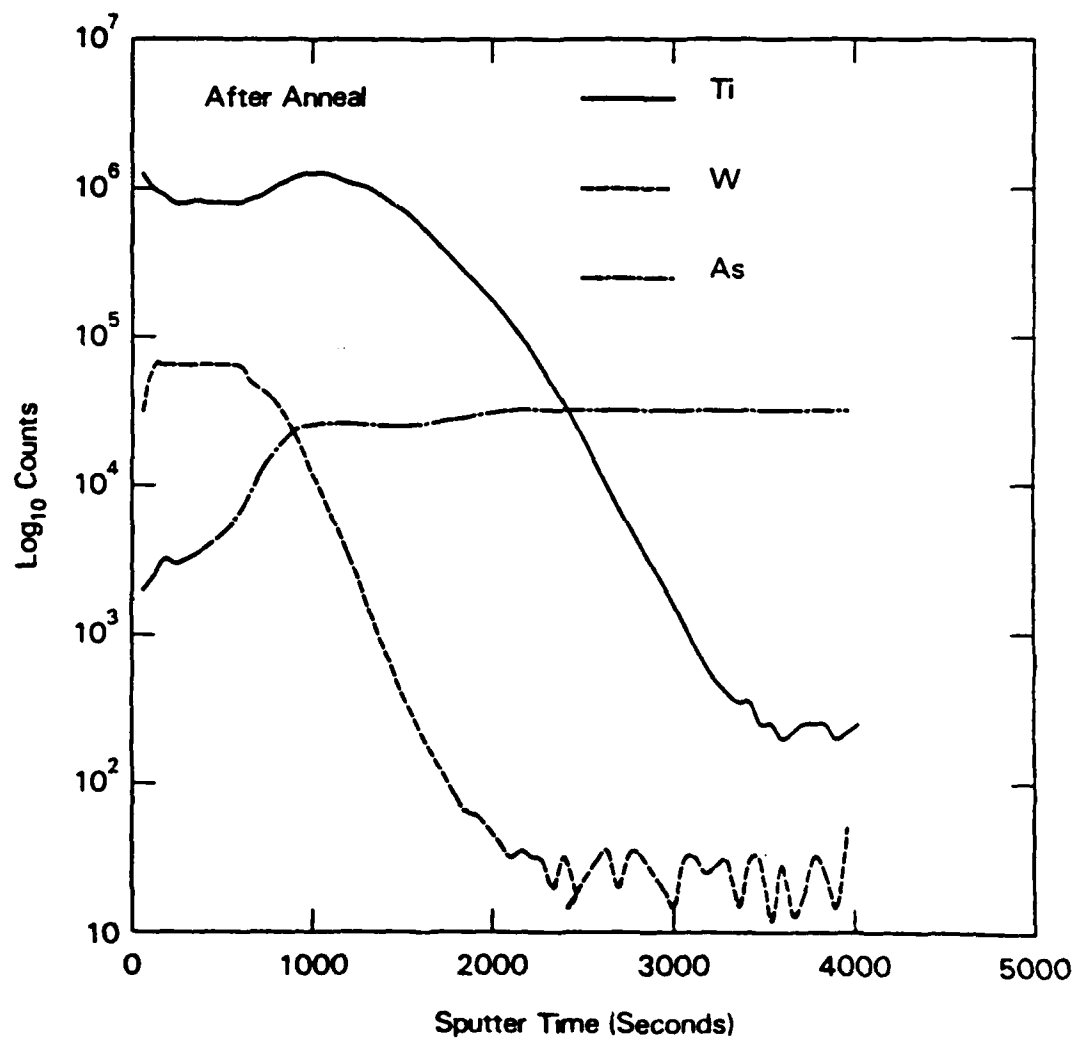
10/86 (T. Jackson)

SIMS: Ti/W Film



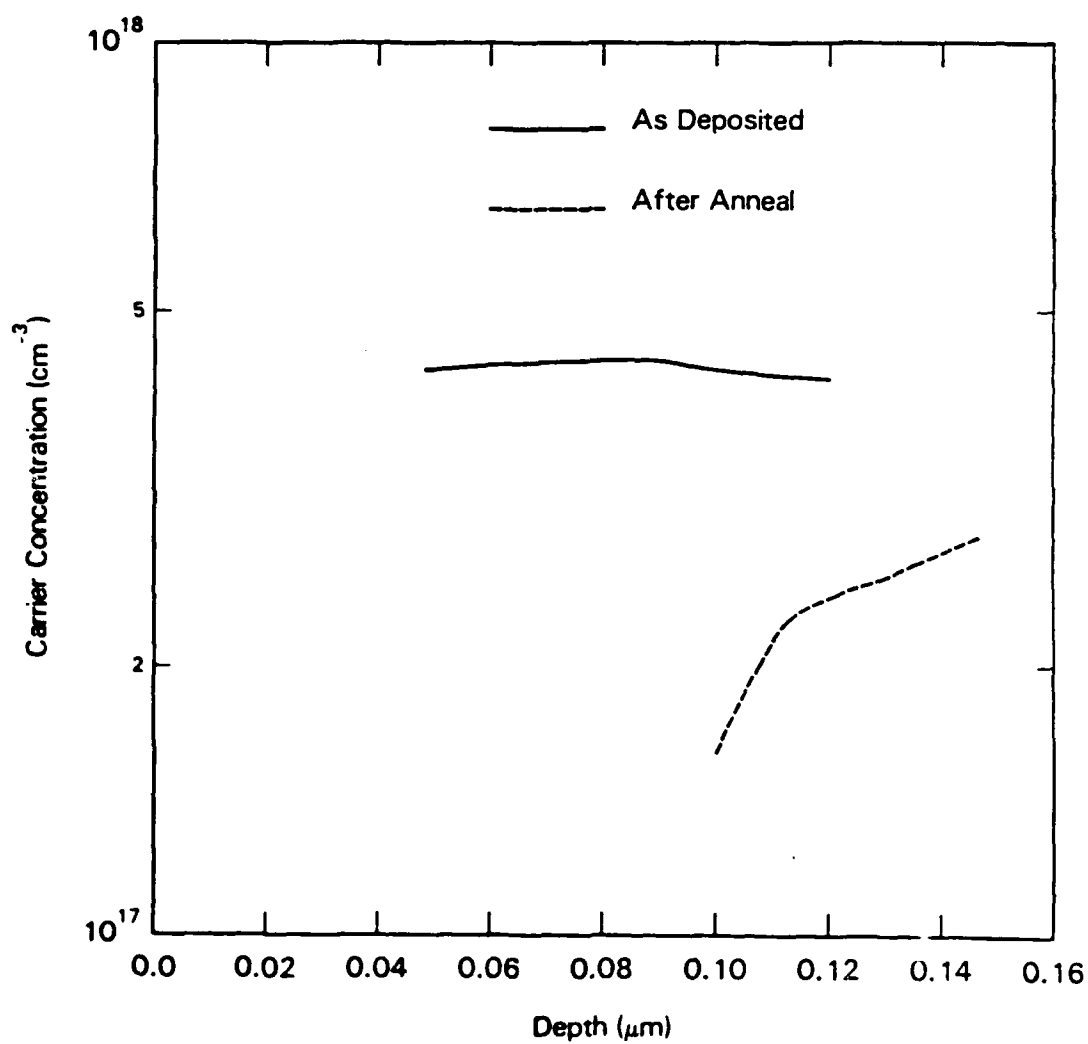
As Deposited

SIMS: Ti/W Film



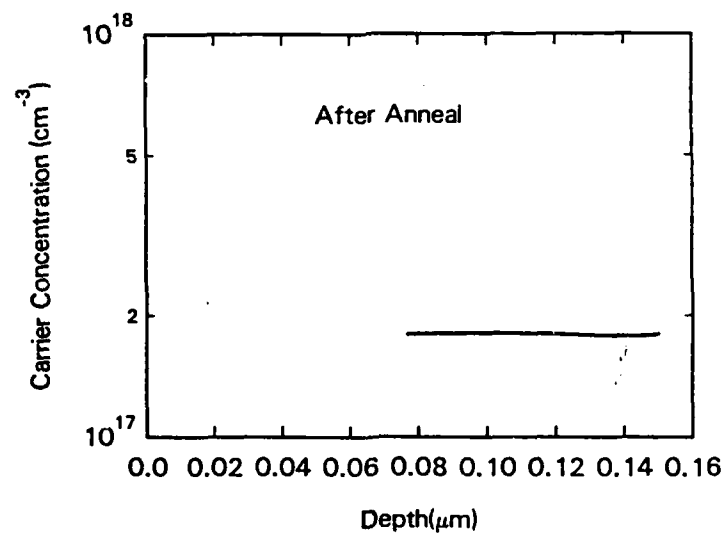
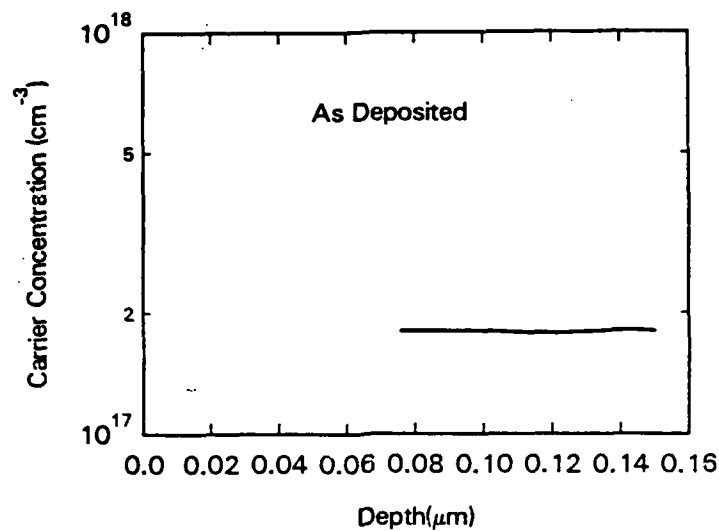
Annealed: 850° C, 15 min.

C-V: Ti/W



As deposited and after 850° C, 15 min. anneal

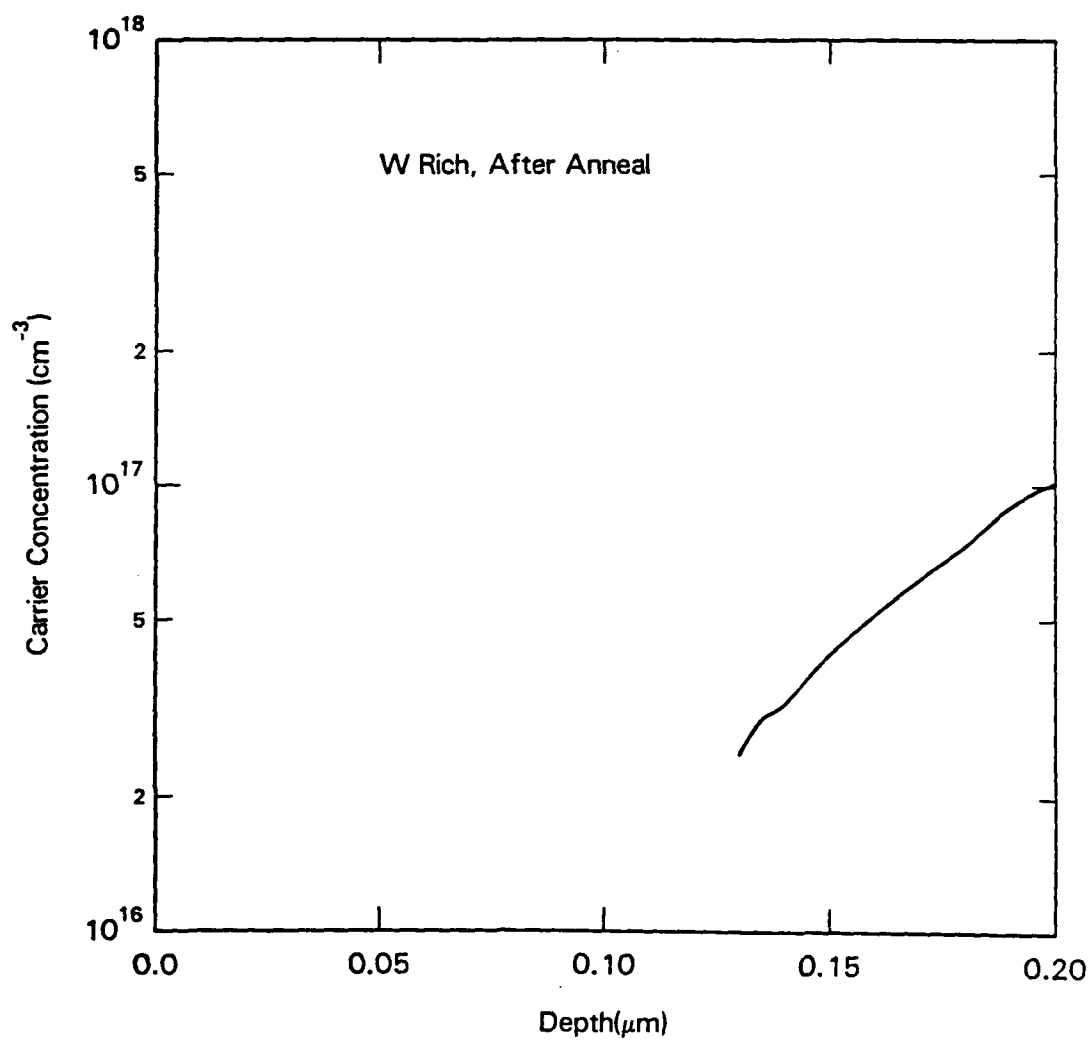
C-V: "Good" W/Si



Annealed: 850°C , 20 min.

$\sim\text{W}_3\text{Si}$

C-V: W Rich W/Si

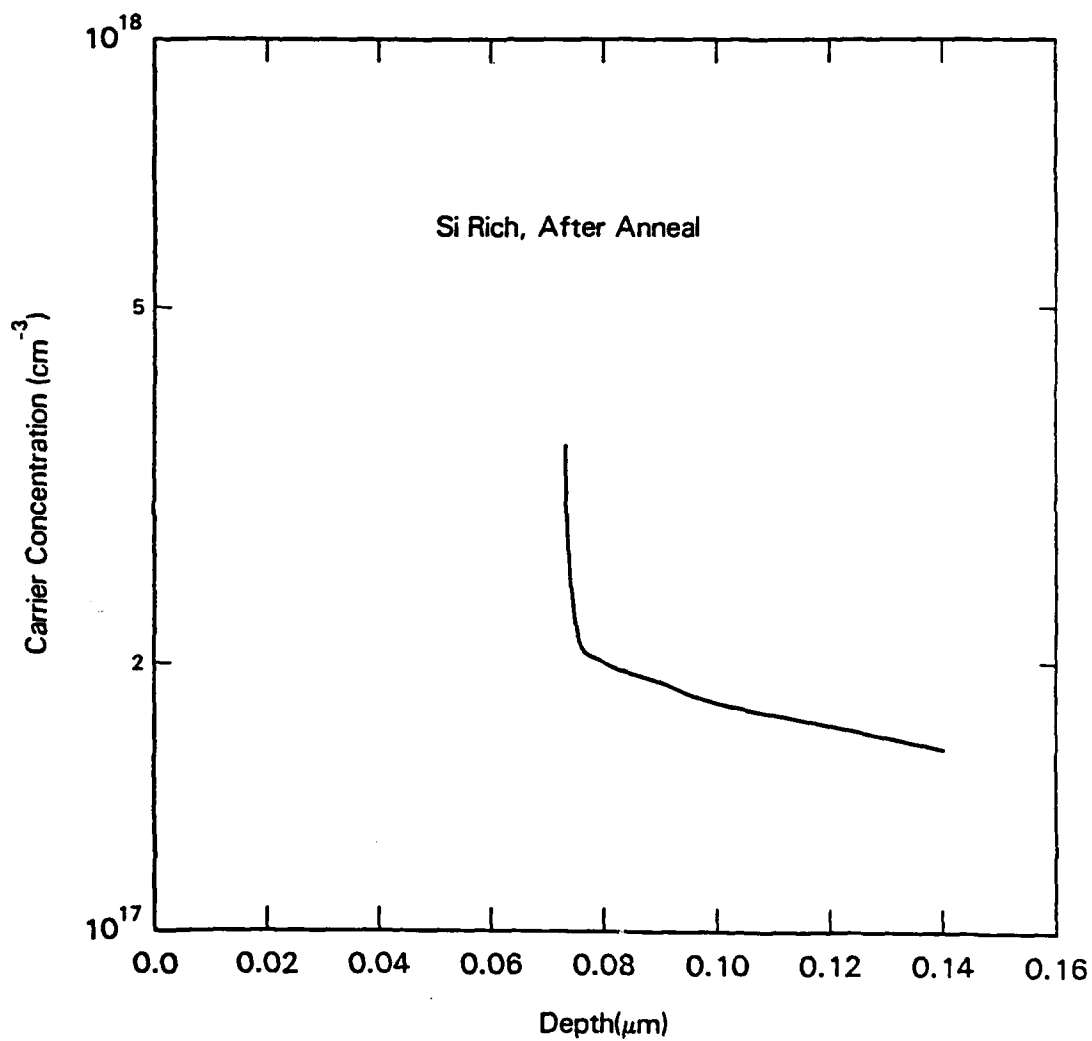


Annealed: 850° C, 20 min.

385

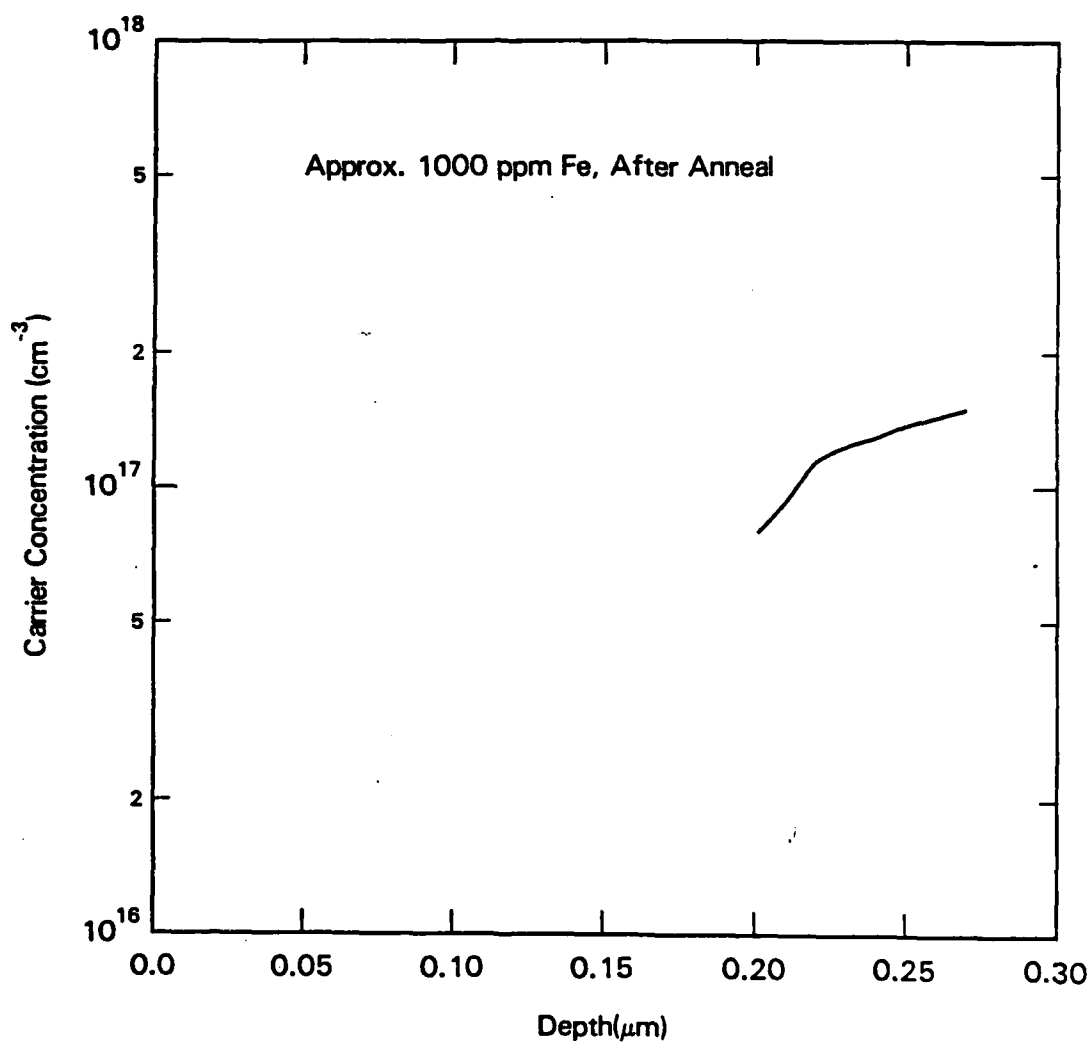
10/86 (T. Jackson)

C-V: Si Rich W/Si



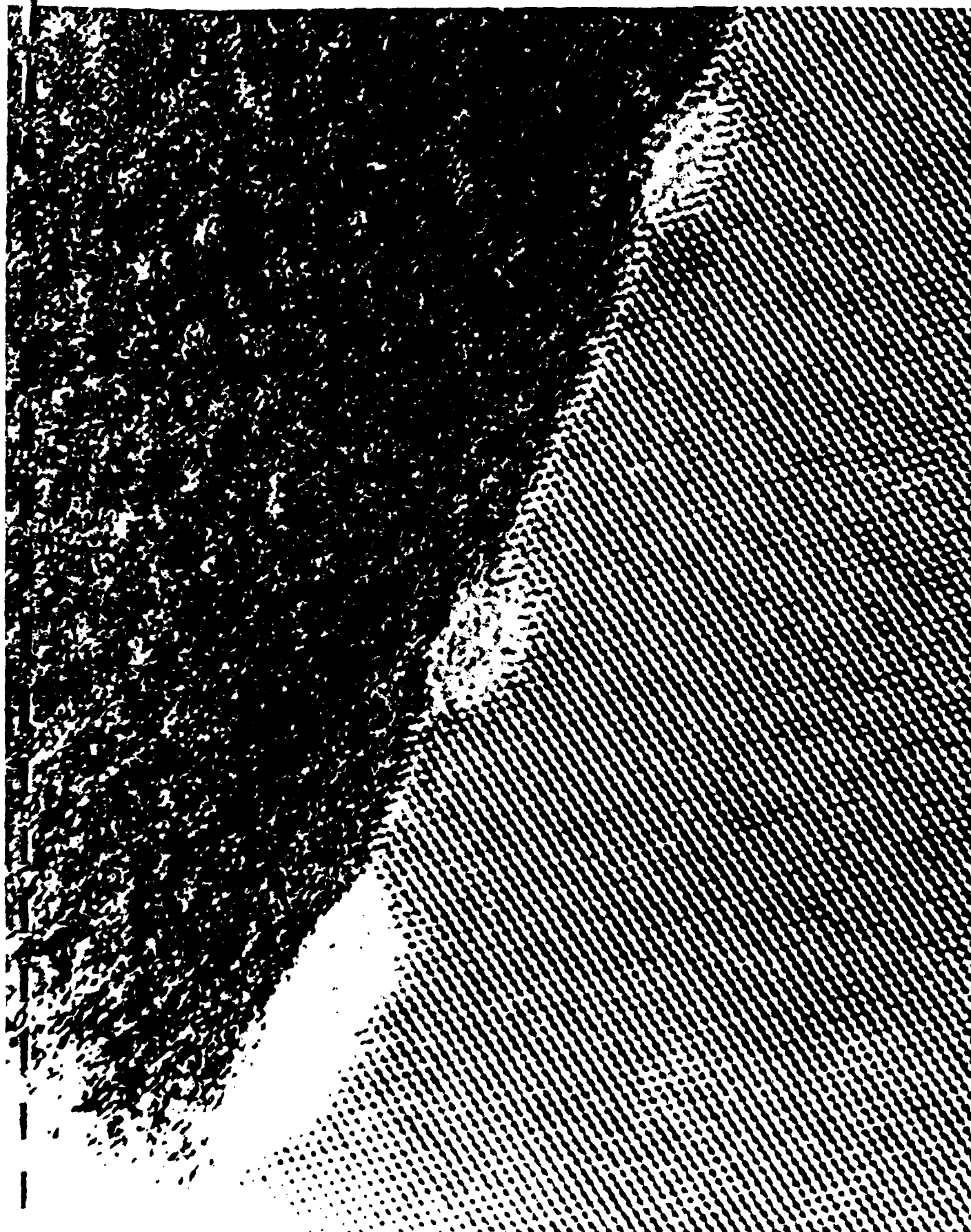
Annealed: 850° C, 20 min.

C-V: Fe Contaminated W/Si



Annealed: 850° C, 20 min.

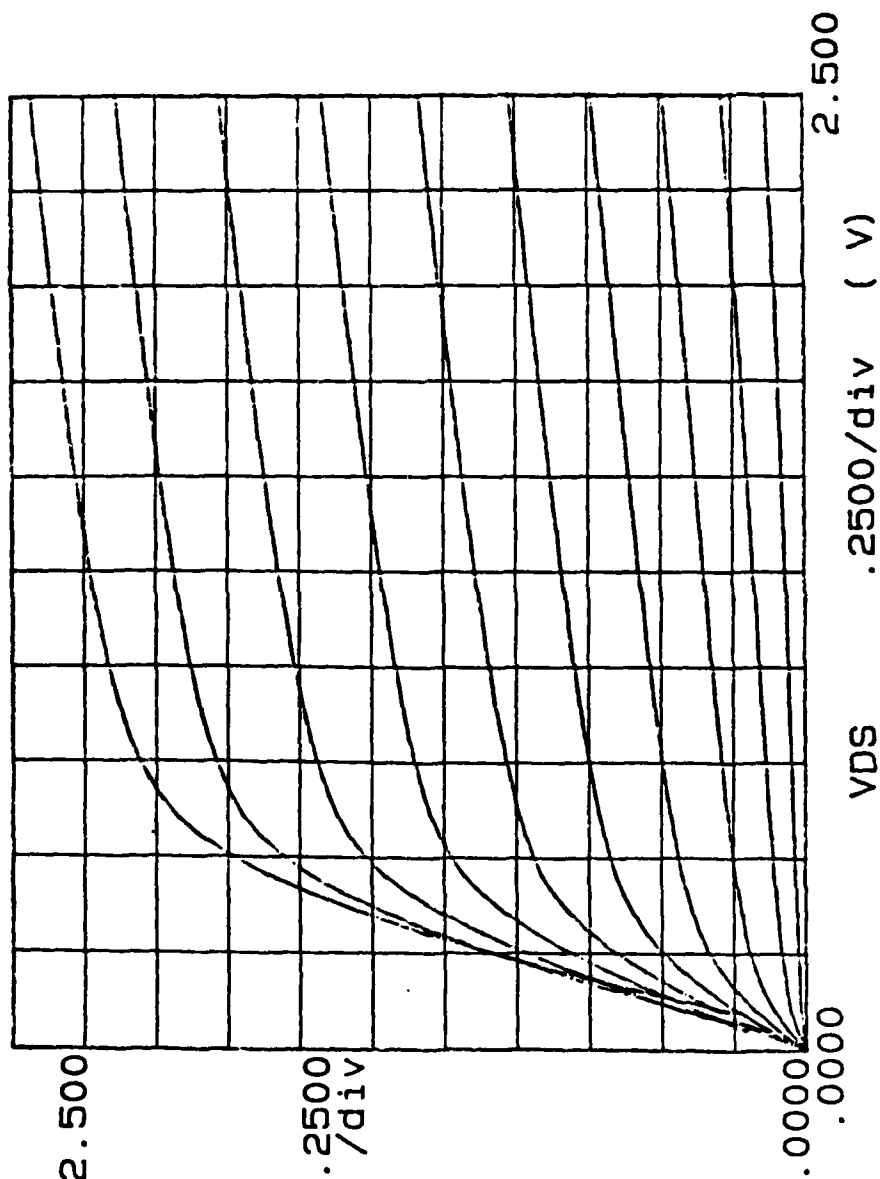




390

***** GRAPHICS PLOT *****

ID (mA)

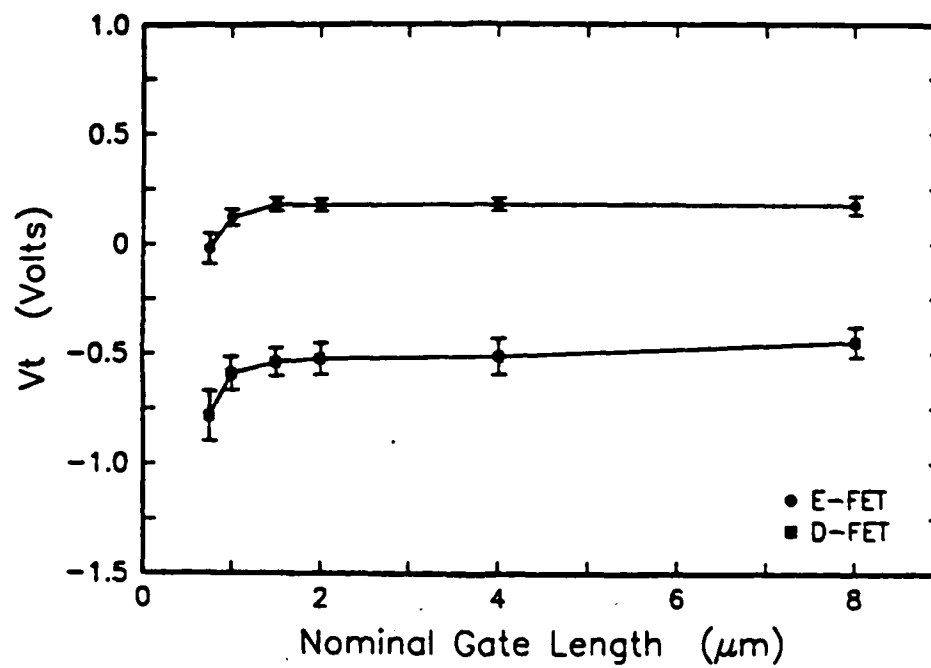


Variable1:
VDS -Ch2
Linear sweep
Start .0000V
Stop 2.5000V
Step .0500V

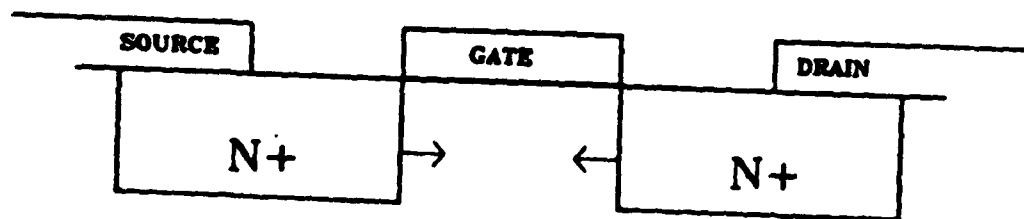
Variable2:
VGS -Ch3
Start .0000V
Stop .8990V
Step .1000V

Constants:
VS -Ch1 .0000V

Short Channel Effects



**"No-Channel"
FET**



SI GaAs

V_t for "No-channel" MESFETs

0.4 micron thick W/Si gate MESFETs with no channel implant. N⁺ implant = $5 \times 10^{13}/\text{cm}^2$. Anneal 800° C, 10 min.

Gate Length	Threshold Voltage

0.25 micron	-2.0 V

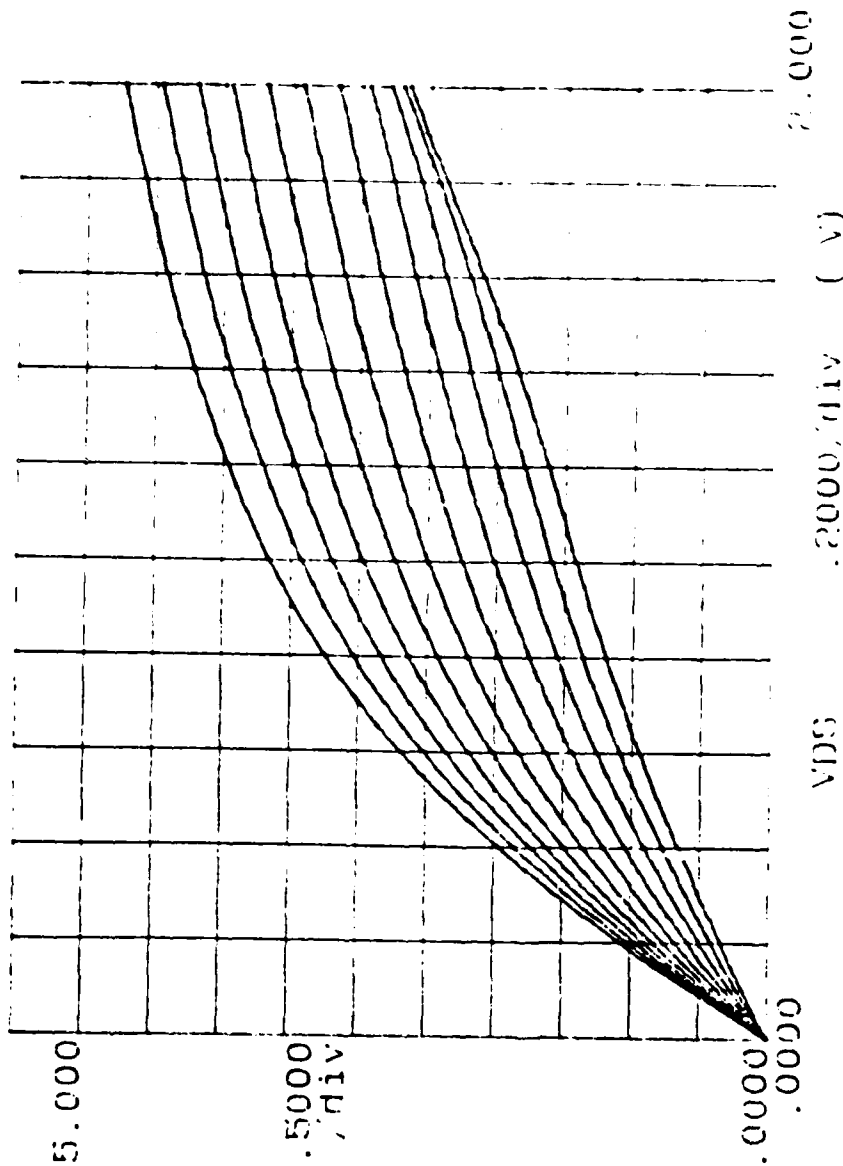
0.5 micron	+0.5 V

1.0 micron	+1.0 V

Companion structures with W/Si removed prior to anneal showed only small conduction even at 0.25 micron gate length.

***** GRAPHICS PLOT *****
 2.2 .2*10 NO CHANNEL

ID (mA)



Variable1:
 VDS -Ch2
 Linear sweep
 Start .0000V
 Stop 2.0000V
 Step .0500V

Variable2:
 VGS -Ch3
 Start .0000V
 Stop -2.0000V
 Step -2000V

Constants:
 VS -Ch1 .0000V

4000 μ w/s:

Stress Effects

- FETs with no channel implant.
- Short channel effects for convention MESFETs.
- Interacting silicide films show enhanced interaction at pattern edges.
- Samples annealed without capping dielectric and insufficient As overpressure show preferential As loss near gate edge.

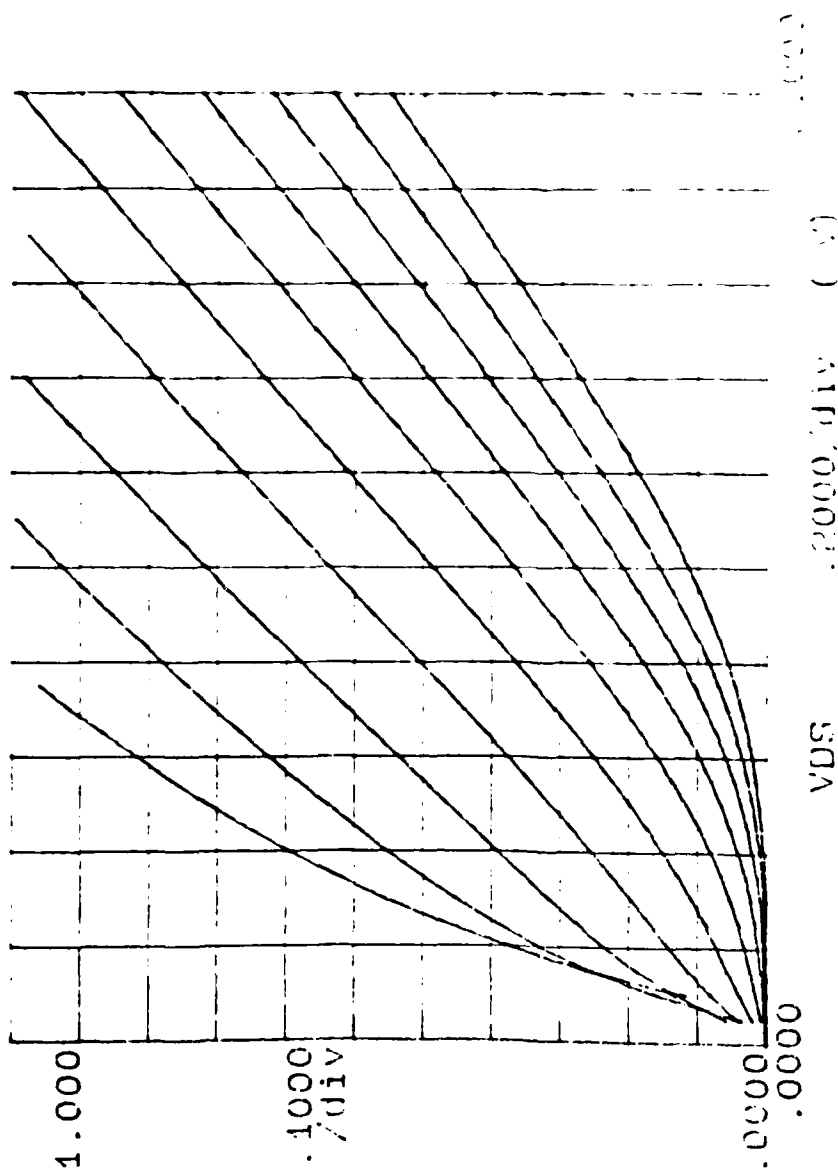
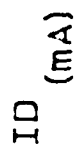
→ Flash Anneal

→ One step farther from equilibrium

***** GRAPHICS PLOT *****

0.5×10^{-4} 800°C - 10' Anneal

4000 A w/s;



Variables:

VD8 -CH2

Linear sweep

Start

8100

0025

-0000v

2.000V

.0500v

var1ab102:

vs -CH3

2025

STOP

5025

.0000v

0990.

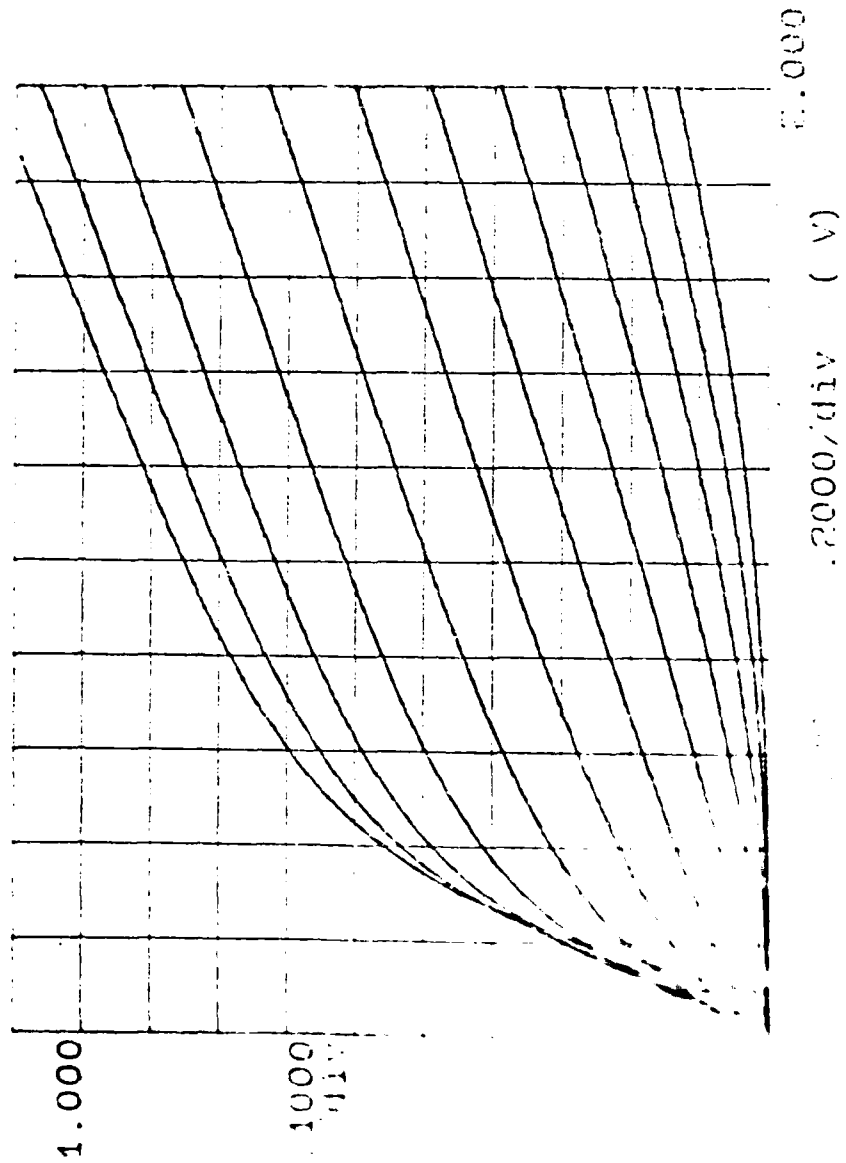
- 1000V

Contents:

VS -Ch1

***** GRAPHICS PLOT *****
 0.5x10_{um} 850°C - 6" Flash (Arlene)
 4000 Å w/s:

ID (mA)



Variable1:
 VDS -Ch2
 Linear sweep
 Start .0000V
 Stop 2.0000V
 Step .0500V

Variable2:
 VG -Ch3
 Start .0000V
 Stop 1.0990V
 Step .1000V

Constants:
 VS -Ch1
 .0000V

AD-A183 158

A WORKSHOP ON 3-5 SEMICONDUCTOR: METAL INTERFACIAL
CHEMISTRY AND ITS EFFECTS (U) STANFORD UNIV CA
W E SPICER ET AL. 05 NOV 86 N00014-87-G-0038

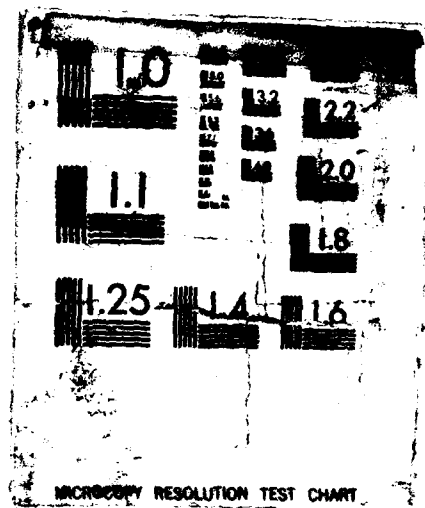
5/7

UNCLASSIFIED

F/G 20/12

NL

57



Flash Anneal

- Reduces short channel effects.
- Makes "bad" silicide look better.
- Makes silicide phase formation and silicide-GaAs interaction even harder to understand.

10/86 (T. Jackson)

Opinion

- Refractory gate materials exist that permit fabrication of self-aligned MESFET circuits at LSI level.
- Performance may be compromised by gate material limitations.
- Understanding of GaAs - refractory gate interface and interaction is rudimentary.
- "Realistic" problems difficult to attack; in general not being worked on much.
- Things will get tougher as channels become shorter and shallower.

Capacitance-voltage characterization of silicide-GaAs Schottky contacts

T. N. Jackson and J. F. DeGelormo

IBM, T. J. Watson Research Center, Yorktown Heights, New York 10598

(Received 5 June 1985; accepted 25 July 1985)

Capacitance-voltage carrier concentration profiling has been used to investigate the high temperature stability of refractory metal silicide films on GaAs. This technique is more sensitive to silicide-semiconductor interactions than is forward I - V characterization since tenacious surface Fermi level pinning of GaAs can yield stable diode barrier height and ideality factor measurements even for some cases of gross silicide-semiconductor interaction. Using C - V characterization we have found tungsten silicide film compositions that exhibit excellent high temperature stability on GaAs and have suggested failure mechanisms for other less stable film compositions.

INTRODUCTION

High-performance GaAs MESFET circuits fabricated using refractory gates to allow self-alignment offer attractive process simplicity. However, such processes require excellent stability of the refractory gate material on GaAs after high temperature (~ 800 – 1000°C) anneals. To date, silicide films, particularly W-Si films, have been used most successfully for this purpose. However, in contrast to the silicide films used in silicon technology, the films used for GaAs technology have usually had compositions near W_3Si_3 , not WSi_2 . Also, the films used for GaAs technology are deposited at the desired composition since there is neither opportunity nor desire to react with the substrate. Because of this only a small fraction of the knowledge gained from the study of silicide films on silicon is applicable to the study of silicide films on GaAs.

EXPERIMENTAL

Previous workers^{1,2} have concentrated on diode I - V characteristics as a means for evaluating the stability of silicide films on GaAs. This is somewhat surprising since the device of interest, the MESFET, uses the depletion layer characteristics of the diode, and since it is well known that the GaAs surface Fermi level position is tenaciously pinned near the middle of the forbidden region for a wide variety of surface interactions and anneals.^{3,4} It is suggested that C - V is a more useful tool for evaluating the electrical stability of silicide (and other) films on GaAs. To illustrate this, Fig. 1 shows the apparent stability of a Ti-W-Si film deposited on Si-doped GaAs ($n \sim 4 \times 10^{17}/\text{cm}^3$) by magnetron sputtering from Ti-W and Si targets. As can be seen, there is no significant change in barrier height or ideality as determined by diode forward I - V characteristics, even for anneals at temperatures as high as 900°C . The urge to call this a stable film and claim no interaction with the GaAs is strong. However, C - V measurements show that this film is not stable, at least in the sense required for successful use as a self-aligned MESFET gate. Figure 2 shows the results of C - V carrier concentration profiling for the films of Fig. 1 before and after an 850°C , 20 min anneal. The C - V measurements were done using a 1 MHz capacitance meter and a computer-controlled data acquisition system. For each measurement the capacitance

was measured in reverse bias only, and the value of carrier concentration found nearest the sample GaAs-silicide interface is for zero bias. Before anneal the results show a carrier concentration near the surface of about $4 \times 10^{17}/\text{cm}^3$ and a zero bias depletion depth of about 50 nm. After the 850°C anneal the sample shows a marked reduction in carrier concentration near the surface and the zero-bias depletion depth has increased to about 100 nm. Since a typical channel thickness for self-aligned MESFET's is 50–200 nm, this amount of interaction is not negligible.

The results of SIMS measurements on the Ti-W-Si films of Figs. 1 and 2 are shown in Figs. 3(a) and 3(b). Figure 3(a) shows the composition profile for the as-deposited film. Figure 3(b) shows the SIMS composition profile for the film after an 850°C , 15 min anneal. There is obviously substantive movement of Ti into the GaAs from the deposited film, and of As out of the GaAs and into the film. Although Figs. 2 and 3 show that the interaction of this Ti-W-Si film with GaAs is gross, the I - V results by contrast suggest film stability.

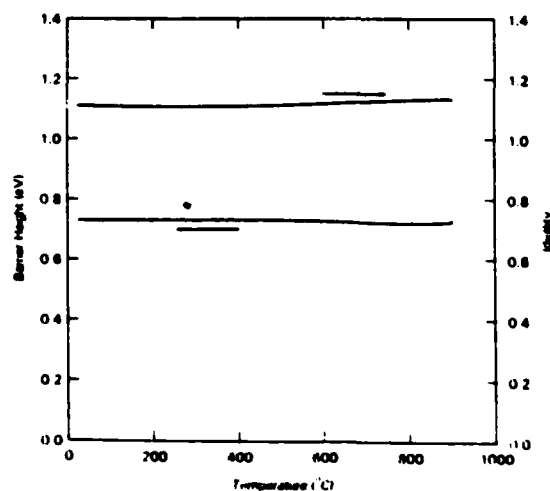


FIG. 1. Barrier height and ideality factor as a function of anneal temperature for Ti-W-Si diodes on bulk-doped GaAs ($n \sim 4 \times 10^{17}/\text{cm}^3$, 15 min anneal).

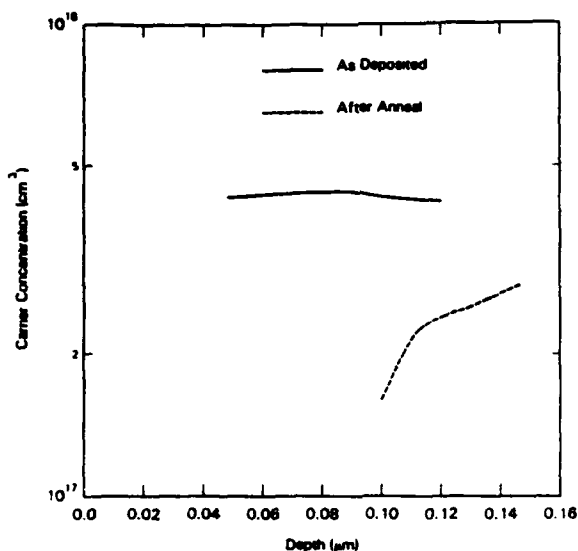


FIG. 2. C-V carrier concentration profiling results for Ti-W-Si diodes on bulk-doped GaAs before and after an 850 °C, 15 min anneal ($n \sim 4 \times 10^{17} / \text{cm}^3$).

Using C-V profiling as a sensitive measure of silicide-GaAs interaction we have characterized co-sputtered W-Si films as a function of composition. The films were sputter deposited from planar magnetron elemental sources with both sources depositing simultaneously onto a rotating substrate holder. The substrates were Si-doped GaAs with $n \sim 2 \times 10^{17} / \text{cm}^3$. Some previous workers¹ have had difficulty depositing a wide range of W-Si compositions because of stress (film failure) at some compositions. By using the

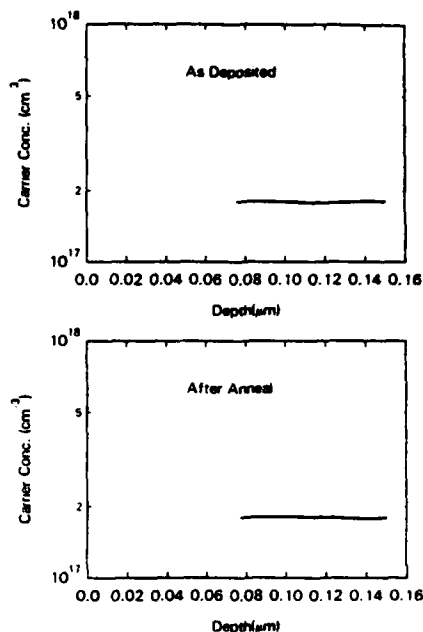


FIG. 4. C-V carrier concentration profiling results for a W-Si film with composition near W_3Si on bulk-doped GaAs ($n \sim 2 \times 10^{17} / \text{cm}^3$) before and after an 850 °C, 20 min anneal.

results of Ref. 5 (an "atomic peening" stress control model) we have had no difficulty in depositing films across the entire compositional range from pure W to pure Si with approximately constant film stress. After deposition, the films were patterned into diodes for C-V analysis by reactive ion etching with $\text{CF}_4 + \text{O}_2$ and then annealed in an anneal system that provides an arsenic overpressure to prevent GaAs decomposition.

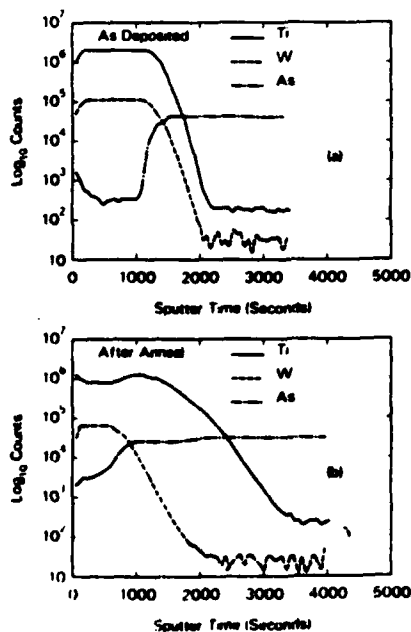


FIG. 3. SIMS profiles for a Ti-W-Si film on GaAs before and after an 850 °C, 15 min anneal.

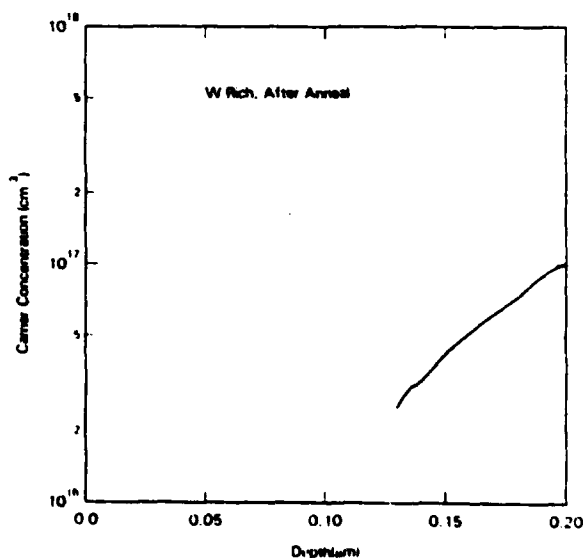


FIG. 5. C-V carrier concentration profiling results for a W-Si film with ~40 at. % W on bulk-doped GaAs ($n \sim 2 \times 10^{17} / \text{cm}^3$) after an 850 °C, 20 min anneal.

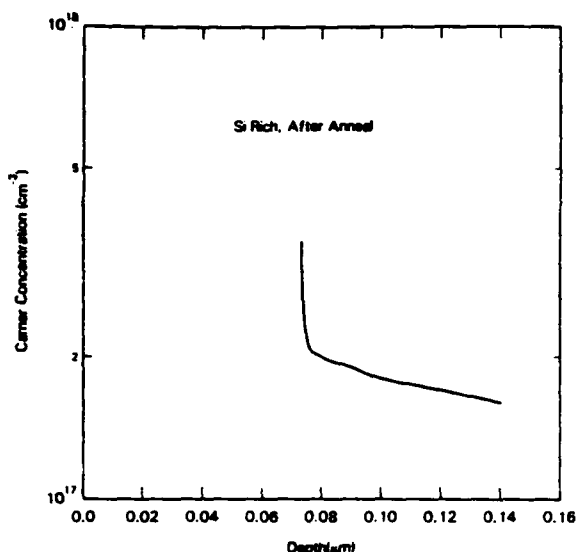


FIG. 6. C - V carrier concentration profiling results for a W-Si film with ~ 45 at. % Si on bulk-doped GaAs ($n \sim 2 \times 10^{17} / \text{cm}^3$) after an 850°C , 20 min anneal.

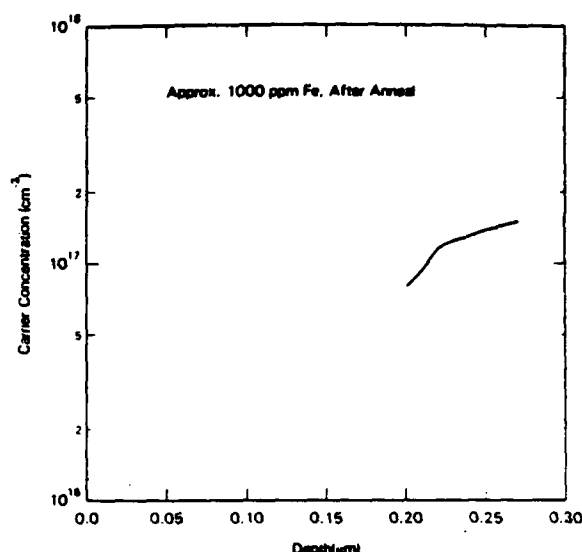


FIG. 7. C - V carrier concentration profiling results for a W-Si film with composition near W_3Si containing ~ 1000 ppm Fe on bulk-doped GaAs ($n \sim 2 \times 10^{17} / \text{cm}^3$) after an 850°C , 20 min anneal.

Figure 4 shows that W-Si films with excellent C - V stability can be obtained as described above. The results shown are for a film composition of approximately W_3Si . Such films also show excellent I - V characteristic stability, as expected. Other workers¹ have found stable W-Si films with about 37.5–39 at. % Si (W_3Si_2). While we also find that films of these compositions can be stable, the scatter in the C - V results is greater than for films near W_3Si . We have used W-Si films with compositions near W_3Si to fabricate GaAs MES-FET devices and circuits with excellent characteristics.

Figure 5 shows the C - V profile results for a film with large W content (~ 90 at. %) before and after an anneal at 850°C for 20 min. As can be seen, there is a large increase in zero-bias depletion width and significant carrier concentration decrease near the surface. I - V measurements showed only small changes in barrier height and ideality (0.02 eV and 0.1) after such anneals. Also, SIMS could not resolve any interaction between the deposited film and the doped GaAs. This is not wholly surprising, since the required interaction need only be of the order of the GaAs doping concentration ($\sim 2 \times 10^{17}$) and this level of interaction between a W-Si film and the GaAs substrate is difficult to probe by SIMS due to dynamic range difficulties.

Figure 6 shows C - V profiling results for a film with large Si content (~ 45 at. % Si) before and after an 850°C , 20 min anneal. Note that the zero-bias depletion depth for the annealed film is now decreased compared to the unannealed film and there is a significant enhancement of the carrier concentration near the surface. In this case, the I - V characteristics for the diode also showed large changes after anneal (~ 0.3 eV decrease in barrier height) and the diodes became "leaky" in reverse bias. These results are similar to those obtained for WSi_2 films and may indicate that Si diffuses into GaAs from W-Si films under some conditions.

DISCUSSION

The above results show some trends for interaction between W-Si and GaAs. There are three main regions of interest: a high Si content regime that exhibits C - V characteristics consistent with Si diffusion into GaAs, a high W regime that shows doping concentration reduction near the silicide-GaAs interface perhaps due to W diffusion, and an intermediate region of relative film stability. It is expected that the boundaries between these regions will be soft, with fine variations for small composition changes. This is expected due to the nature of the film formation process. Consider: The silicide films as-deposited are nearly amorphous (x-ray diffraction analysis shows only slight coordination). The films are then annealed and react to form polycrystalline W-Si of varying phase or phases depending at least on composition and anneal. It is likely that the interaction phenomena for such films are strong functions of the kinetics of the silicide formation which is in turn a function of many variables such as the details of the anneal conditions and impurities in the deposited films. Also, it is known that the diffusion of Si into GaAs is a strong function of the arsenic pressure in the anneal system.⁶

It is also quite possible to have impurities present in W-Si films whose presence can have as large an effect on film stability as major changes in film composition. For example, Fig. 7 shows the C - V profiling results before and after an 850°C , 20 min anneal for a film with the same W-Si composition as that of Fig. 4, but with about 1000 ppm Fe added to the film. It can be seen that this small addition of Fe has caused a change in zero-bias depletion width of almost 100 nm! This is particularly alarming since it is known that silicide sputtering targets may contain several impurities in amounts as high as 100 ppm.⁷

CONCLUSION

Stable refractory metal silicide films are important components of some high-performance self-aligned GaAs MES-FET fabrication processes. While film formation technology has been adequate to date to allow progress with these processes, the details of film stability are poorly understood. Improvements in characterization and analysis of silicide films with compositions far from WSi_2 should be fruitful.

¹T. Ohnishi, N. Yokoyama, H. Onodera, S. Suzuki, and A. Shibatomi, Appl. Phys. Lett. 43, 601 (1983).

²W. F. Tseng and A. Christou, IEDM Tech. Dig. 1982, 174.

³J. M. Woodall and J. L. Freeouf, J. Vac. Sci. Technol. 19, 794 (1981).

⁴W. E. Spicer, P. W. Chye, P. R. Skeath, C. Y. Su, and I. Lindau, J. Vac. Sci. Technol. 16, 1422 (1979).

⁵D. W. Hoffman and J. A. Thornton, J. Vac. Sci. Technol. 20, 355 (1982).

⁶G. R. Antell, Solid-State Electron. 8, 943 (1965).

⁷S. C. Liang, J. Vac. Sci. Technol. B 2, 714 (1984).

404

MOVPE GROWTH OF III-V MATERIALS AND INTERFACES

T.F. Kuech
IBM T.J. Watson Research Center
Yorktown Heights, N.Y.

- I. Introduction - MOVPE Growth**
- II. Bulk Growth of GaAs**
- III. Growth of V-V' Alloys**
- IV. Doping**
- V. Summary**

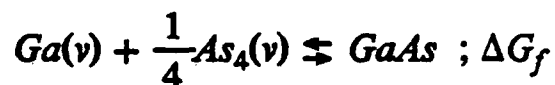
IBM

10/86 (T.F. Kuech)

405

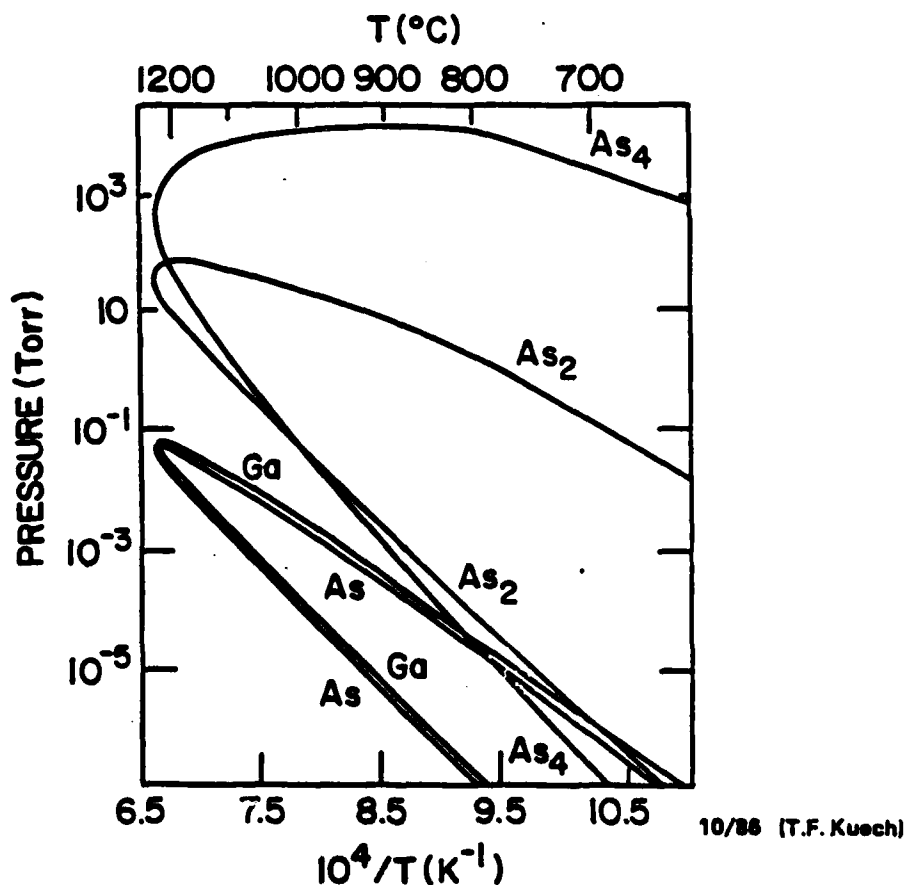
GaAs and Crystal Growth

At Thermal Equilibrium



$$K_{eq}^{-1} = P_{Ga}^o P_{As_4}^o{}^{\frac{1}{4}}$$

- The Ga and As activities (pressures) are interdependent and can assume a range of values.



Crystal Growth and Thermodynamic Equilibrium

For crystal growth to occur, a supersaturation must be present in the growth ambient.

$$P_{Ga} P_{As_4}^{\frac{1}{4}} > P_{Ga}^o P_{As_4}^{o\frac{1}{4}}$$

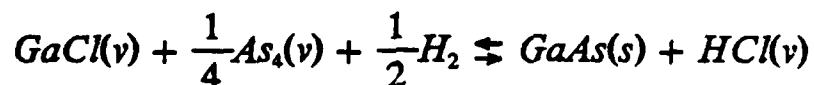
In CVD this supersaturation is due to the decomposition of reactive chemical precursors.

- Near Equilibrium
 - small supersaturation
 - fast reaction kinetics

- Liquid Phase Epitaxy



- Halide Growth



- Growth chemistry far from chemical equilibrium

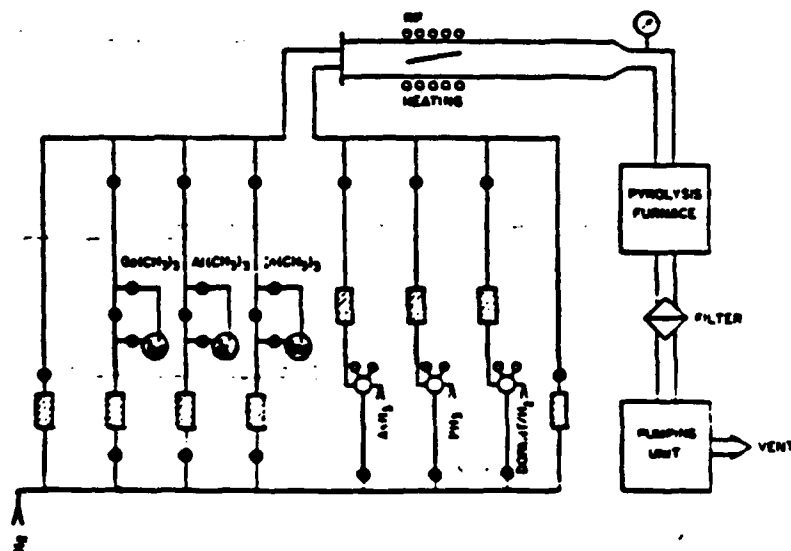
Metal-organic Vapor Phase Epitaxy

IBM

10/86 (T.F. Kuech)

MOVPE Growth

An open tube, cold wall epitaxial growth Technique which utilizes metal-organic and hydride growth precursors in a H_2 or N_2 carrier gas.



Growth Conditions

Growth Rate	$= 0.5 - 6.0 \mu\text{m/hr}$
Growth Rate	$\propto X_{MO}$
Gas Composition:	
Metal-Organic	$X_{MO} \approx 10^{-3} - 10^{-6}$
Hydride	$X_{Hydride} \approx 5 - 100 X_{MO}$
P_{reactor}	$= 0.01 - 1 \text{ atm.}$
Growth Temperature	$= 550 - 800^\circ\text{C}$
Carrier Gas	$H_2, N_2, \dots$

IBM

10/86 (T.F. Knecht)

MOVPE Growth Precursors

A wide variety of growth precursors are available increasing the versatility of this growth technique.

An ideal vapor source should possess:

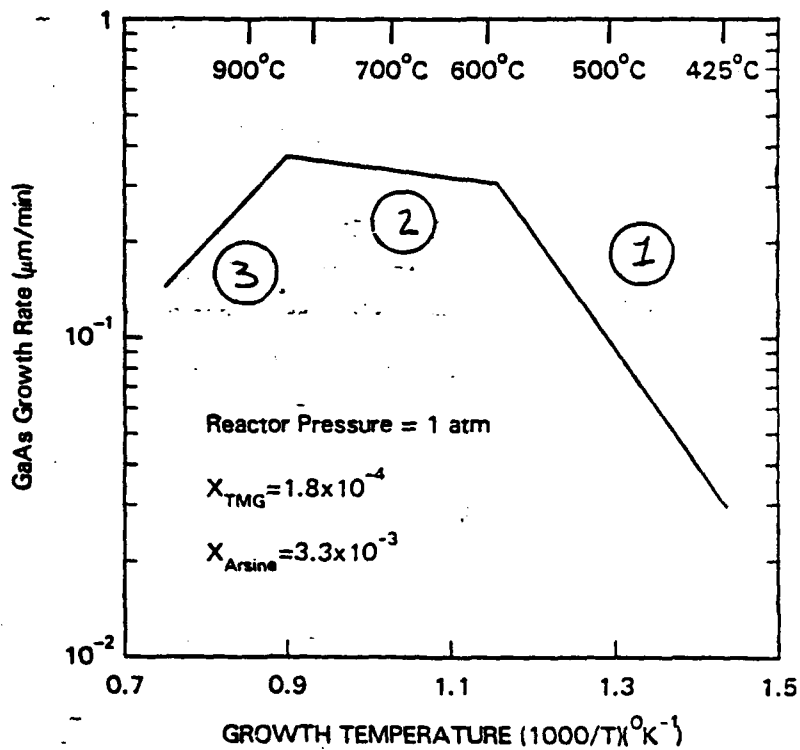
- Adequate vapor pressure
- Suitable purification routes
- Suitable pyrolysis temperatures (RT stability)
- No interaction with growth apparatus
(Stainless steel, ..)
- Appropriate reaction routes during growth

<u>Cation Source</u>	<u>Anion Source</u>	<u>Compound Semiconductor</u>
$\text{Ga}(\text{CH}_3)_3$	AsH_3	$\left\{ \begin{array}{l} \text{GaAs} \\ \text{Al}_x\text{Ga}_{1-x}\text{As} \\ \text{GaAs}_y\text{P}_{1-y} \\ \text{Al}_x\text{Ga}_{1-x}\text{P} \\ \text{In}_x\text{Ga}_{1-x}\text{Sb} \end{array} \right.$
$\text{Ga}(\text{C}_2\text{H}_5)_3$	$\text{AsH}(\text{C}_2\text{H}_5)_2$	
$\text{Al}(\text{CH}_3)_3$	+ PH_3	
$\text{Al}(\text{C}_2\text{H}_5)_3$	$(\text{CH}_3)_3\text{PH}_2$	
$\text{In}(\text{CH}_3)_3$	$\text{Sb}(\text{CH}_3)_3$	

IBM

10/88 (T.F. Kuech)

Temperature Dependence



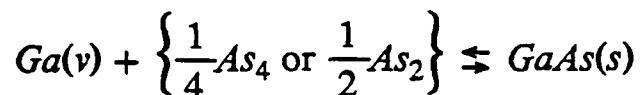
1. Chemical Kinetic Limitation
2. Gas Phase Mass Transport
3. Ga Desorption (?) with $P_{Ga} \approx P_{TMG}$

IBM

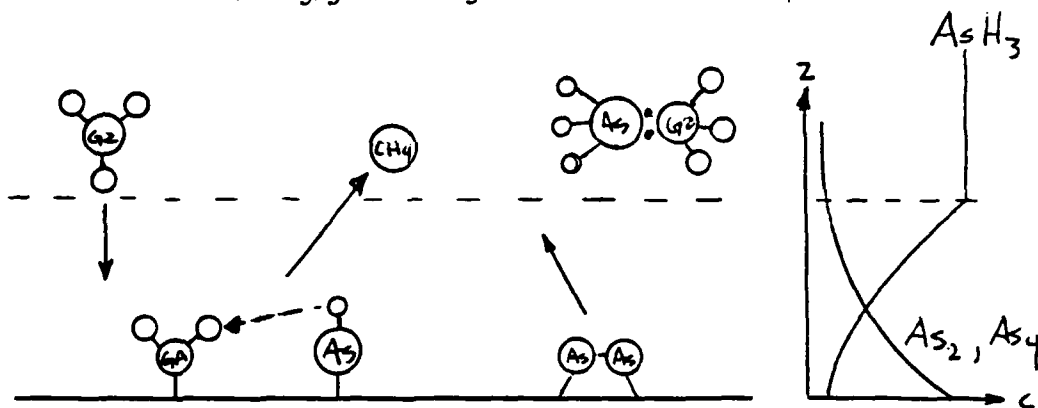
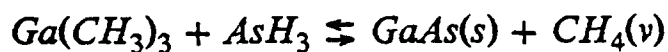
10/86 (T.F. Kuech)

Near the Growth Surface

Phase Equilibrium

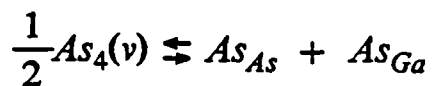
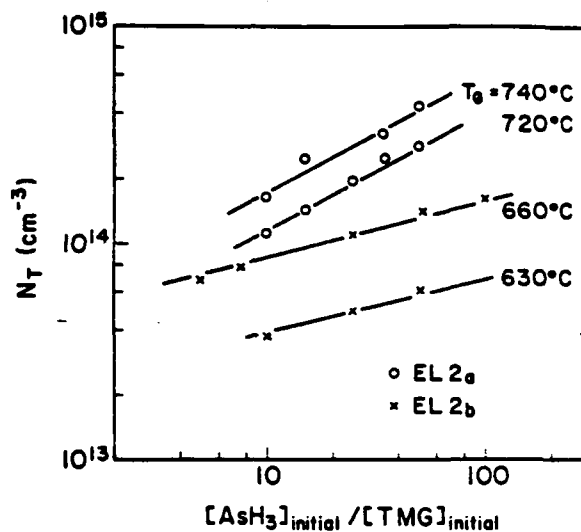


Chemical Equilibrium



- Gas Phase Reactions
- Metal-organics react to completion at or near surface
- As Activity determined by the generation of As(v) at the surface and diffusion of As(v) away from the surface.

Stoichiometric Defects



$$K_{eq} = [As_{Ga}] P_{As_4}^{-\frac{1}{2}}$$

$$[EL2] = [As_{Ga}] \propto P_{As_4}^{\frac{1}{2}}$$

M.O.Watanabe, A.Tanaka, T.Udagawa, T.Nakainsi, and Y.Zohta, Jap.J.Appl.Phys. Vol.22, (1983) 923.

IBM

10/86 (T.F. Kuech)

Growth Environment Interactions

Hetero-interfaces

III-III'

- residence time
- lattice matching
- large V partial pressures

V-V'

- kinetics of hydride decomposition
- thermodynamics
- residence time
- lattice matching

IBM

06/86 (T.F. Kuech)

III-III' Interfaces

Interface Structure:

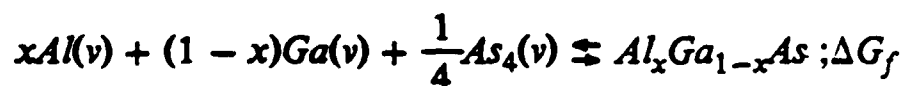
- Large P_v , $(\frac{V}{III}) > > 1$
- Growth rate limited by the mass transport of metal alkyl to the surface
- Interface abruptness
 - limited by the residence time, τ , of the reactants in the reactor
 - interface width, Δw
 $\Delta w \approx GR * \tau$
 - growth interruption; impurity accumulation at the interface
- Lattice mis-matched systems
 - 3-D or island nucleation
 - dislocations

IBM

10/86 (T.F. Kuech)

Al_xGa_{1-x}As-GaAs Interfaces

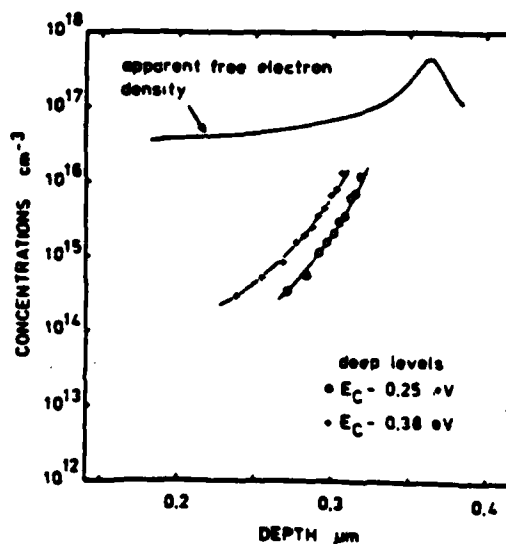
Deep Level and Defects



$$|\Delta G_f^o(AlAs)| > |\Delta G_f^o(GaAs)|$$

$$P_{Al}^o P_{As_4}^{o\frac{1}{4}} < P_{Ga}^o P_{As_4}^{o\frac{1}{4}}$$

- Changes in stoichiometry at fixed As activity
- Defect concentrations may change at interfaces
- Misfit dislocations in lattice mismatched materials



D.Allsop, A.R.Peaker, E.J.Thrush, and G.Wale-Evans, J.Crystal Growth Vol.68, (1984) 295.

V-V' Hetero-interfaces

Growth Environment

- Large $P_{V,V'}$ pressures
- Growth rate limited by mass transport of metal alkyl

Heterojunction Formation

- Rapid switching of all components
- Interface width, Δw , is determined by the residence time of reactants:

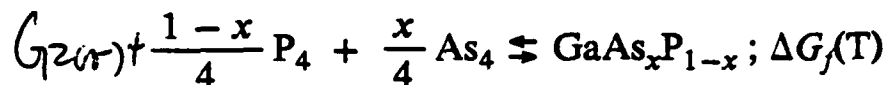
$$\Delta w \approx GR * \tau$$

- Interface structure may reflect changes in the local activity of the group V components.

IBM

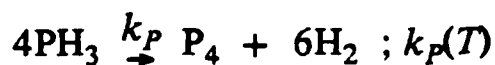
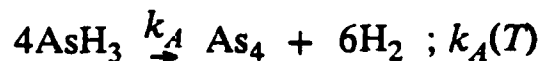
10/88 (T.F. Kuech)

Thermodynamics



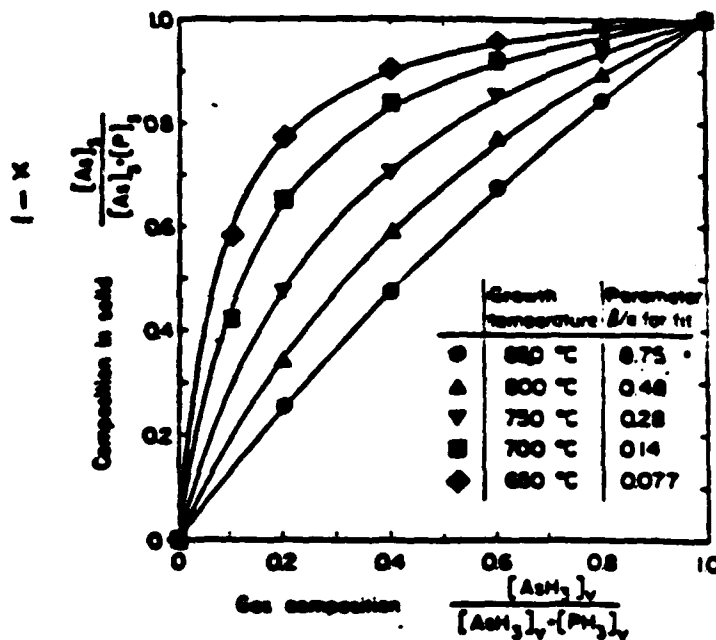
$$\frac{P_{G_2} P_{As_4}^{\frac{x}{4}} P_{P_4}^{\frac{1-x}{4}}}{a_{GaAs_xP_{1-x}}} = K_f(T)$$

Kinetics at the Growth Surface



Composition is a function of growth temperature and may vary over the surface due to local variations in As/P in the gas phase.

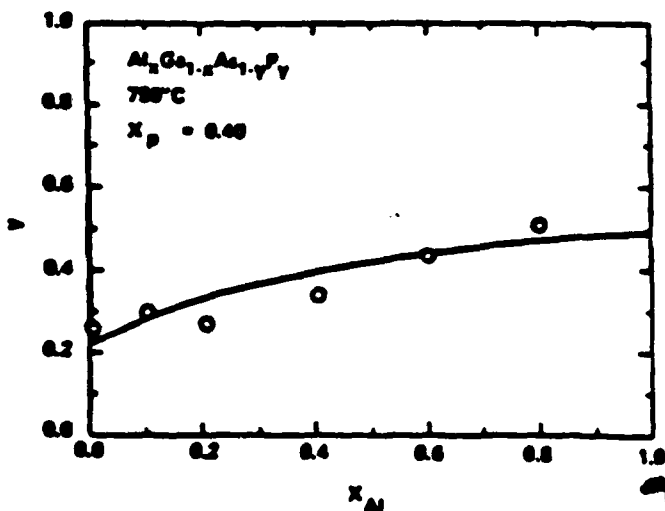
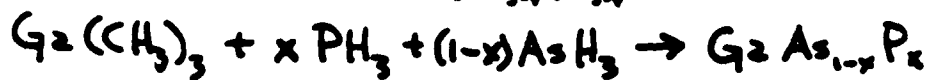
GaAs_{1-x}P_x



Incorporation Rate

$$x = \frac{1}{1 + \frac{\beta}{\alpha} \frac{P_{PH_3}}{P_{AsH_3}}}$$

- Kinetics of Decomposition
- Adsorption Rate



Influence of Alloy Composition

- Influences Decomposition Rate
- Thermodynamic Influences

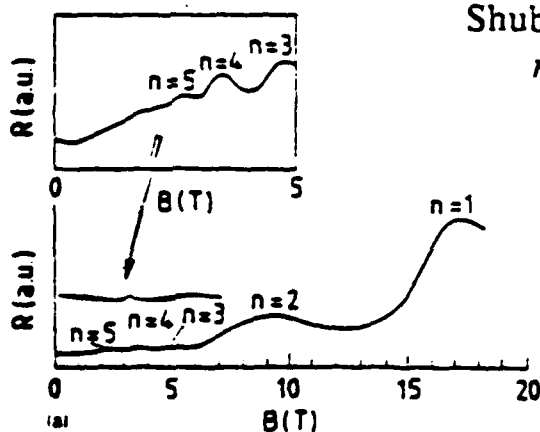
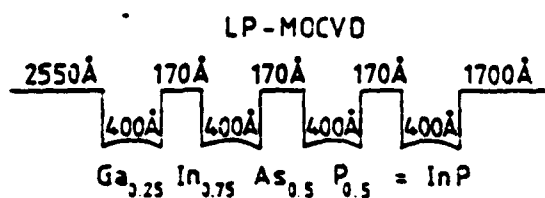
IBM

08/88 (T.F. Kuehn)

$\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}\text{-InP}$ Heterostructures

Multi-Quantum Wells

M. Razeghi, J.P. Duchemin, J.C. Portal
Appl. Phys. Lett. V26 (1985) 46.



Growth Conditions

Low Growth Rate $\sim 3 \text{ Å/sec}$

High Gas Velocity

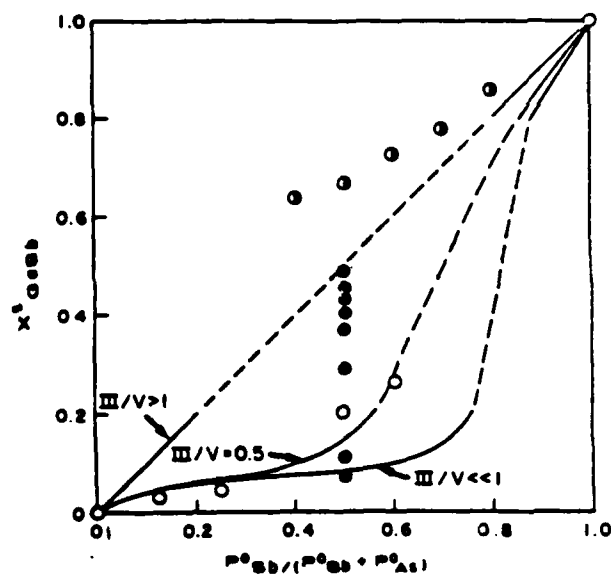
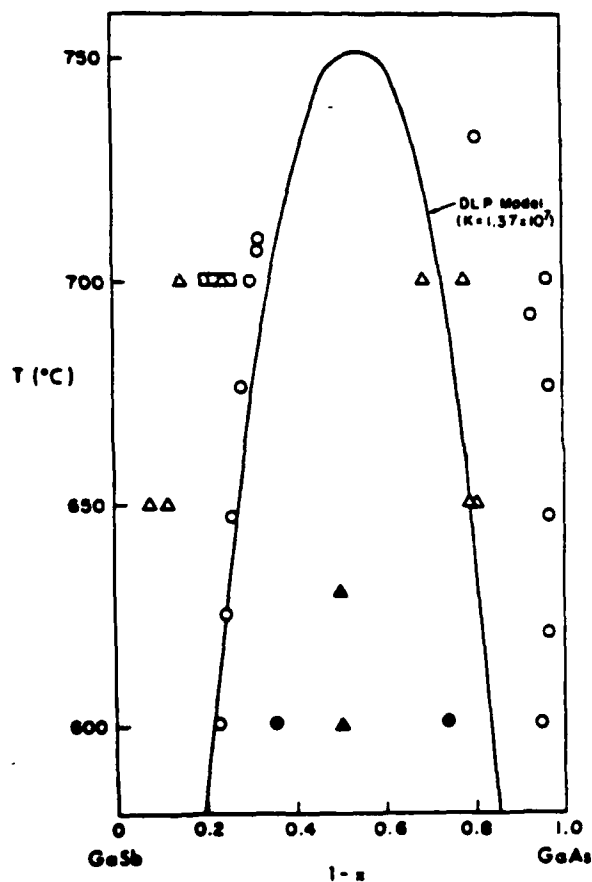
Continuous Growth

- residence time of gases $\sim 1 \text{ sec}$

IBM

08/86 (T.F. Kuech)

GaAs_ySb_{1-y} - Metastable Compositions



G.B.Stringfellow and M.J.Cherng, J.Crystal Growth Vol.64, (1983) 413.
 M.J.Cherng, G.B.Stringfellow, and R.M.Cohen, Appl.Phys.Lett. Vol.44, (1984) 677.

IBM

10/86 (T.F. Kuech)

Growth of $\text{GaAs}_y\text{Sb}_{1-y}$

Input Reactants Decomposed at the Growth Front

$$P_{\text{Ga}(\text{C}_2\text{H}_5)_3} \cong P_{\text{Ga}}, P_{\text{As}(\text{CH}_3)_3} \cong P_{\text{As}_4}, P_{\text{Sb}(\text{CH}_3)_3} \cong P_{\text{Sb}_4},$$

GaAs in $\text{GaAs}_y\text{Sb}_{1-y}$:

$$\frac{a_{\text{GaAs}}^s}{P_{\text{Ga}}^o P_{\text{As}_4}^{o \frac{1}{4}}} = K_{\text{GaAs}}$$

GaSb in $\text{GaAs}_y\text{Sb}_{1-y}$:

$$\frac{a_{\text{GaSb}}^s}{P_{\text{Ga}}^o P_{\text{Sb}_4}^{o \frac{1}{4}}} = K_{\text{GaSb}}$$

Composition:

$$y = \frac{P_{\text{As}_4} - P_{\text{As}_4}^o}{(P_{\text{As}_4} - P_{\text{As}_4}^o) + (P_{\text{Sb}_4} - P_{\text{Sb}_4}^o)}$$

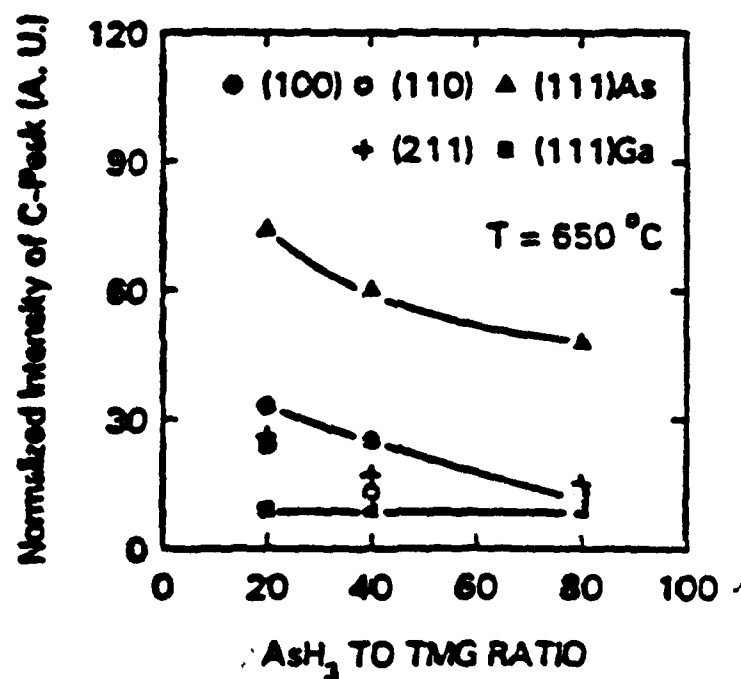
Stoichiometry:

$$(P_{\text{Ga}} - P_{\text{Ga}}^o) = 4(P_{\text{As}_4} - P_{\text{As}_4}^o) + 4(P_{\text{Sb}_4}^o - P_{\text{Sb}_4})$$

IBM

10/88 (T.F. Kuech)

Growth of GaAs from $\text{Ga}(\text{CH}_3)_3$ and AsH_3



- N_{carbon} $\Rightarrow$ increases with T_{growth}
- $\Rightarrow$ decreases with P_{arsine}
- $\Rightarrow$ increases with As surface site density

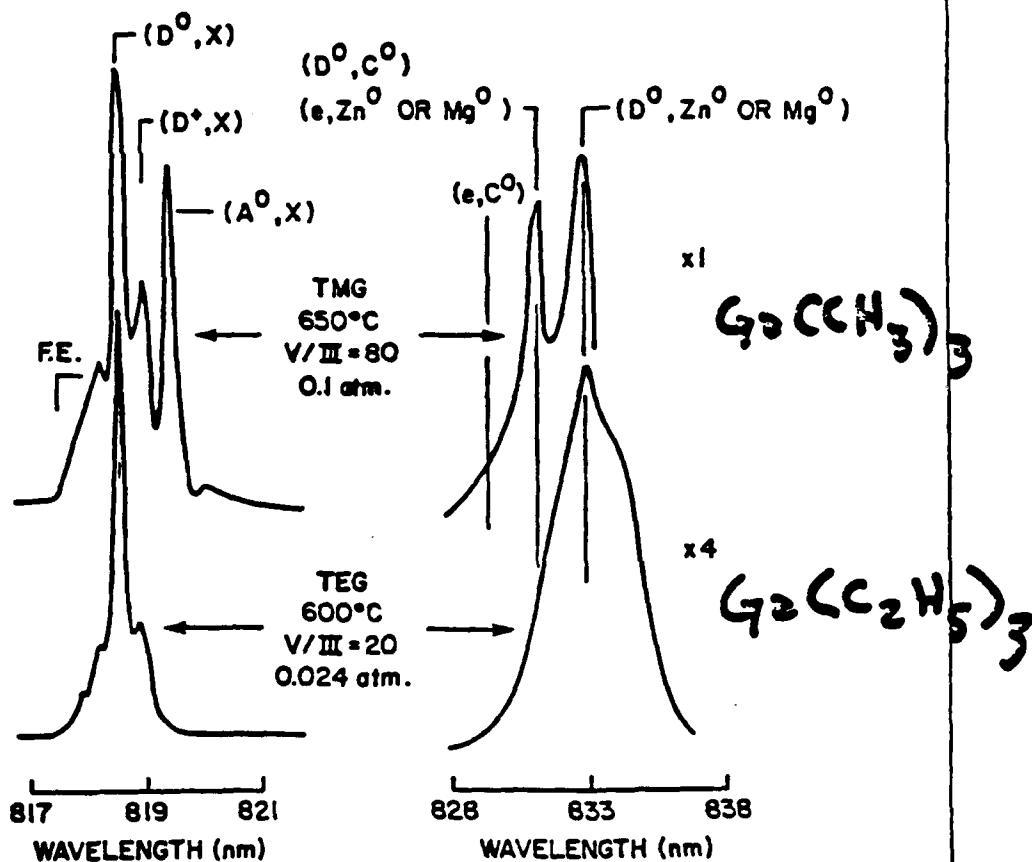
T.F.Kuech and E.Veuhoff, J. Crystal Growth, 68, 148(1984).

IBM

Carbon Reduction with the Ethyl Based Chemistry

Low Temperature (2K) Edge Luminescence

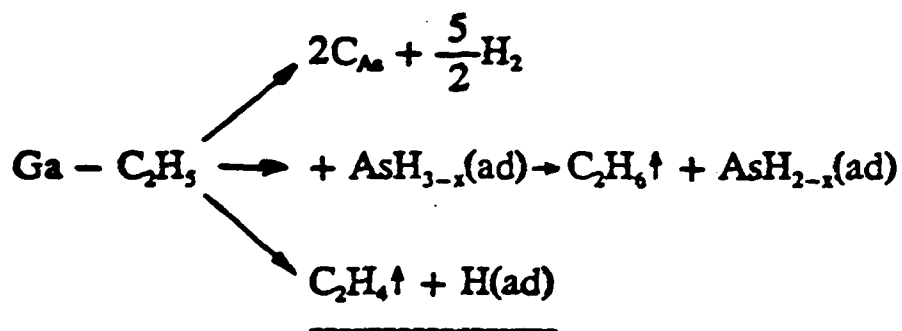
Low carbon content films are possible with the ethyl based chemistry. Zinc is then the dominant residual acceptor with these materials.



IBM

Ethyl Based MOVPE Growth

Possible Reaction Paths:



The use of larger hydrocarbon radicals:

1. weakens the metal-carbon bond
2. introduces new reaction paths for decomposition and carbon elimination.

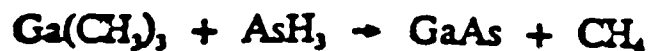
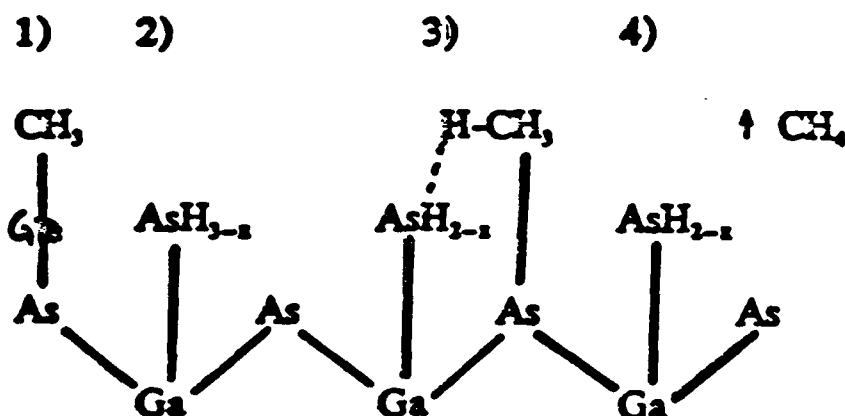
IBM-THORNTON

IBM

12/85 (T.F. Kuech)

Model of Carbon Incorporation for Methyl Based Growth of GaAs

1. Adsorption of CH_3 on As atoms
2. Adsorption of AsH_{2-x} on Ga atoms
3. Hydrogen Transfer Reaction
 $\text{CH}_3(\text{ad}) + \text{AsH}_{2-x} \rightarrow \text{CH}_4(\text{ad}) + \text{AsH}_{2-x}(\text{ad})$
4. Desorption of CH_4
 $\text{CH}_4(\text{ad}) \rightarrow \text{CH}_4(\text{g})$

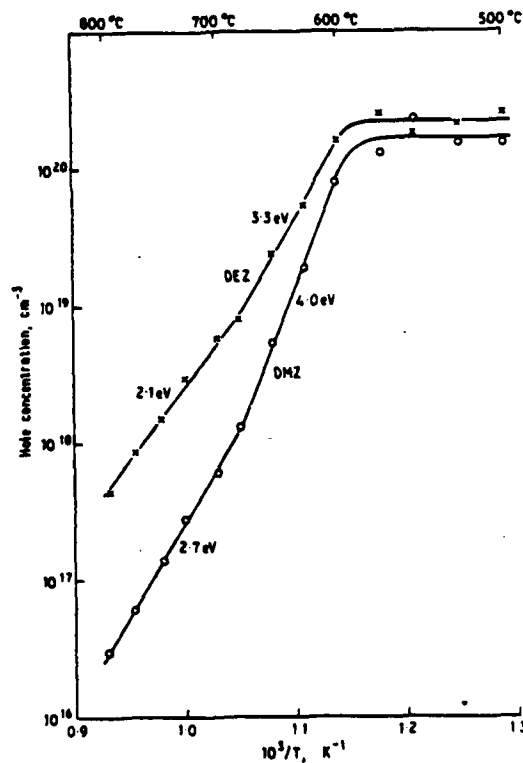


IBM

12/85 (T.F. Kuech)

Zinc Incorporation

Zinc has a high elemental vapor pressure at temperatures encountered in MOVPE growth. The Zn can interact with the growth environment with the subsequent Zn concentration in the solid being dictated by the Zn partial pressure above the growth surface.



R.W.Glew, J.Crystal Growth Vol.68, (1984) 44.

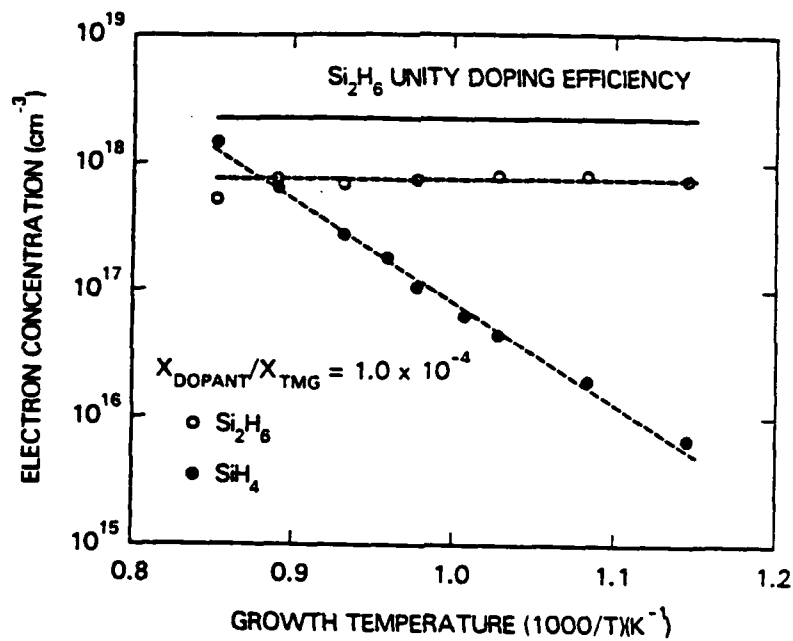
IBM

10/86 (T.F. Kuech)

SiH₄ versus Si₂H₆

SiH₄ - Surface Reaction Limited

Si₂H₆ - Mass Transport Limited



For a high degree of doping uniformity, the dopant incorporation must be mass transport limited in its behavior:

such that at the growth front,

$$J_{\text{dopant}} \propto J_{\text{Ga}} \rightarrow \Delta n \propto \Delta \left[\frac{J_{\text{dopant}}}{J_{\text{Ga}}} \right]$$

IBM

Summary

Little is known about the actual growth reactions taking place during the MOVPE process. There is substantial evidence that during the MOVPE growth of a III-V materials the growth front is in near thermal equilibrium.

- Stoichiometric Defects
- Alloy Composition in V-V' Materials

The growth environment can affect the electrical properties of interfaces due to changes in the defect structure of the materials as the composition is altered across an interface. The change in the chemical composition near the growth front dictates, in part, the structure of the interface.

IBM

10/86 (T.F. Kuech)

Studies of Buried Interfaces

using

**Total External Reflection
of X-Rays**

and

**Extended X-Ray Absorption
Fine Structure**

EXAFS

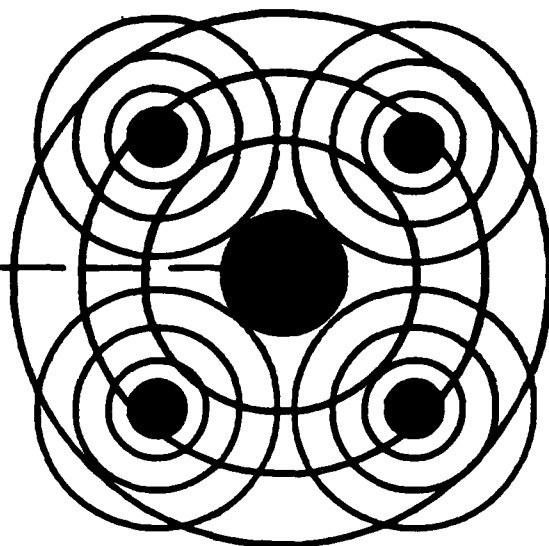
**Bruce A. Bunker
Notre Dame**

E X A F S

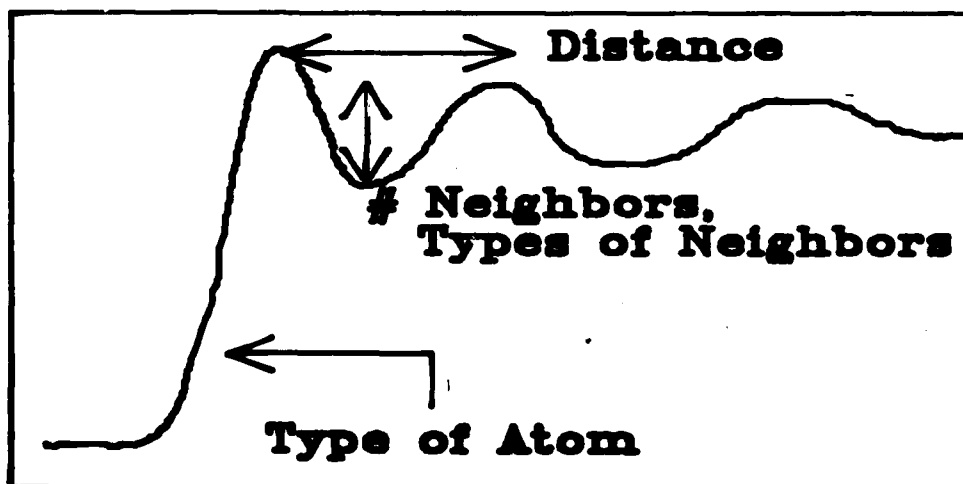
Extended X-Ray Absorption Fine Structure

Incident X Ray

**Interference
Modulates
X-Ray Absorption
Coefficient**



Absorption Coefficient

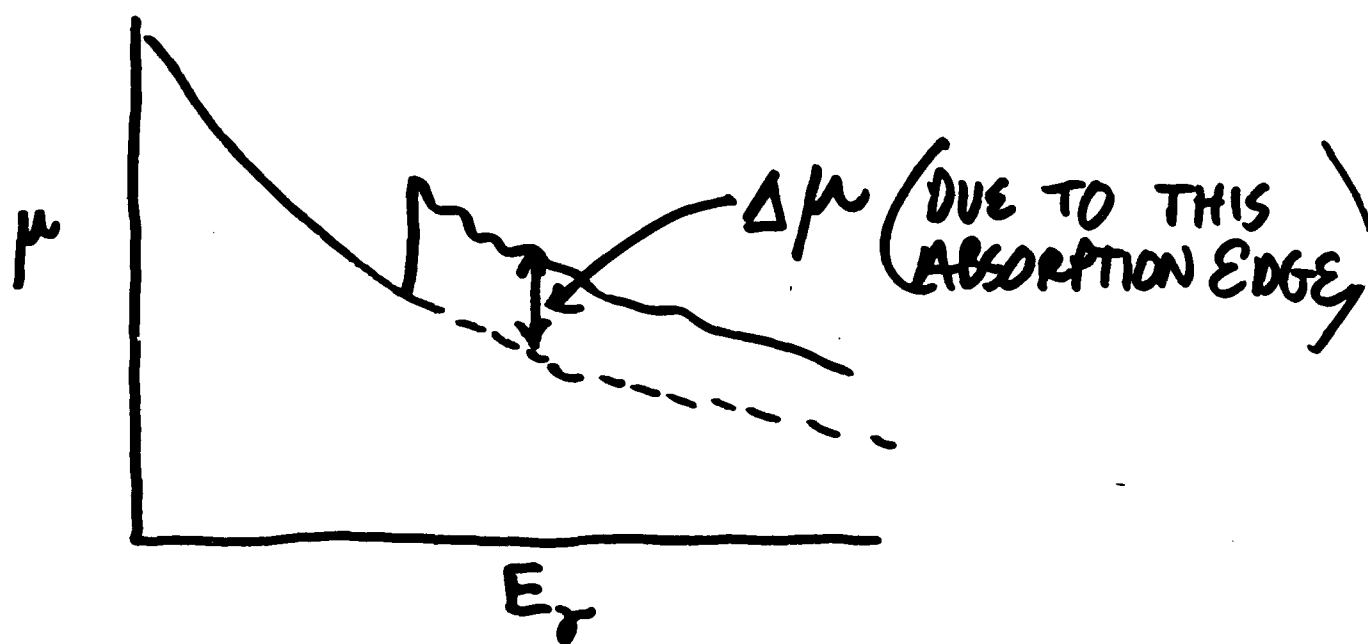
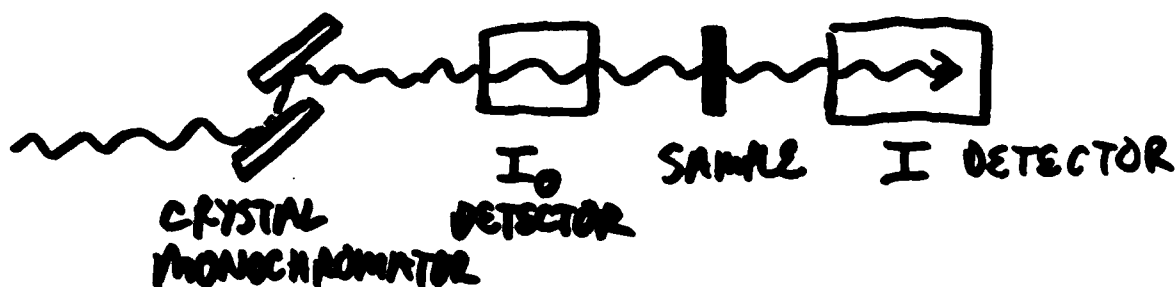


X-Ray Energy

- o Atom-Specific
- o Local Environment
- o 1st, 2nd, sometimes 3rd shells

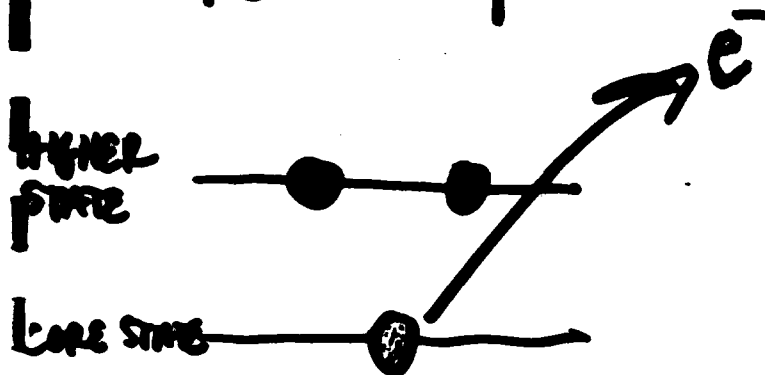
EXPERIMENTAL METHODS

(1) TRANSMISSION



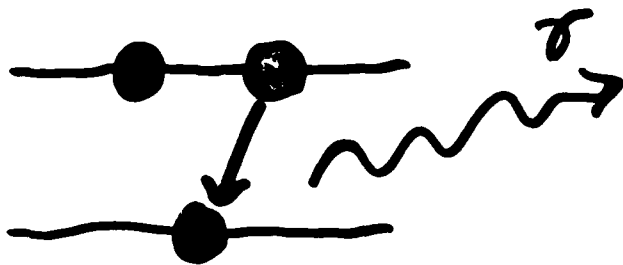
$\Delta\mu \sim \# \text{CORE HOLES PRODUCED}$
AS A FUNCTION OF X-RAY
ENERGY

CREATION & DECAY OF CORE HOLES

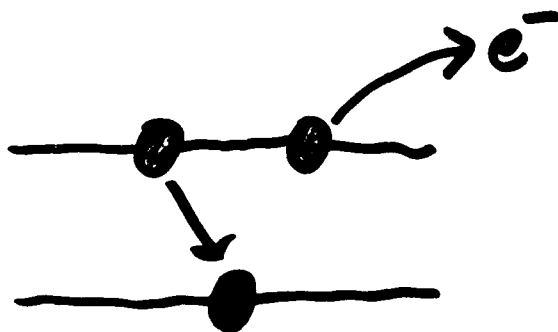


ABSORPTION

CREATING OF CORE HOLE



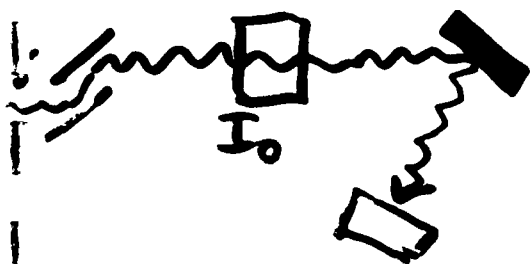
X-RAY FLUORESCENCE
DECAY OF CORE HOLE,
EMISSION OF X-RAY
PHOTON



AUGER ELECTRON
EMISSION

DECAY OF CORE HOLE,
EMISSION OF SECOND
ELECTRON

FLUORESCENT X-RAYS EMITTED AT
CONSTANT ENERGY (DIFFERENCE BETWEEN
ATOMIC LEVELS)



Major Strength of EXAFS:

LOCAL PROBE

Extreme Example:
Impurity in Semiconductor

**Focus on Impurity Atom,
determine:**

- * Types of Neighbors**
- * Number of Neighbors**
- * Distance to surrounding
1st and 2nd shell atoms**
- * Vibrational Properties**
- * Site Symmetry**
(from Near-Edge Structure)

Local Environment About Impurities in Semiconductors:

The Fe Site in Fe-Implanted Si

with: P. Bandyopadhyay

Determine:

- impurity site**
 - lattice relaxation**
 - impurity complex formation**
-

Experimental Technique:

- Grazing Incidence
(Impurities near surface)**
- Fluorescence Detection
(dilute impurities)**
- Sample Rotating During Data
Acquisition
(suppress Laue diffraction lines
contaminating data)**

Results: Fe Site in Fe-Implanted Si

- o Tetrahedral Interstitial Site
- o First Shell Expands $0.10+0.05\text{\AA}$
- o Second Shell Contracts $0.07+.06!$

Precision measurement:

Beats in EXAFS Amplitude yield

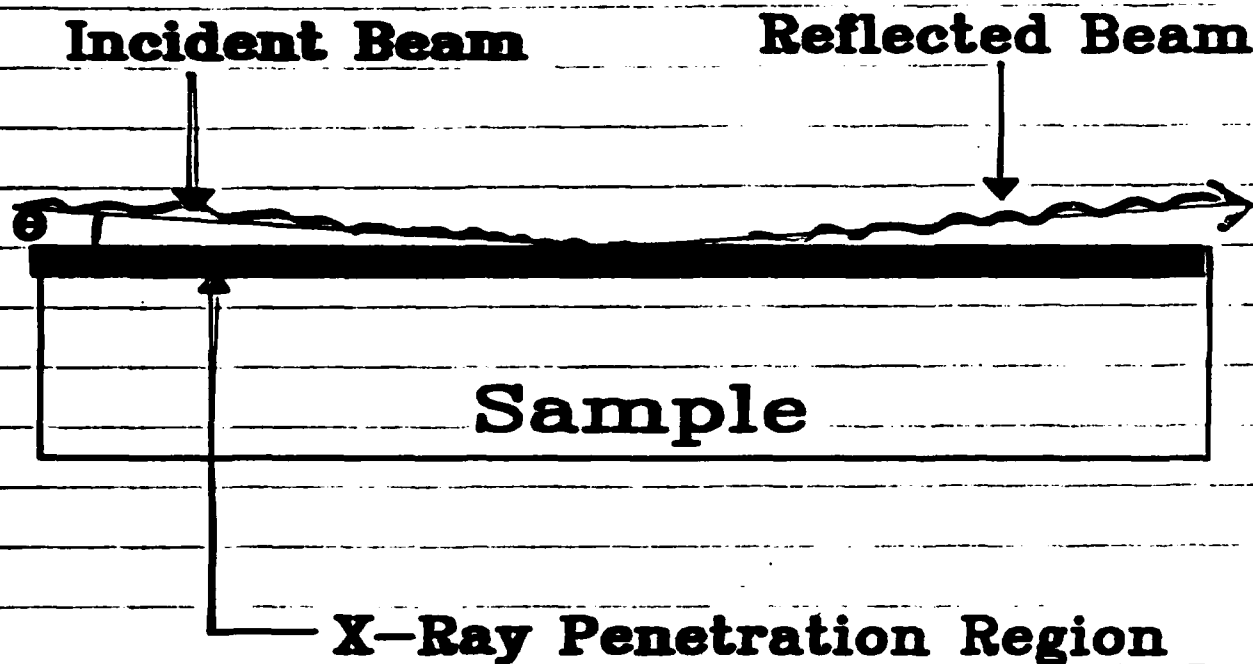
Distance Difference $R_2 - R_1$

If Undistorted:	$0.35\text{\AA}$
We Find:	$0.18 \pm 0.03\text{\AA}$

**Excellent Agreement With Theory:
Zunger, et al.: $0.17\text{\AA}$**

--- agreement within $0.01\text{\AA}$!

Total External Reflection of X Rays...



For $\theta > \theta_c$, $d = \sim 1000\text{\AA} - 20\mu$
 $\theta_c \approx 0.5^\circ$

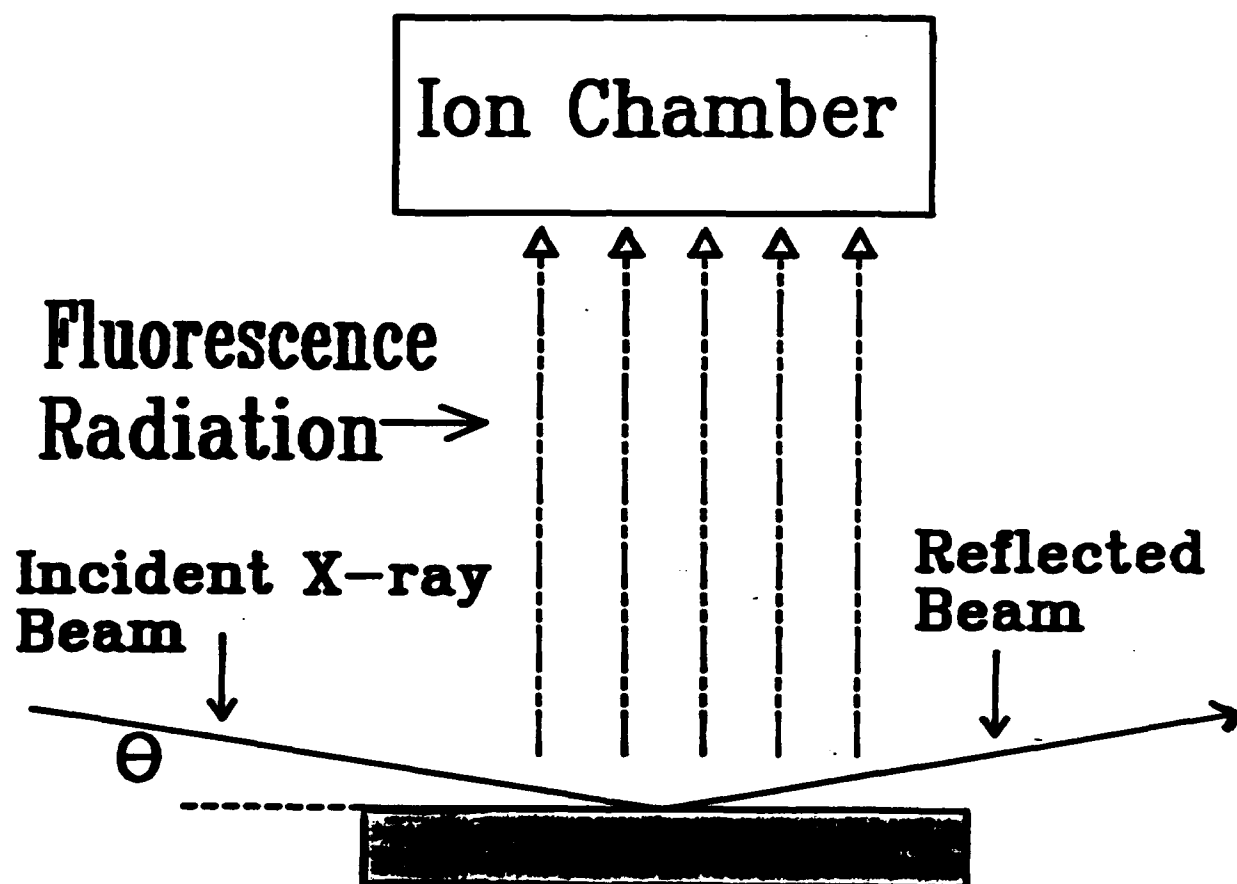
in x-ray region, index of refraction $n < 1$

---> total external reflection possible
 for grazing incidence

For $\theta < \theta_c$, $d = \sim 10 - 30\text{\AA}$

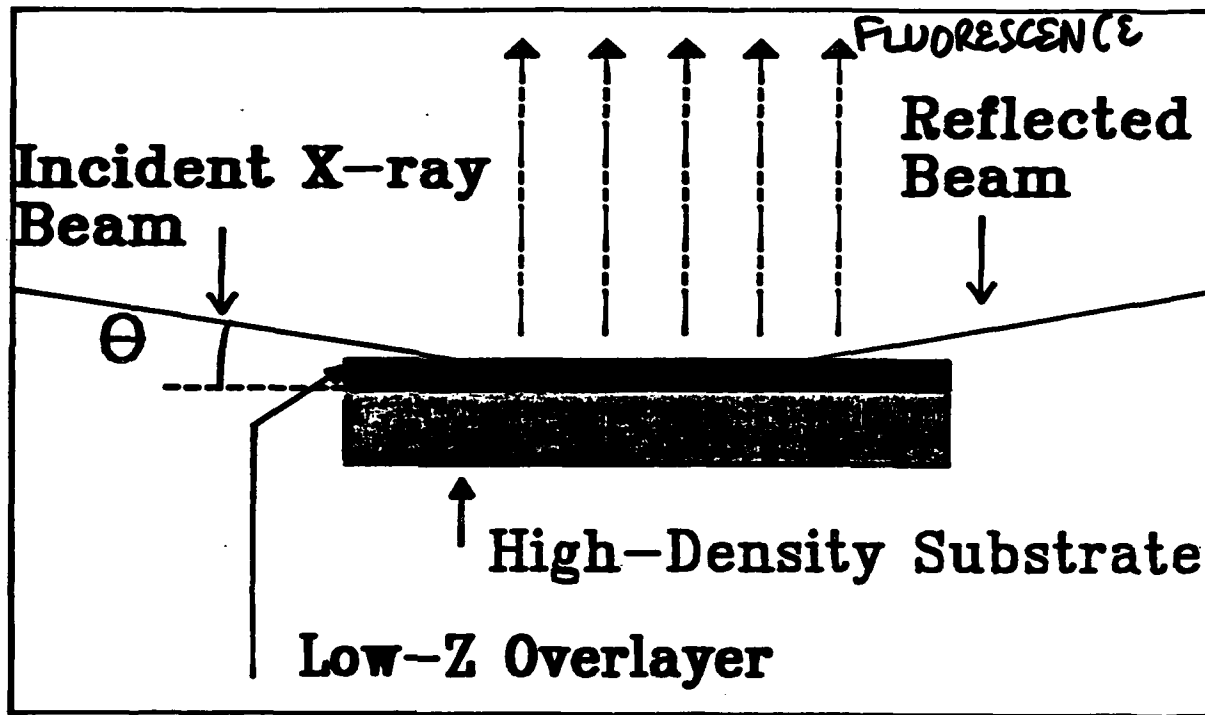
--- Surface Sensitivity

Total External Reflection
+ Fluorescence Detection
= Surface Sensitivity



Probe Local Environment
within ~ 10 Å of Surface
MUCH MORE SENSITIVE THAN "SEXAFS"
→ .01-.001 MONOLAYER DETECTABLE

Low-Z Overlayers e.g. Al on GaAs



Tune θ : $\theta_{\text{Al}} < \theta < \theta_{\text{GaAs}}$

-- Sensitive to As atoms within
 $\sim 10\text{\AA}$ of Buried Interface

Study: Diffusion
Compound Formation
Defect Complex Formation
Schottky Barriers (?)

SAMPLES

GAS, MBE GROWN

500 Å AL DEPOSITED IN-SITU

(1) 500°C DEPOSITION TEMP.

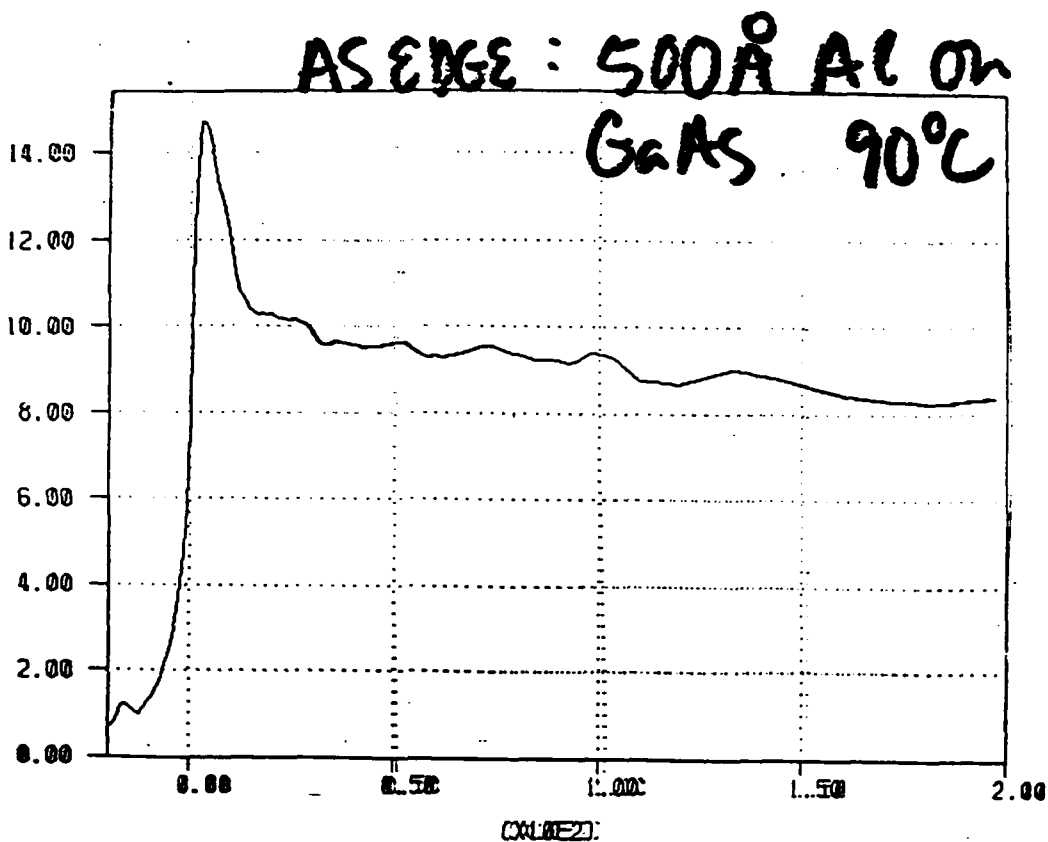
(2) 90°C " "

FRANK CHAMBERS

AMOCO RESEARCH LABS

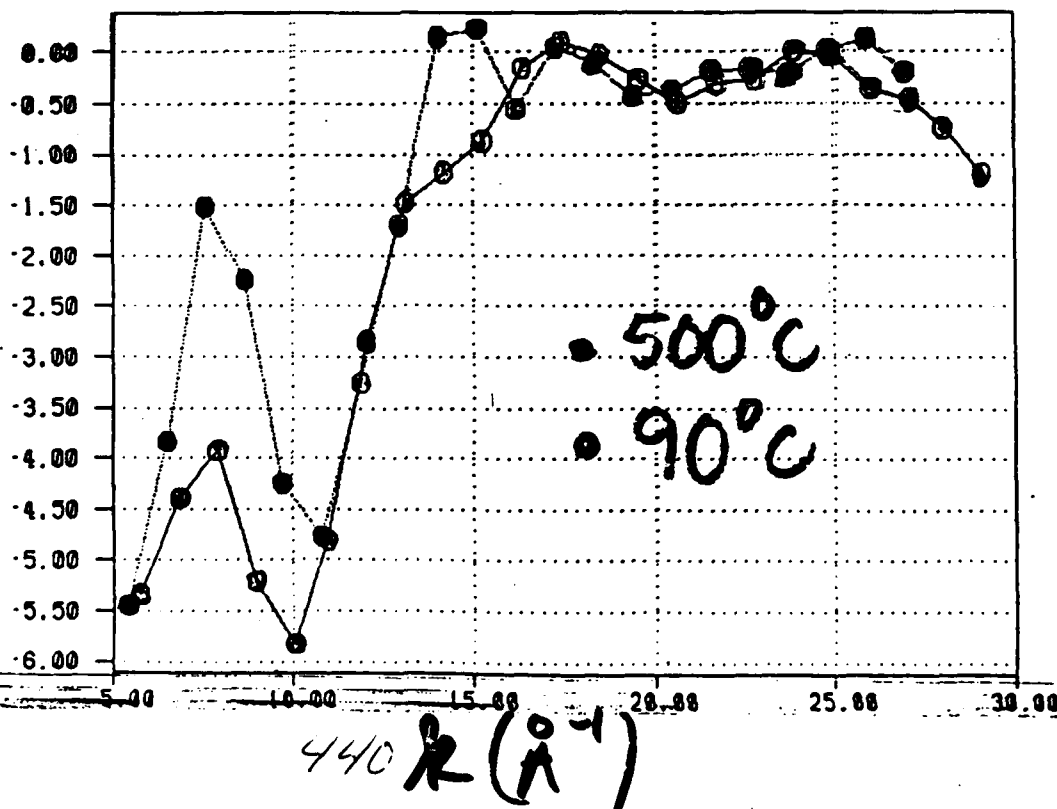
NAPERVILLE, IL

FLUORESCENCE
SIGNAL (X10E-1)



X-RAY ENERGY - EDGE ENERGY

$d(\text{Fluor})/dE$
(X10E-4)



FUTURE WORK

- MORE CAREFUL **DEPTH PROFILING**
BY SWEEPING ANGLE
- IN-SITU **ANNEAL DURING MEASUREMENT**
- STUDY OF **DOPANT ATOMS**
MIGRATION TO INTERFACE?

Summary

Reflection - Mode EXAFS

- Probe Adsorbed Species

~ 1 monolayer

- Probe Buried Interfaces

Study Atomic Environment For

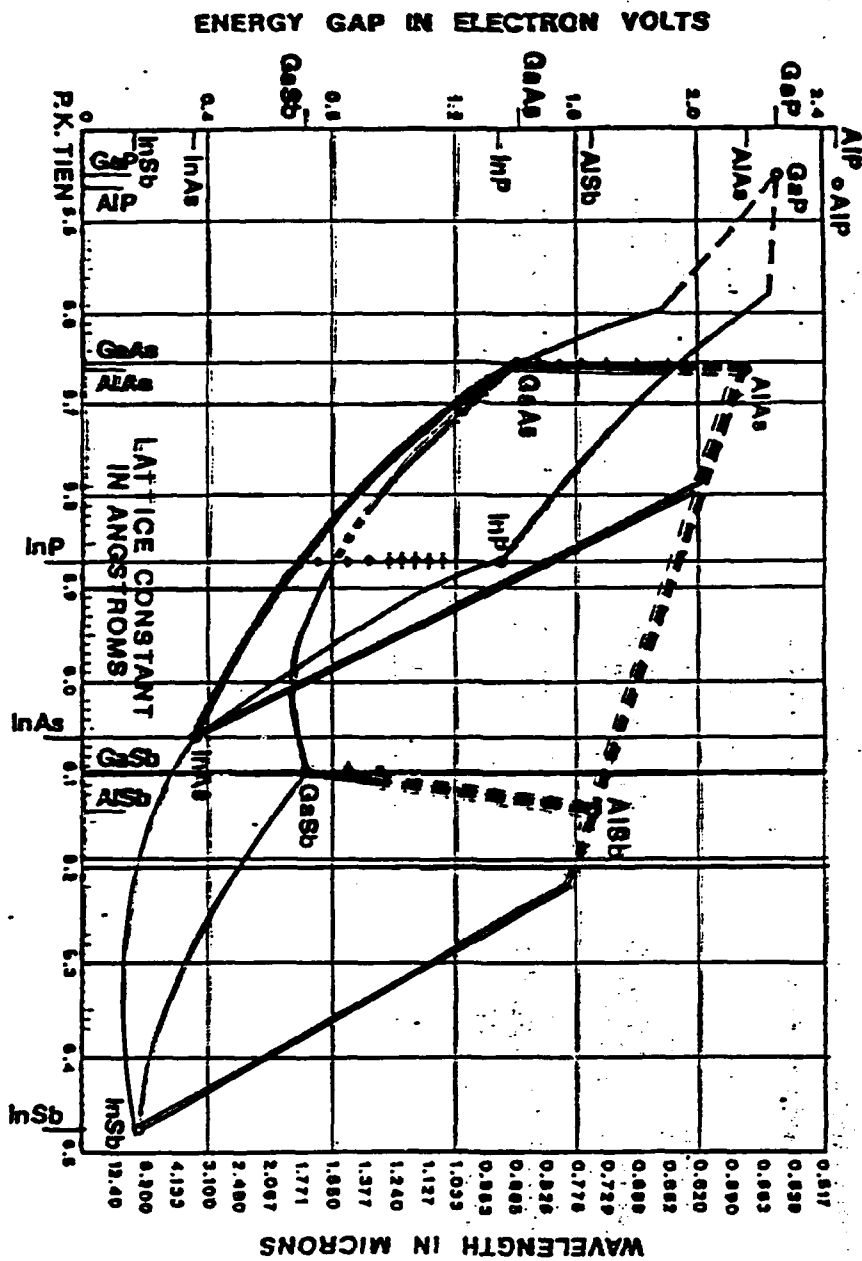
Atoms Within $\sim 10 \text{ \AA}$ of Interface

Around Each Species

- Types of Neighbors
- Number of Neighbors
- Bond Lengths

Composition Dependence of Metal In $\text{Al}_x\text{Al}_{1-x}$
Barrier Height and Its Application

Harry Wieder
University of California - San Diego



$\text{In}_x\text{Al}_{1-x}\text{As} / \text{InP}$

lattice matched, $x=0.52$

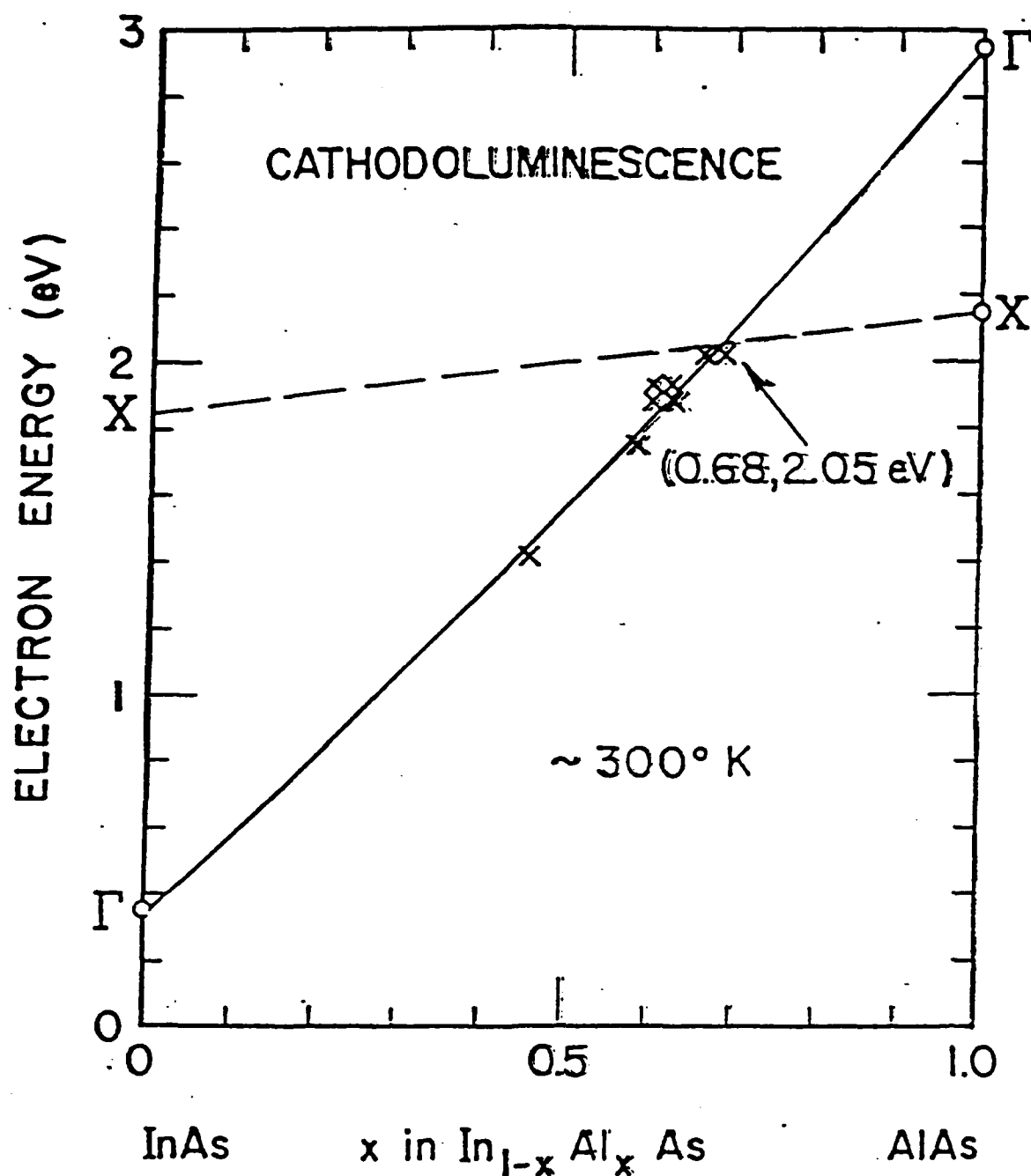
staggered band line-up

$$\Delta E_c = 0.52 \text{ eV}$$

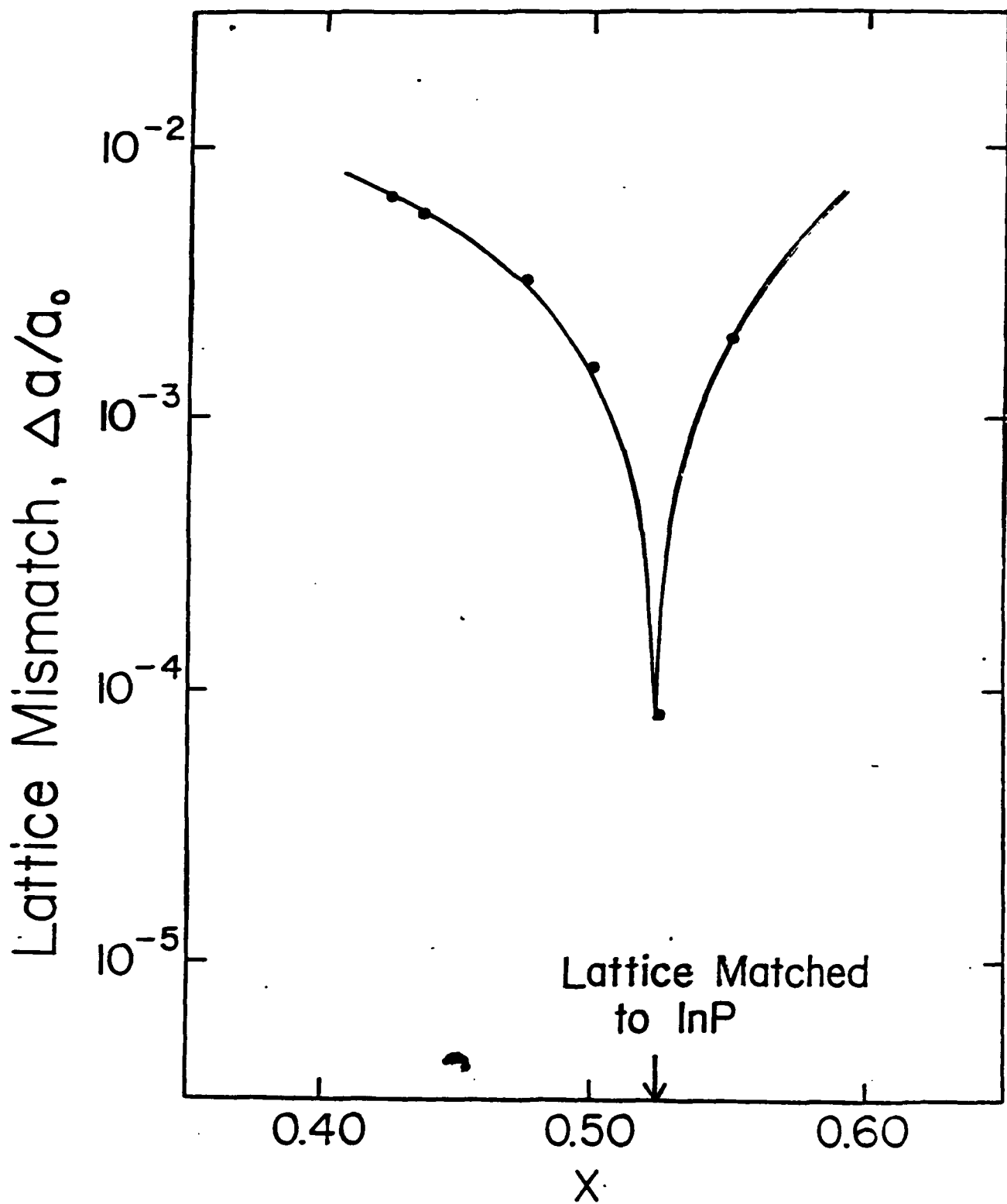
$$\phi_{\text{Bn}} = 0.8 \text{ eV}, \text{ C-V}$$

$$\phi_{\text{Bn}} = 0.6 \text{ eV}, \text{ internal photoemission}$$

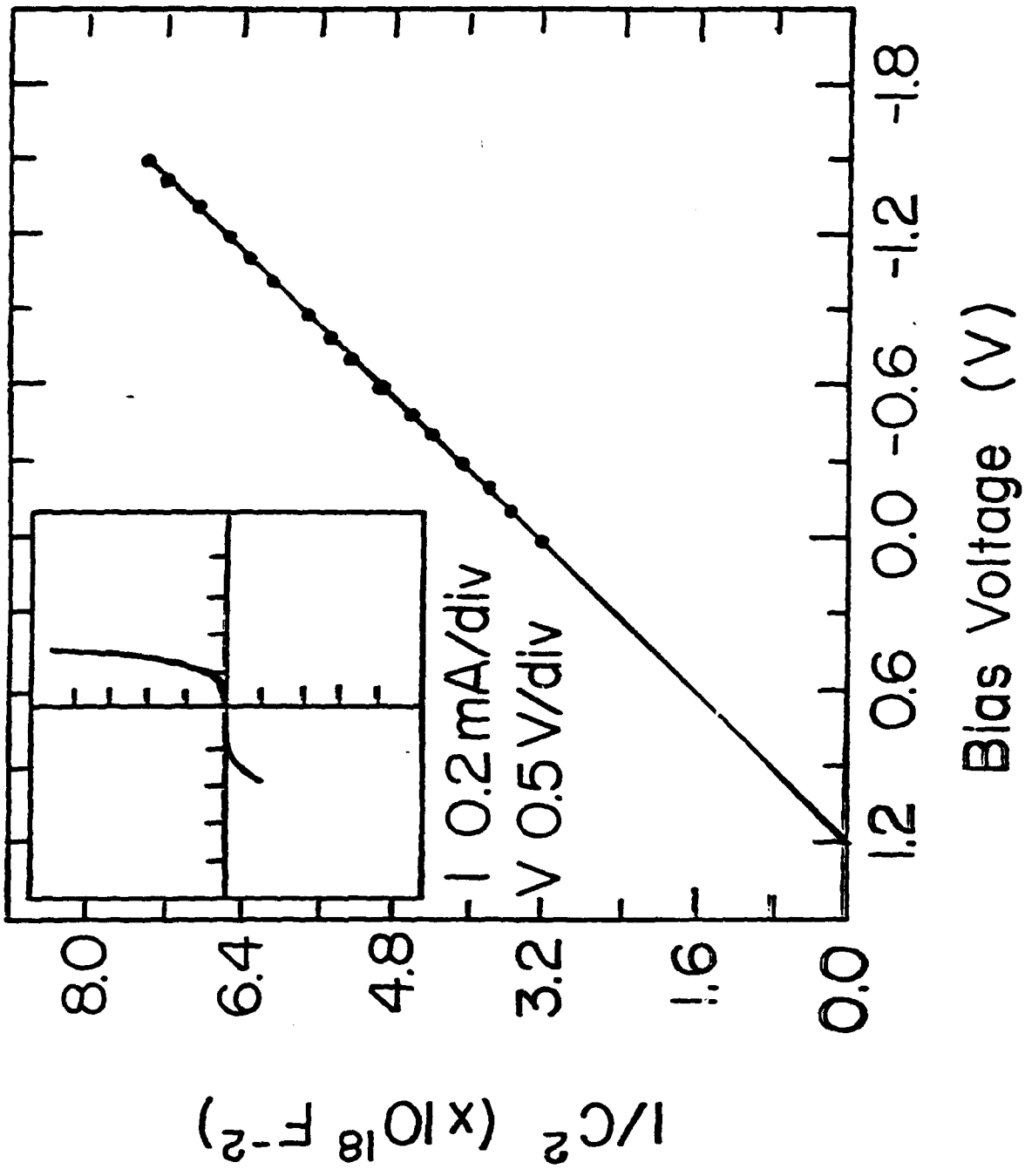
MBE grown, $T_s < 530^\circ\text{C}$ ~SEMI-INSULATING



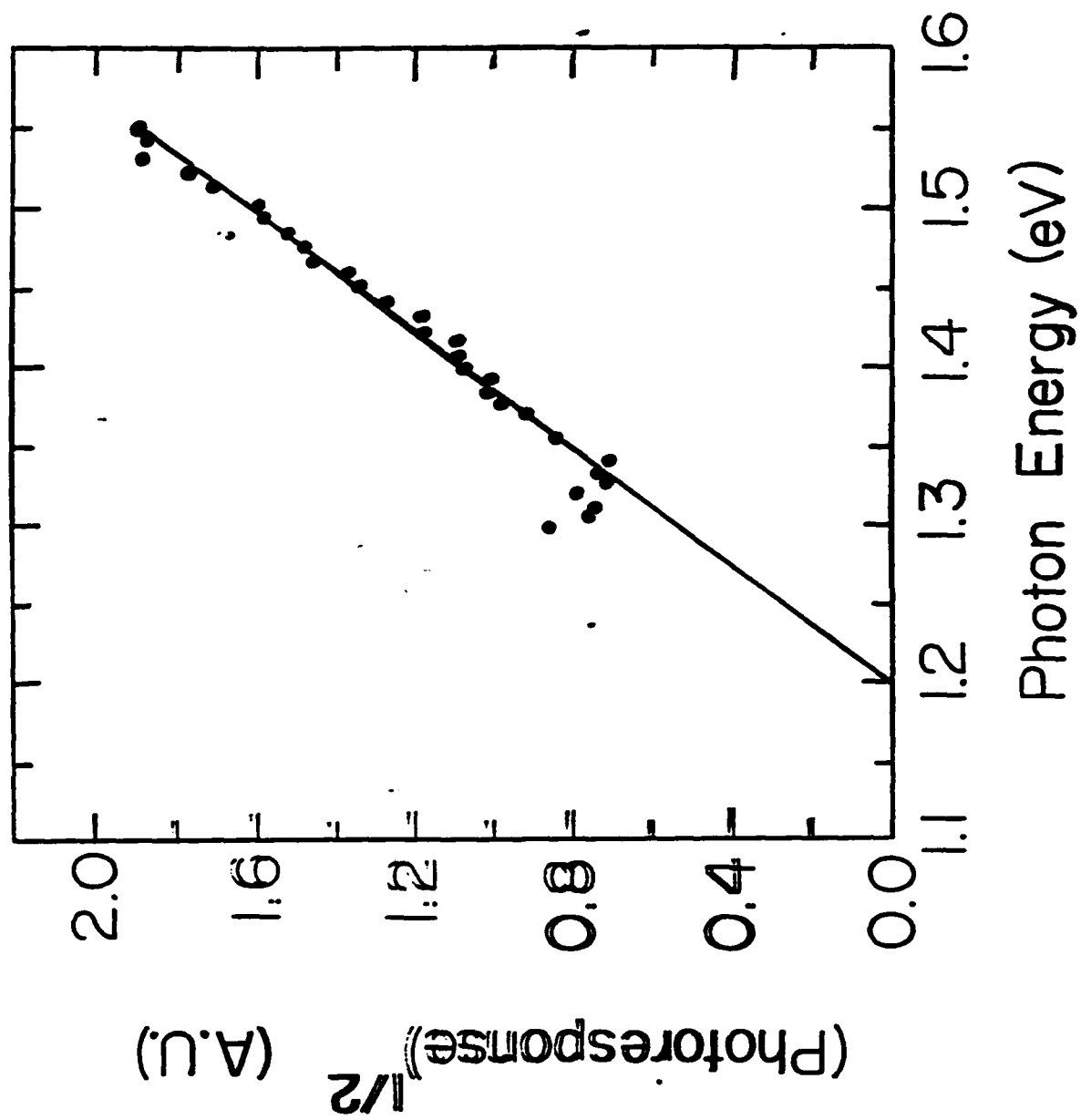
CL peak energies as a function of $\text{In}_{1-x}\text{Al}_x\text{As}$ alloy composition at 300°K. The X conduction band has been extrapolated to InAs on the basis of the conduction band cross overpoint and the X point in AlAs. 446



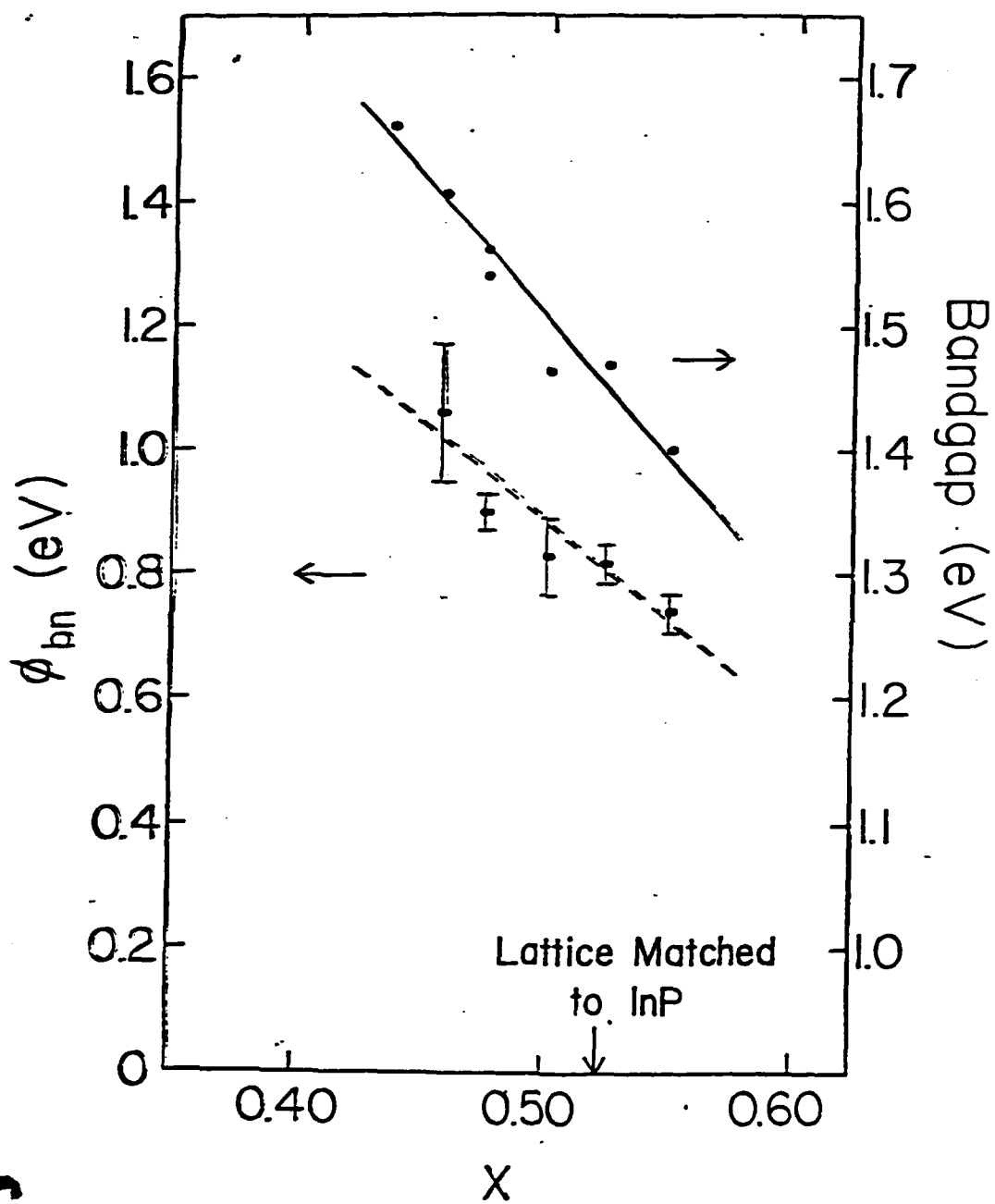
8th



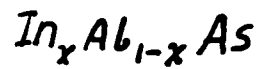
0.43 10⁻⁵ 5.57



InGaAs



450



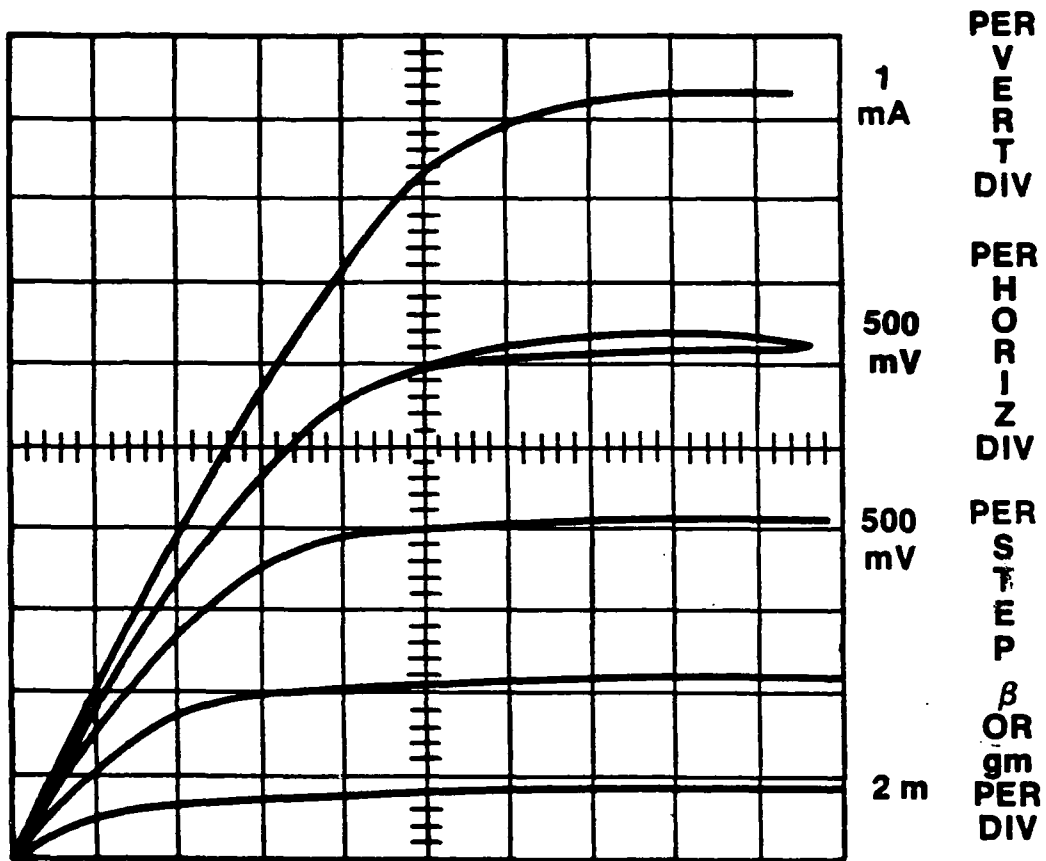
$$\phi_{\text{sn}} = 2.46 - 3.16 x \quad (x > 0.42)$$

$$\phi_{\text{sn}}(\text{AlAs}) = 1.2 \text{ eV} \quad (\text{measured})$$

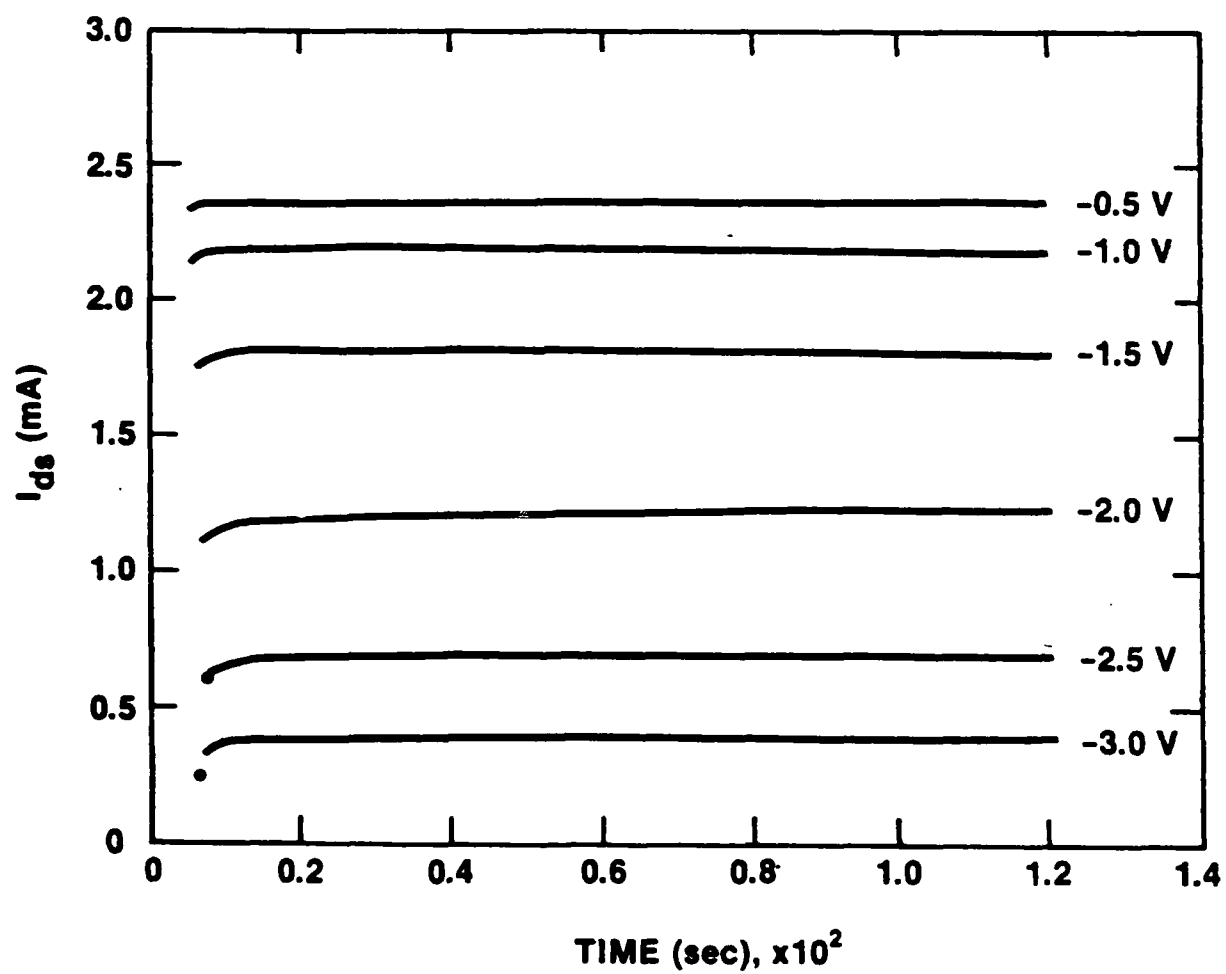
$$\phi_{\text{sn}}(x = 0.32) = 1.45 \text{ eV} \quad (\text{extrapolated})$$

$$\phi_{\text{sn}}(x = 0.78) = 0 \quad "$$

$$\phi_{\text{sn}}(x > 0.78) = \text{inverted surface} \quad "$$



452



453

(In-Situ) contacts to GaAs based on InAs

S.L. Wright
E.D. Marshall (summer student)
R.F. Marks
T.N. Jackson
S. Tiwari
H. Baratte

IBM Watson Research Center
Yorktown Heights, NY.

IBM

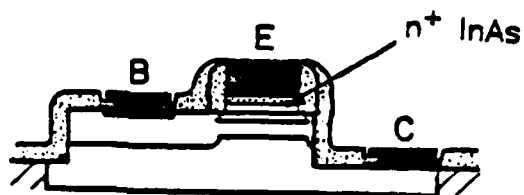
455

In-Situ Epitaxial Contacts: Device Motivation

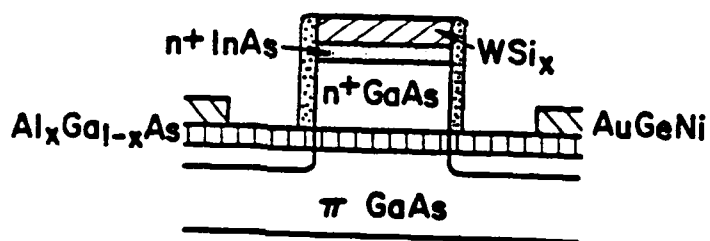
- Bandgap Engineering: improved understanding of ohmic contacts
- superior to Au/Ge/Ni:
 - very uniform and shallow
 - good temperature stability
 - potentially lower contact resistance ?
- compatible with refractory metallization
- good for self-alignment schemes involving small area contacts
- advantages for stop/regrowth applications

Heterostructure Devices with In-Situ Contacts

HBT

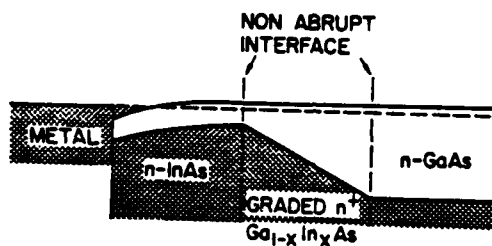


SISFET

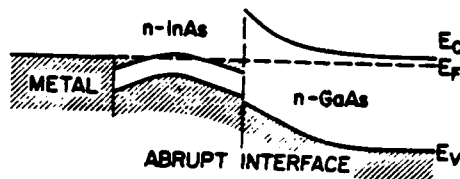


In-Situ Contacts based on (In,Ga)As

graded bandgap contact: (In,Ga)As/GaAs (Woodall et al. 1981)



abrupt junction: InAs/GaAs

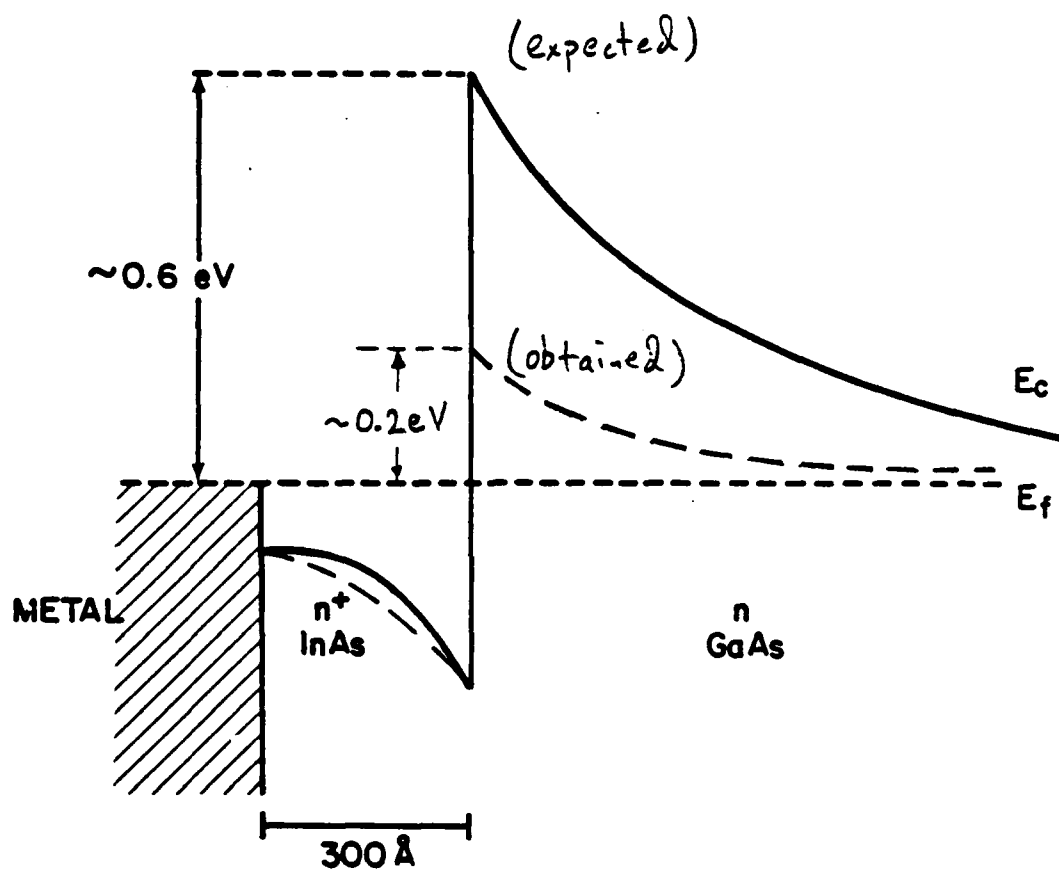


- Reproducible growth and processing
- May require less material than "graded" contact
- May require heat treatment

IBM
458

01/86 (S.L. Wright)

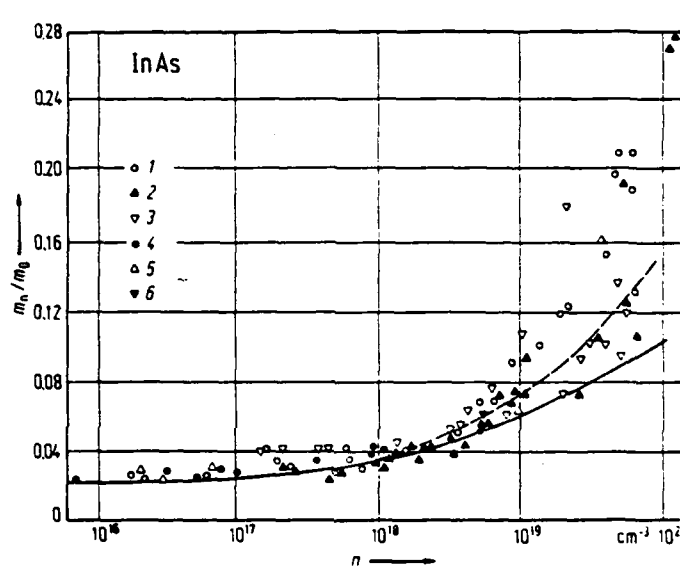
InAs/GaAs Band Diagram



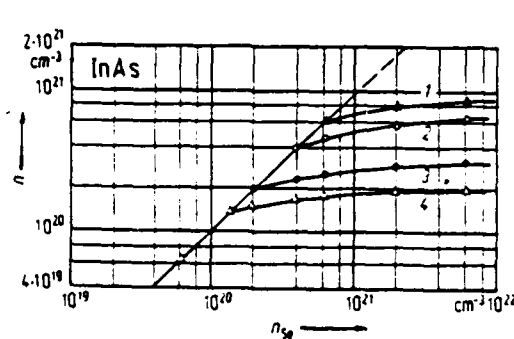
- Fermi level pinning
- Bulk InAs and GaAs Fermi level (doping)
- Conduction band discontinuity
- Strain and dislocations?

GOOD news and BAD news

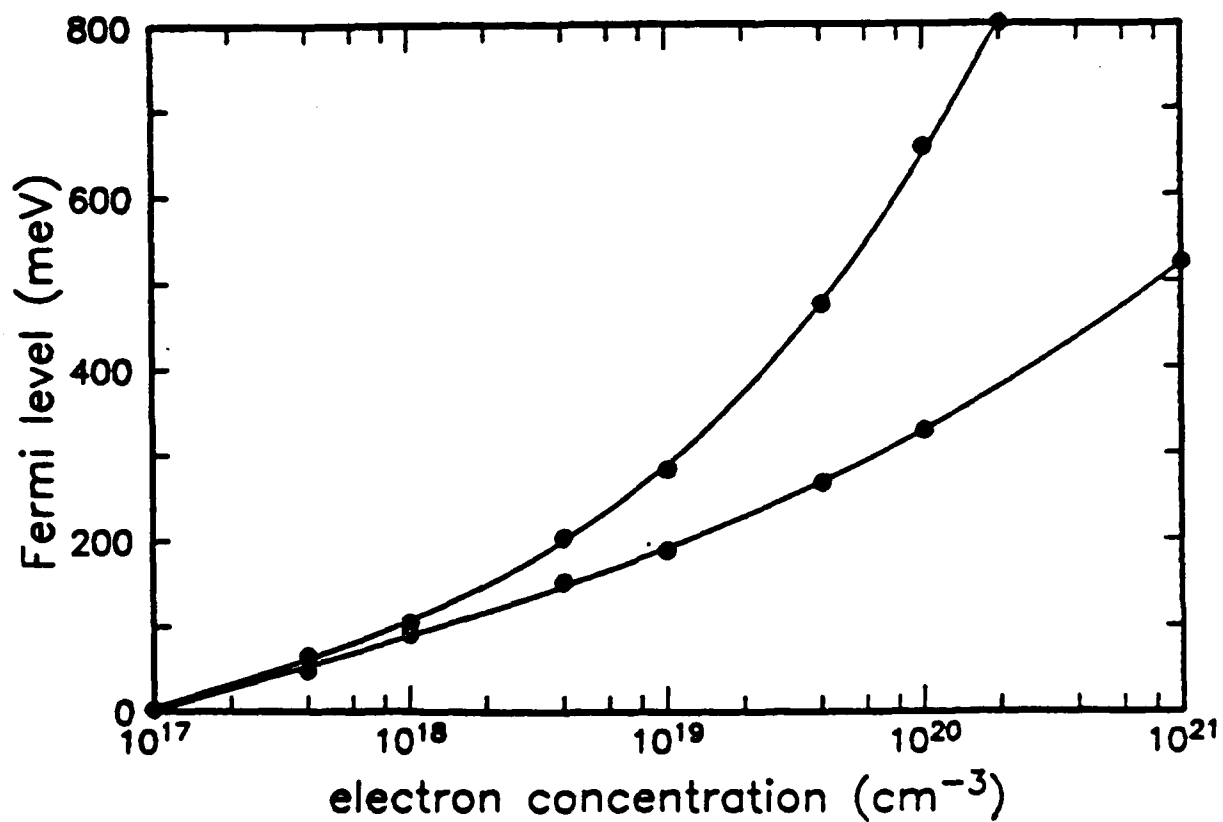
- m^* increases sharply with doping (and fermi level)



- InAs can be doped with electrically active concentrations approaching 10^{21} cm⁻³



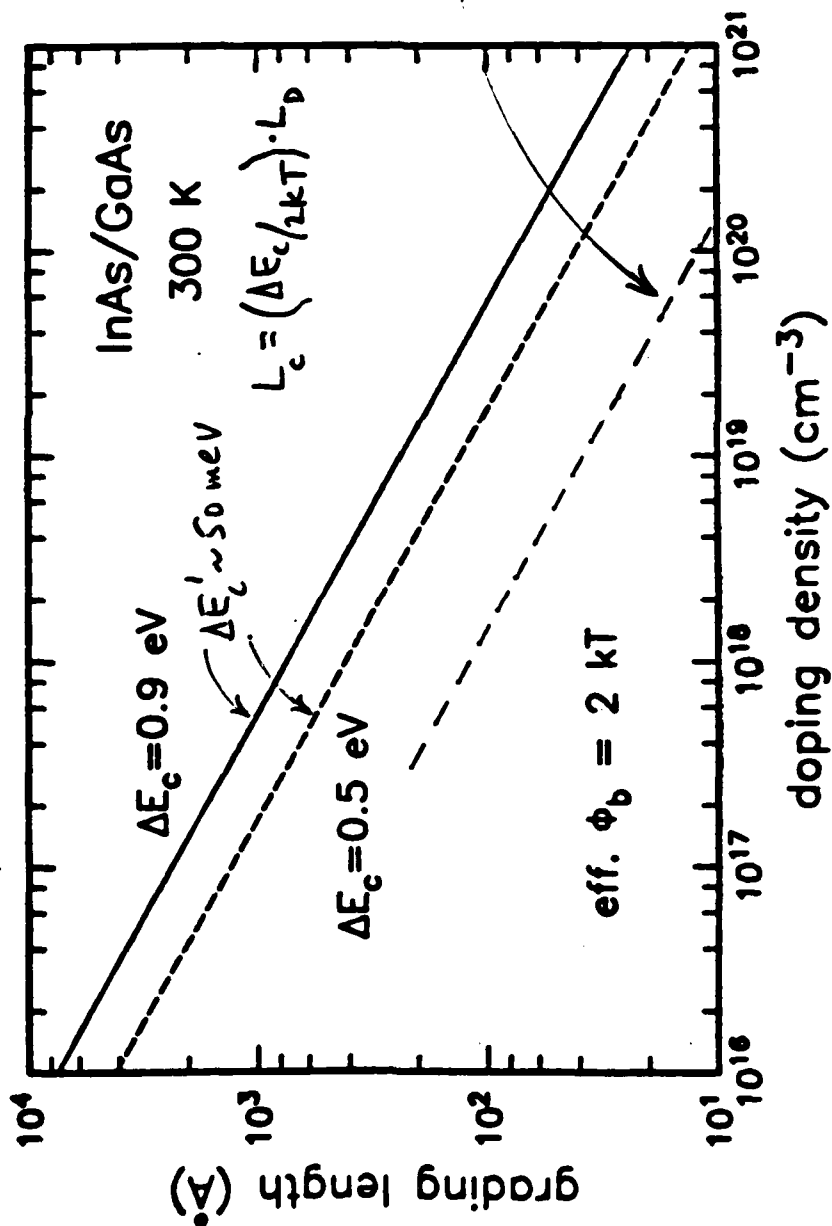
InAs bulk Fermi level



09/86 (S.L. Wright)

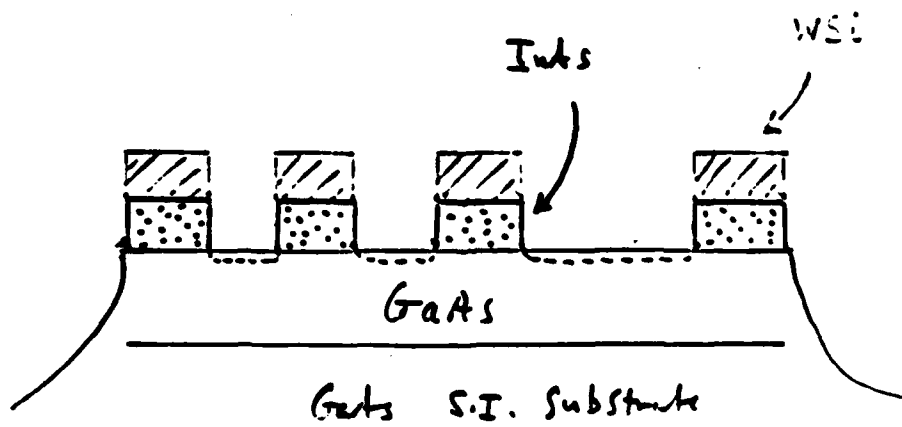
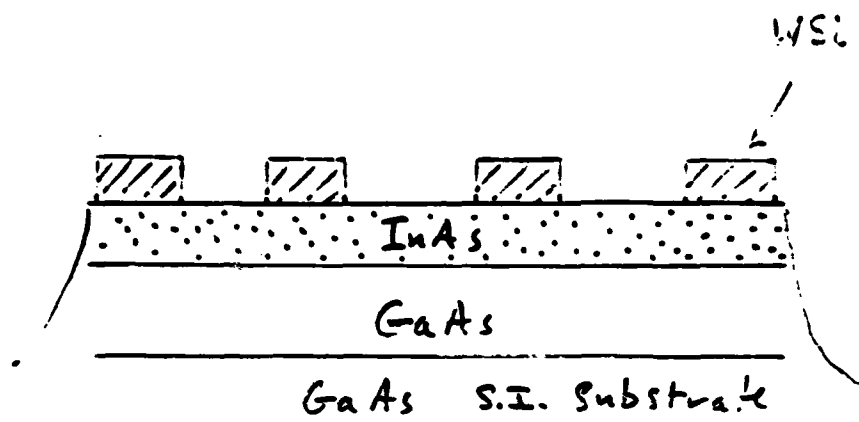
IBM

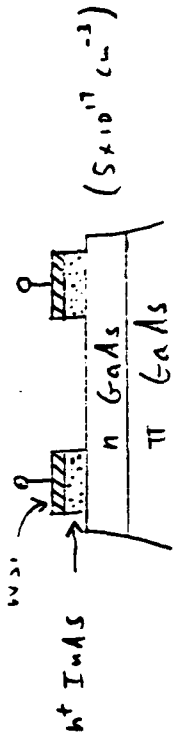
461



$\Delta E'_c \sim 200 \text{ meV}$
assuming
 $\Delta E'_c \propto 1/L$

Transmission Line Structures



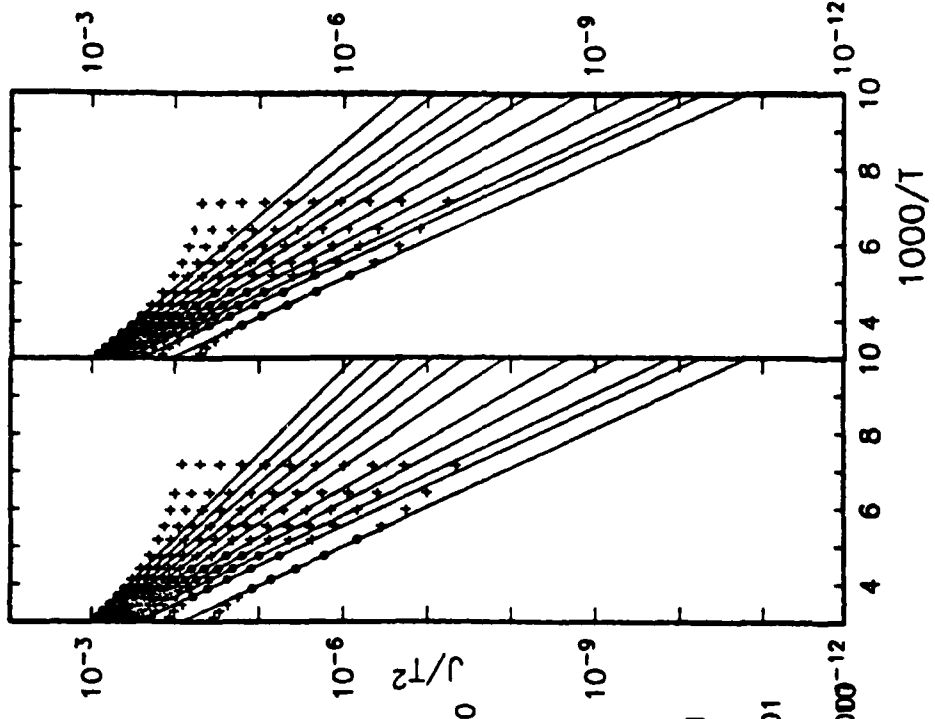
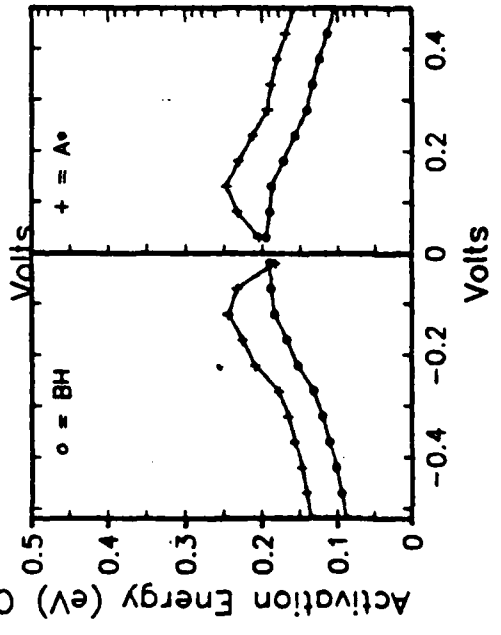
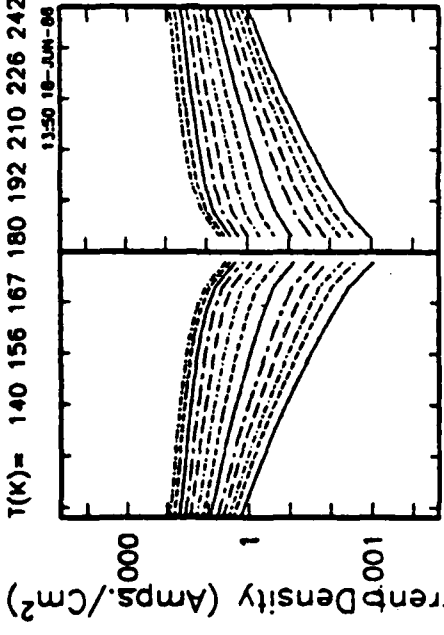


V844A16 INAS/GAAS TLM NON ANNEALED

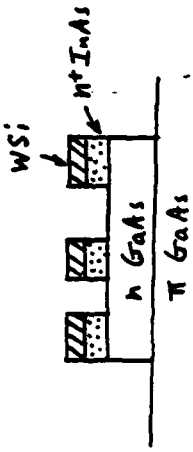
T(K) = 140 156 167 180 192 210 226 242 257 271 287 303 318

MANUAL DATA SELECTION

SIZE = 0.010.0 UMS

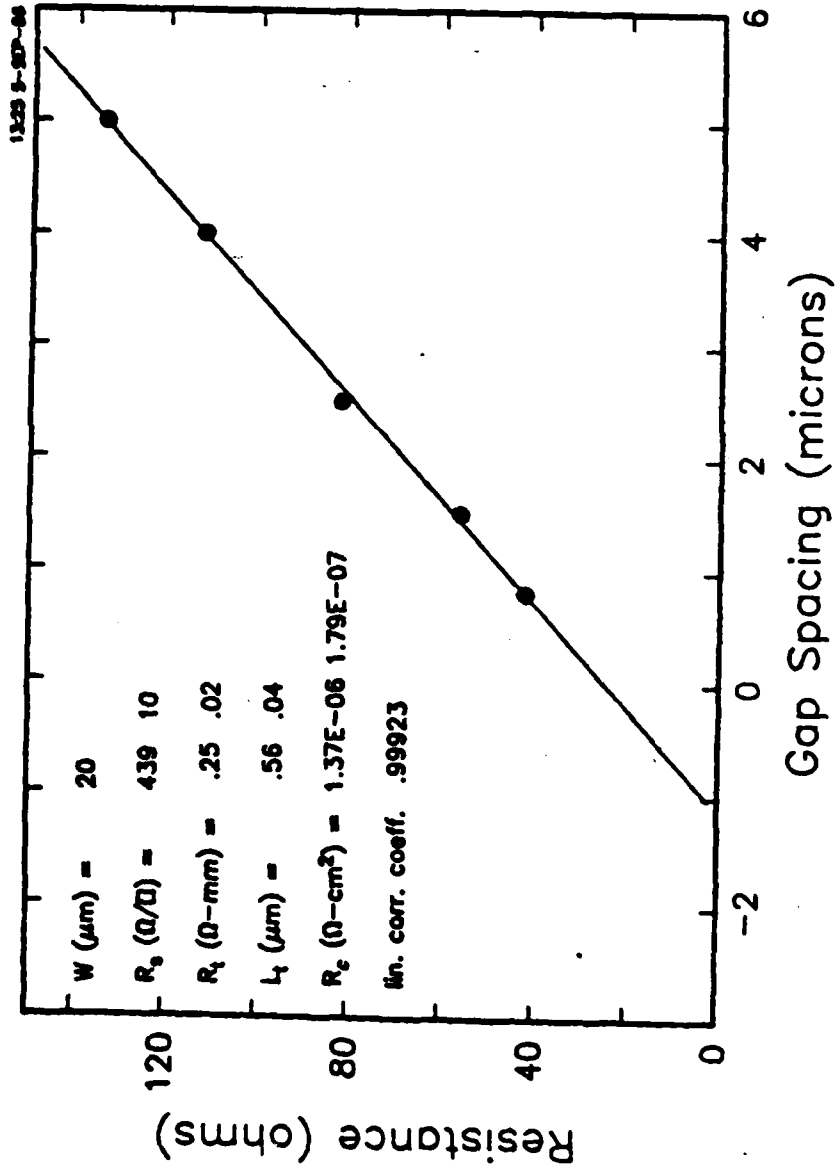


h 2/h



VB44 200A etch
obrupt. Se17 GaAs
1s 880 C anneal

gop	.8	1.5	2.5	4.0	5.0	11	.0
R	42.0	56.0	82.0	112.0	134.0	11	.0



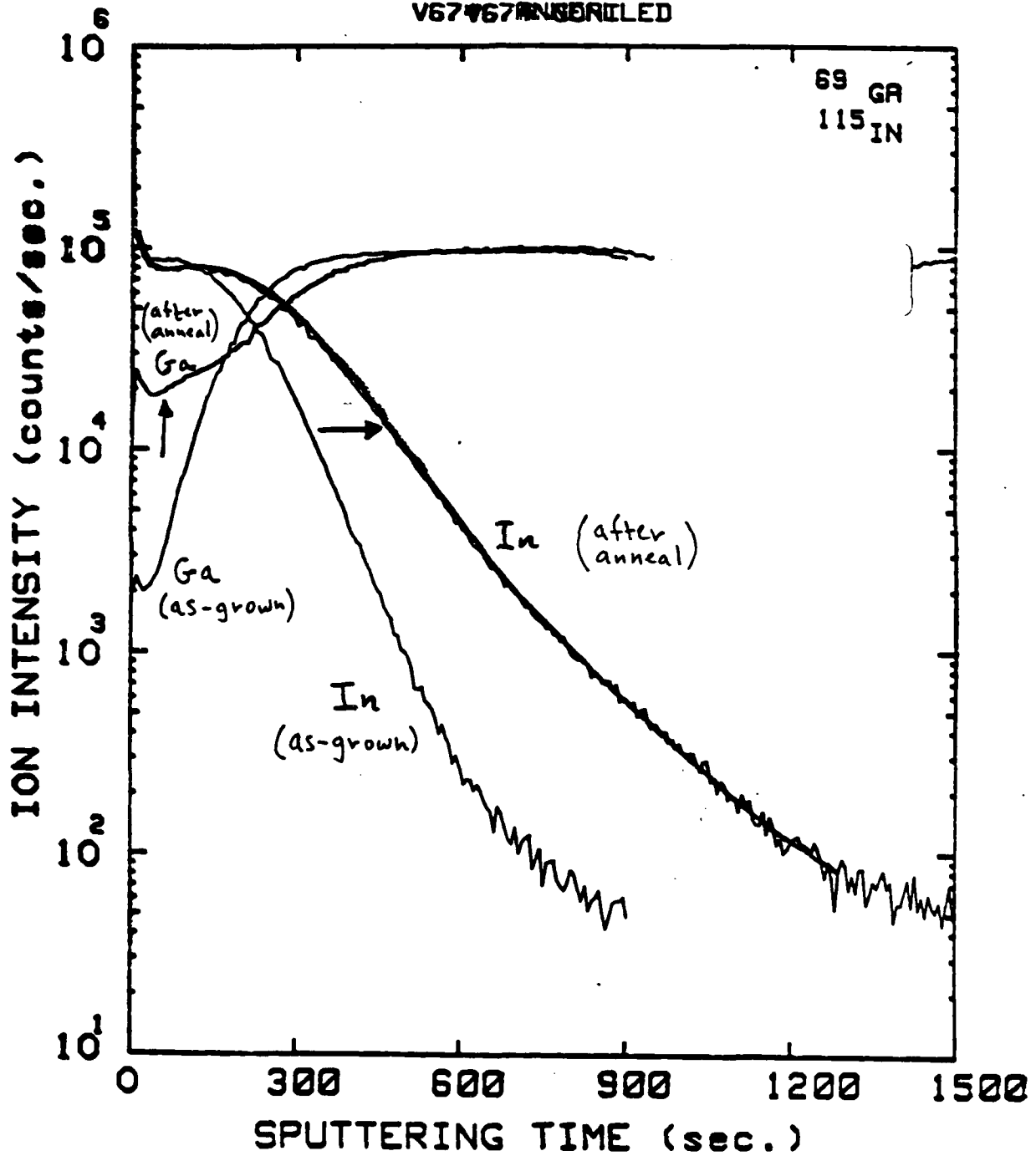
465



SIMS DEPTH PROFILE 08-13-86

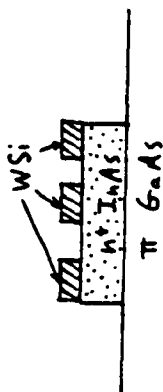
62258

V67 V67 INSERTE

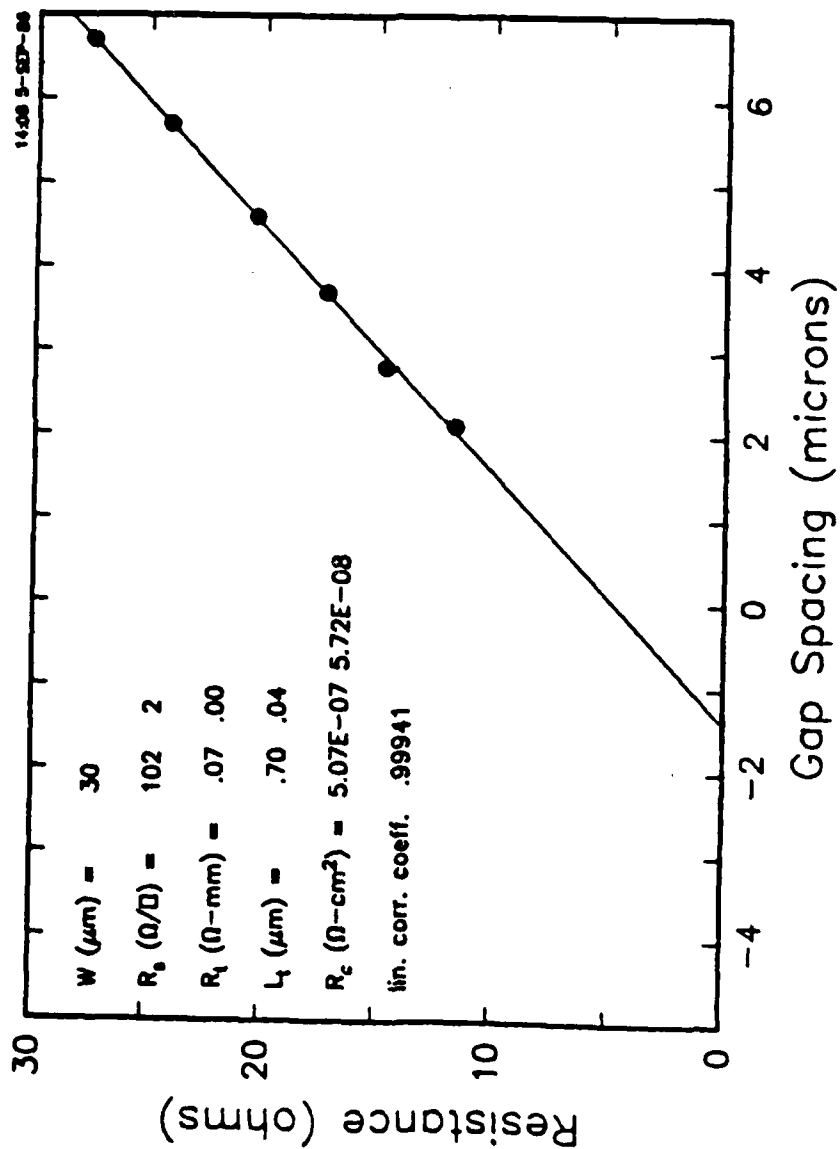


Abrupt Structures: typical results

sample	GaAs doping (cm^{-3})	$R_s(\Omega\text{-mm})$	$\rho_c(\Omega\text{-cm}^2)$
V671 300Å n+InAs 850°C, 3 sec	2×10^{17}	0.47	9×10^{-6}
V844 200Å n+InAs 880°C, 1 sec	5×10^{17}	0.3	1×10^{-6}
V917 300Å n+InAs 750°C, 5 min	1×10^{18}	0.17	2.6×10^{-6}
850°C, 18 sec		0.23	2.2×10^{-6}



V903 1B3 gap 2.1 2.6 3.7 4.6 5.7 6.7 11 .0
 n+ InAs on pl R 11.7 14.7 17.3 20.4 24.2 27.6 11 .0
 18s 850 C anneal



Metal/InAs interfacial contact resistance

ex) V903: 500Å n+ InAs/ π GaAs buffer

Hall (300K): $n_s \sim 2.6 \times 10^{14} \text{ cm}^{-2}$
 $\mu \sim 300 \text{ cm}^2/\text{V-s}$
 $R_s \sim 80 \Omega/\square$

heat treatment	$R_t(\Omega\text{-mm})$	$\rho_c(\Omega\text{-cm}^2)$
as-grown	0.07	$3\text{-}5 \times 10^{-7}$
650°C, 5 min	0.06	3.6×10^{-7}
750°C, 5 min	0.06	3.3×10^{-7}
850°C, 5 min	0.09	2.3×10^{-7}
850°C, 18 sec	0.07	4.0×10^{-7}

- finite WSi/InAs interface resistance
 $\rho_c \leq 5 \times 10^{-7} \Omega\text{-cm}^2$
- NOT a limiting factor in most cases

Graded Structures: typical results

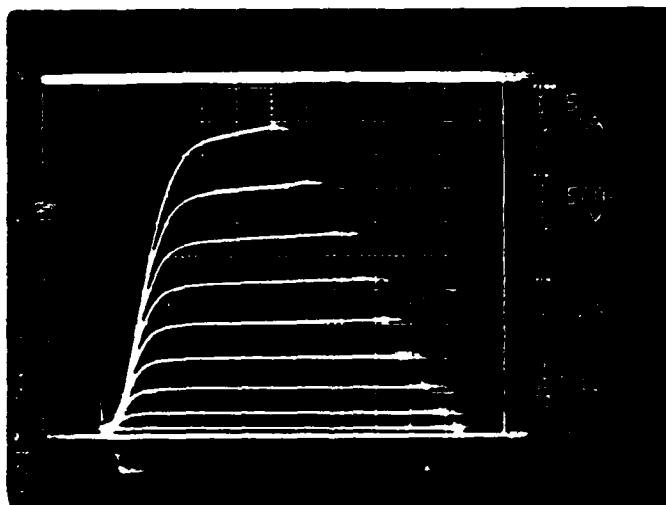
0.2 μ m 1×10^{18} GaAs channel/ graded layer/ 200 Å n+ InAs

contact layer etched down to channel in gap regions.

5 min. 750 °C arsine anneal

sample	$R_s(\Omega/\square)$	$R_t(\Omega\text{-mm})$	$\rho_c(\Omega\text{-cm}^2)$
V914 as-grown	213	0.09	4×10^{-7}
600Å grade			
V914 annealed	458	1.0	2×10^{-5}
V907 as-grown	192	0.08	3.5×10^{-7}
320Å grade			
V907 annealed	209	0.19	1.7×10^{-6}
V905 as-grown	207	0.09	4×10^{-7}
180Å grade			
V905 annealed	176	0.07	3×10^{-7}

HBT characteristics



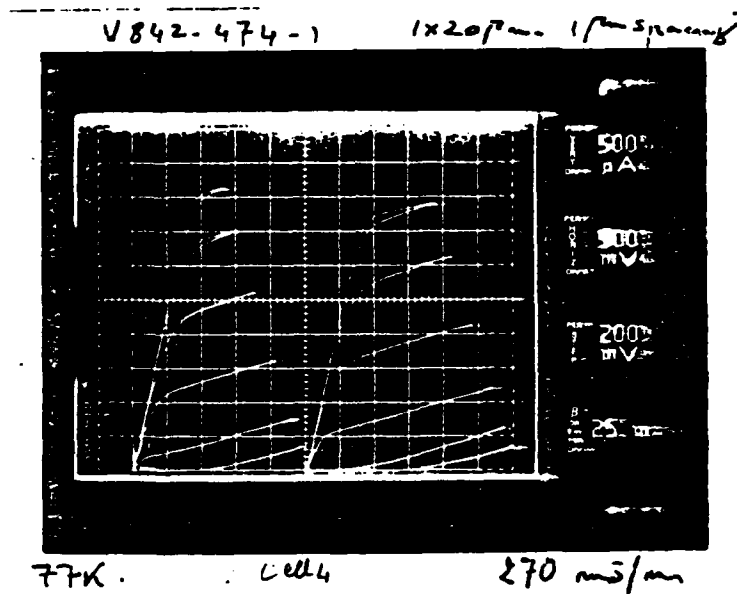
vertical npn structure on n+ substrate
25 μm diameter emitter
WSi/InAs self-aligned ohmic contact
p+ implant; 850 $^{\circ}\text{C}$, 2-3 s anneal

06/86 (S.L. Wright)

IBM

471

GaAs Gate FET with In-Situ contact

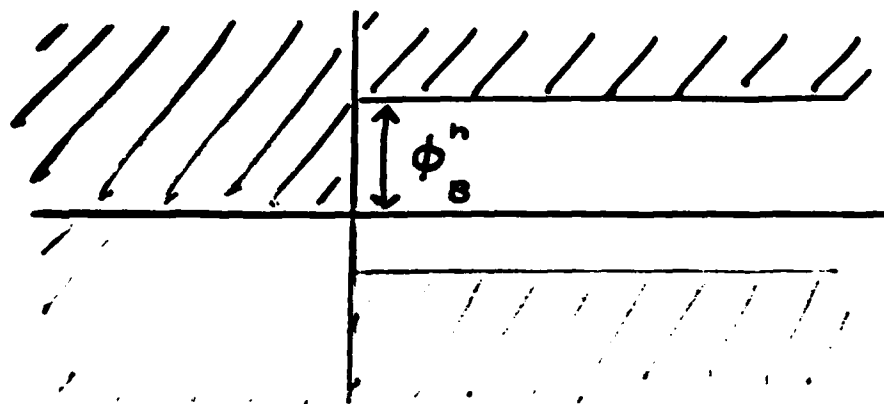
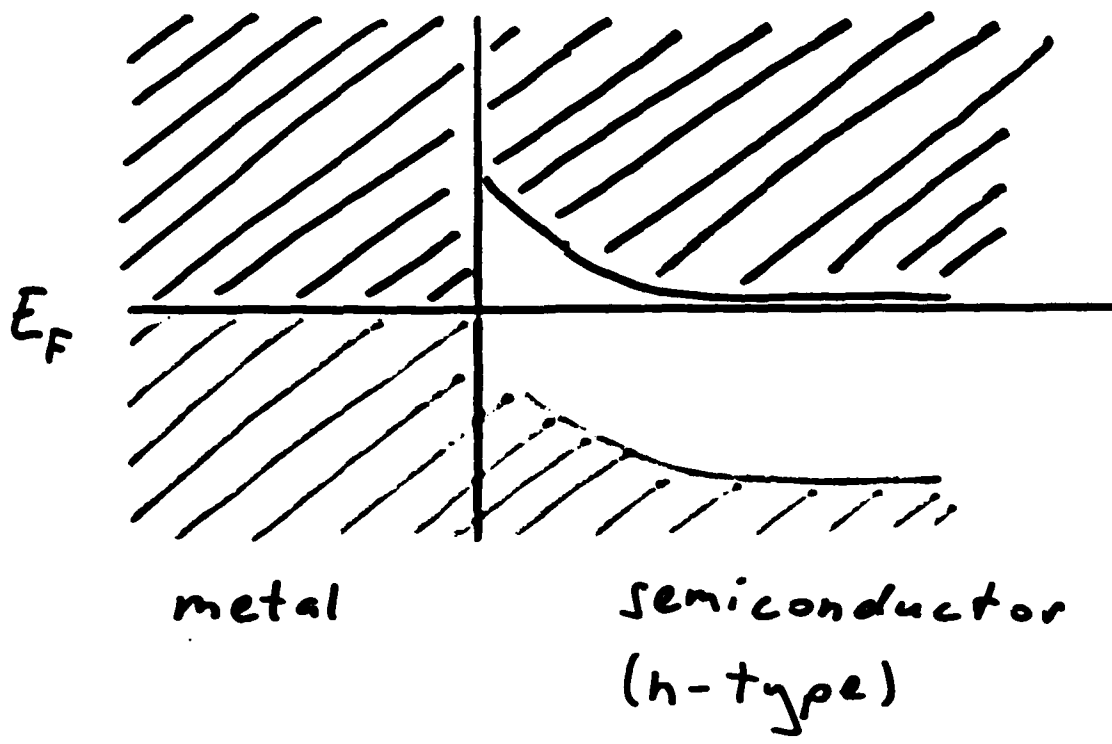


Summary

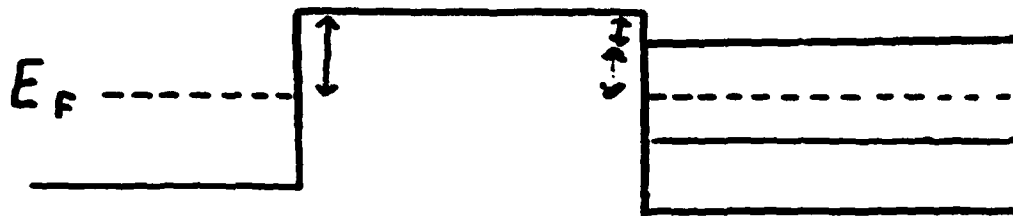
- In-Situ Contacts: solution for self-aligned SISFET and HBT structures.
- Good morphology and electronic properties at small InAs thicknesses
- Transport data: $\Delta E_c(\text{InAs/GaAs}) \sim 0.5\text{-}0.6\text{ eV}$
HJ Fermi level NOT pinned near mid-gap.
- Abrupt structures which are capped are compatible with implant activation anneals. For 10^{18} cm^{-3} GaAs:
as-grown: $\rho_c \sim 1\text{-}5 \times 10^{-5}\ \Omega\text{-cm}^2$ (non-linear)
annealed: $\rho_c \sim 1 \times 10^{-6}\ \Omega\text{-cm}^2$, ($R_t \leq 0.3\ \Omega\text{-mm}$)
- WSi/InAs interfacial resistance: $\rho_c \leq 5 \times 10^{-7}\ \Omega\text{-cm}^2$
- as-grown graded structures have low contact resistance
 $\rho_c \leq 4 \times 10^{-7}\ \Omega\text{-cm}^2$, $R_t \leq 0.1\ \Omega\text{-mm}$
- tendency for graded structure contact resistance to degrade with heat treatment. spinodal decomposition?
- improvements are anticipated with optimal growth conditions and more heavily doped layers.

INTRINSIC MECHANISMS
FOR
FERMI-LEVEL PINNING
AT
SURFACES AND INTERFACES

JERRY TERSOFF
IBM WATSON CENTE.



Schottky (1940)

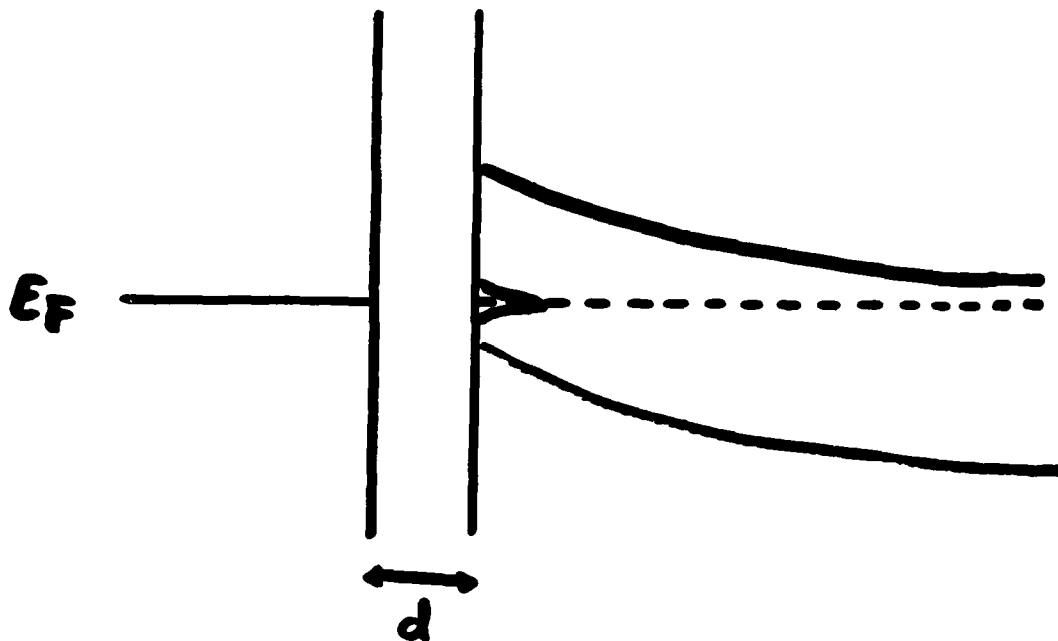


ϕ_b = metal work function
- semiconductor e affinity

Terrible

Fermi level "pinned"

BARDEEN (1947)



$d \rightarrow \infty$ 10^{12} states/cm² with μ at E_F
 $d \rightarrow 0$ need 10^{14}

Cf. true interface: "MIGS" etc.

HEINE (1965)

LOUIS et al. (1976)

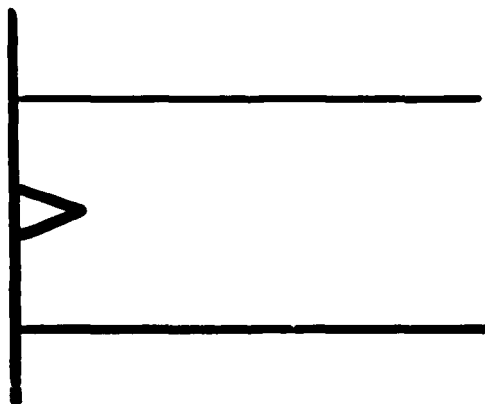
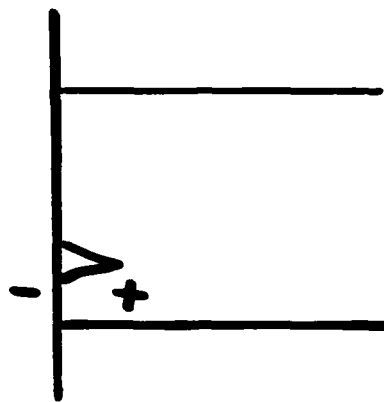
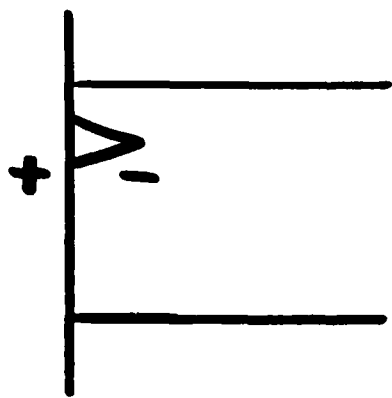
TEJEDOR et al. (1977)

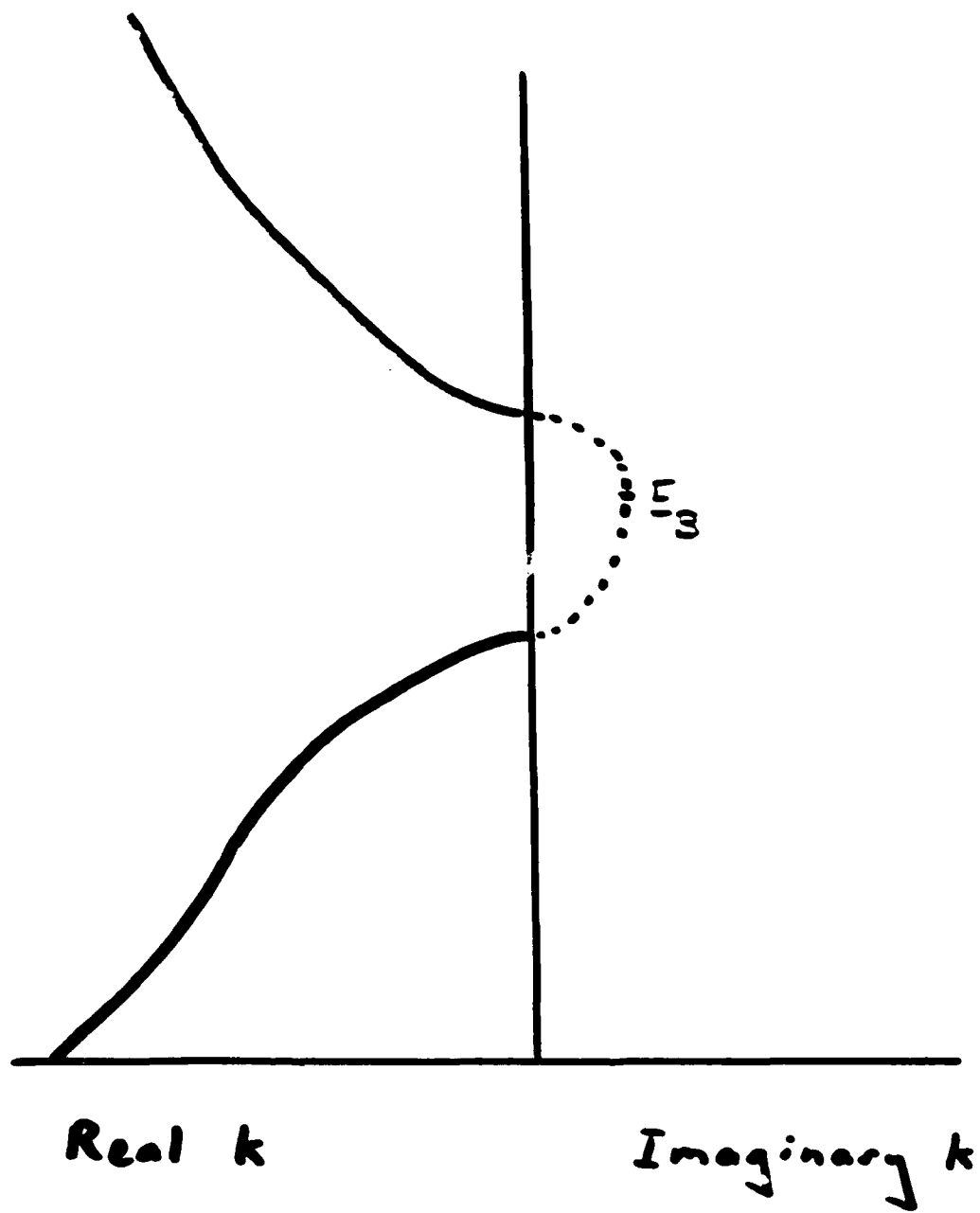
TERSOFF (1984)

WHAT IS ϕ_b ? $\Rightarrow$ WHAT IS E_{ss} ?

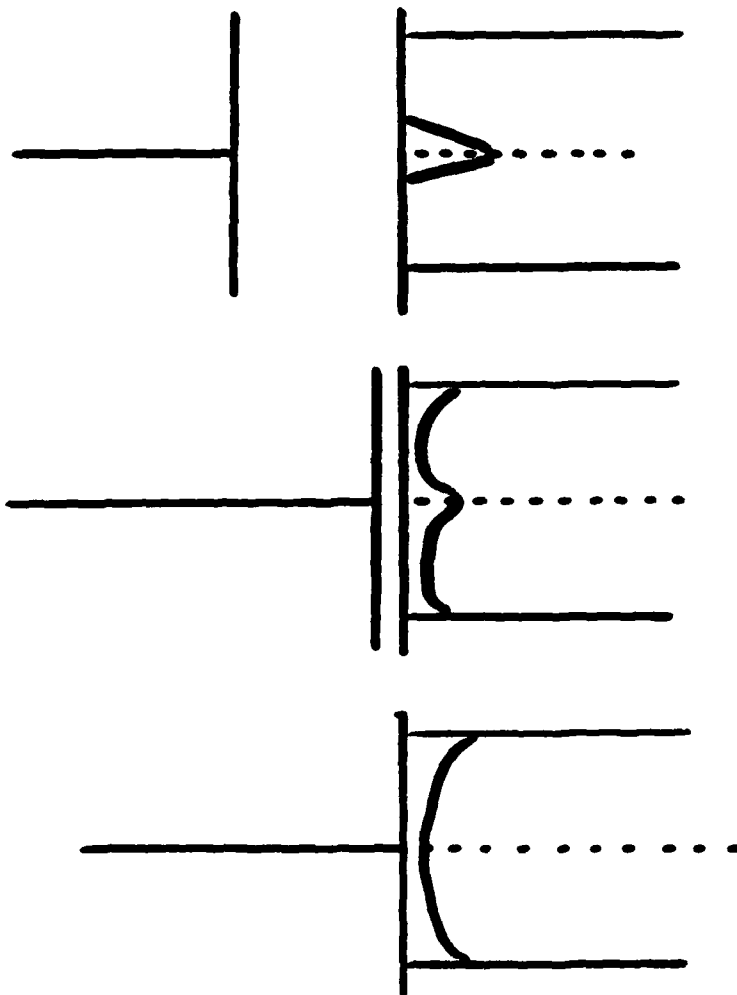
APPELBAUM + HAMANN (1974):

ROLE OF SELF-CONSISTENT DIPOLE





SURFACE VS. INTERFACE



TEJEDOR + FLORES (1978)

SURFACE STATES AND INTERFACE STATES (MIGS) BOTH PIN E_F AT E_B

GENERALIZE TO 3-D, HETEROPOLAR



FOR BARE SURFACE,

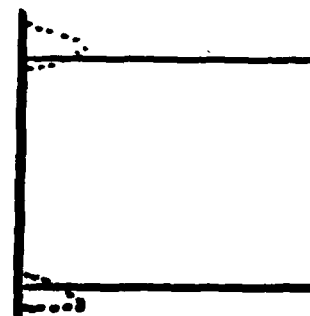
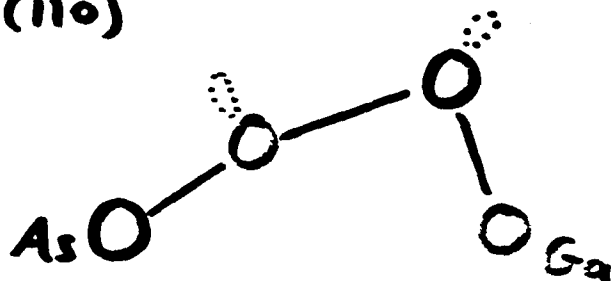
$$\phi_{lp} + \phi_{ln} = E_g - E_g^s.$$

ADDING METAL BROADENS
STATES ($\rightarrow$ MIGS).

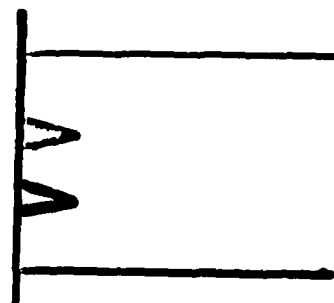
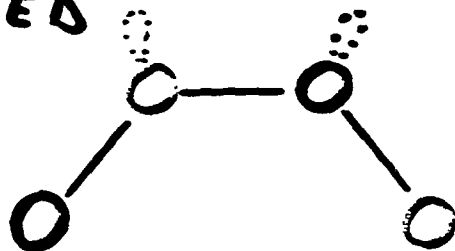
THEN $E_g^s \rightarrow 0$, E_F PINNED MIDWAY,
 $E_F \rightarrow E_g$

POSSIBLE INTERPRETATION OF STANFORD EXPERIMENTS

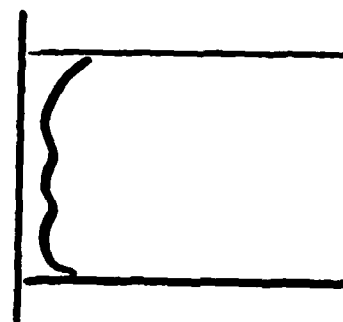
GaAs (110)



UNBUCKLED



METALLIZED



PREDICTING SCHOTTKY BARRIERS

- AT BARE SURFACE, SURFACE STATES PIN E_F AROUND EFFECTIVE GAP CENTER E_B
(BARDEEN, APPELBAUM & HAMANN)
- AT METAL-SEMICONDUCTOR INTERFACE, SURFACE STATES HYBRIDIZE WITH METAL STATES, BECOME "MIGS";
 E_F STILL PINNED NEAR E_B
- CALCULATE E_B

Generalize to three dimensions

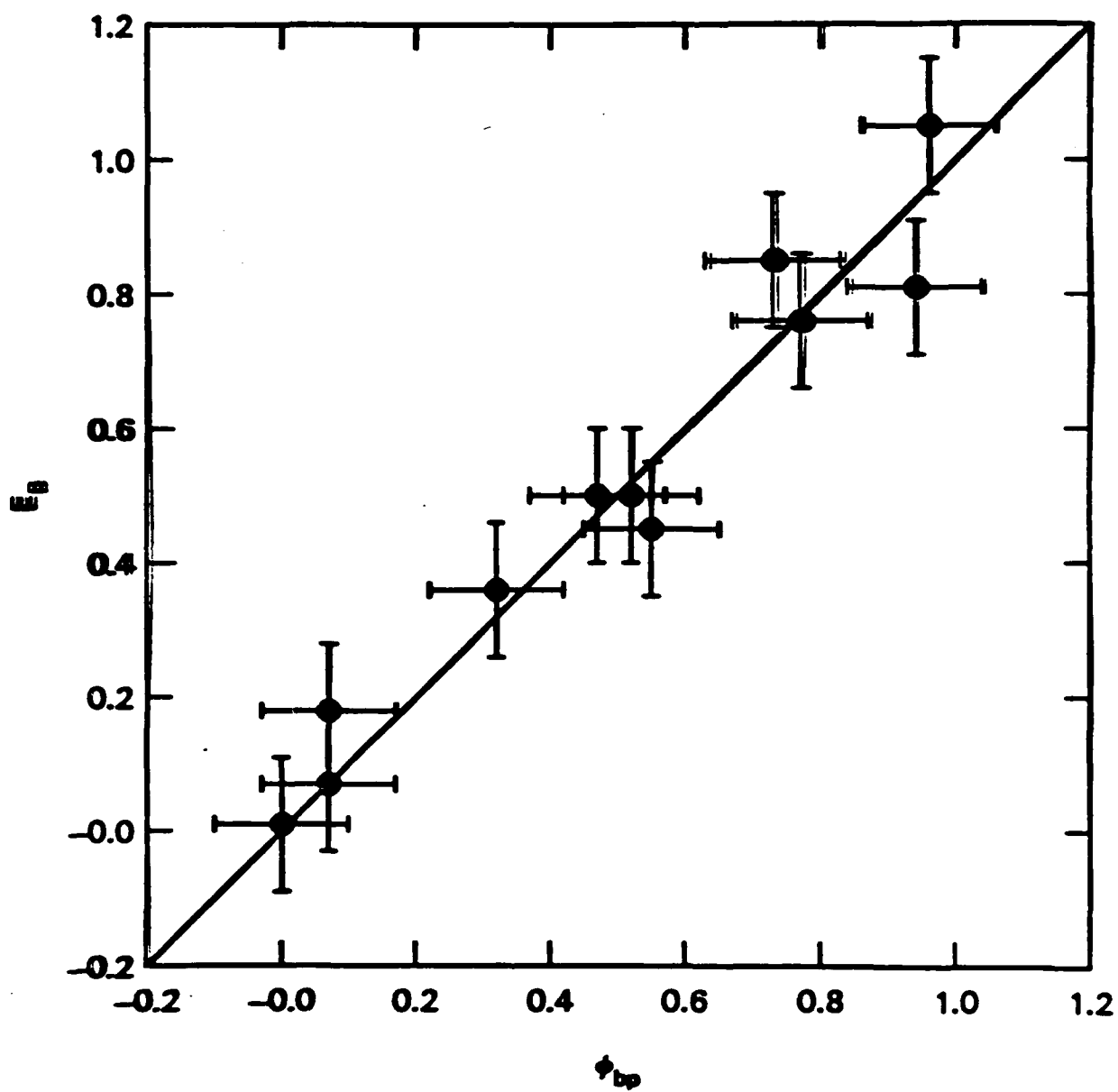
$$G(\vec{R}, E) \equiv \int d\vec{r} \sum_{nk} \frac{\psi^*(\vec{r}) \psi(\vec{r} + \vec{R})}{E - E_{nk}}$$
$$= \sum_{nk} \frac{e^{i\vec{k} \cdot \vec{R}}}{E - E_{nk}}$$

Locate E_B where valence + conduction
bands contribute equally to $G(\vec{R}, E)$

Reduces to branch point in 1-dimension

Calculation:

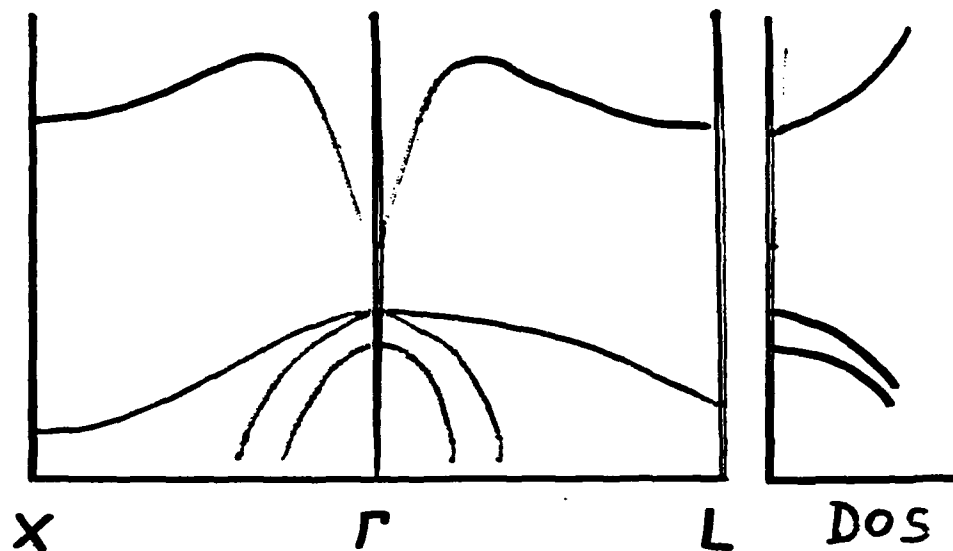
Input only E_{nk}
LAPW method
band gap problem
strain



485

REAL SEMICONDUCTOR

LINE UP "CENTER" OF GAP



WHERE IS CENTER?

Effective gap center

$$E_o = (\bar{E}_v + \bar{E}_c) / 2$$

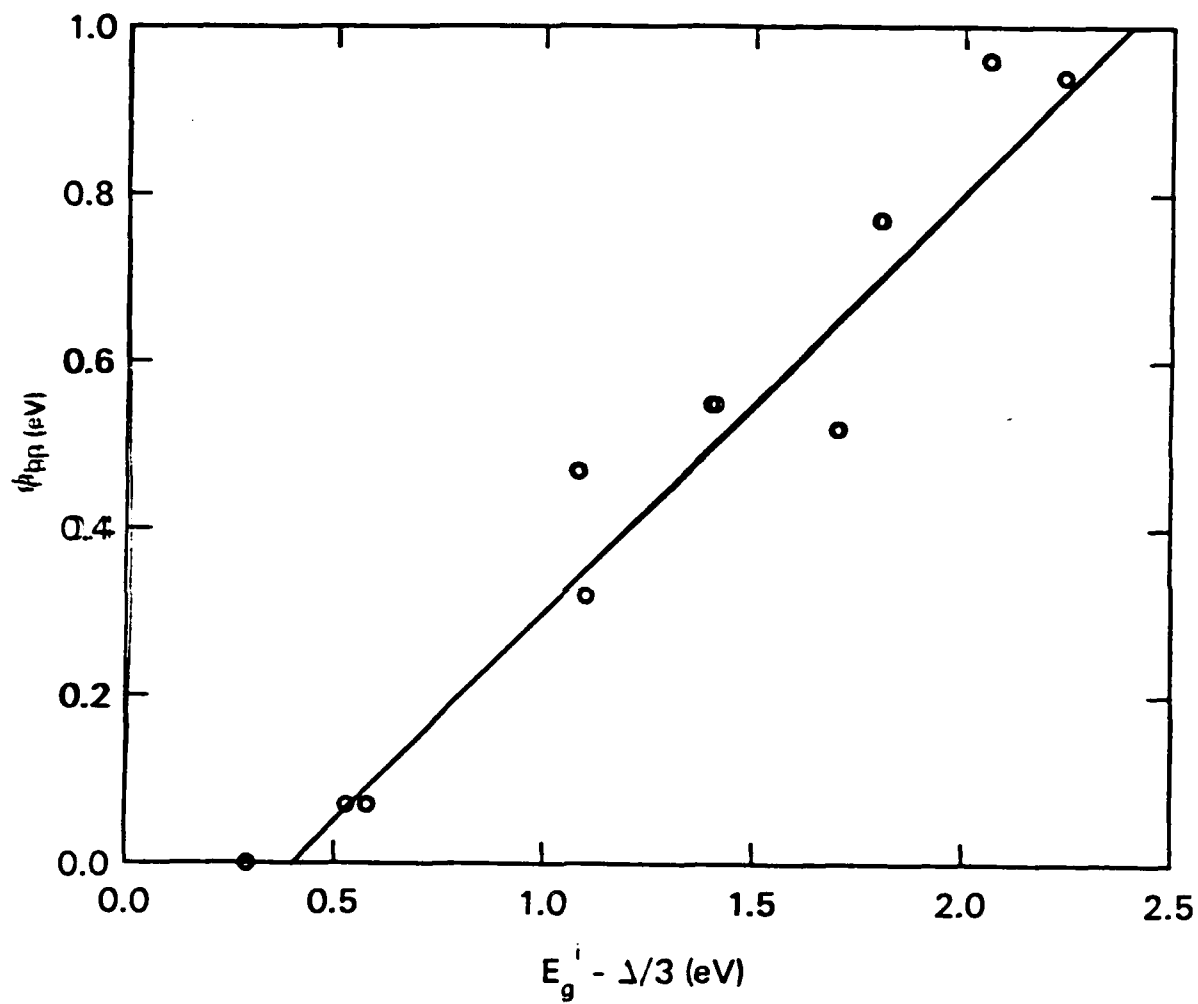
$$\bar{E}_v = E_v - \Delta / 3$$

$$\bar{E}_c = E_v + E_g^i$$

$$\begin{aligned}\bar{E}_B &= E_o - E_v = \frac{1}{2}(E_v - \frac{\Delta}{3} + E_v + E_g^i) - E_v \\ &= \frac{1}{2}(E_g^i - \frac{\Delta}{3})\end{aligned}$$

need some adjustable parameter

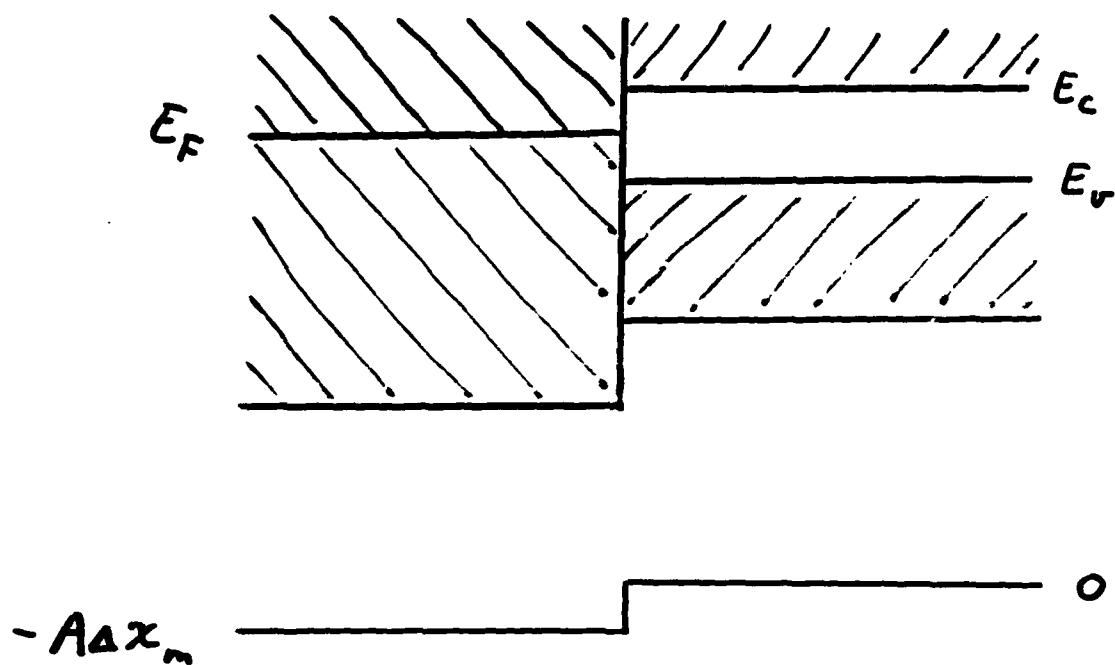
$$\Rightarrow E_B = \frac{1}{2}(E_g^i - \frac{\Delta}{3}) + \delta_m$$



$$\delta_m = -0.20 \text{ eV}$$

$$rms = 0.07 \text{ eV}$$

$$max = 0.13 \text{ eV}$$



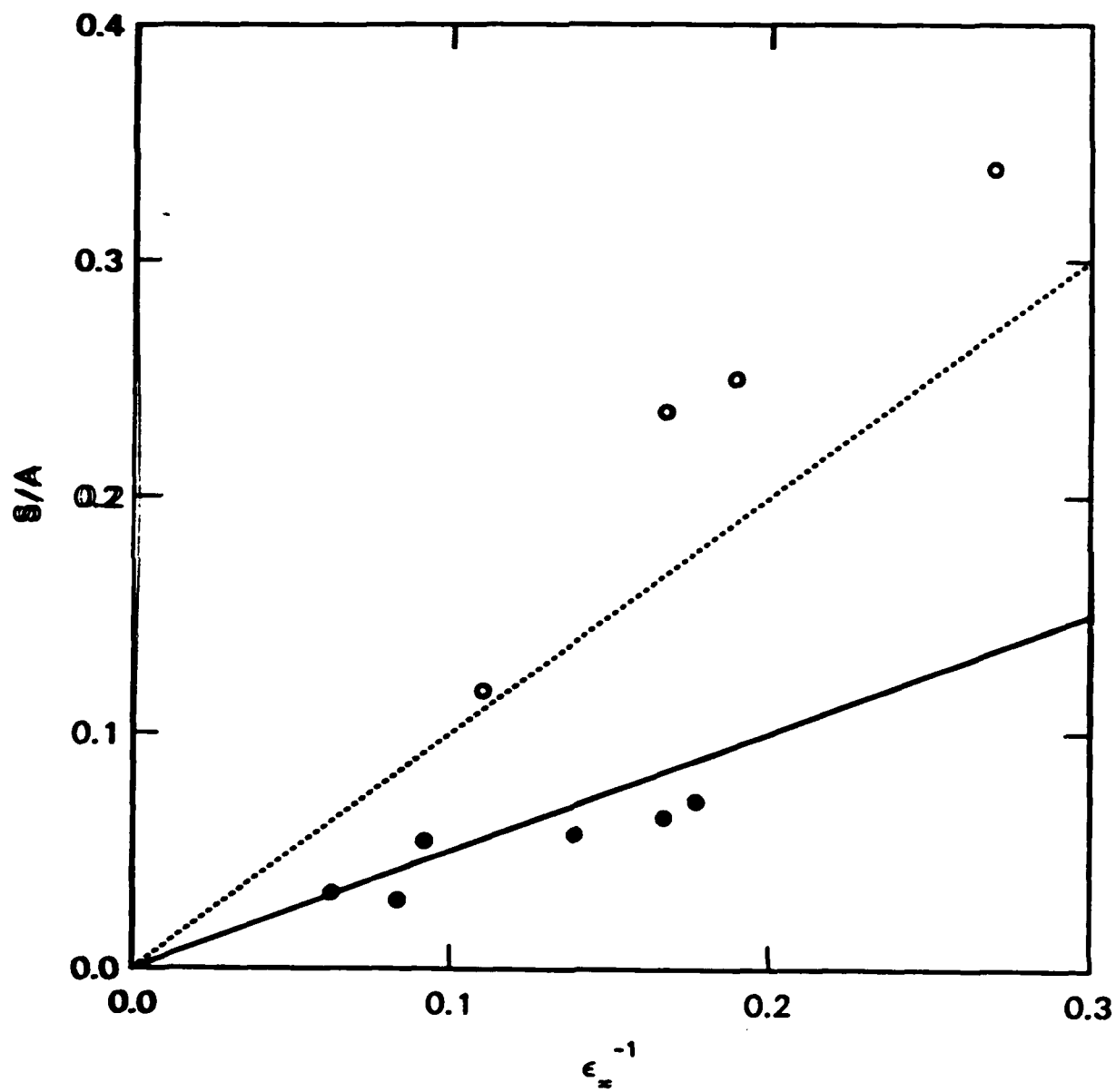
$$S = \frac{d\phi_{bn}}{d\chi_m}$$

$$\bar{S} = S/A \quad A \approx 2.8 \text{ eV}$$

$$\Delta\phi_{bn} = S \Delta\chi_m = A \Delta\chi_m / E_{eff}$$

$$\Rightarrow \bar{S} = 1/E_{eff}$$

$$0 \leq \bar{S} \leq 1/E_{eff} \quad \text{guess} \quad \bar{S} \approx 1/2E_{eff}$$



ROLE OF INTERFACE IDEALITY

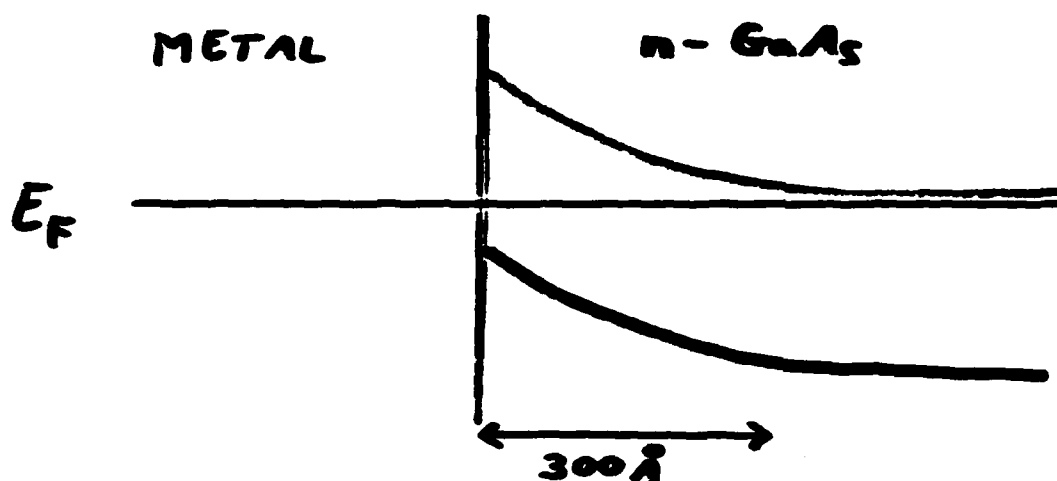
THEORY ONLY VALID FOR "IDEAL"
SURFACE, INTERFACE?

- E_F PINNED BY GAP STATES
- STATES DETERMINED BY BOTH SEMICONDUCTOR BULK AND INTERFACE.
[SCHRÖDINGER EQ. AND BOUNDARY COND.]
- WHEN INCLUDE DIPOLE SELF-CONSISTENTLY, FIND STATES DISTRIBUTED SO E_F FALLS AT E_B .

EXPECT E_F PINNED NEAR E_B
FOR WIDE VARIETY OF STRUCTURES

IMPORTANCE OF INTERFACE CHEMISTRY, STRUCTURE

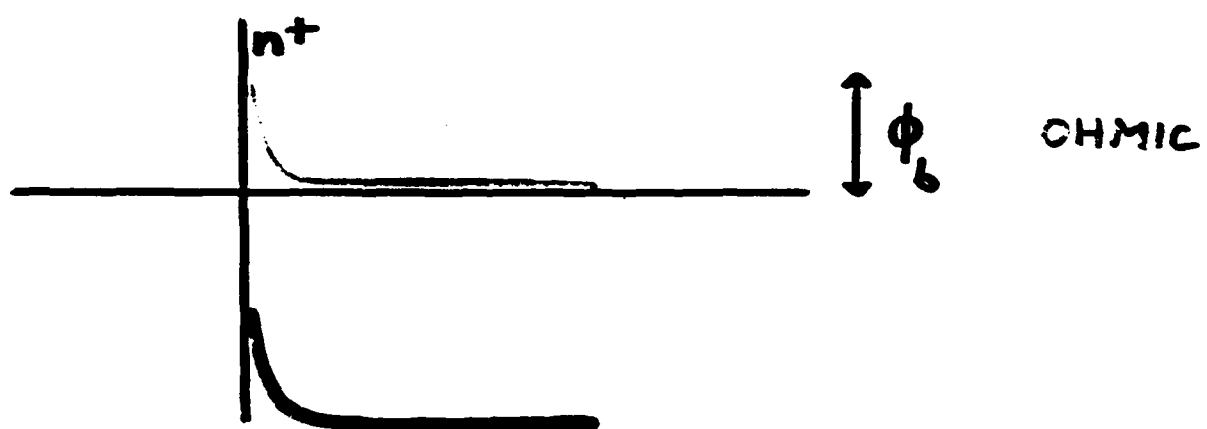
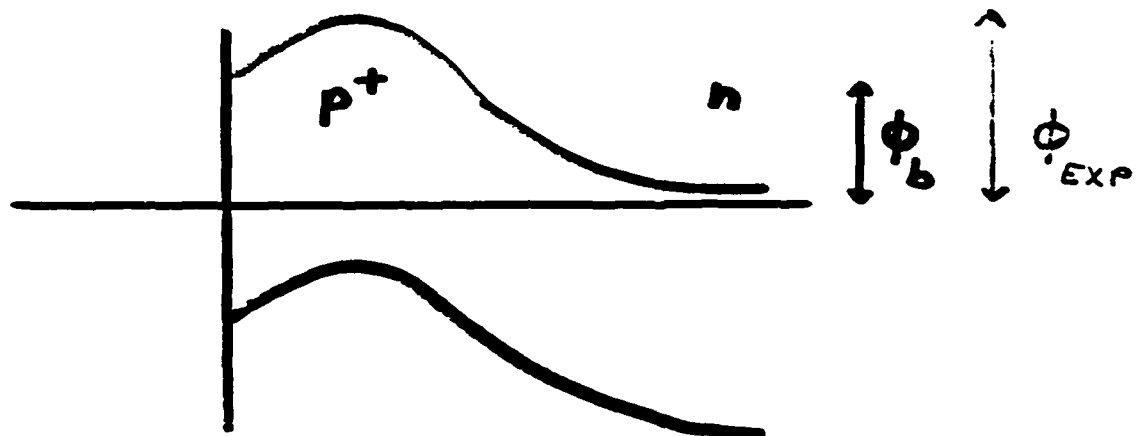
SCHOTTKY BARRIER NOT IMPORTANT!
TRANSPORT IS IMPORTANT!



IDEAL INTERFACE: $\phi_b \rightarrow$ TRANSPORT

OTHER POSSIBILITIES.

SIMPLE EXAMPLES



MORE COMPLEX POSSIBILITIES

LATERAL INHOMOGENEITY

RESONANT TUNNELING, HOPPING

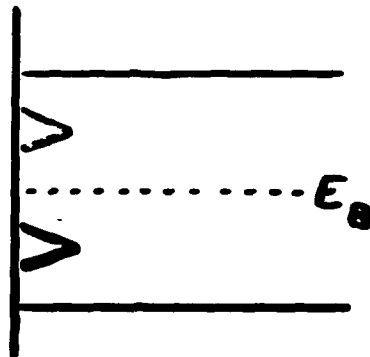
EXCHANGE REACTION (Al-GaAs)

IMPORTANCE OF EXPERIMENTALLY
CHARACTERIZING TRANSPORT

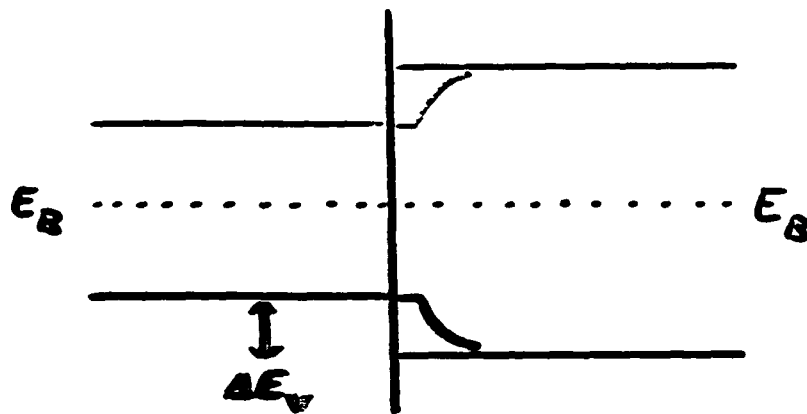
I-V vs. T; IDEALITY

C-V vs. V

CONNECTION WITH HETEROJUNCTIONS
HAD GAP STATES SYMMETRIC ABOUT E_B



SIMILARLY, AT HETEROJUNCTION,
ALIGN TWO E_B 'S.



$$\Delta E_V = \Delta E_B = \Delta E_C$$

AD-A183 158

A WORKSHOP ON 3-5 SEMICONDUCTOR: METAL INTERFACIAL
CHEMISTRY AND ITS EFFECTS (U) STANFORD UNIV CA
W E SPICER ET AL. 05 NOV 86 N00014-87-G-0038

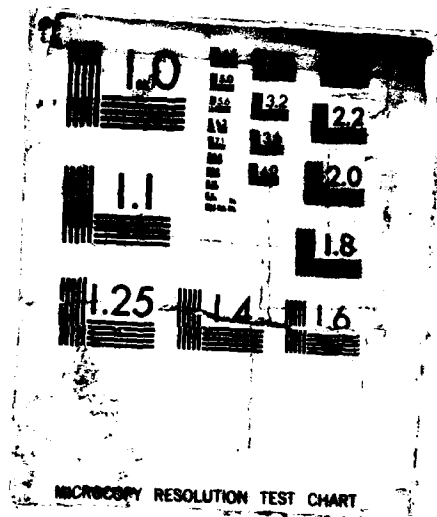
6/7

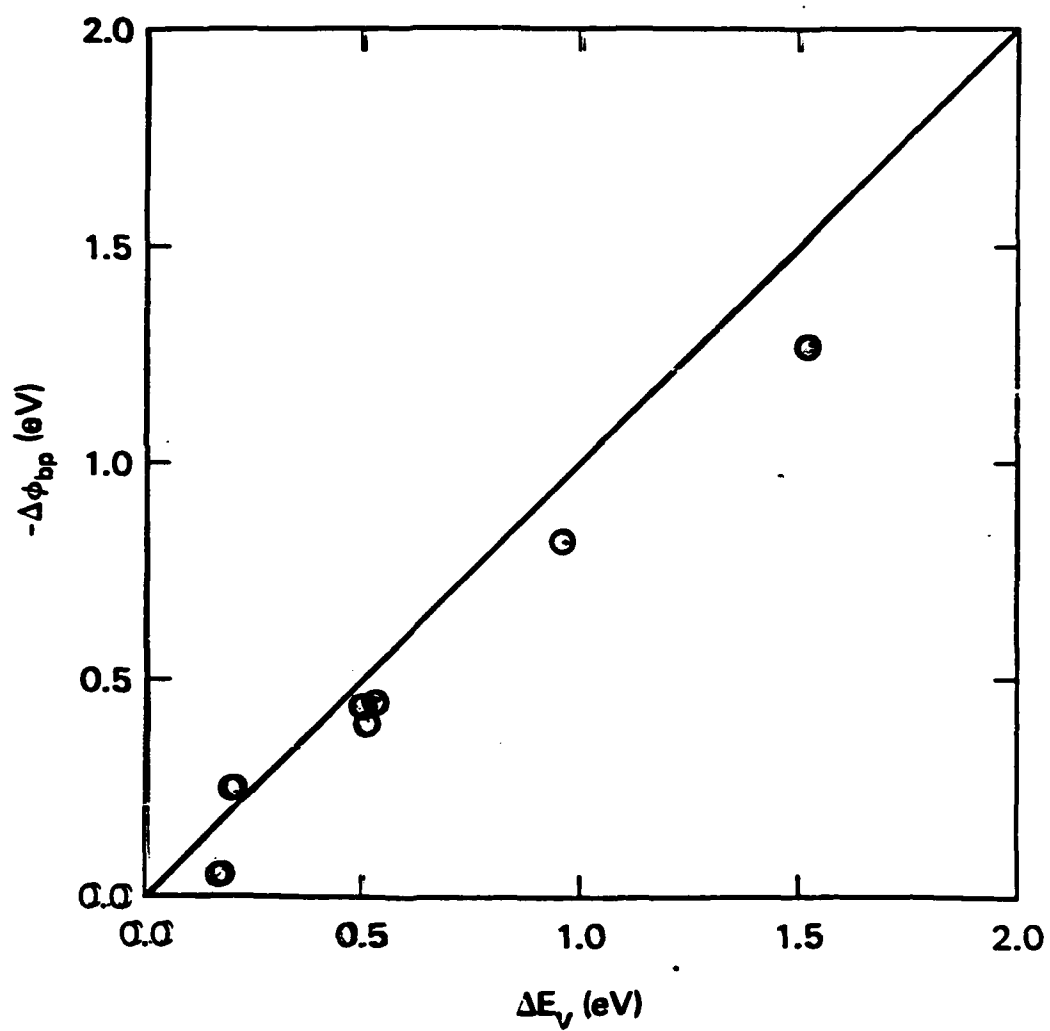
UNCLASSIFIED

F/G 20/12

NL

ST





496

SUMMARY

- INTRINSIC SURFACE OR INTERFACE STATES PIN E_F NEAR E_B
- EXCELLENT AGREEMENT WITH EXP
- $E_B \sim \frac{1}{2} E_g^2$
- METAL DEPENDENCE: $S \sim 1/\epsilon_\infty$
- DIRECT CONNECTION WITH BAND LINEUPS
- EVIDENCE AGAINST EXTRINSIC MECHANISM

**Recent Photoemission and Cathodoluminescence
Spectroscopy Studies of III-V
Semiconductor-Metal Interfaces**

Leonard J. Brillson

Xerox Corporation

RECENT PHOTOEMISSION AND
CATHODOLUMINESCENCE SPECTROSCOPY STUDIES OF
III-V SEMICONDUCTOR-METAL INTERFACES

- **CHEMISTRY OF CLEAN $\text{In}_x\text{Ga}_{1-x}\text{As}$ METAL INTERFACES**
- **CHEMICAL DEPENDENCE OF $\text{In}_x\text{Ga}_{1-x}\text{As}$ E_F MOVEMENTS**
- **DIRECT OBSERVATIONS OF III-V/METAL INTERFACE STATES**
- **SPECTRAL CORRELATION WITH ELECTRONIC AND CHEMICAL STRUCTURE**

Supported in Part by the Office of
Naval Research

COLLABORATORS

Enrique Viturro
Michael Slade

Xerox Webster Research Center
Xerox Webster Research Center

Michael Kelly
Lila Tache
Douglas Kilday
G. Margaritondo

University of Wisconsin-Madison
University of Wisconsin-Madison
University of Wisconsin-Madison
University of Wisconsin-Madison

Peter Kirchner
Dave Pettit

IBM Yorktown
IBM Yorktown

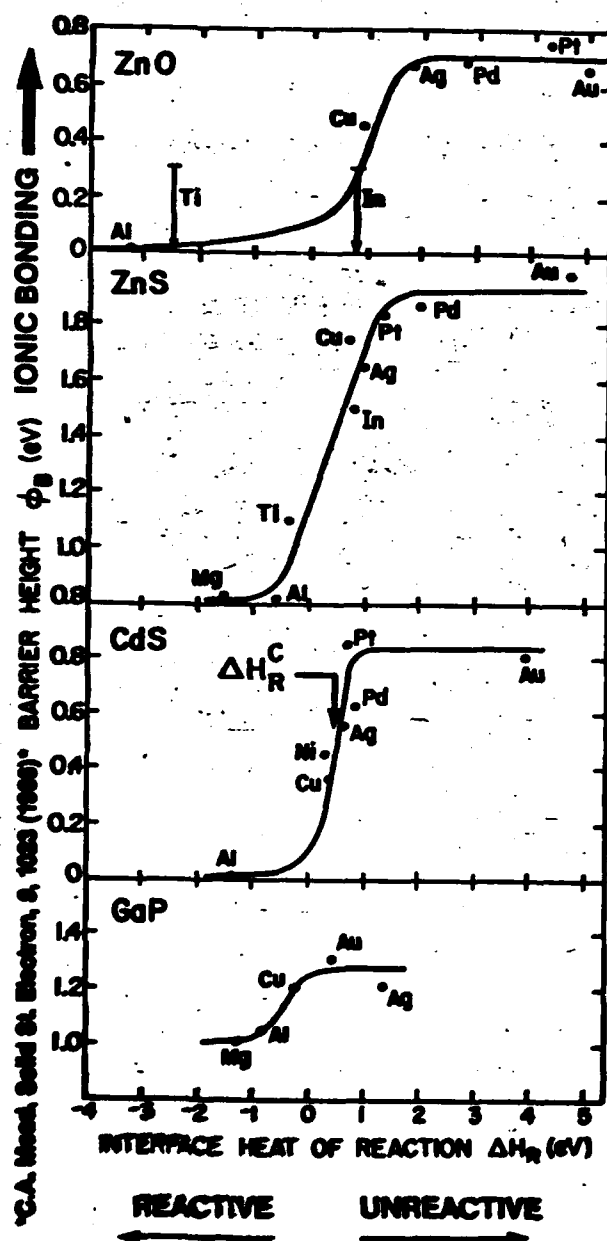
Jerry Woodall
Steve Wright

IBM Yorktown
IBM Yorktown

Piero Chiaradia

Istituto Struttura Materia, Frascati

TRANSITION IN SCHOTTKY BARRIER FORMATION WITH CHEMICAL REACTIVITY

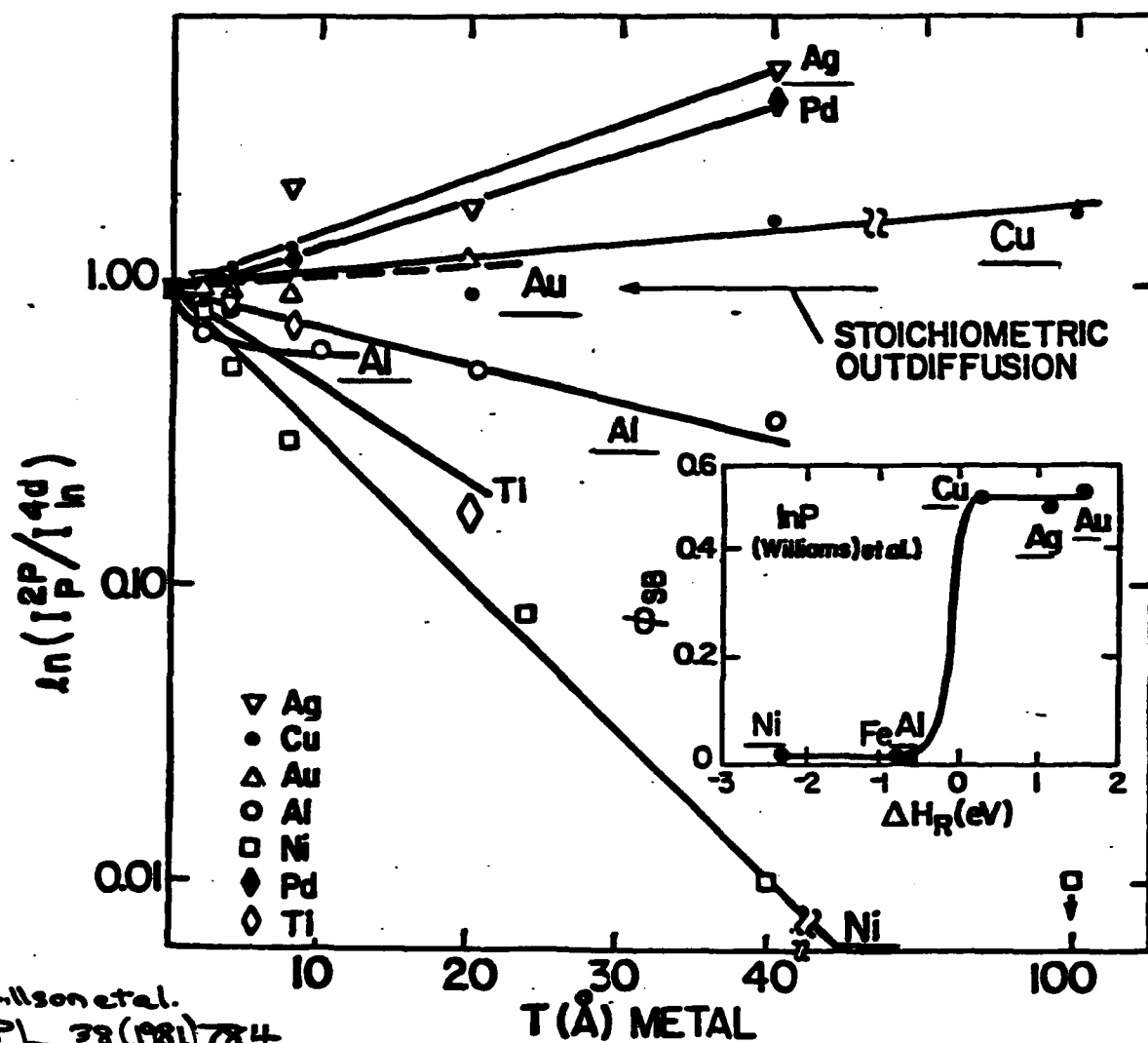


SAME TRANSITION FOR IONIC AND COVALENT SEMICONDUCTORS

TRANSITION AT EXPERIMENTALLY DETERMINED ΔH_R

L.J. Brillson
Phys. Rev. Lett. 40, 280 (1978)

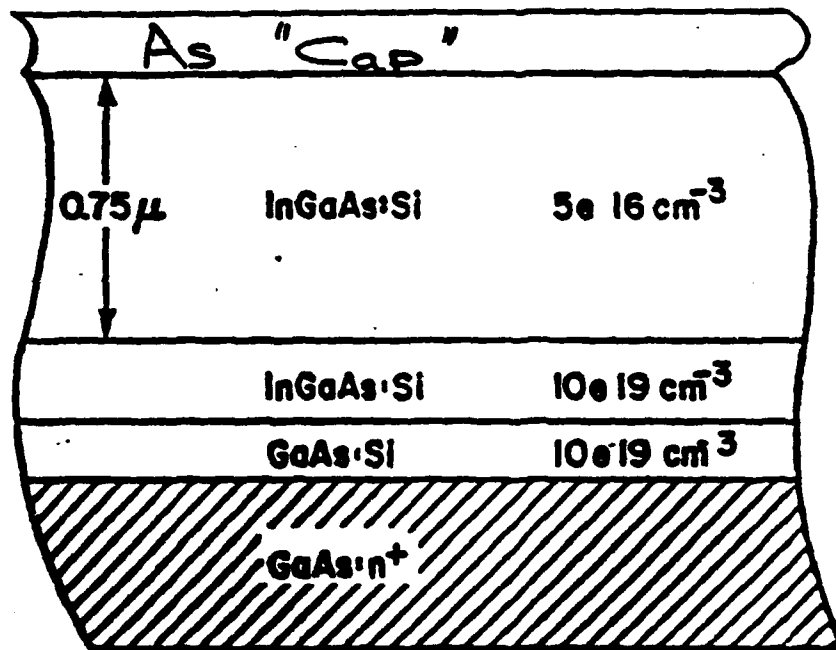
STOICHIOMETRY OF OUTDIFFUSION VS SCHOTTKY BARRIER HEIGHT



Brillson et al.
A.P.L. 38 (1981) 784

**STRENGTH OF INTERFACE CHEMICAL BONDING
DETERMINES ELECTRICITY - ACTIVE SITES (III-V's)**

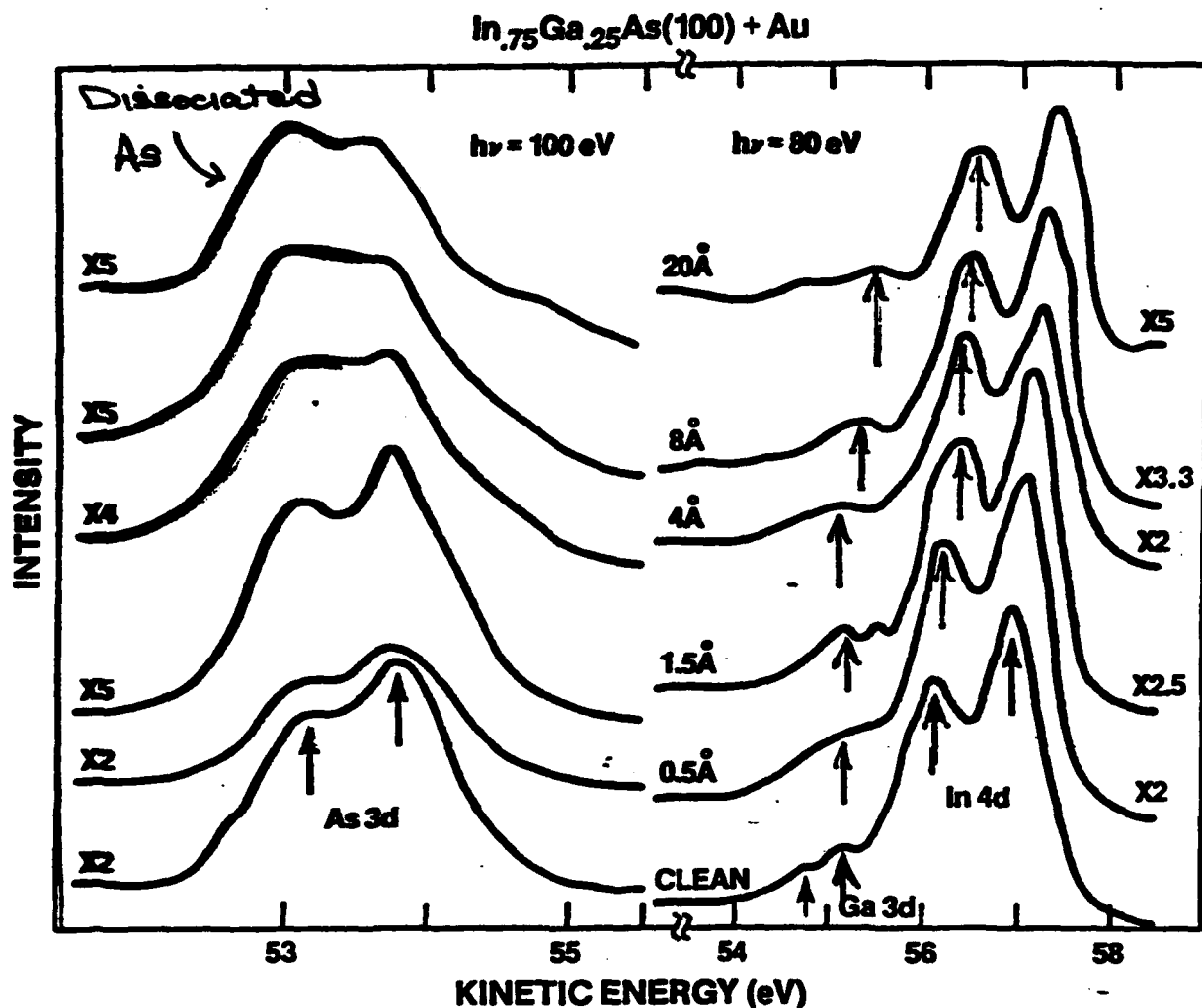
Thermal Cleaning of As- "Capped" $\text{In}_x\text{Ga}_{1-x}\text{As}(100)$



Woodell, Pettit, Kitchner, & Wright

- Clean, Ordered $\text{In}_x\text{Ga}_{1-x}\text{As}$ Grown By MBE
- "Ohmic" Back Contacts
- De-"capping" of As Protective Layer in JHV

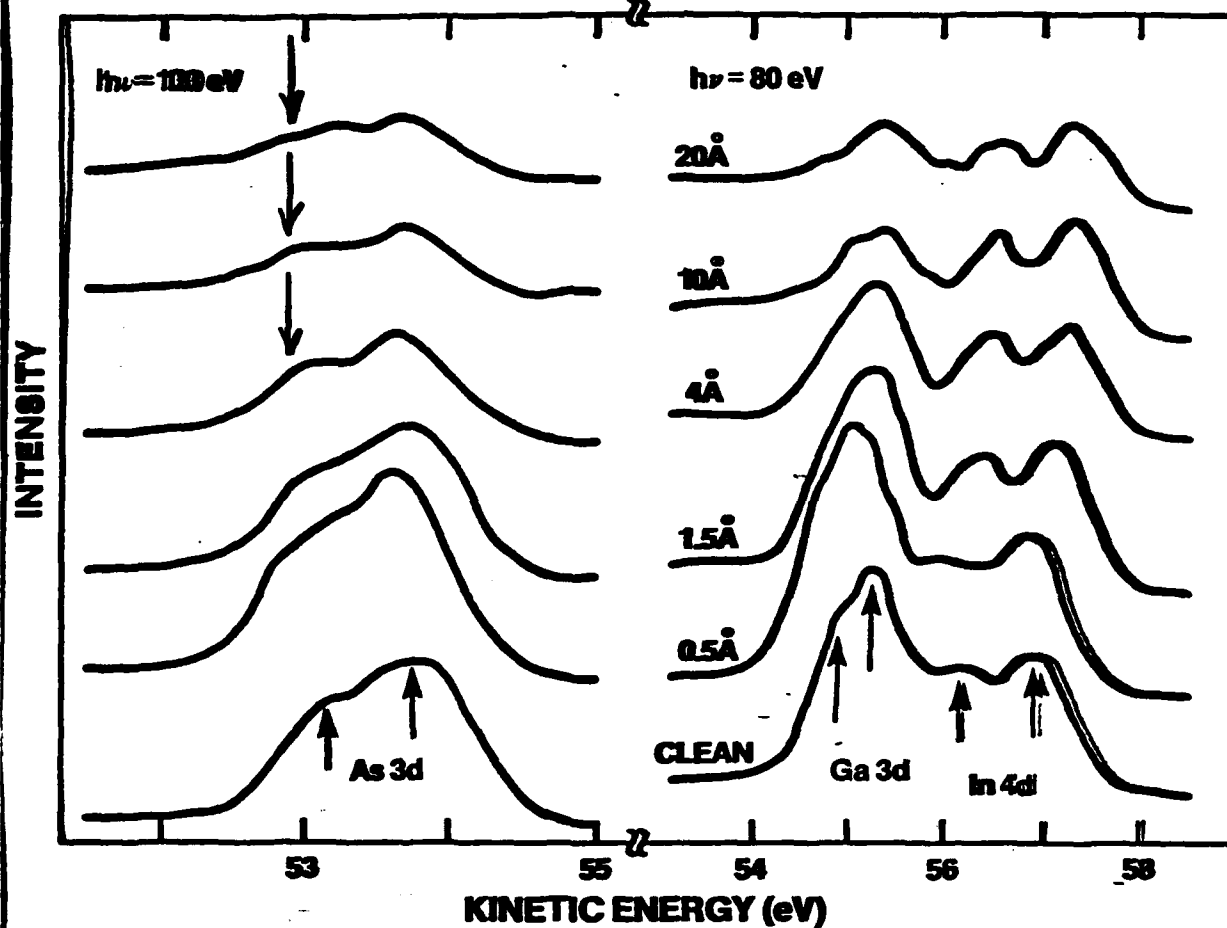
Interface Dissociation



- As - Rich Outdiffusion
- No Strongly Dissociated In or Ga
- E_F Shift: Lower Binding Energies

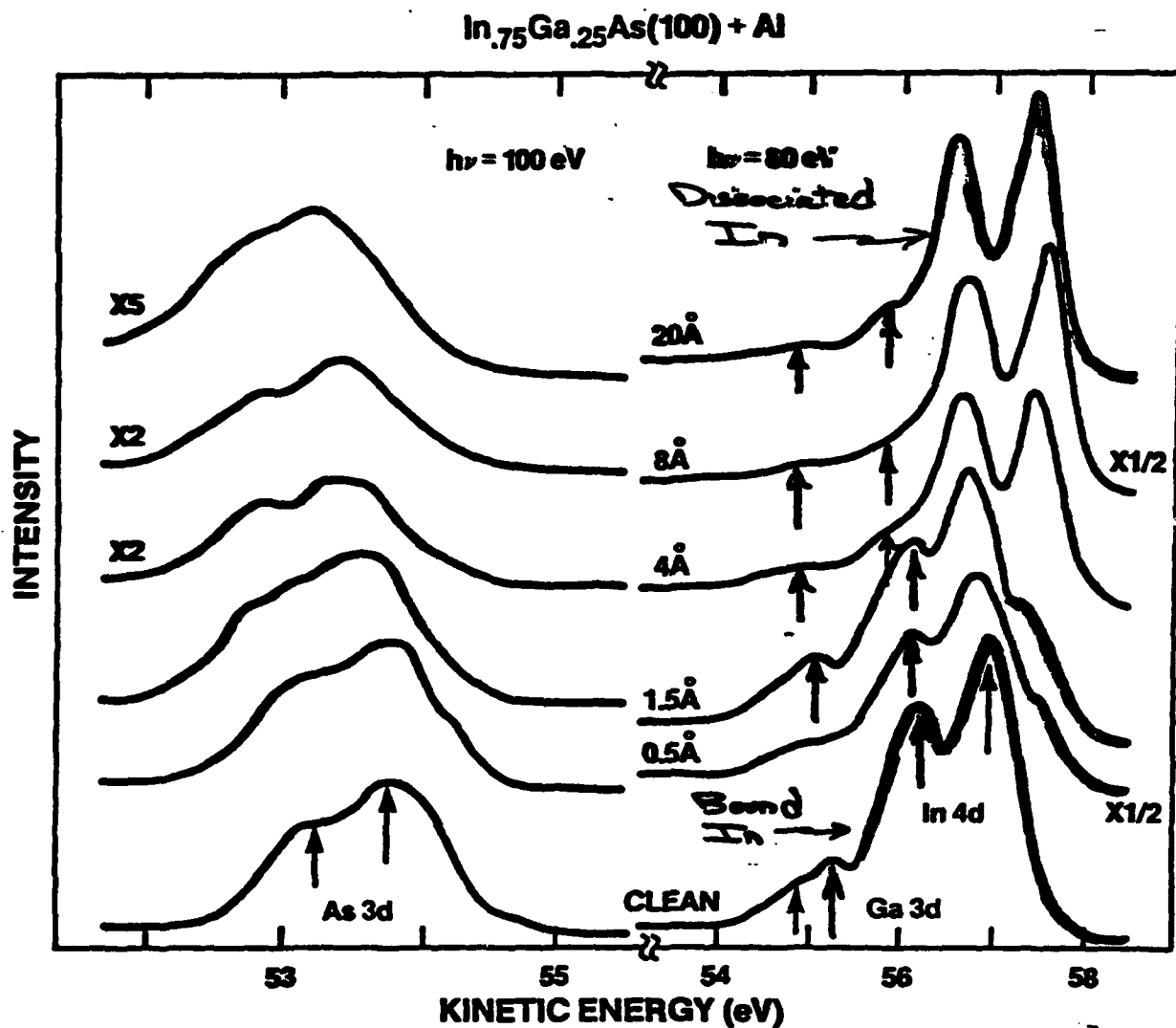
Interface Dissociation: Low In Alloy

$\text{In}_{25}\text{Ga}_{75}\text{As}(100) + \text{Au}$



- Little if Any Dissociated As
- No As-Rich Outdiffusion
- Contrast with High In Alloy

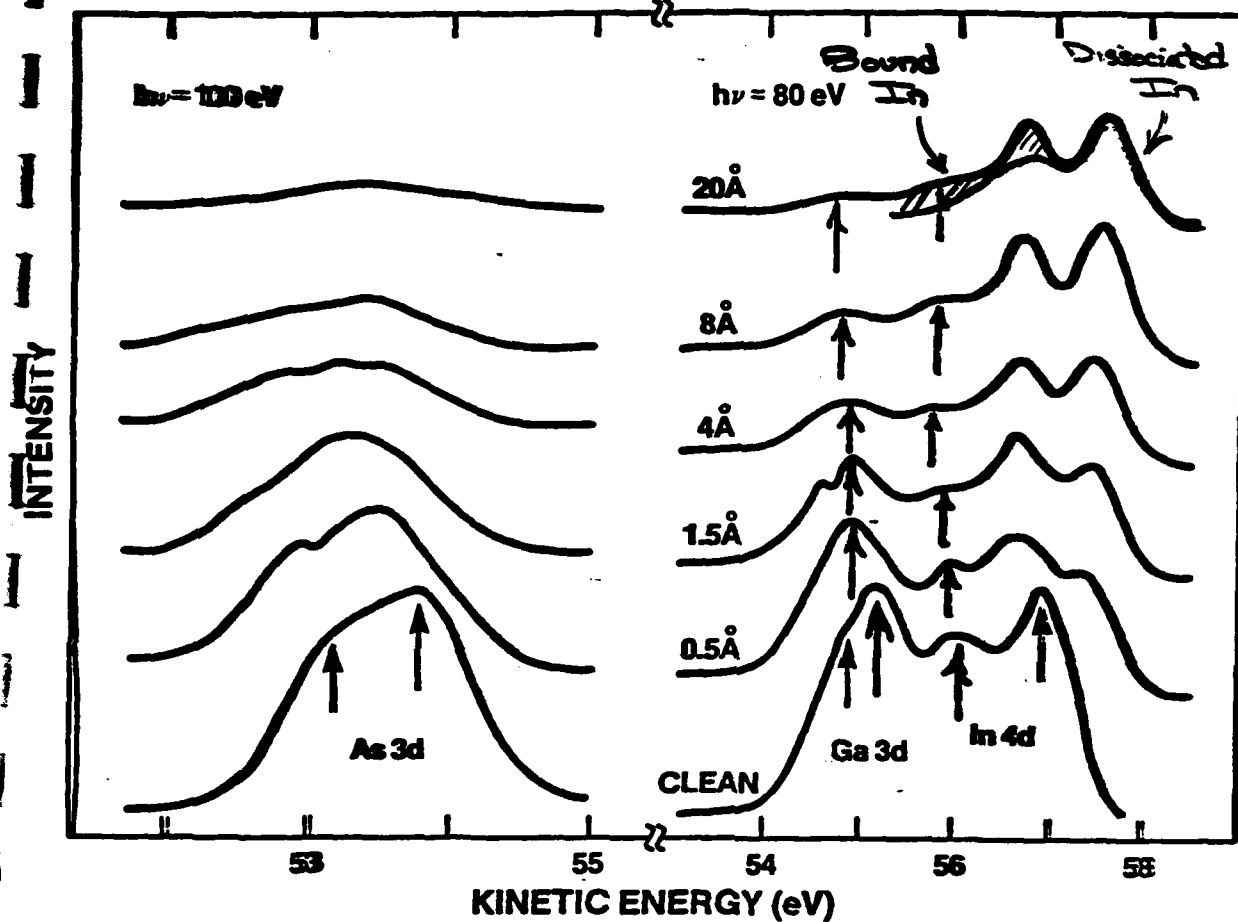
Interface Exchange Reaction



- Al Replaces In in InGaAs Lattice
— Low $\text{Bound In} / \text{Bound Ga}$
- No Ga Dissociation
- E_F Shift: Higher Binding Energies
- Little As Outdiffusion

Interface Exchange Reaction

$\text{In}_{25}\text{Ga}_{75}\text{As}(100) + \text{Al}$



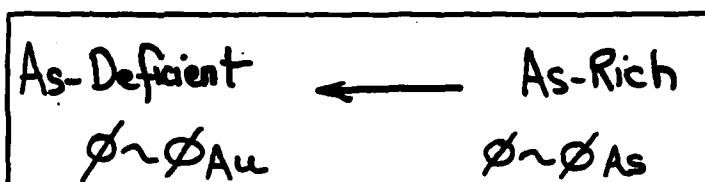
- Lower Proportion of Dissociated/Bound In
- Higher Proportion of Bound In/Bound Ga

⇒ KINETIC LIMITATION TO REPLACEMENT REACTION

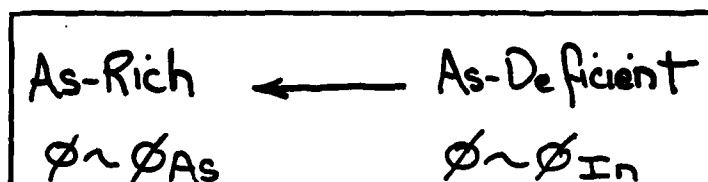
- Higher Proportion of Surface As

Metal-Semiconductor Interface Composition

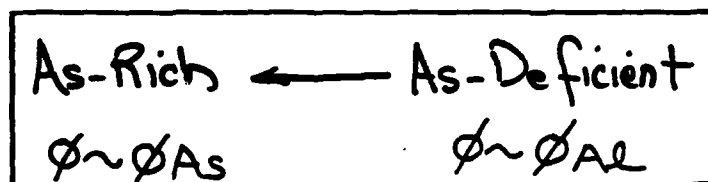
Au



In

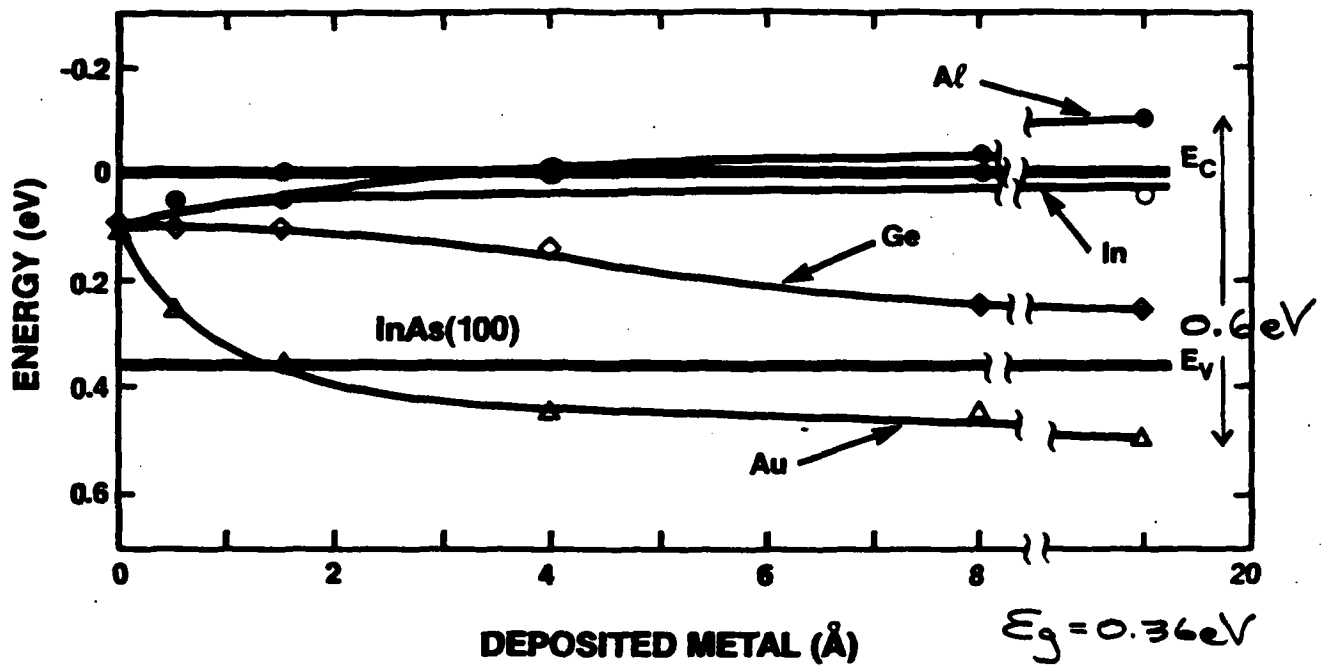


Al



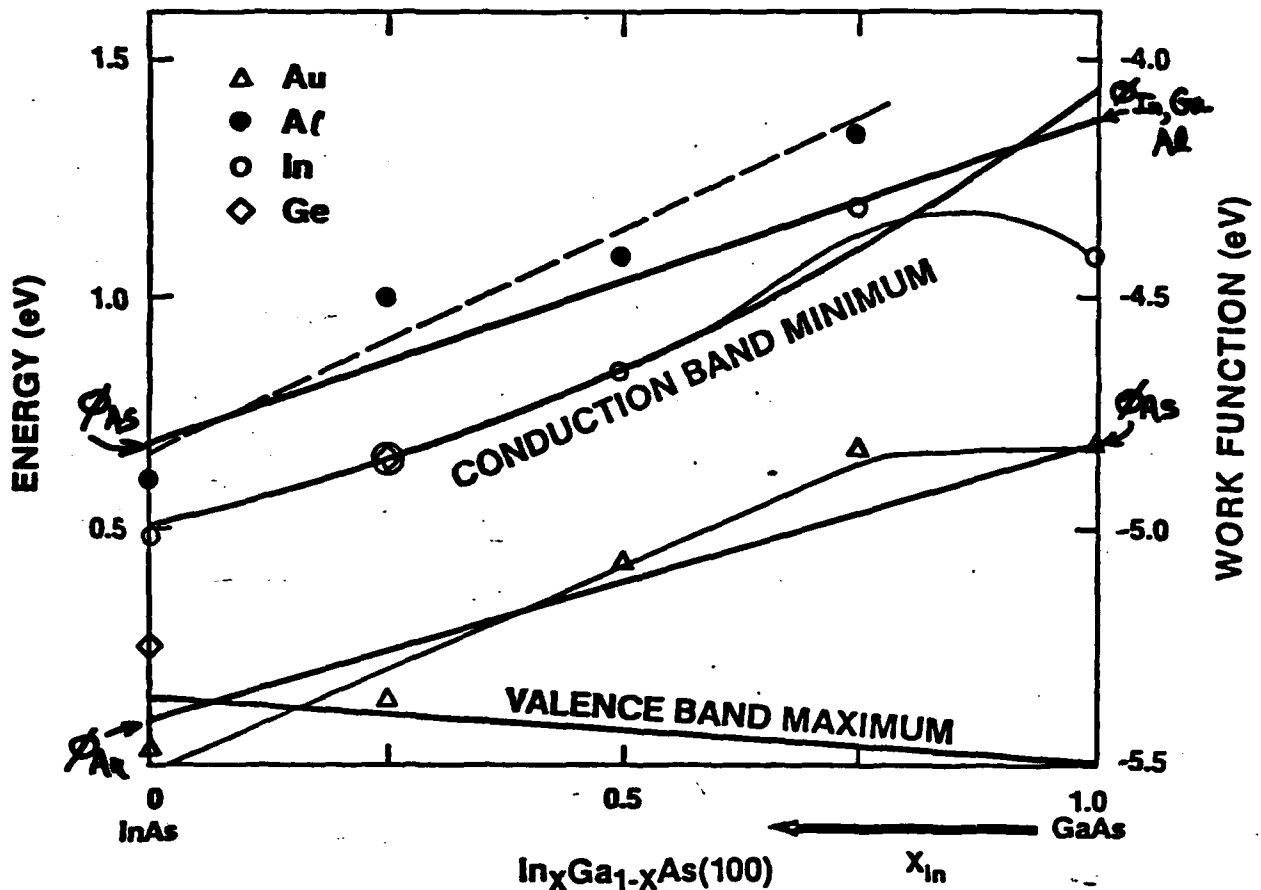
InAs $In_xGa_{1-x}As$ GaAs

Fermi Level Movement With Metal Deposition - InAs(100)



- Wide Range of E_F Stabilization
- E_F Movement Above Monolayer Coverage

E_F Stabilization Energies For Metals on $\text{In}_x\text{Ga}_{1-x}\text{As}$ (100)

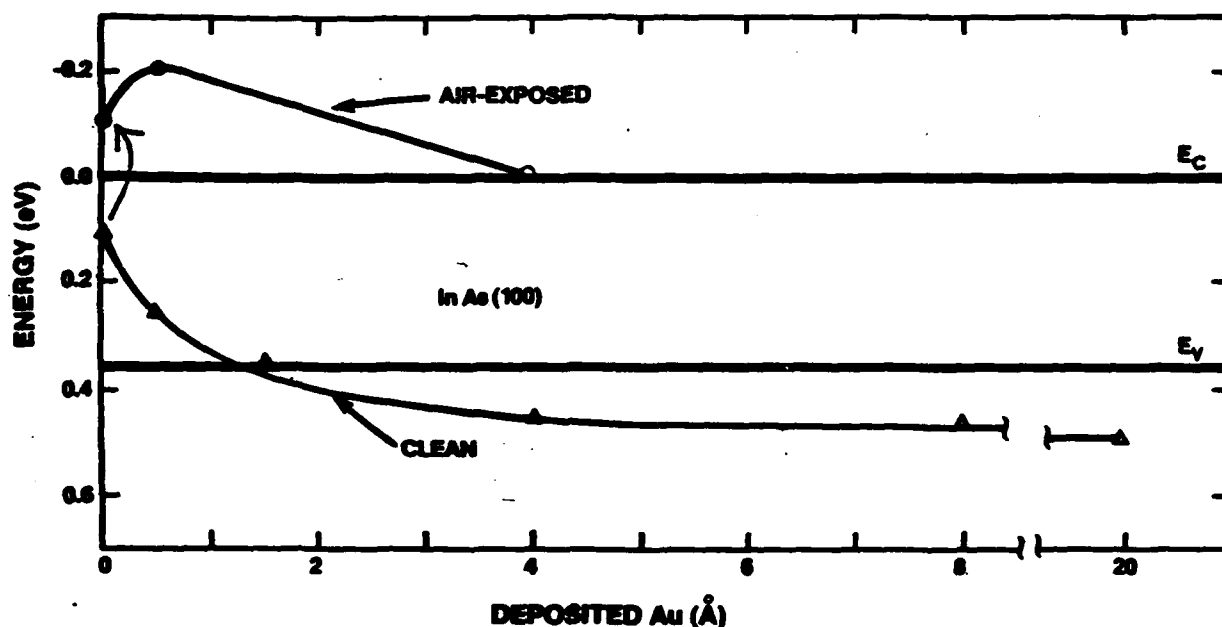


- E_F Not "Pinned"
- Regular Trends Across Alloy Series
- Tracking With Conduction Band
- Air-Exposed Surfaces: Different

Appl. Phys. Lett.,
in press
48, 1458 (1986)

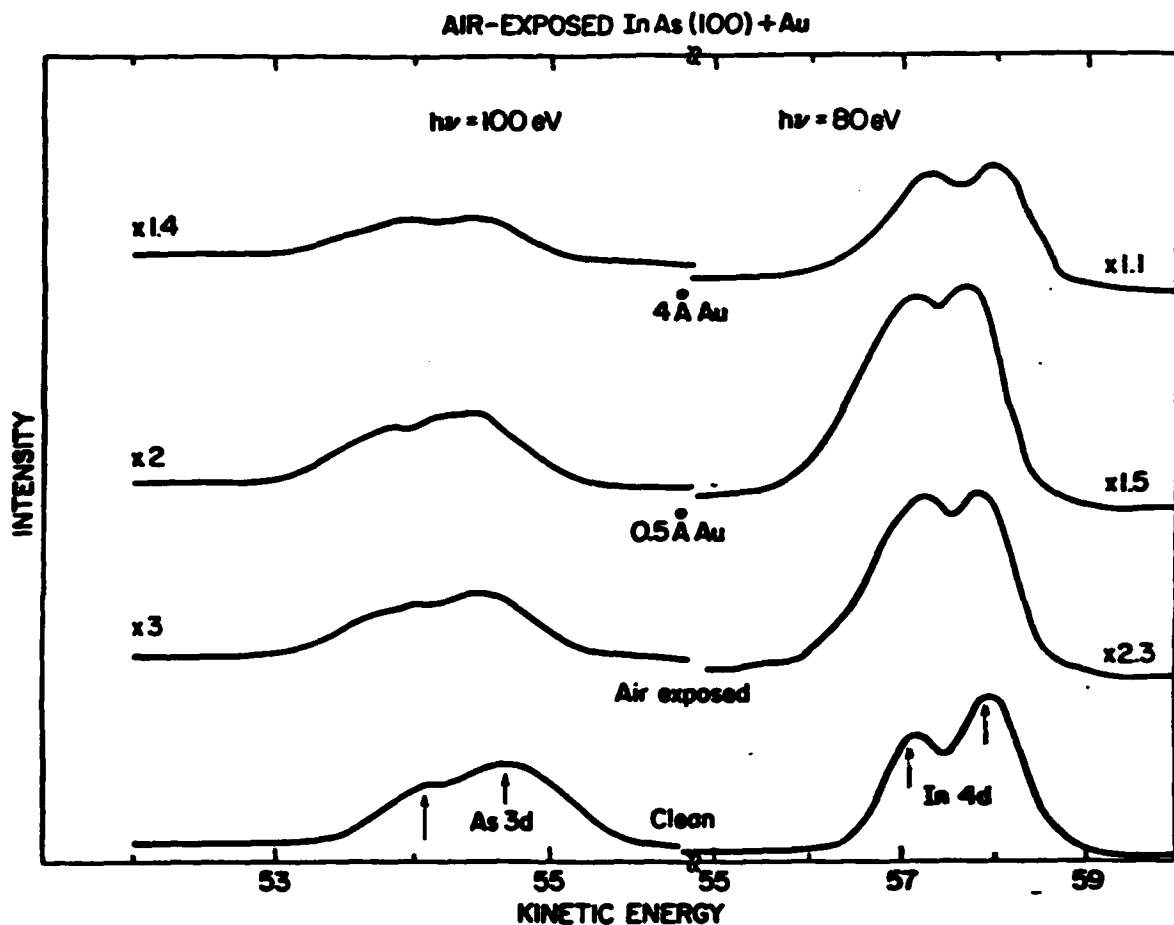
Influence of Air Exposure - In As(100)

All Initial Surfaces: Clean, Ordered



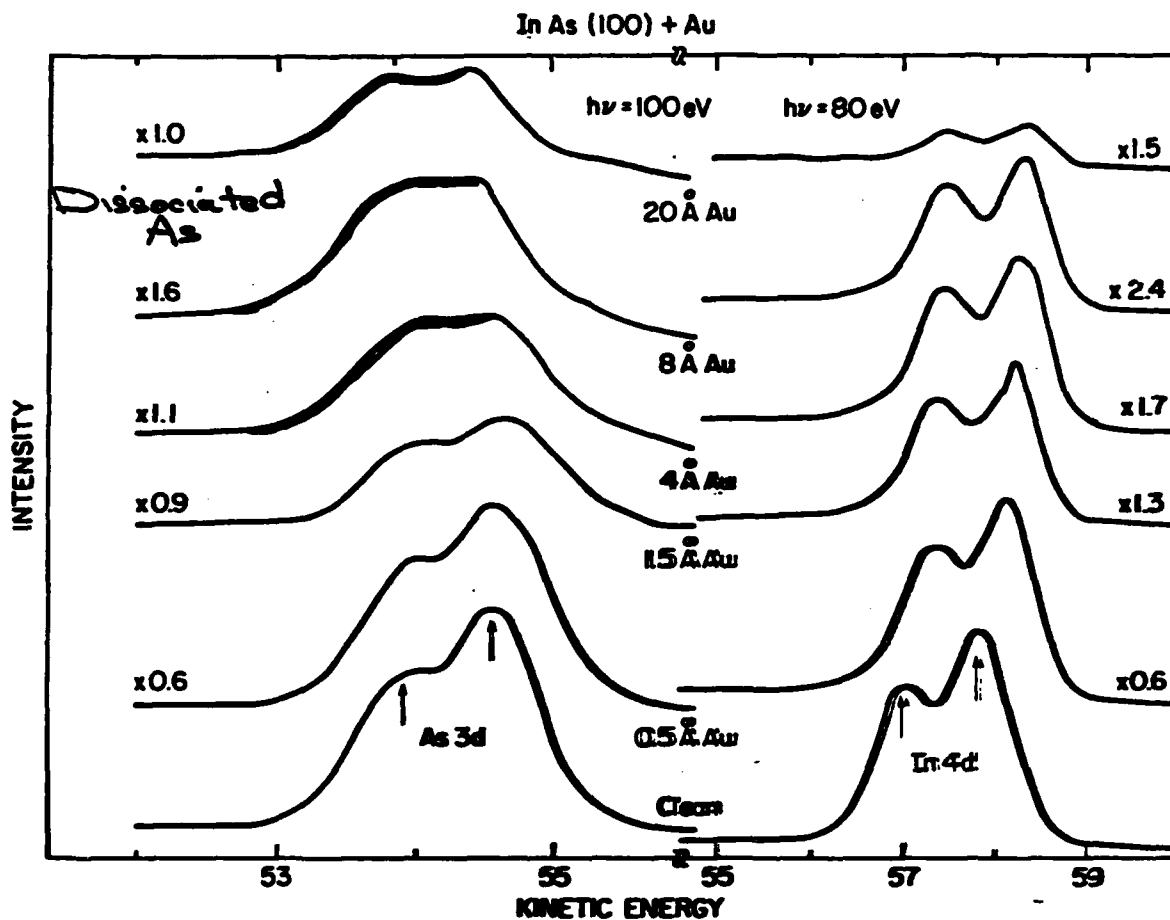
- Major Changes With Air Exposure
- Accounts For Previous Electrical Data

Effect of Air Exposure on Au-InAs Interface Dissociation



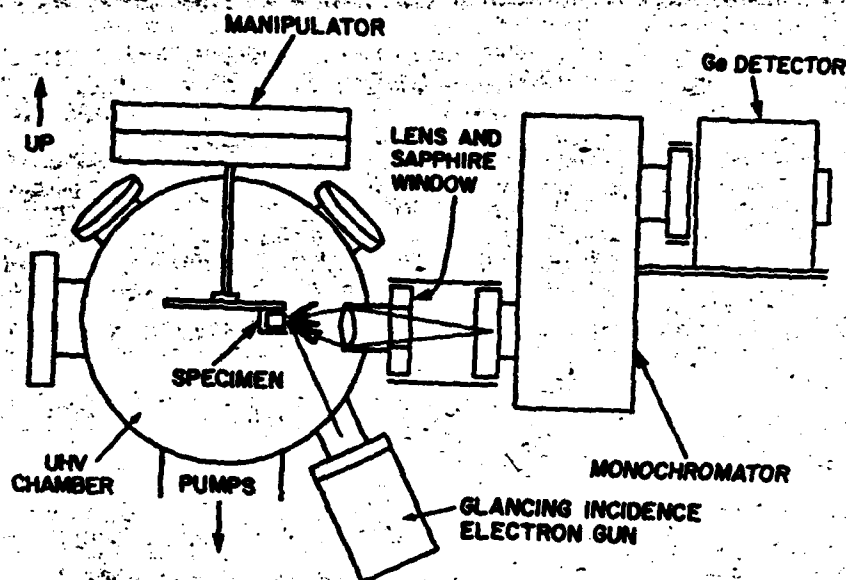
- Little Dissociated. As
- As/In Decreases with Au Coverage
- As outdiffusion Twice as Large for Clean InAs

Au-InAs Interface Dissociation



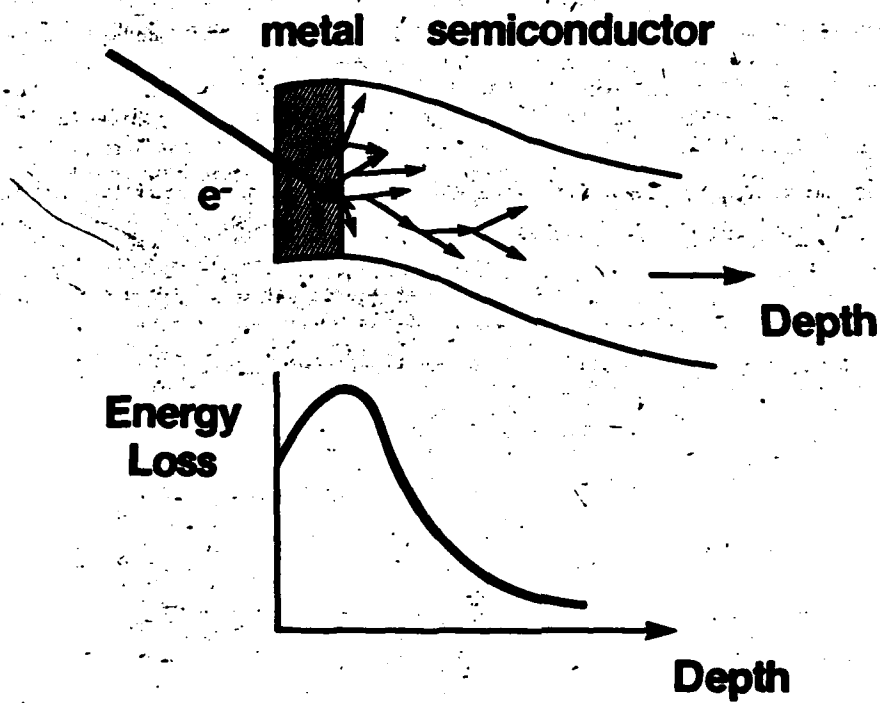
- Significant Dissociated As
- As / In Increases with Au Coverage

Cathodoluminescence Spectroscopy



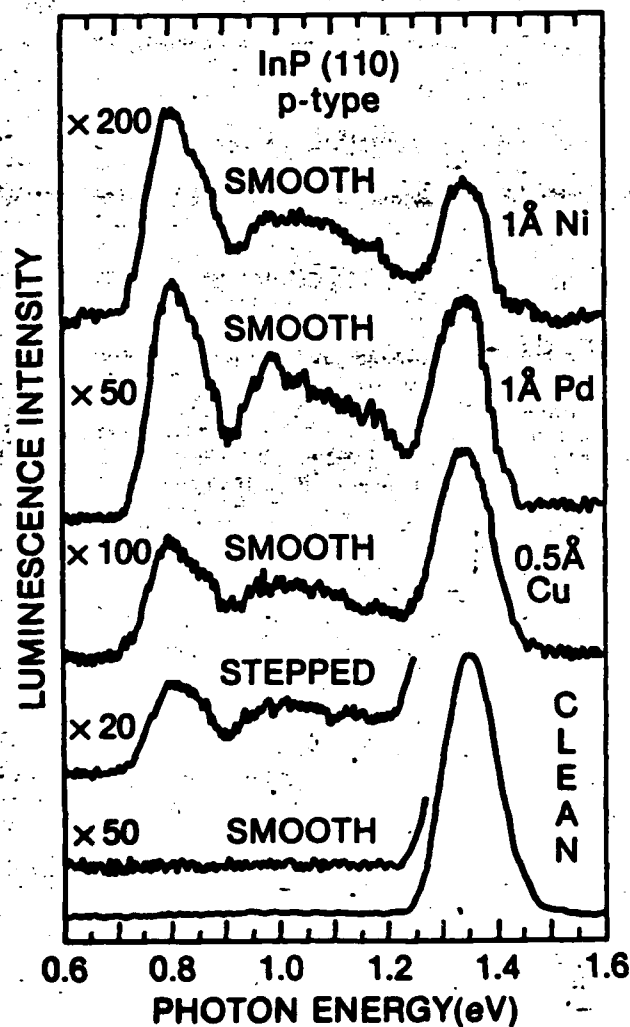
- UHV Surface Preparation
- Low Electron Energy & Glancing Incidence
- IR Sensitivity ($h\nu > 0.6\text{eV}$)

Spatial Range of Interaction



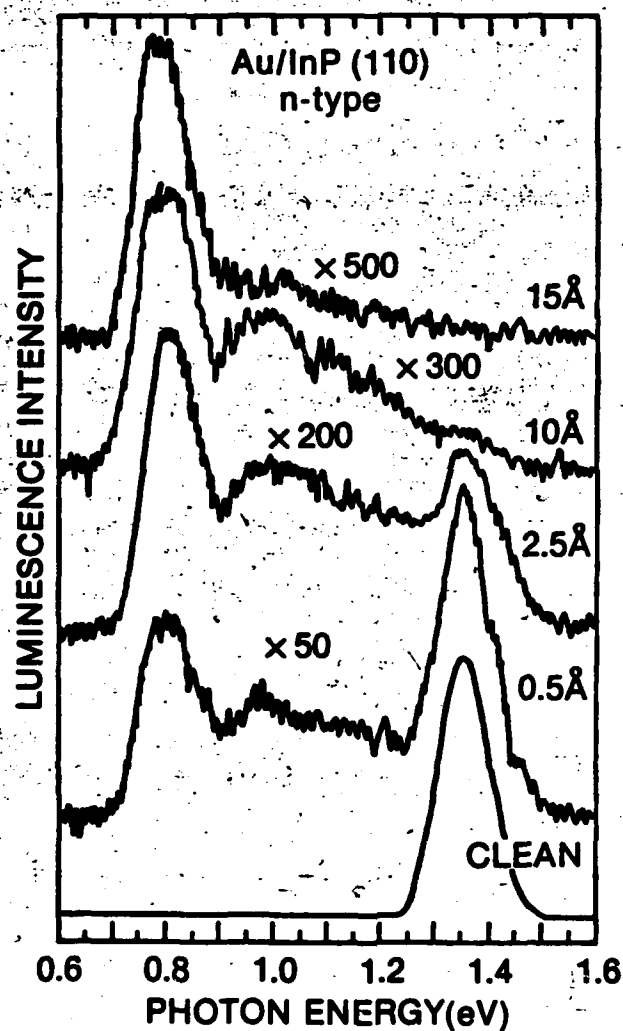
- Near Surface Excitations
- Depth Resolution

Extrinsic Interface States: InP (110)



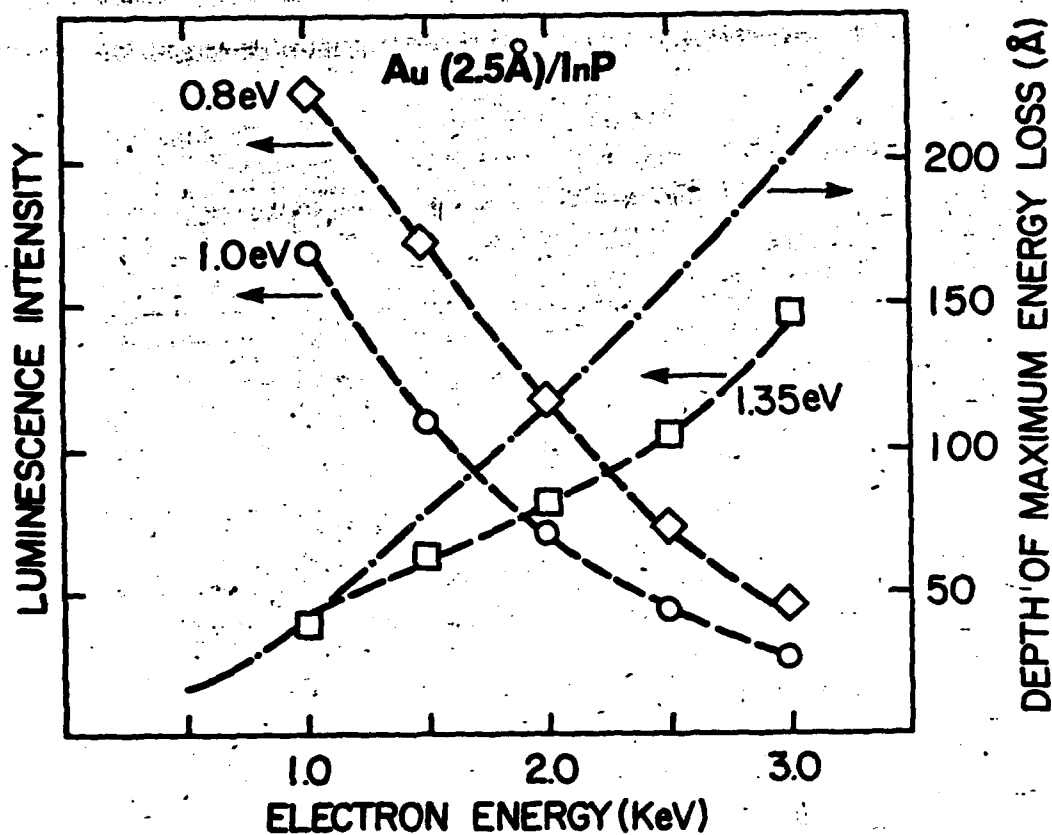
**Submonolayer Metal Deposition & Cleavage Steps
Produce Broken Bonds**

Spectral Shape vs Multilayer Metal Deposition: Au/InP



**0.78 eV Peak Dominates
at Multilayer Coverage**

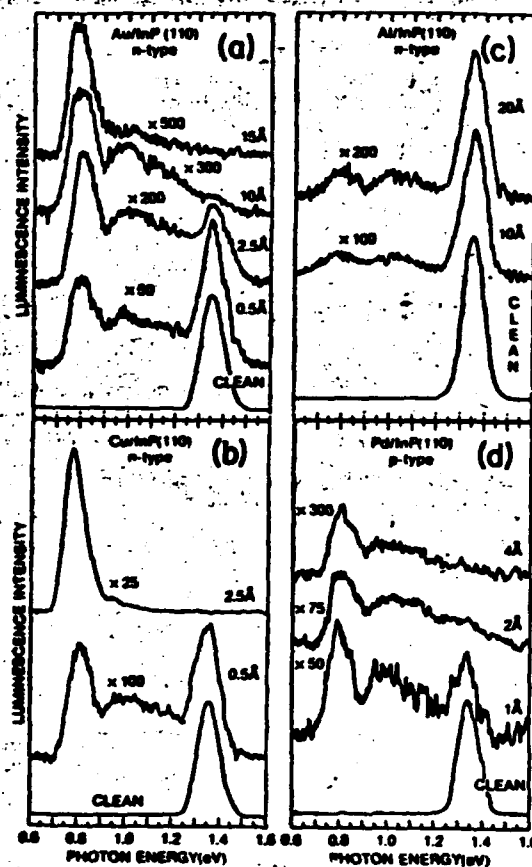
Depth Resolved CLS



- Near Surface Localization of Recombination Centers

- "Buried" Interfaces

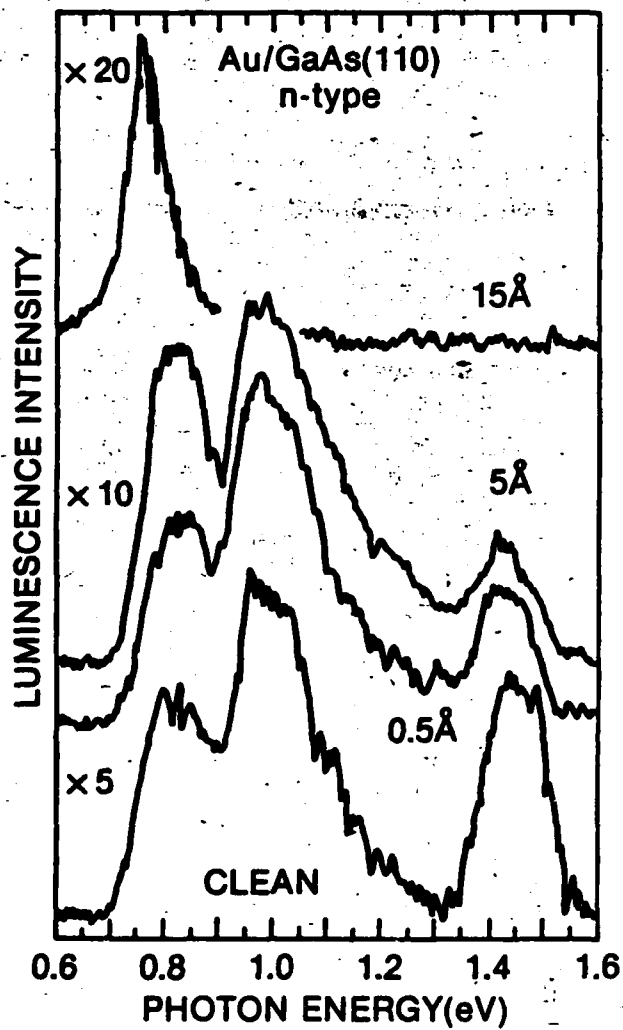
Optical Emission from Metal-Induced States



C. Viturro et al.,
Phys. Rev. Lett.
57, 487 (1986)

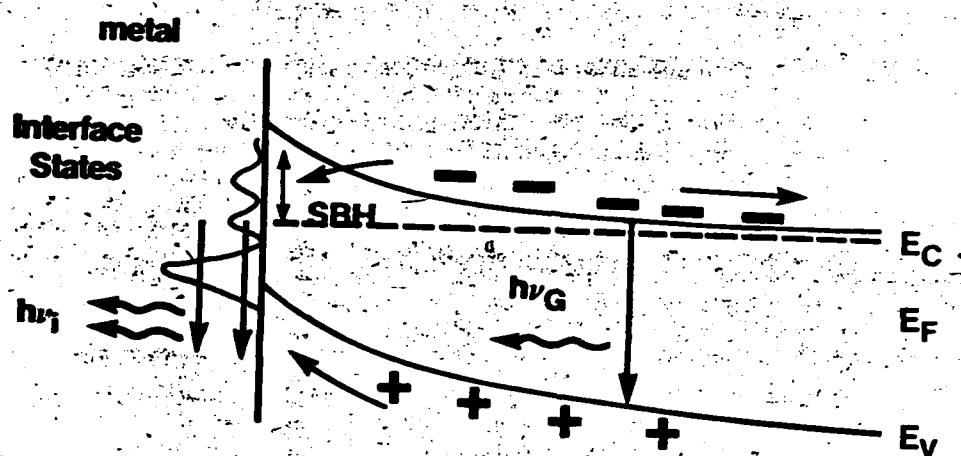
- Deep Level Interface States
- Multilayer Coverage Evolution
- Band Bending Correlation

Metal-Induced vs Bulk Trap States



- Metal-Induced States Dominate at Multilayer Coverage

Correlation with Schottky Barrier Heights



InP (110) n-type

Metal

Schottky
Barrier

$E_G - h\nu_i$

Au, Cu
Al

~ 0.5eV
0-0.25eV

0.57 eV
0, 0.2-0.5 eV

GaAs (110) n-type

Au

0.8-0.9eV

0.7 eV

CONCLUSIONS

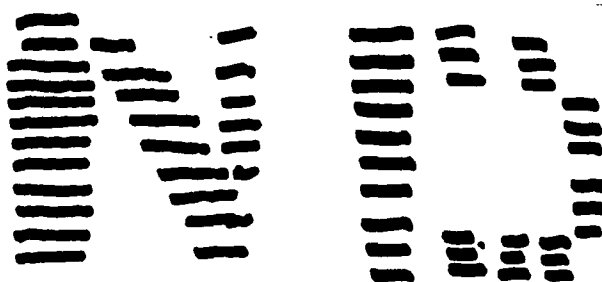
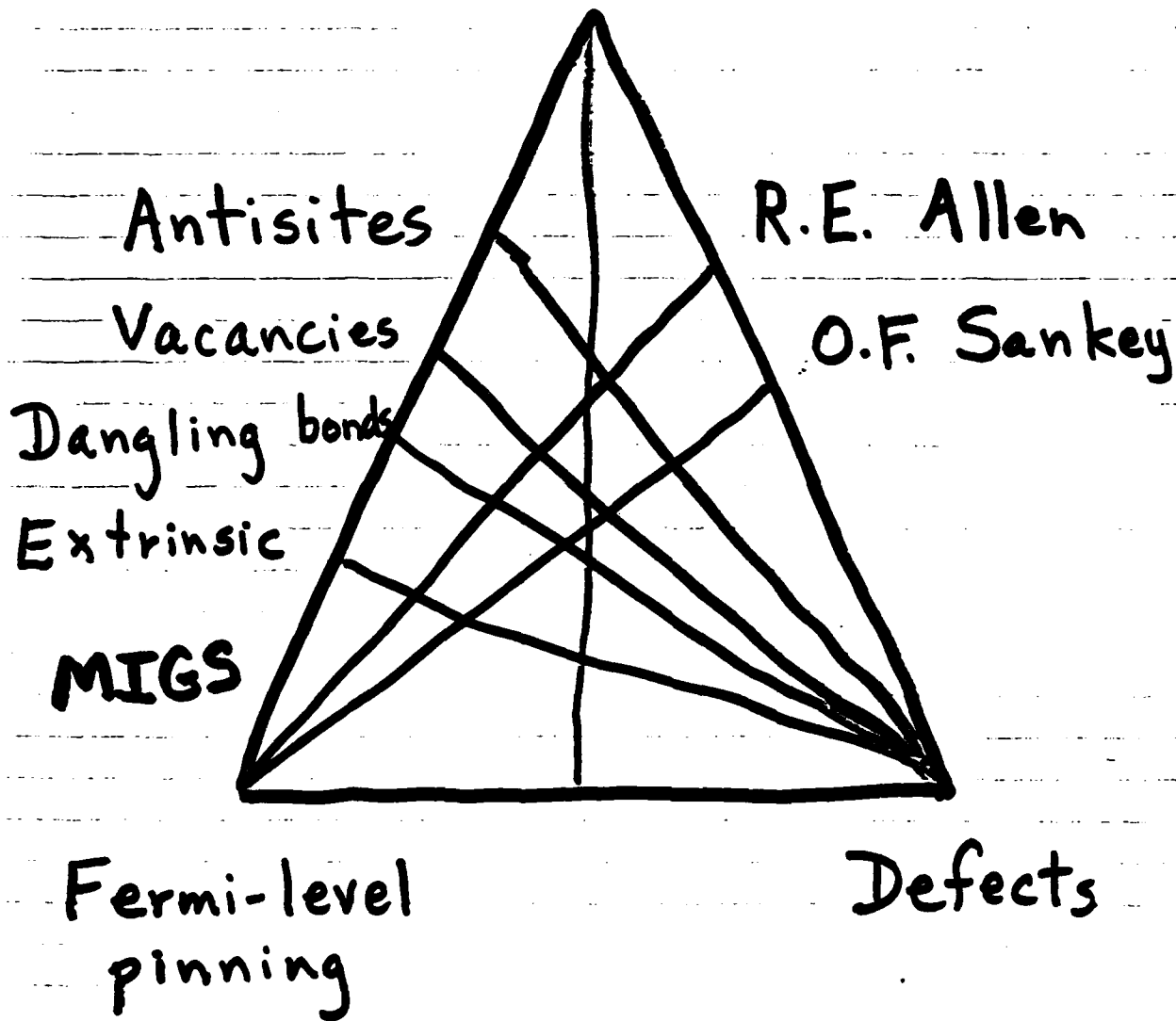
- METAL DEPENDENT CHEMICAL TRENDS ACROSS $\text{In}_x\text{Ga}_{1-x}\text{As}$ ALLOY SERIES
 - CHEMICALLY-MODIFIED WORK FUNCTION MODEL
 - EFFECTS OF AIR EXPOSURE
-
- DIRECT OPTICAL EMISSION FROM INTERFACE STATES
 - METAL, MORPHOLOGY, MONOLAYER AND MATERIAL DEPENDENCES
 - SPECTRAL CORRELATION WITH ELECTRONIC AND CHEMICAL STRUCTURE

Antisite Defects and Schottky Barriers

Jack Dow

Notre Dame University

Schottky barriers



OUTLINE

① Schottky barriers are due to Fermi-level pinning by surface deep levels (Bardeen)

② Native defects (formed during deposition of metal contact) provide the pinning levels (Spicer).

③ Chemical reactions can determine which defects are dominant (Brillson)

④ In III-V's, normally
antisites
vacancies
extrinsic

Co-authors:

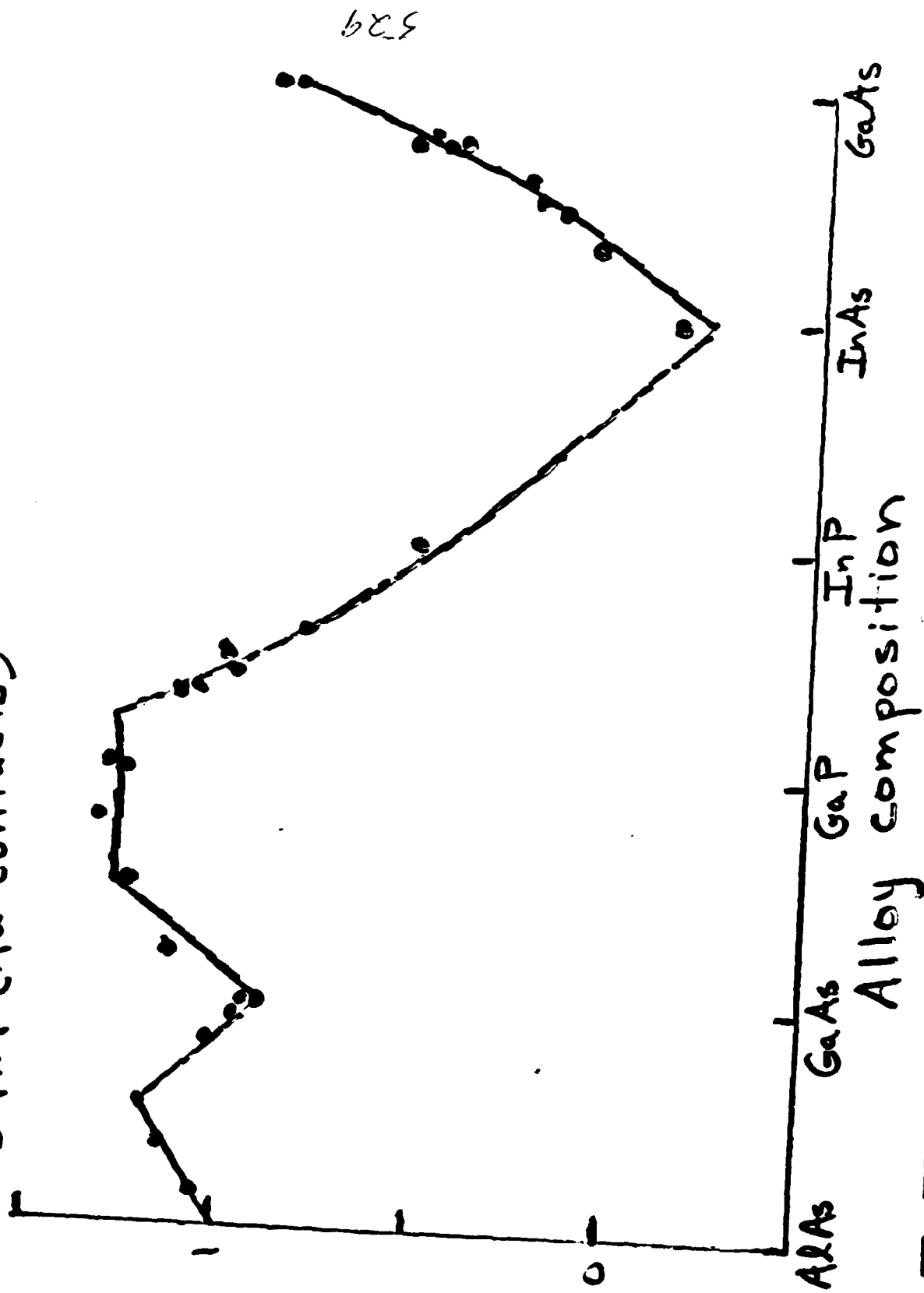
R.E. Allen

527

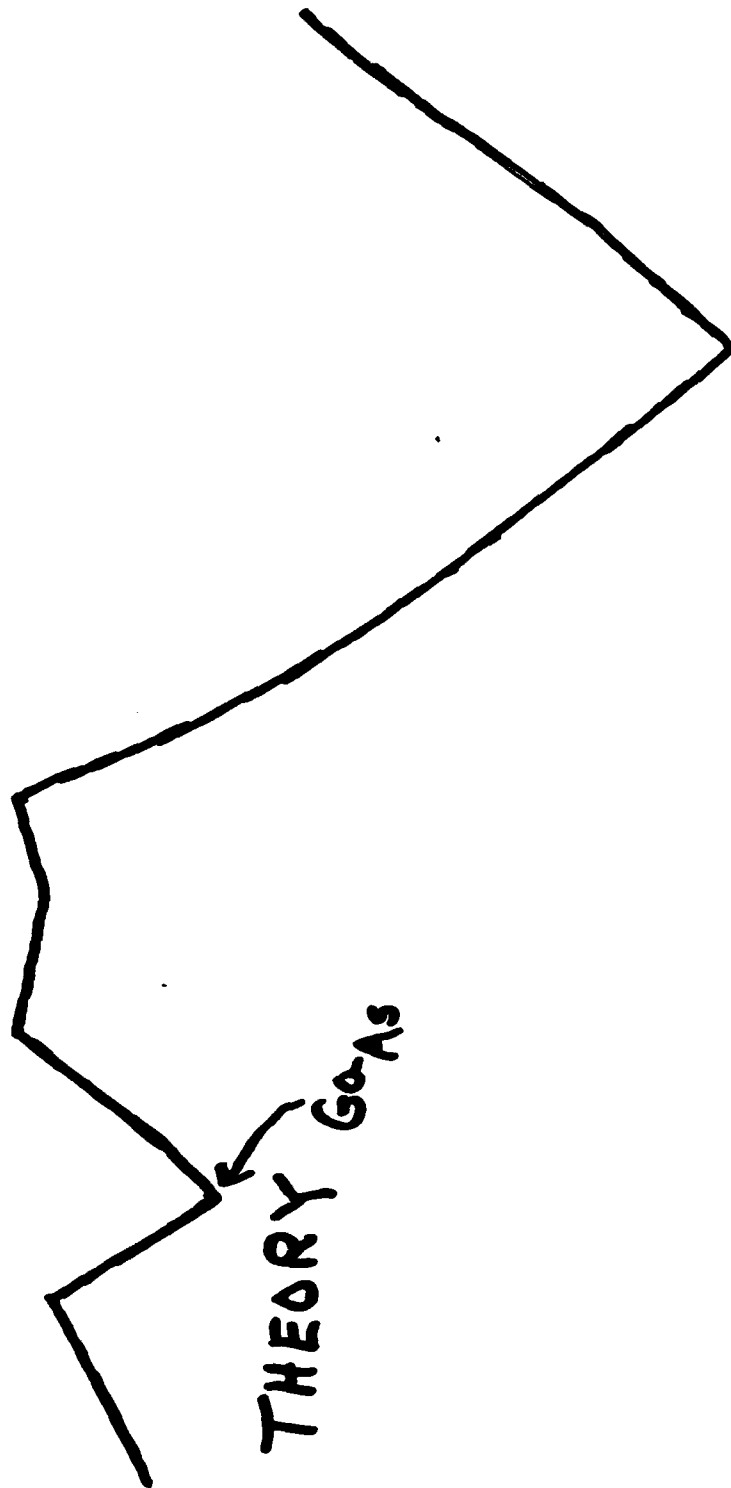
O.F. Sankey

Schottky Barrier Height (eV)

DATA (Au contacts)

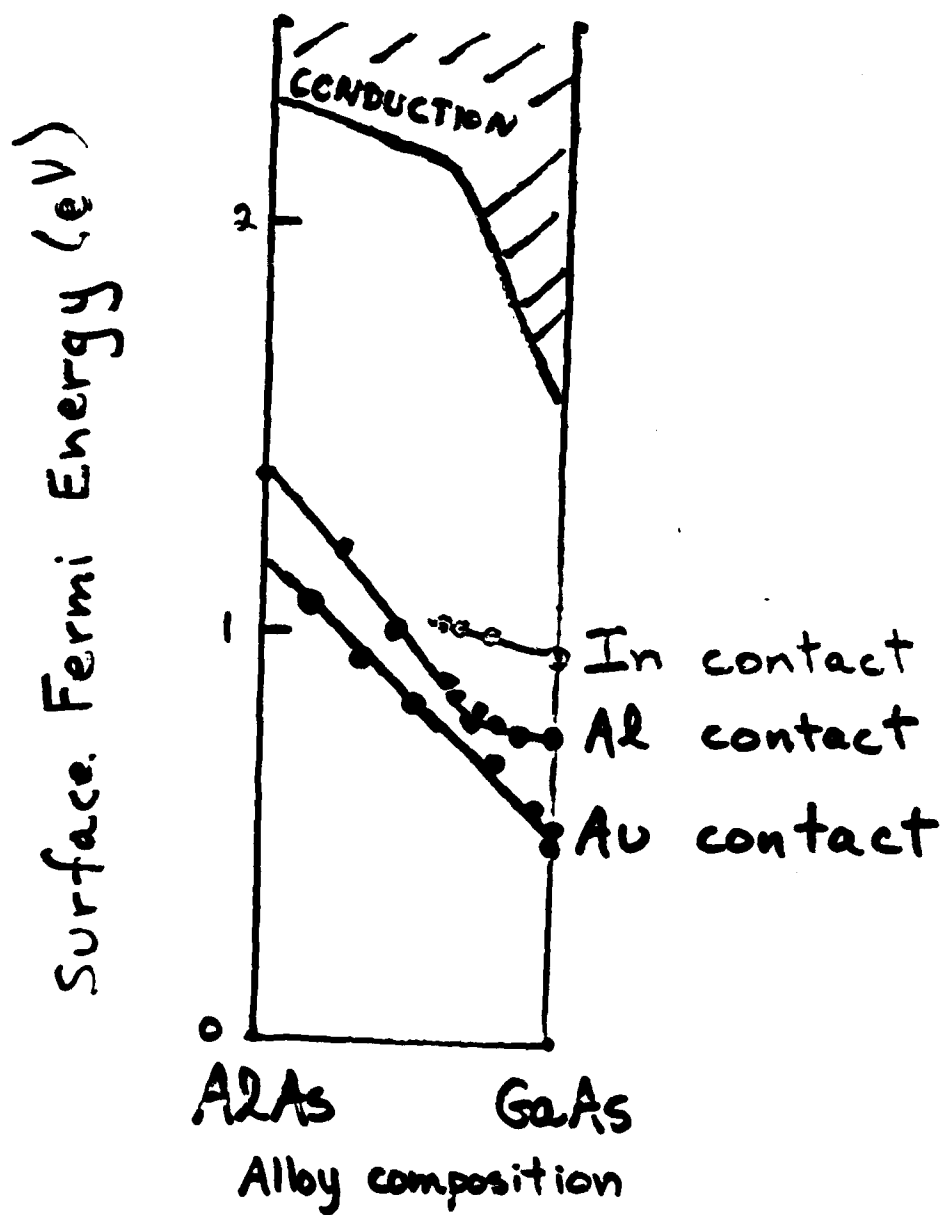


530

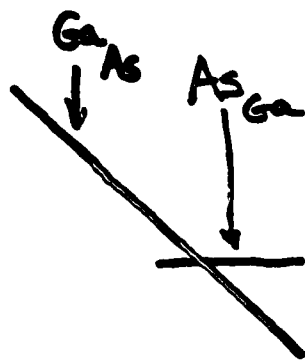


THEORY GO-As

Dependence
on contact



THEORY



GaAs

—

Ga_{As}

—

—●—●—

As_{Ga}

—

—●—●—

DATA

Explains:

① # Donors $\approx$ # Acceptors (Mönch)

$$\begin{array}{ccc} \text{---} & = & \text{---} \\ \text{or} & & \\ \# \text{Ga}_{\text{As}} & \approx & \# \text{As}_{\text{Ga}} \end{array}$$

② Chemisorption defect $\neq$ cleavage defect
 $\text{Ga}_{\text{As}} \neq \text{As}_{\text{Ga}}$ (Mönch)

③ Abrupt change of barrier
at T_{anneal} (antisite); (Mönch)

a) p-barrier --- As_{Ga}

b) n-barrier remains --- Ga_{As}

④ Surface levels $\neq$ bulk levels

All impurities produce

a) ∞ shallow levels if $\Delta z \neq 0$

b) 4 deep levels if s. p-bonded

Deep: $V_{\text{central-cell}}$

Shallow: $-\frac{\Delta z e^2}{\epsilon r}$

SHALLOW
IMPURITY

———— $T_2(p)$
———— $A_1(s)$

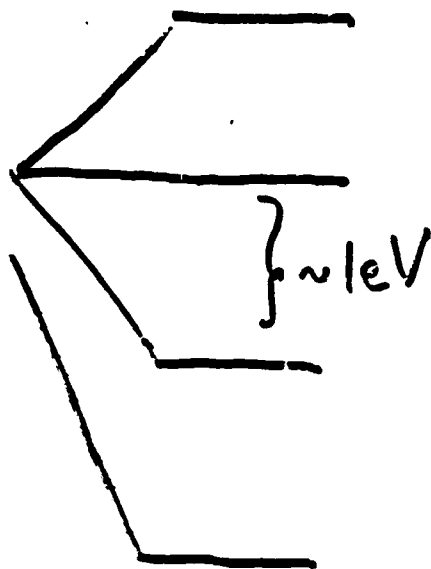
DEEP
IMPURITY

———— $T_2(p)$

E_{gap} ————— CONDUCTION
Shallow Shallow

———— $A_1(s)$
deep

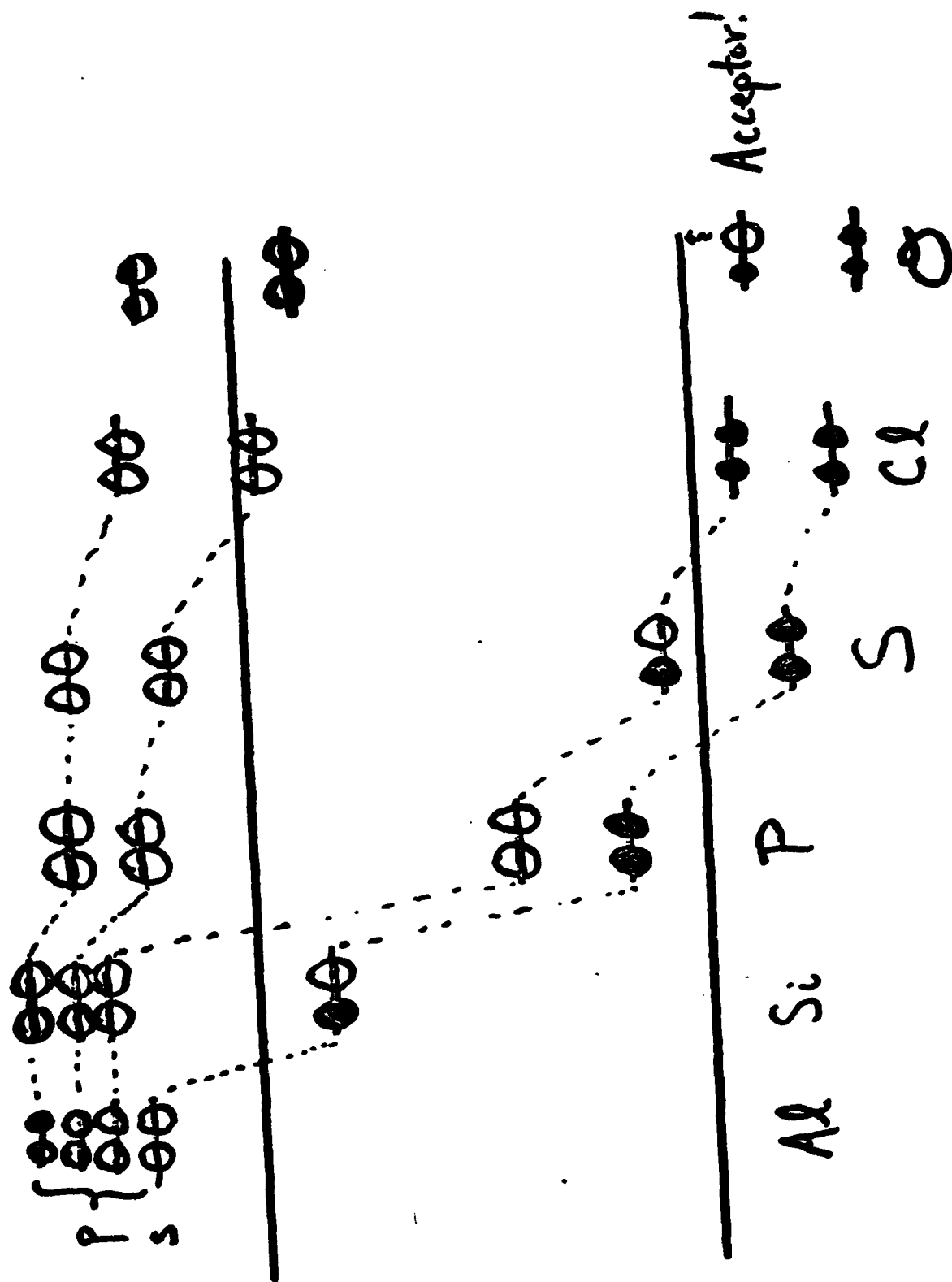
○ ————— VALENCE



SURFACE
or other
non- T_d

Surface levels $\neq$ bulk levels

Surface Ga site: Doping anomaly



PART II:

Si/Transition-metal silicide

Schottky barriers

O.F. Sankey, R.E. Allen, + J.D. Dow
Solid State Commun. 49, 1 (1984).

FACTS:

(A) On $\sim 1\text{eV}$ scale, barrier is independent of

- i) transition metal (Ni , Pt , Pd)
- ii) crystal structure (NiSi , NiSi_2 , Ni_2Si)
- iii) Si surface
- iv) stoichiometry

(B) On $\sim 0.1\text{eV}$ scale barrier depends on

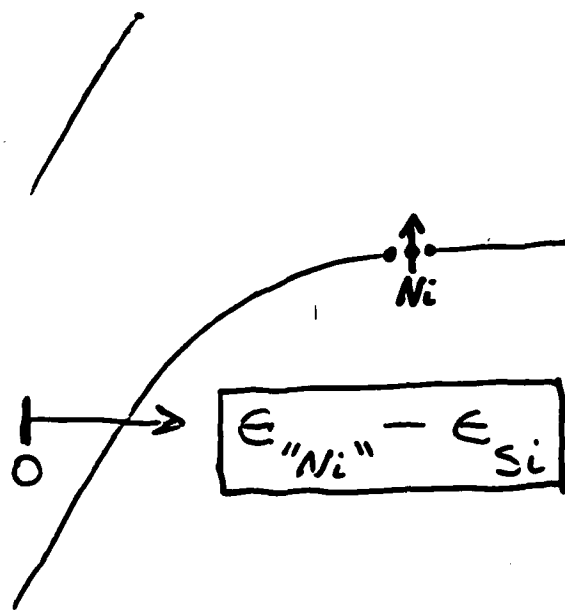
- i) transition metal ($\sim \epsilon_{\text{atomic}}$)
- ii) crystal structure

(C) Barrier forms with < 1 monolayer of transition metal

(D) $\phi_n + \phi_p \approx E_{\text{gap}}$

(E) Si is similar to III-V's

Ni
 $- \epsilon_{s,p}$



No crossing
 makes level
 independent
 of Ni, etc

$54/2$
 $- \epsilon_d^{Ni}$

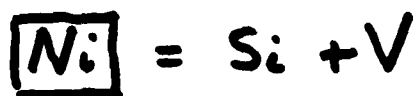
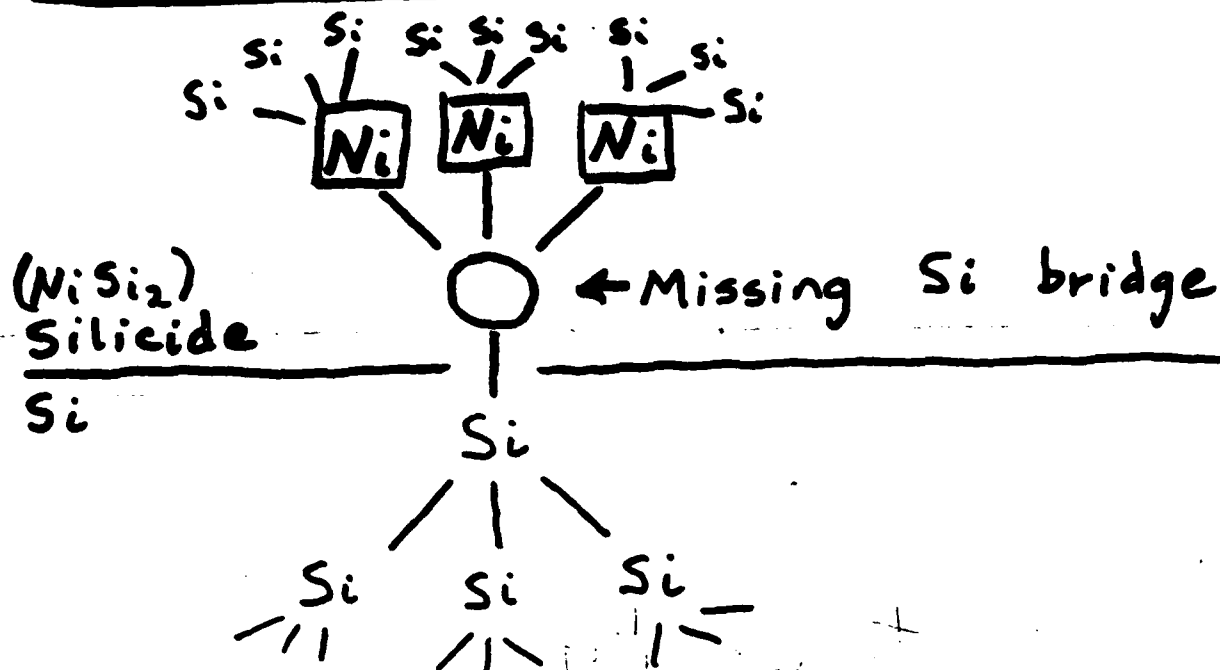
CONDUCTION

$V_{Si}(T_2)$ —

VALENCE

$V_{Si}(A_1)$ —

Schottky barriers in silicides



Si/T-metal silicide

$\frac{CB}{\frac{\phi}{VB}}$

Schottky barriers ϕ

- ① ϕ independent of T-metal on 1 eV scale (Ni, Pt, Pd)
- ② ϕ : chemical trends with T-metal on 0.1 eV scale
- ③ < 1 monolayer of T-metal gives ϕ
- ④ ϕ : independent of crystal structure (on > 0.1 eV scale): $NiSi$, $NiSi_2$, Ni_2Si .
- ⑤ ϕ : independent of stoichiometry, Si surface (on > 0.1 eV scale)
- ⑥ $\phi_n + \phi_p \approx E_{gap}$
- ⑦ Si is similar to III-V's.

Summary

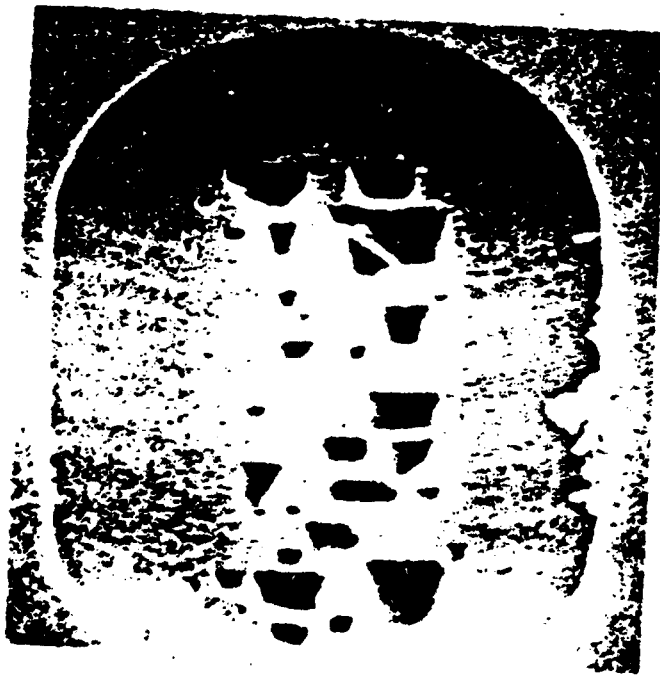
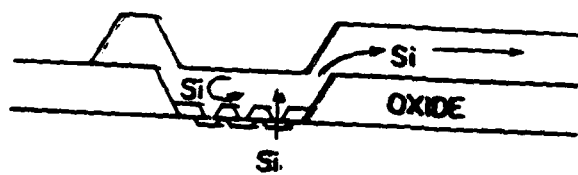
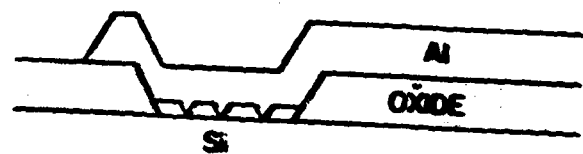
- ① Fermi level pinning
(Bardeen)
- ② By defects at interface
 - Antisites: III-V/non-reactive
 - Vacancies: III-V/reactive
 - Dangling bonds: Si/TM silicide
 - Extrinsic: n-InP: S, Sn(Spicer)
- ③ Chemical reactions
produce various defects
(Brillson)
- ④ New field: surface defect
spectroscopy

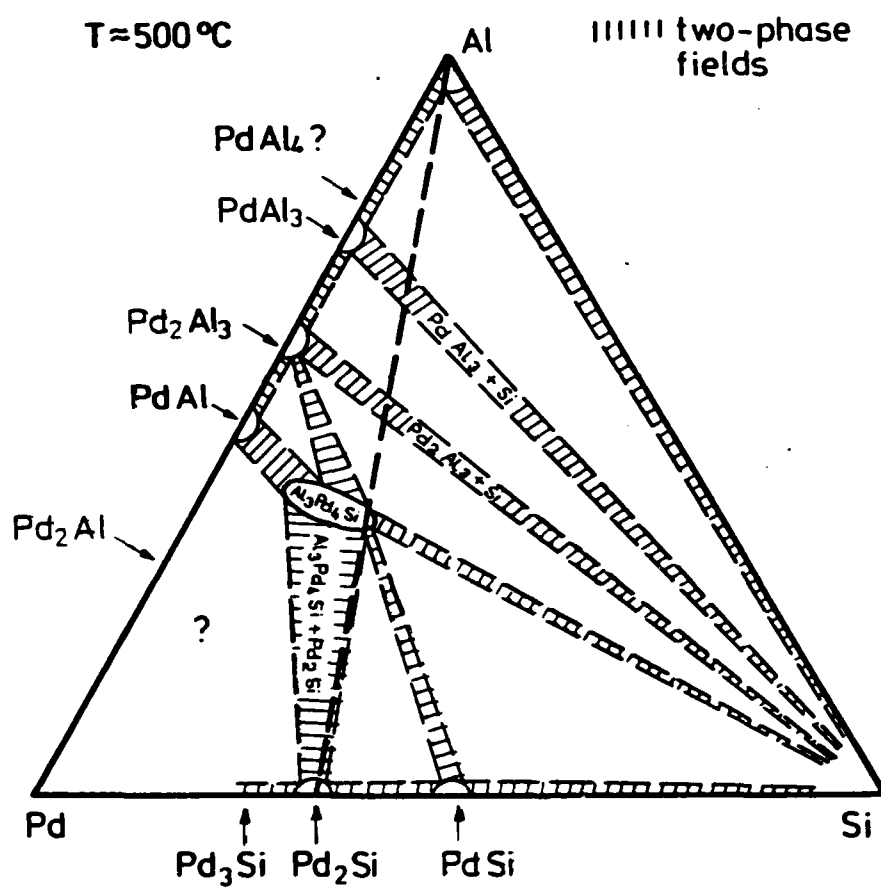
Scattering by barriers

**Direct Measurements of Electronic States
at Metal/GaAs Interfaces**

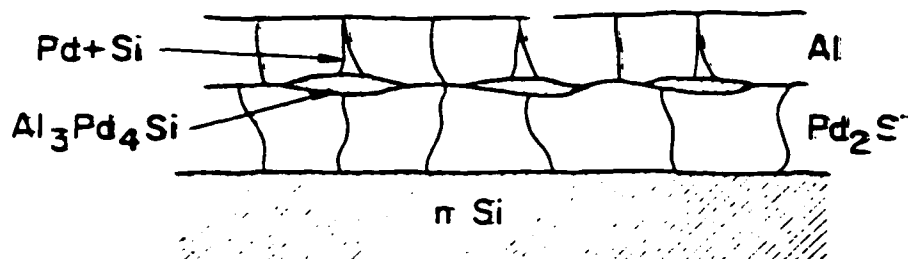
Paul Ho

IBM - Yorktown Heights

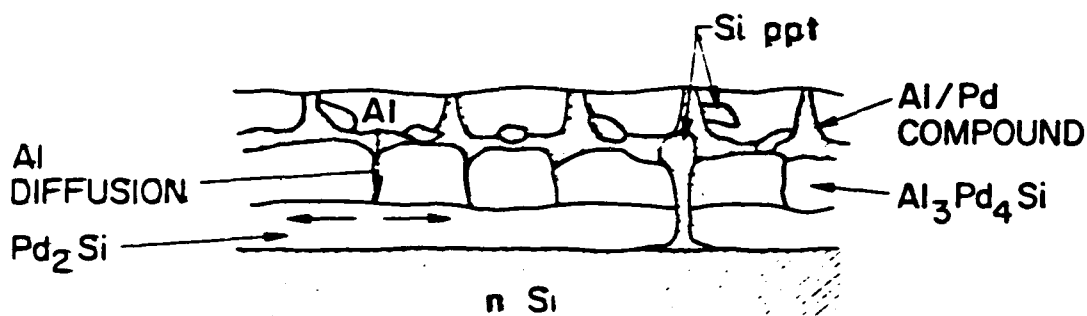




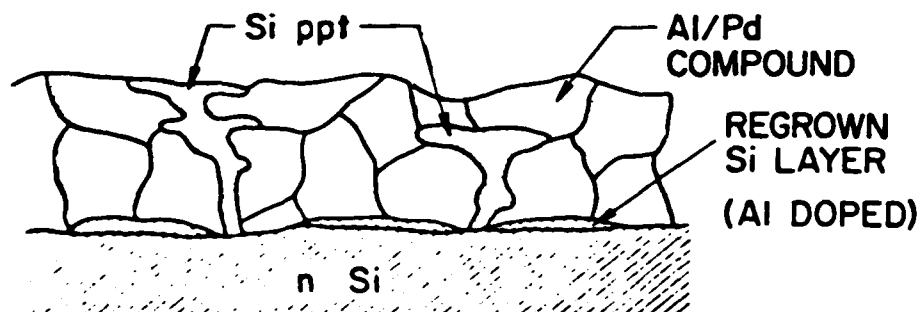
SCHEMATIC PRESENTATION OF Al/Pd₂Si/Si REACTION



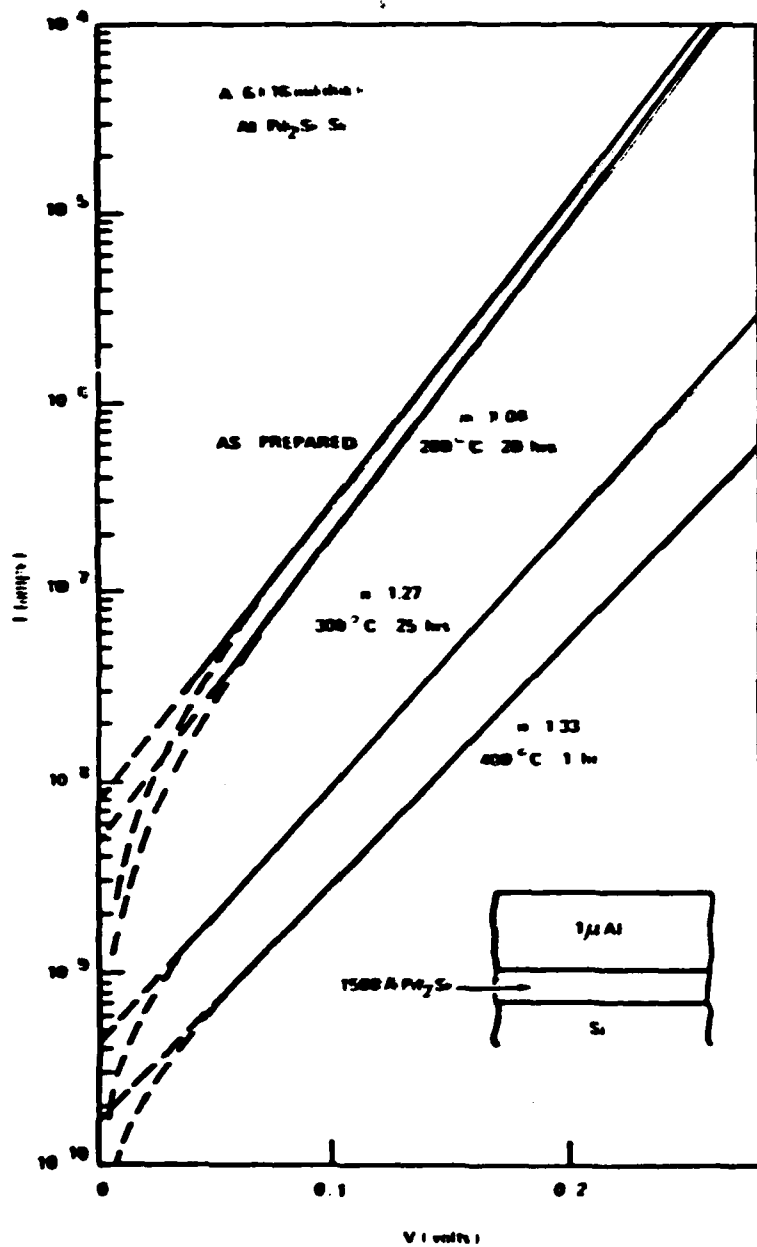
a) INITIAL STAGE



b) INTERMEDIATE STAGE



c) FINAL STAGE



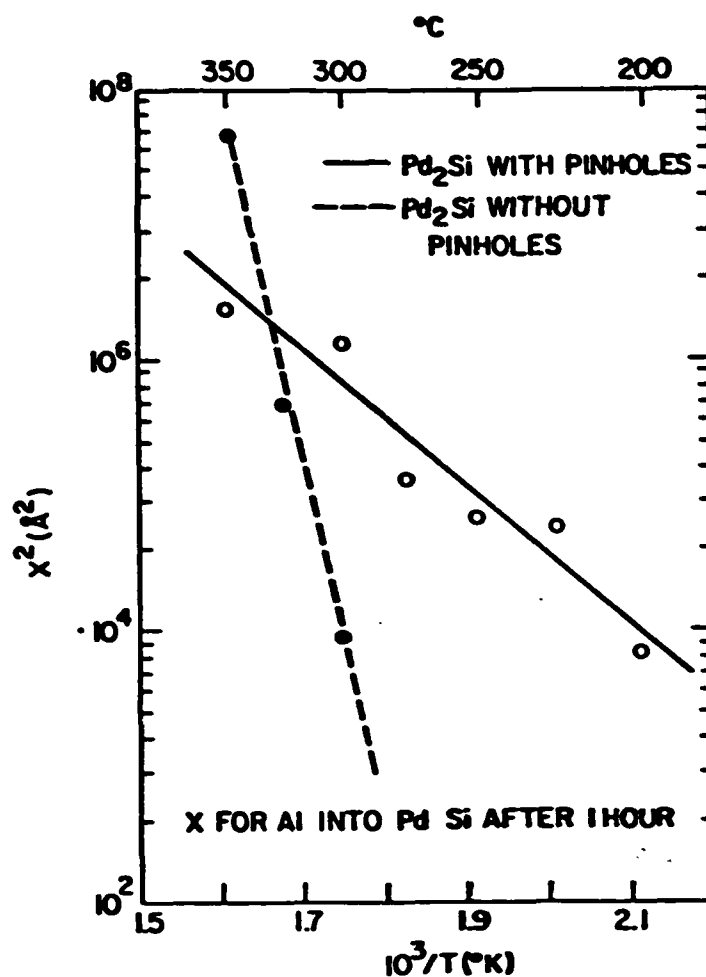


Fig. 7. Comparison of the rates of Pd_2Si dissociation in Al/ Pd_2Si /Si contacts for polycrystalline Pd_2Si films containing pinholes on Si(111) and pinhole-free on Si(100). The rate of dissociation was measured from the distance X of Al penetration into Pd_2Si . Data are normalized to 1 hr and plotted vs. X^2 because of the kinetics.

1. Microstructure, e.g. grain boundaries,
Interface & Layer composition important

KINETICS FACTOR AND CONTROL

2. The thermodynamic tie line is
a band reflecting the phase field.

M_xGa_yAs particularly relevant to
the stability.

3. Electrical properties can't be observed
by TEM or spectroscopy techniques

4. Precipitates (particularly As) on
the electrical interface important.

COOLING CYCLE !!!

DIRECT OBSERVATION OF INTERFACE STATES

R. Haight, N. Amer, E. Yang & P. Ho

GOAL

To study the characteristics of the interface
states

Energy distribution

In-depth distribution

Dynamic behavior

TRANSPORT PROPERTIES AT JUNCTIONS

SCHOTTKY BARRIER FORMATION

TECHNIQUES

Laser transient spectroscopy

Time-resolved photoemission

Thin interfaces

High energy resolution. Polarization
Photothermal spectroscopy

Defect characterization

In-depth sensitivity

Spatial - lateral sensitivity

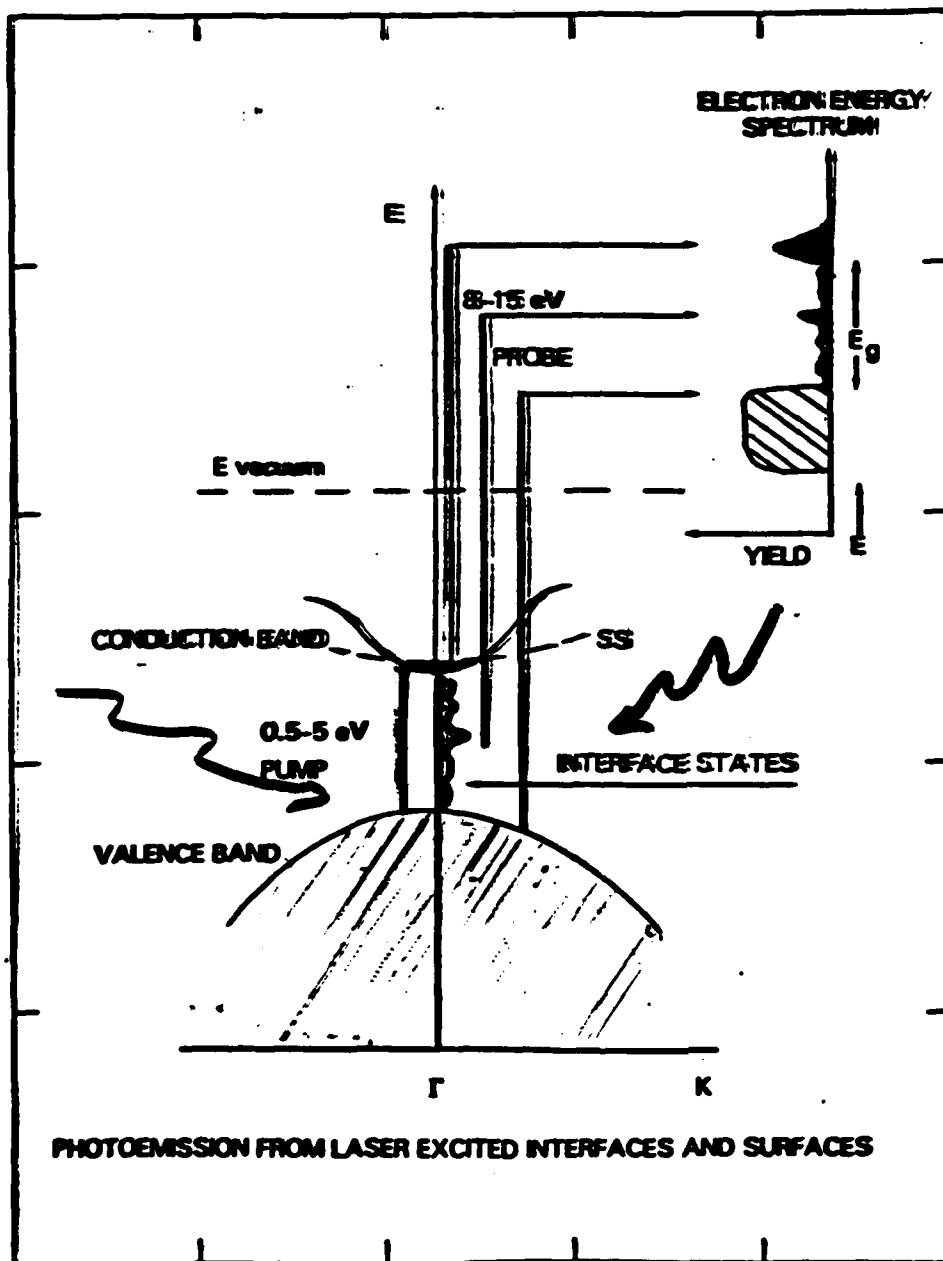
Transport measurement

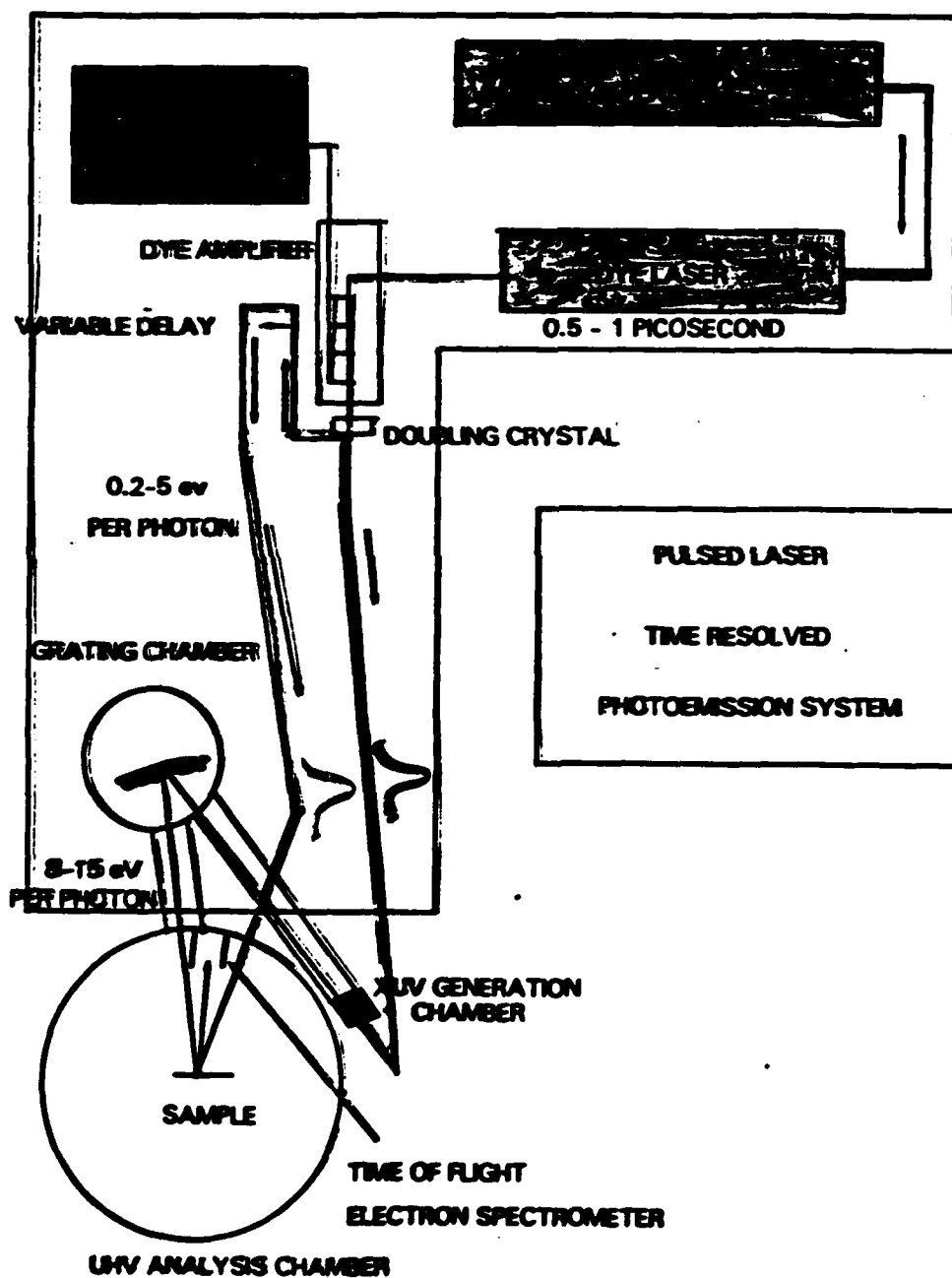
Accurate phase capacitance spectroscopy

Buried interface

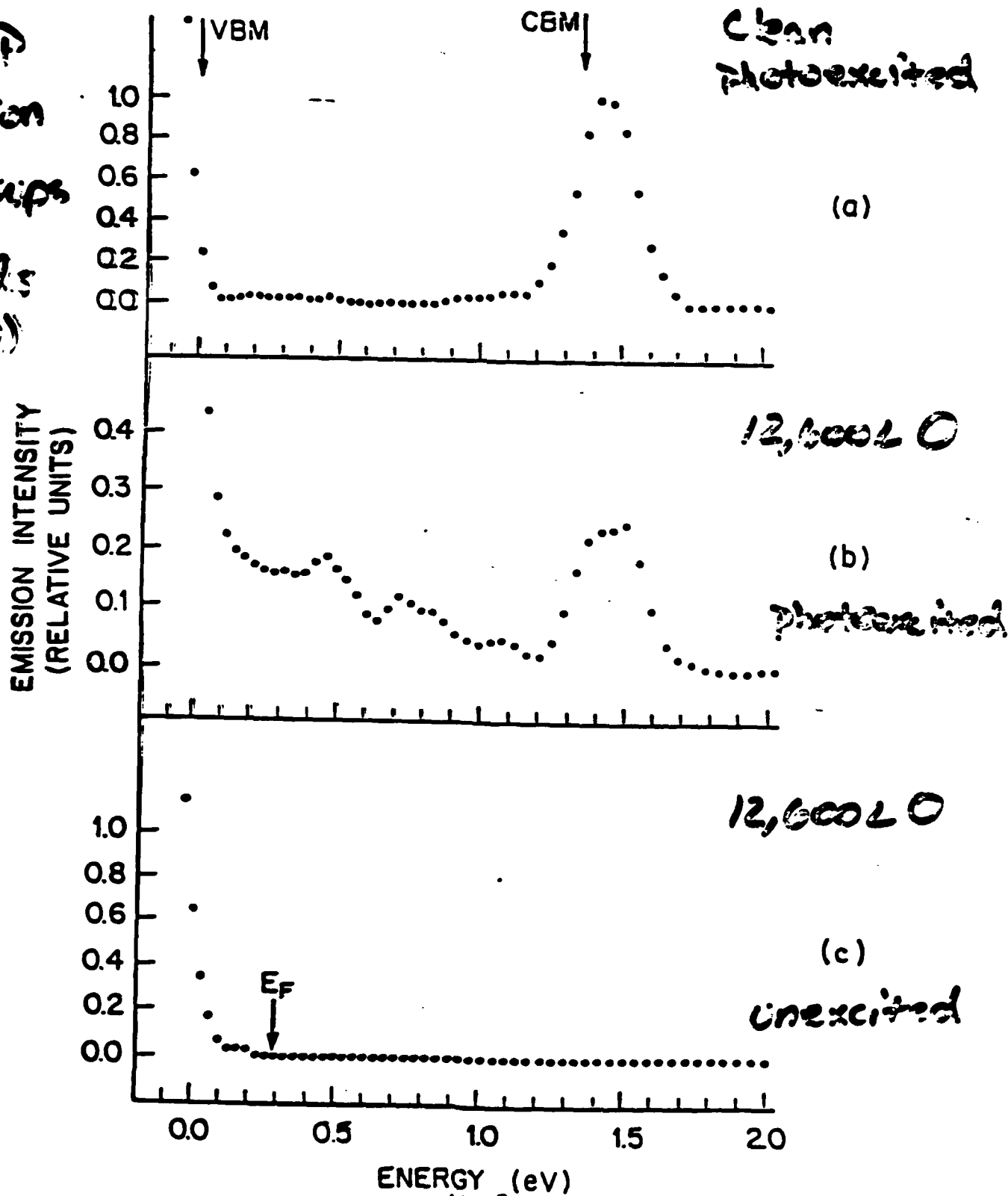
Charge transport at interface.

ALL ARE DYNAMIC TECHNIQUES 555





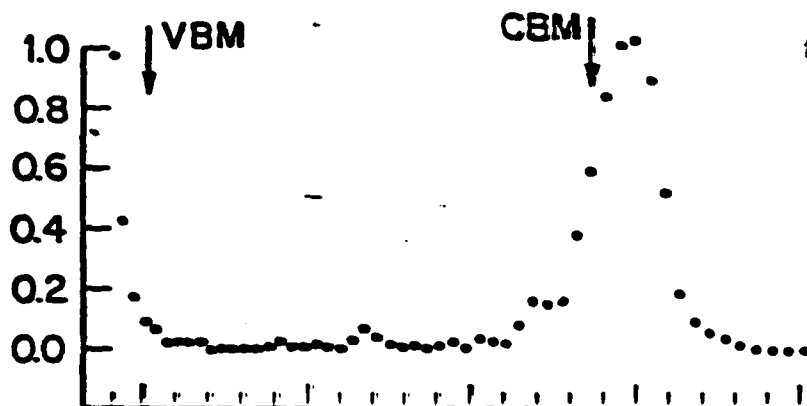
gap
region
occupies
7.25
(110)



gap
region
fluctuations

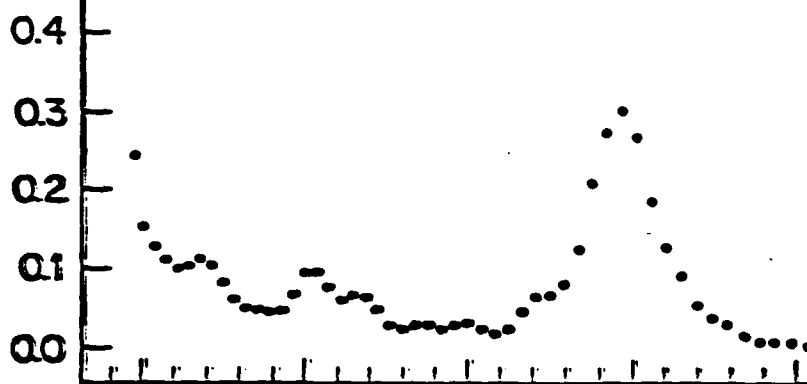
0.2.5
(110)

EMISSION INTENSITY
(RELATIVE UNITS)



Clean
photoexcited

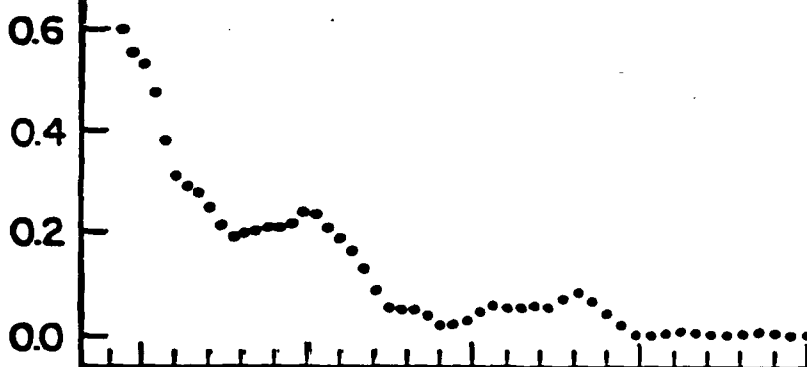
(a)



0.1 ml Au

(b)

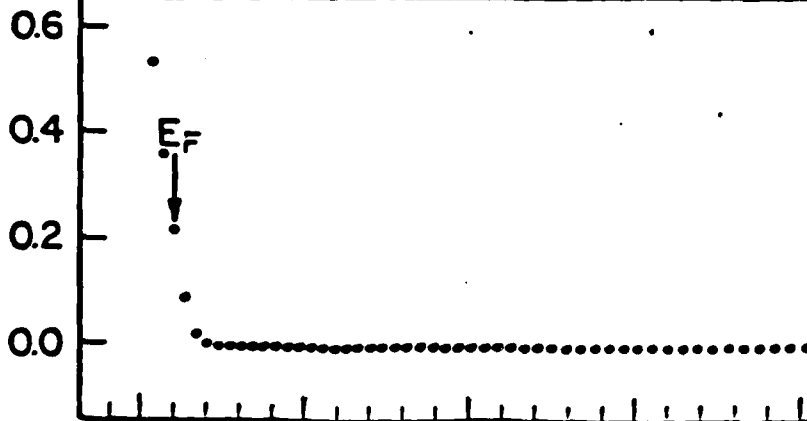
photoexcited



0.35 ml Au

(c)

photoexcited



0.1 ml Au

unexcited

(d)

ENERGY (eV)

559

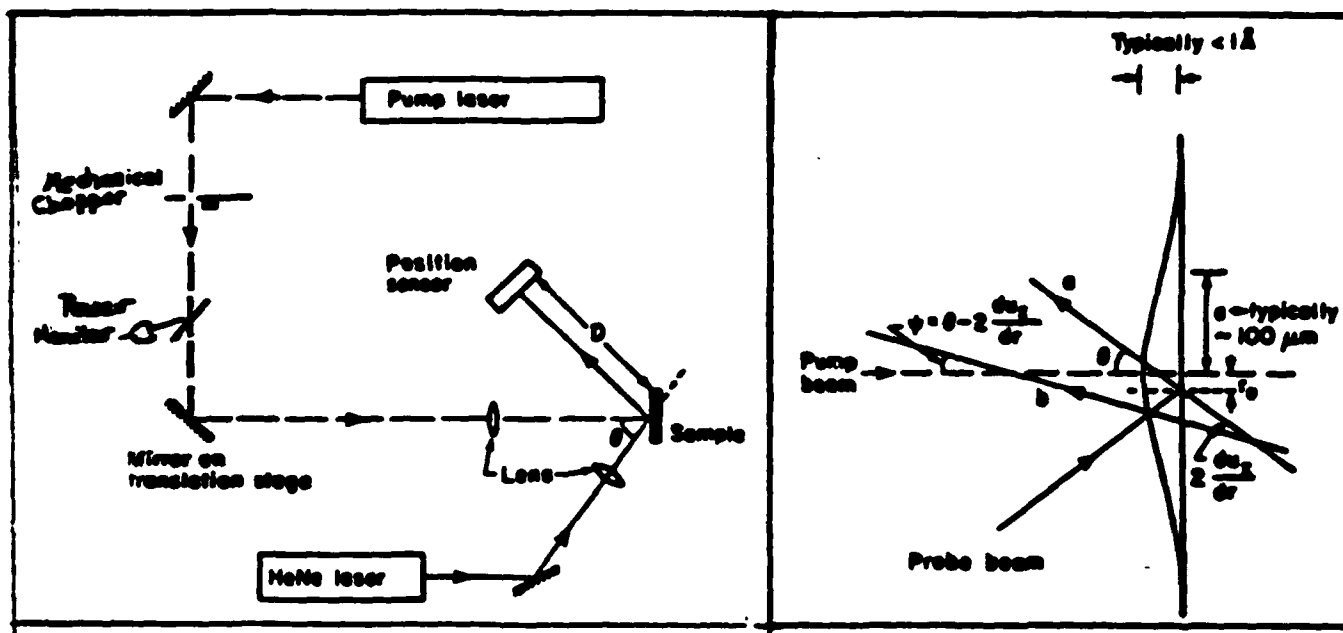
R. Hain

J. G. G. G.

P. R. L.

SL 2846 (1986)

In depth distrib. — freq.
 Interface — optical discontinuity.



Experimental Arrangement and Physical Principle
 of Photothermal Displacement Spectroscopy

Sources of Optical Heating

Non-Radiative Processes:

- **Carrier thermalization $\implies$ lattice heating
 $\implies$ Employed to measure minute optical
absorption ($\alpha l \sim 10^{-7} - 10^{-8}$)**
- **Non-radiative carrier recombination
yields carrier mobility and lifetime; dynamics**

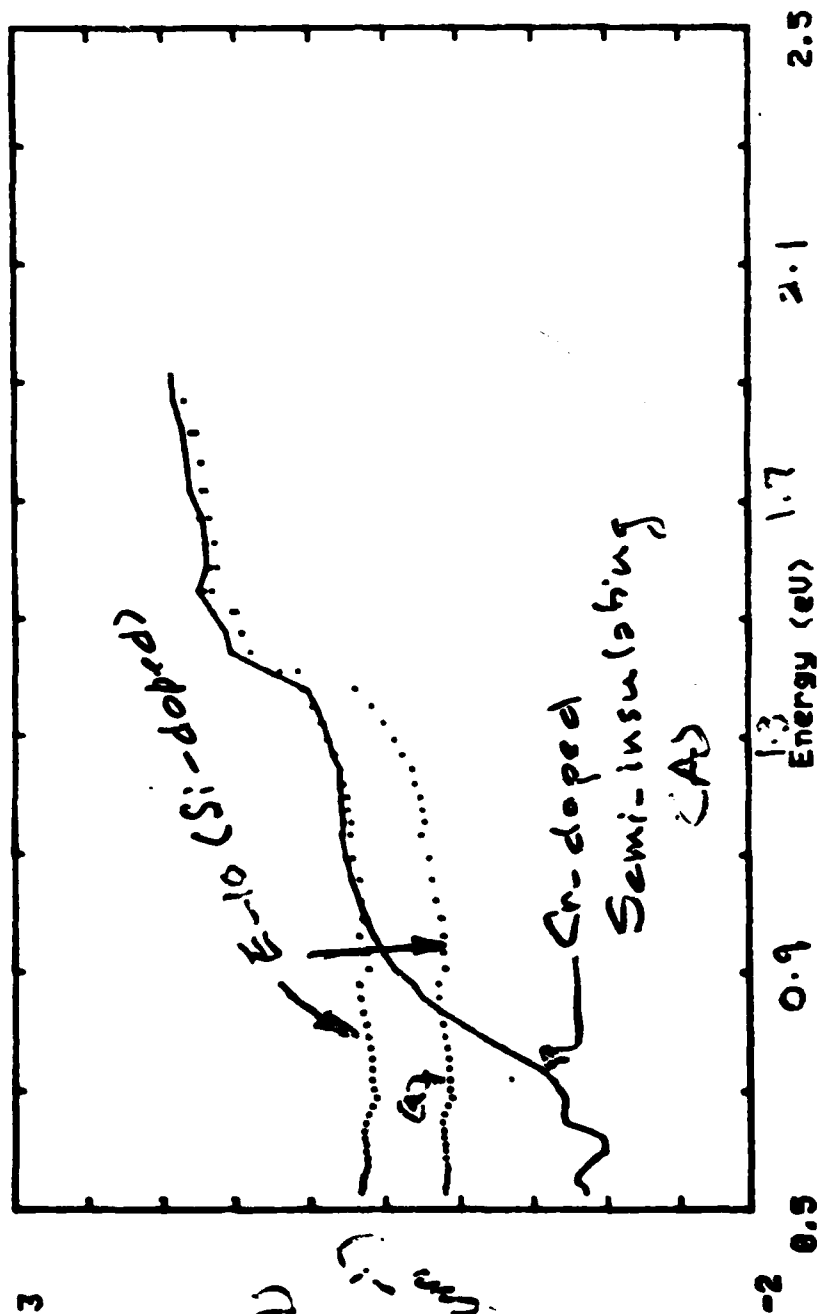
The diagram illustrates a pump-probe experiment setup. A rectangular sample of length l is shown. A "Modulated Pump Beam" (represented by three wavy arrows) is incident on the top surface of the sample. A "Probe Beam" (represented by a straight arrow) is incident on the right side of the sample at a depth x from the top surface. The probe beam travels through the sample, and its deflection angle is labeled $\theta(x)$. The sample is labeled "Sample".

Can measure minority carrier lifetime and diffusion length (on the μm scale)

GaAs

LINE GRAPH: A (T=0.045 cm)
 DOT GRAPH: top E10 (t set at 0.05 cm (t=0.08 cm))
 btm G (t=0.05 cm)

GaAs : A,G,E 10

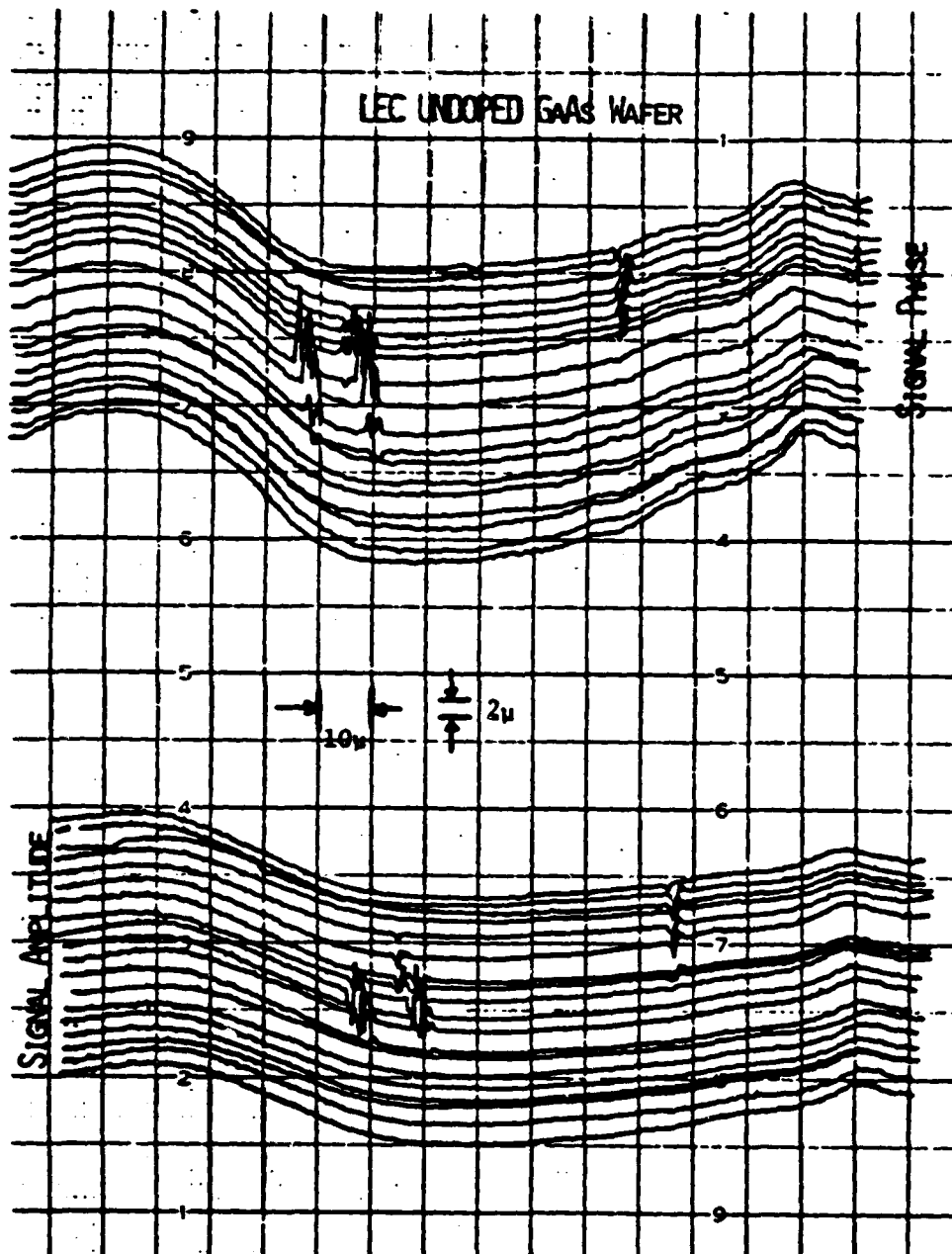


$h\nu$ (eV)

HENLETT-PACKARD

PHASE

AMPLITUDE



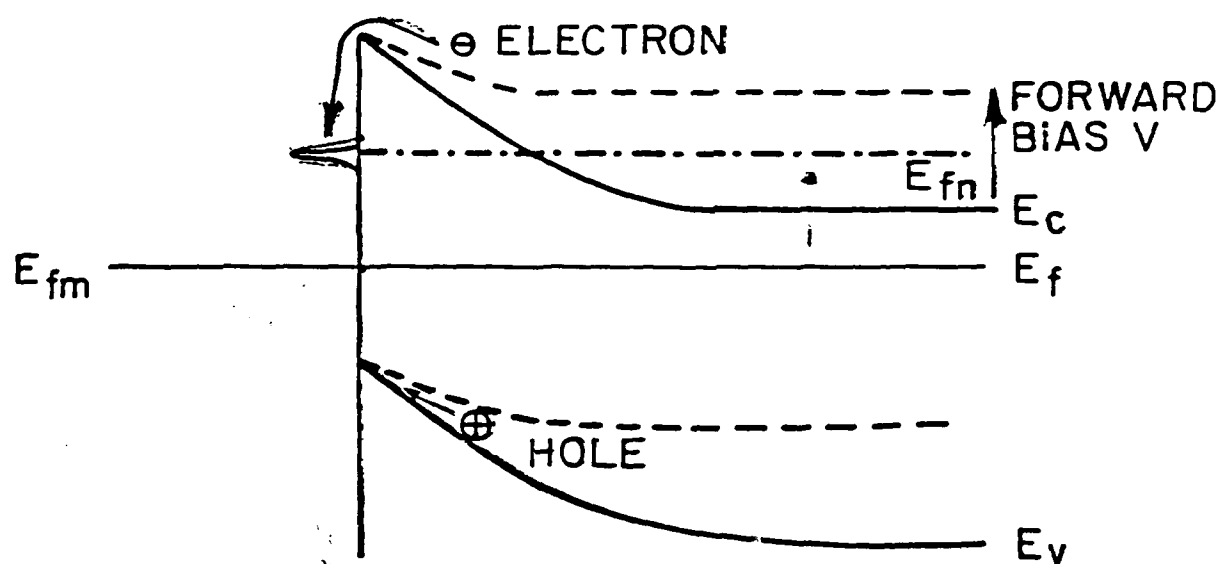
XBL 645-1701

X

Photothermal Scans of GaAs Wafer
Showing Arsenic Inclusions

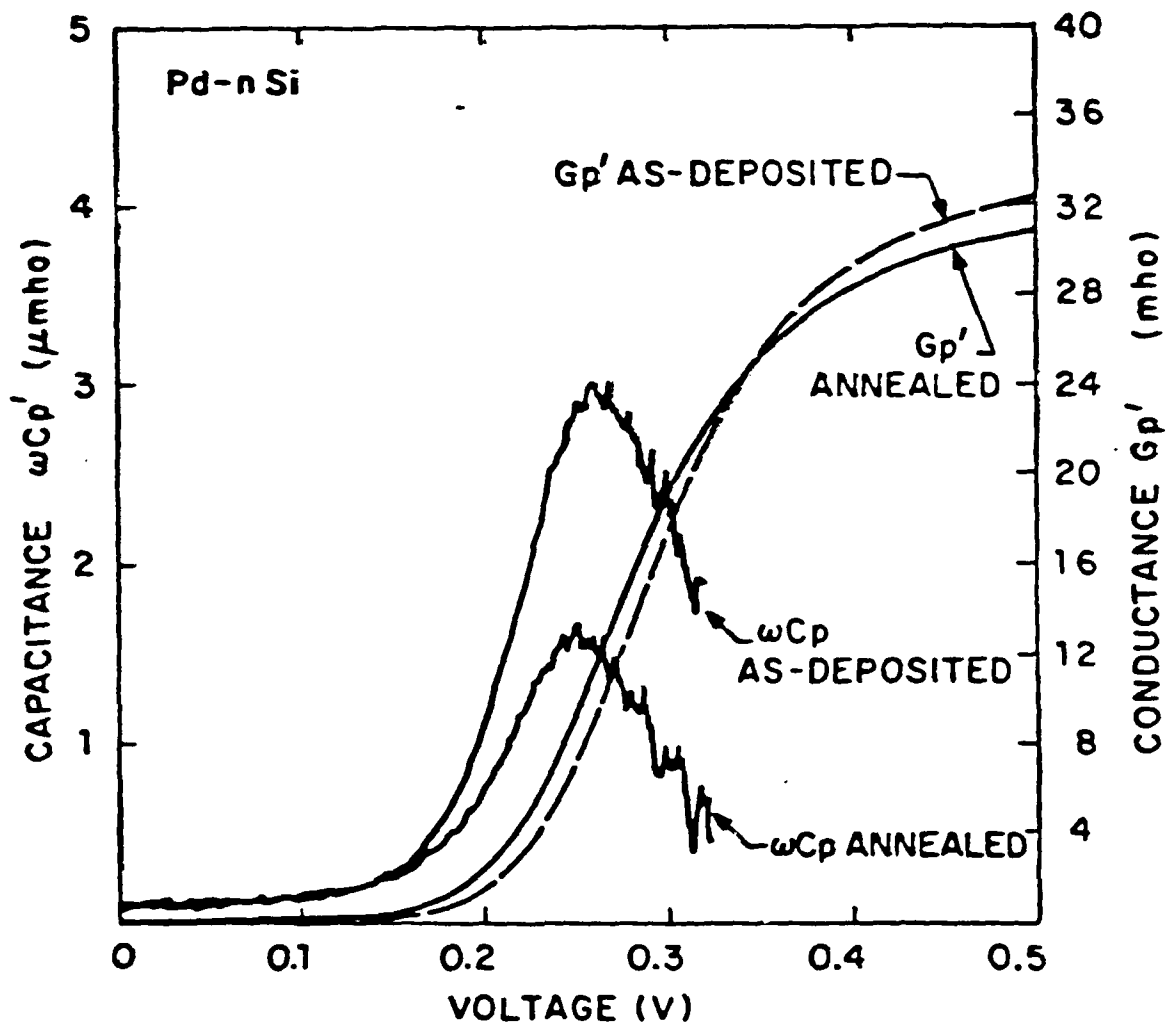
SILICIDE

n-SILICON



INTERFACE STATE CAPACITANCE SPECTROSCOPY

Temp, Freq. Dependence

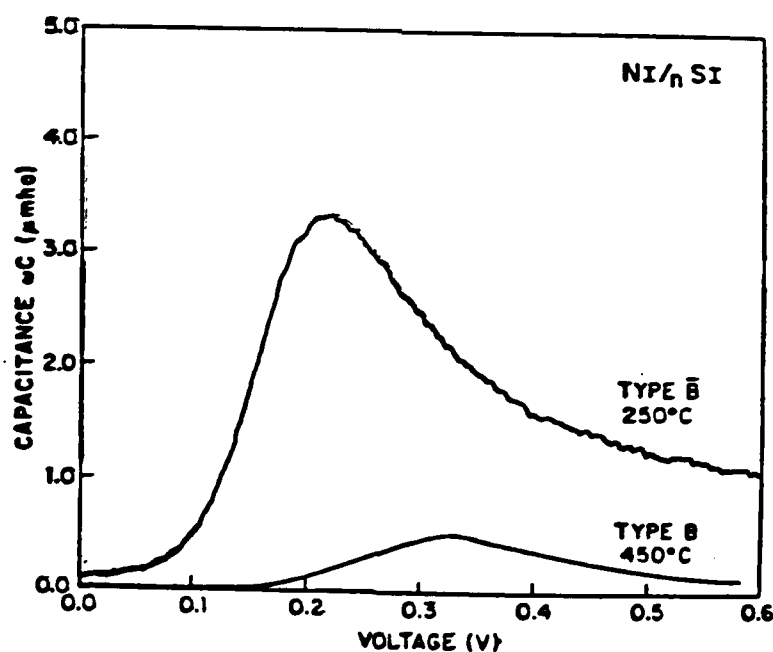


Interface states measurements

- Measures empty interface states in forward bias

Results:

- Low density of states for nearly perfect interfaces
- Ten times higher density for mixed-phase interfaces
- High and low barrier diodes show an energetic separation of their corresponding interface states by about 0.12 eV.



TYPE B vs. TYPE B $\text{NiSi}_2/\text{n-Si}$ DIODES

**THE ROLE OF TRANSITION METAL
IMPURITIES IN SCHOTTKY BARRIER
FORMATION**

R. Ludeke

In Collaboration with:

W. Drube

F.J. Himpsel

G. Hughes

G. Landgren

D. Rieger

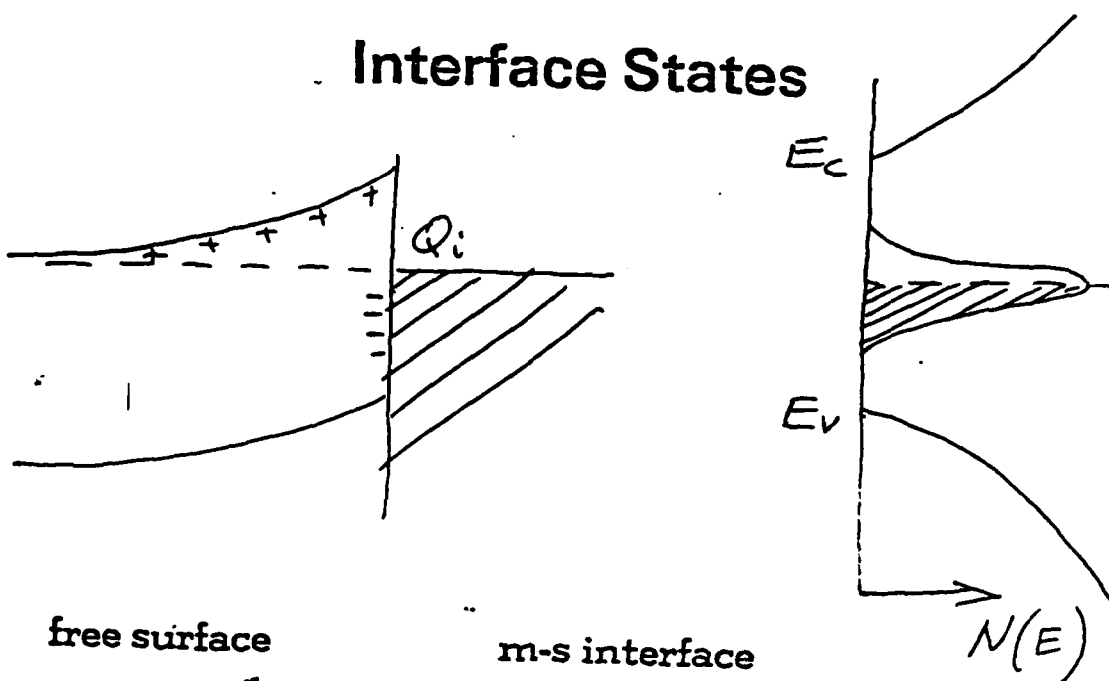
F. Schaffler

D. Straub

OUTLINE

- Limitations of present Schottky models
- "Anomalous" behavior of transition metals
 - range of barrier height values
 - evidence for interface states in gap
- Model for transition metal Schottky barrier:
 - characteristics of substitutional impurities
 - experimental evidence
- Conclusions
 - limitations of model
 - remaining issues

Interface States



free surface

$$(2q\epsilon N_D V)^{1/2} \lesssim Q_i \lesssim$$

m-s interface

$$\frac{\epsilon V}{4\pi d}$$

$$10^{12}$$

$$\lesssim Q_i \lesssim$$

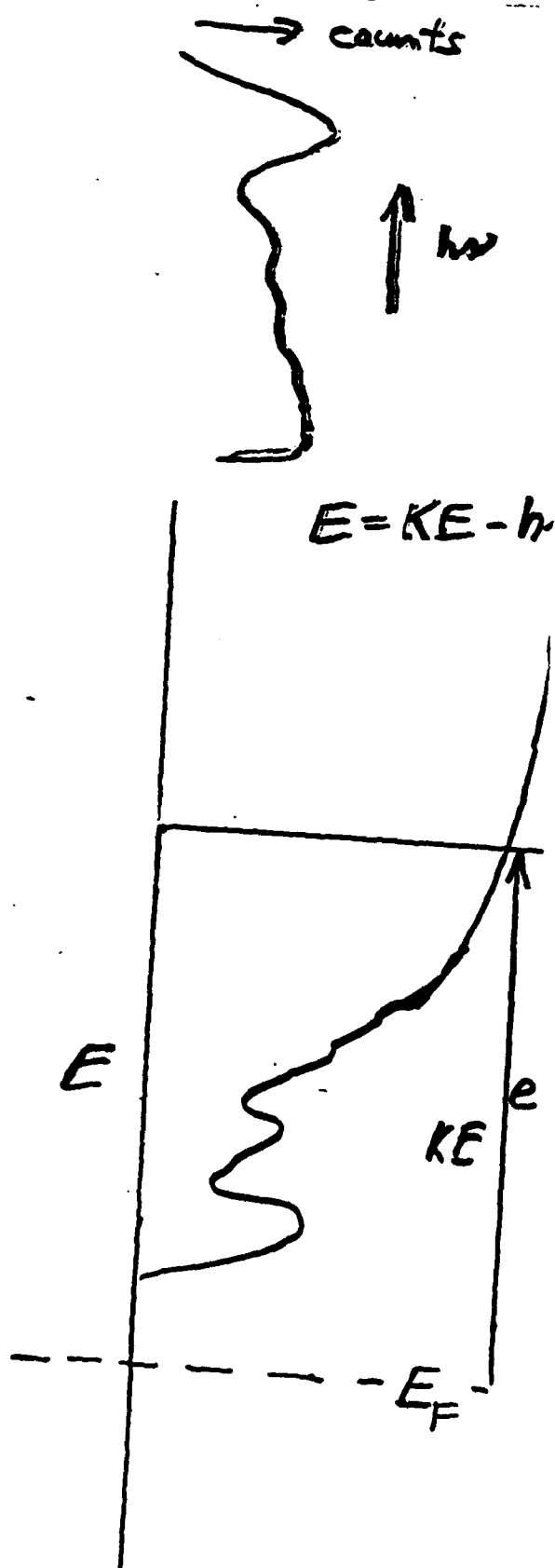
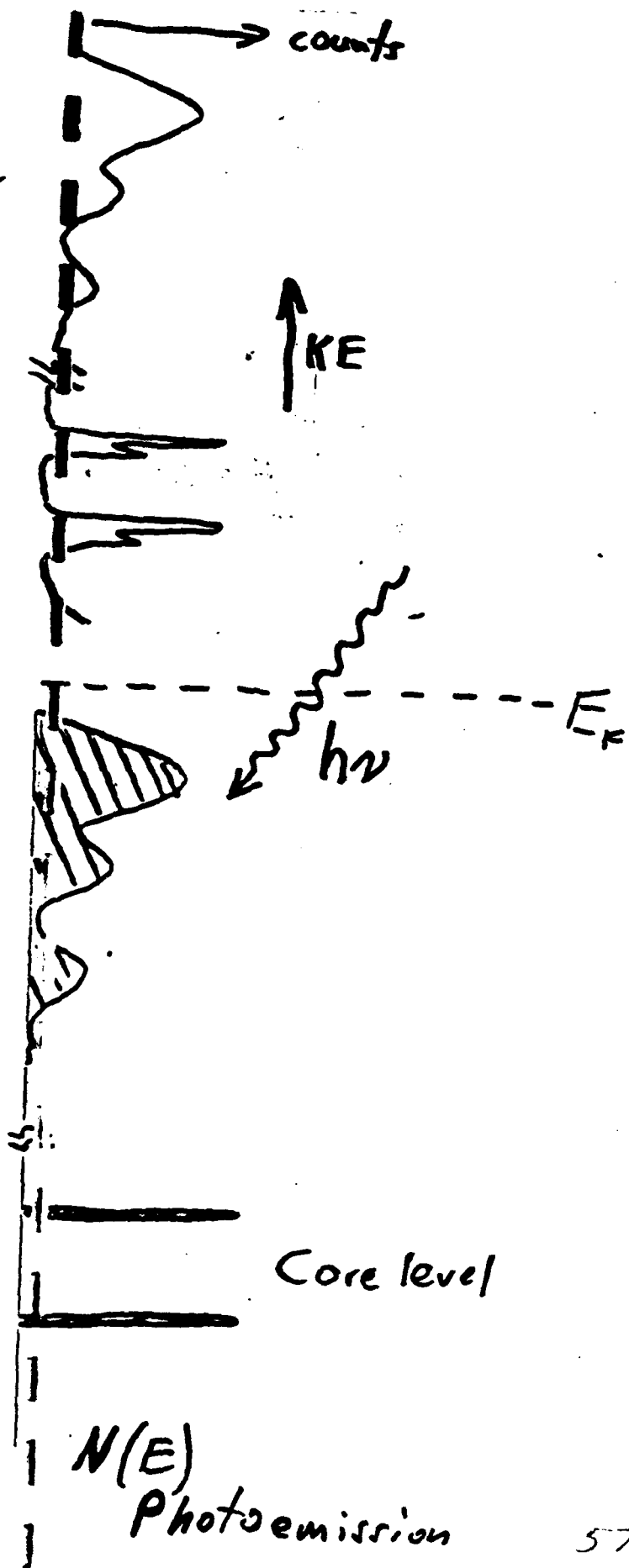
$$10^{14} \text{ e cm}^{-2}$$

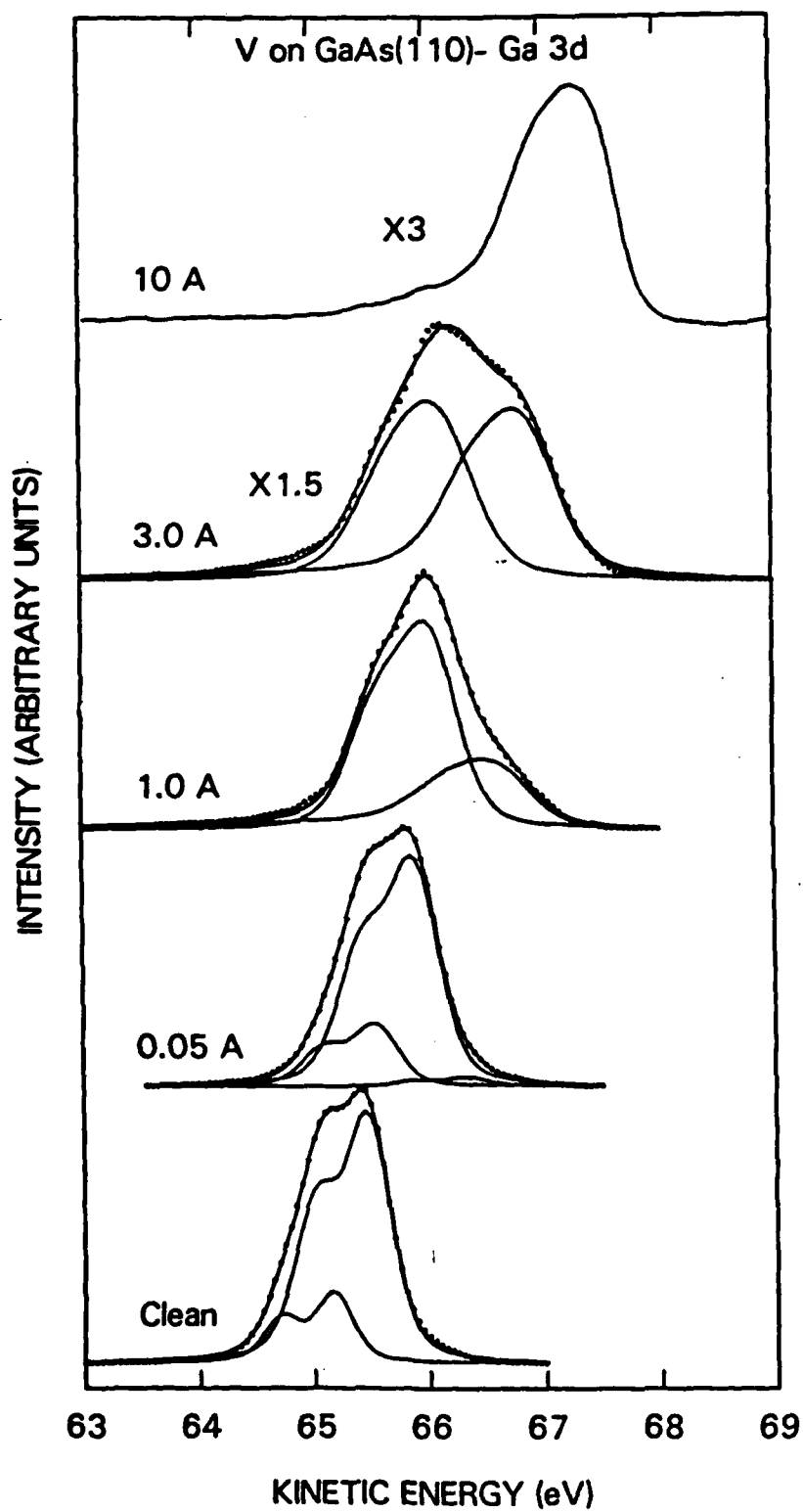
Origin and properties

- "intrinsic" defects
- "extrinsic" interface states
- all:
 - sufficient density
 - acceptor + donor properties
 - $E(\text{donor}) \approx E(\text{acceptor})$
- up to now no definitive identification

CHARACTERISTICS OF SOME SCHOTTKY MODELS

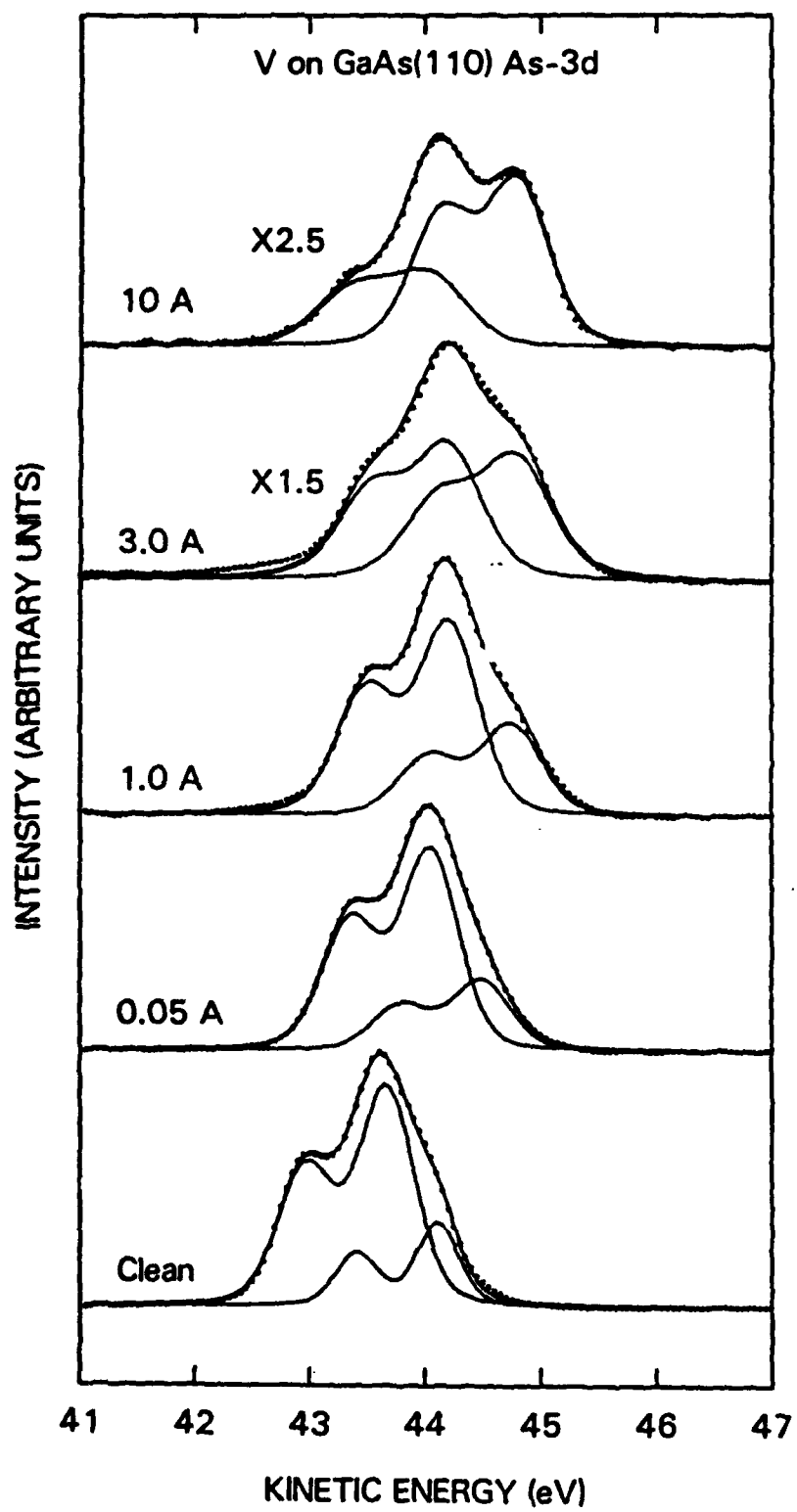
- **Unified defect model**
 - metal independent
 - separate pinning for n & p-type material
 - interface states intrinsic to semiconductor
 - energetically separated acceptor and donor states
- **Effective work function model**
 - metal dependent
 - ϕ (anion) is relevant parameter
 - presence of anion clusters at interface
- **Metal Induced Gapstates**
 - metal independent
 - requires delocalized states (metal)



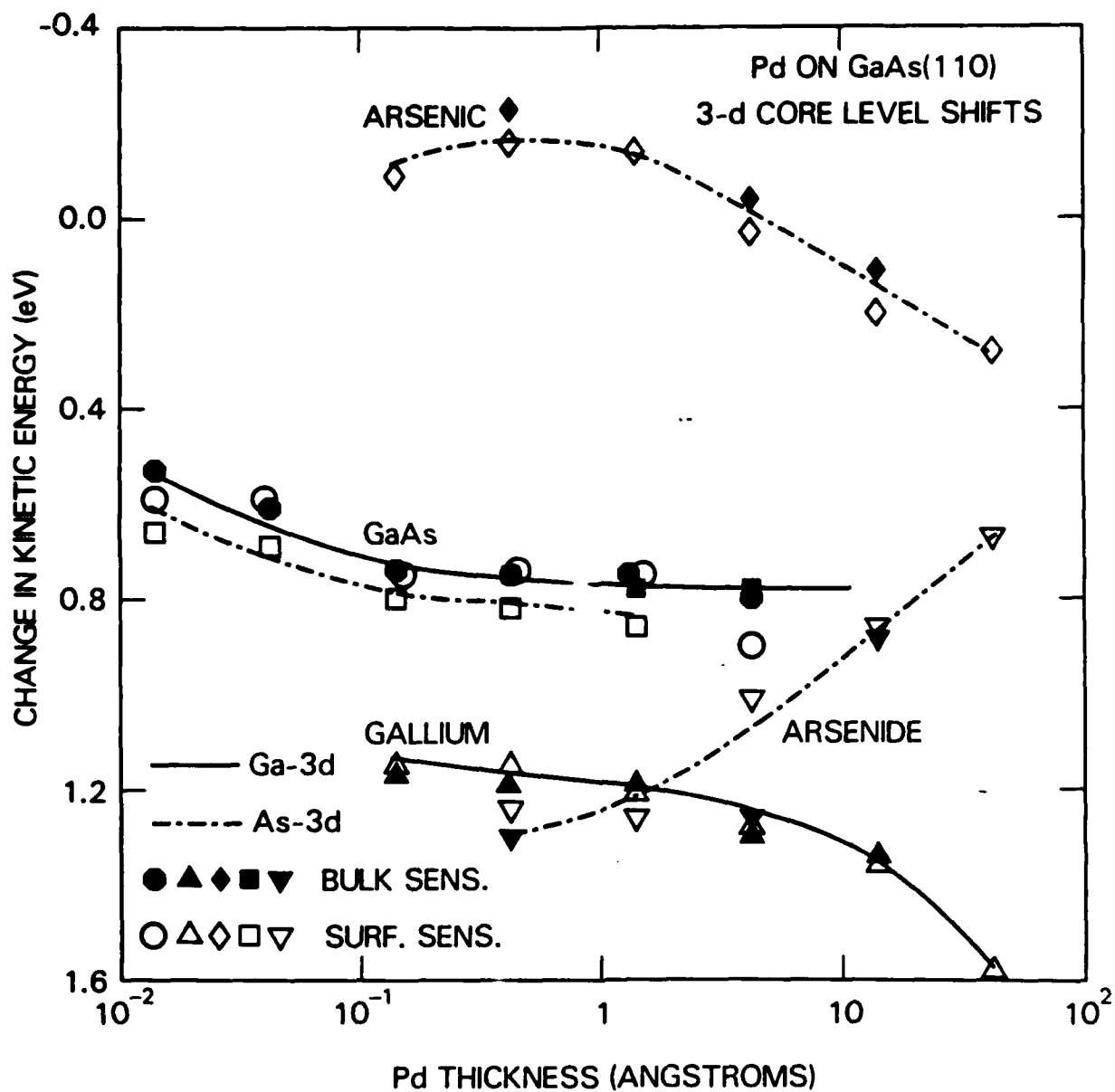


574

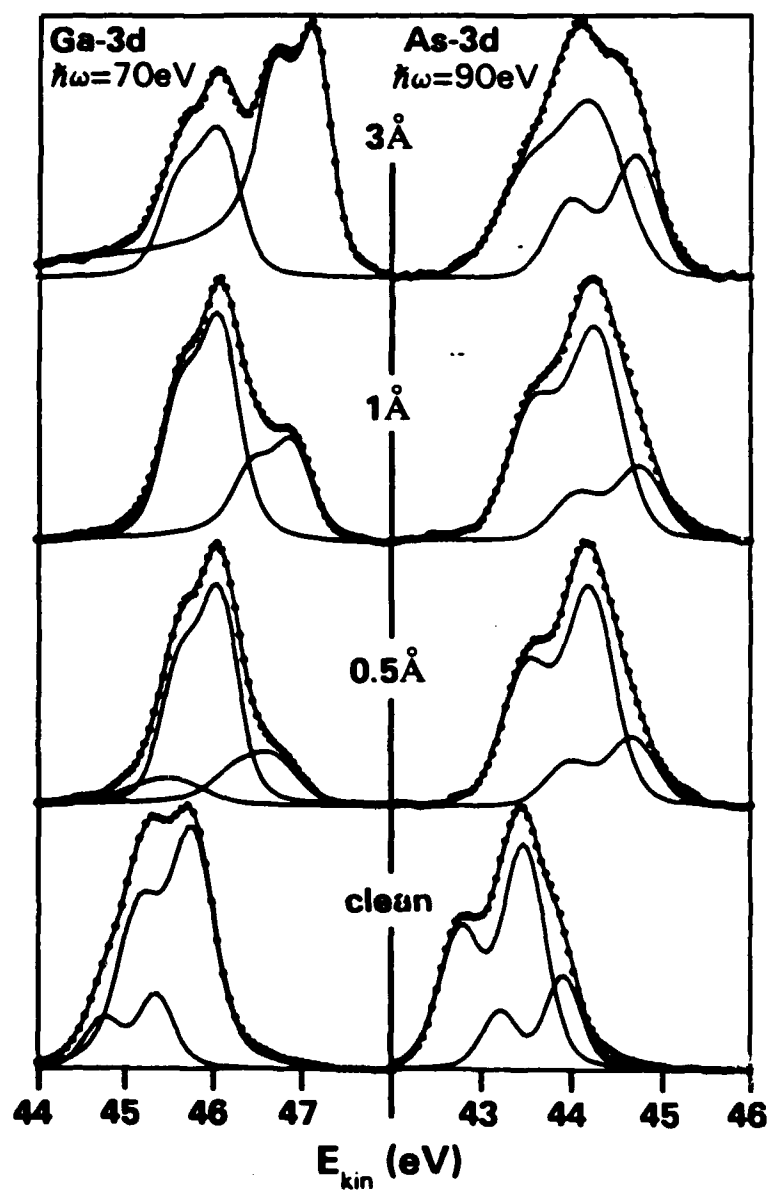
-258

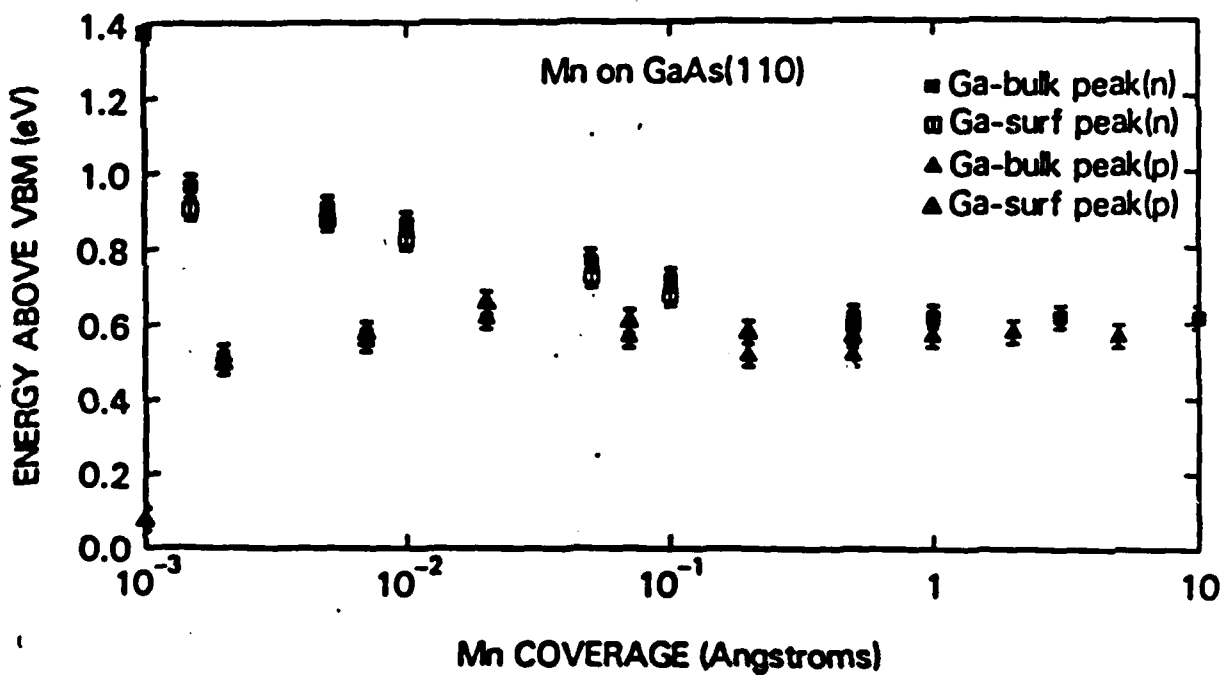
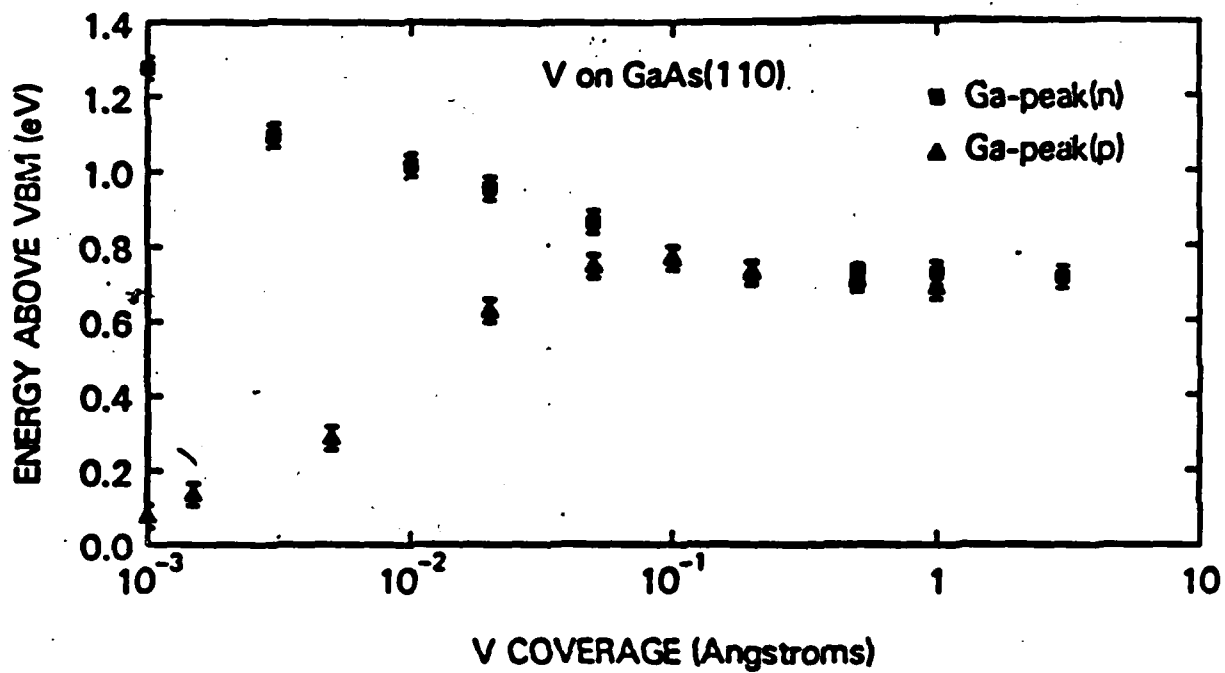


575

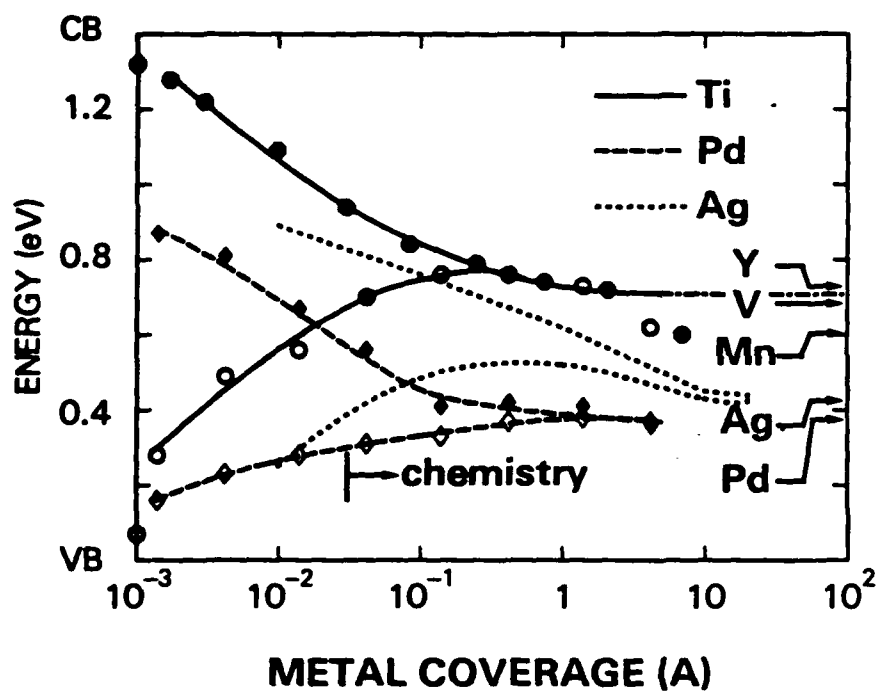


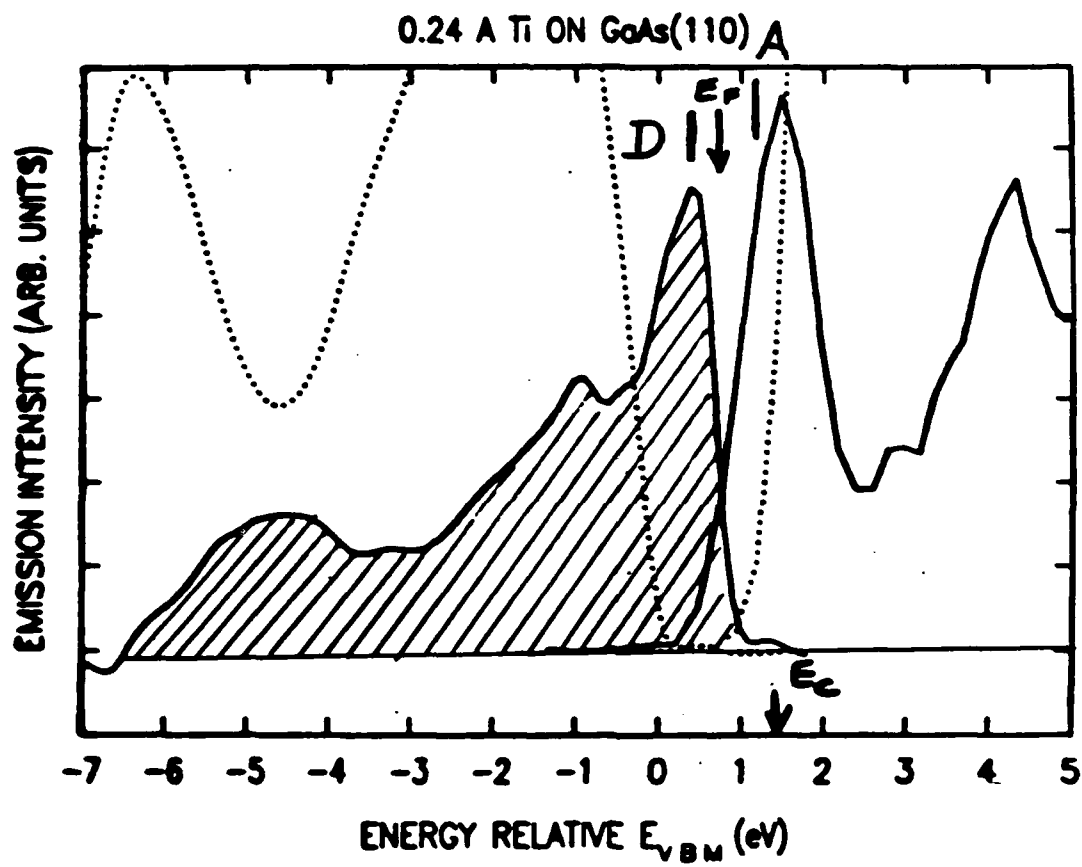
Mn on n-GaAs(110)





FERMI LEVEL AT GaAs(110) INTERFACE

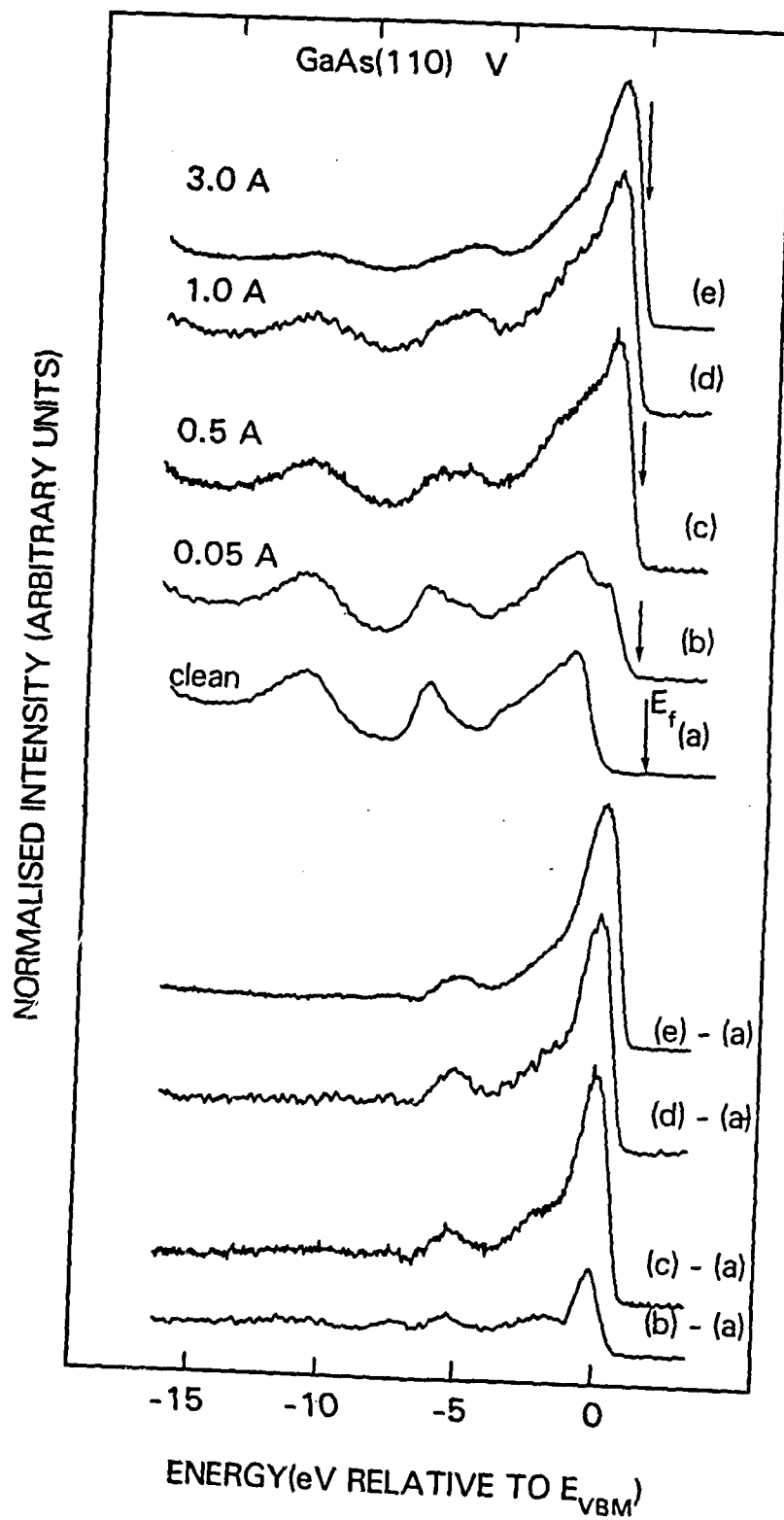




bonding

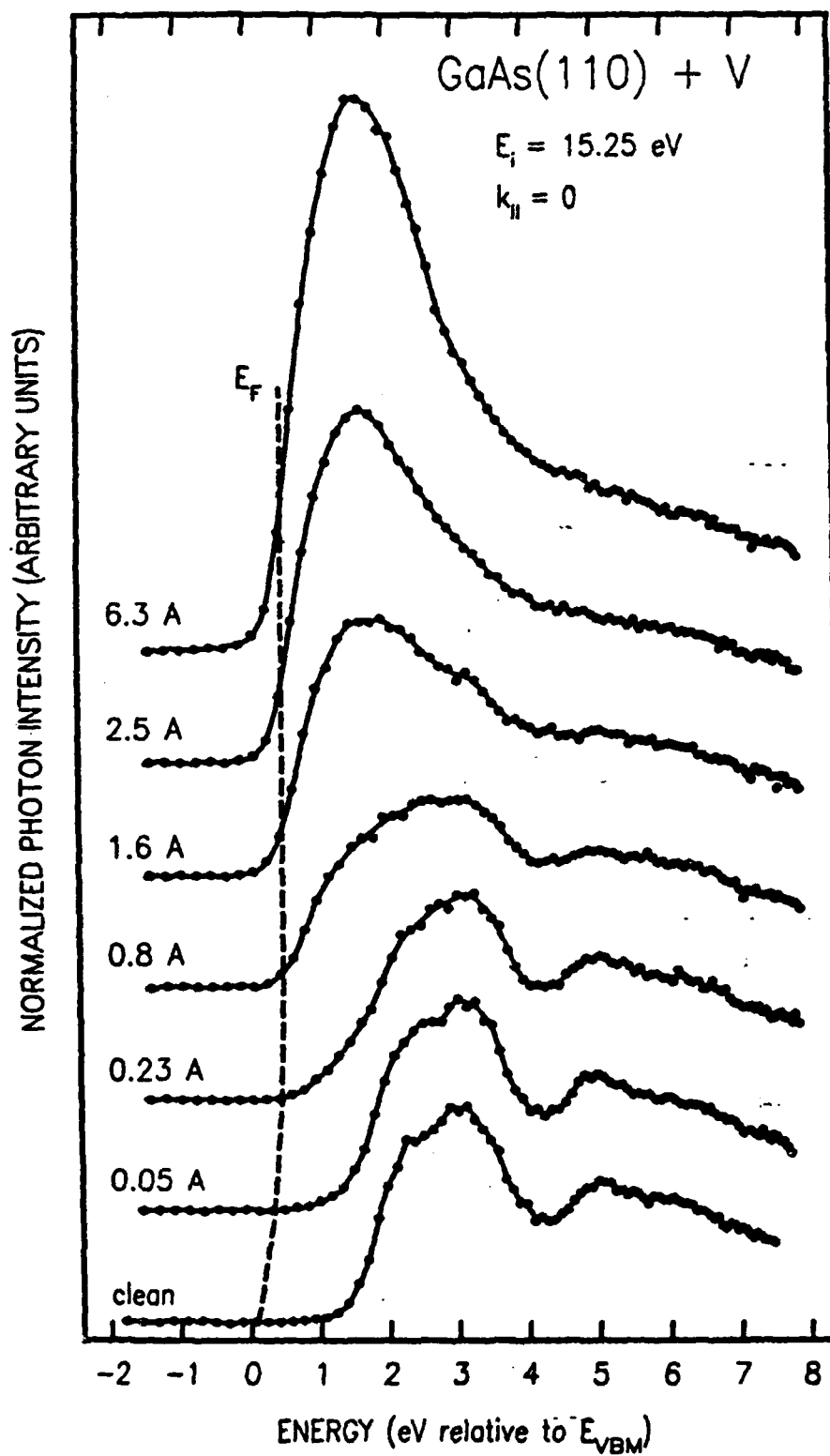
non-bonding

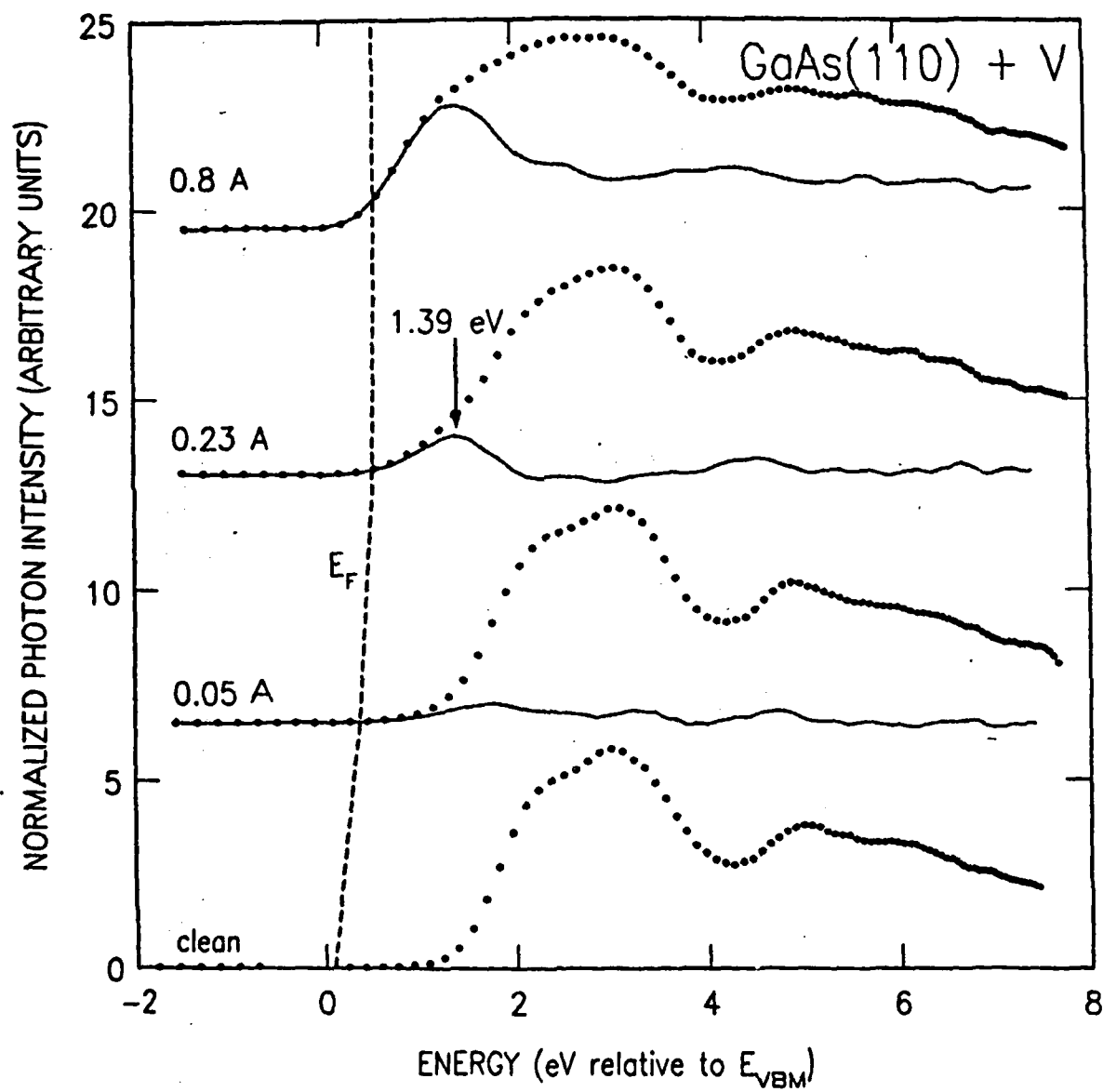
anti-bonding

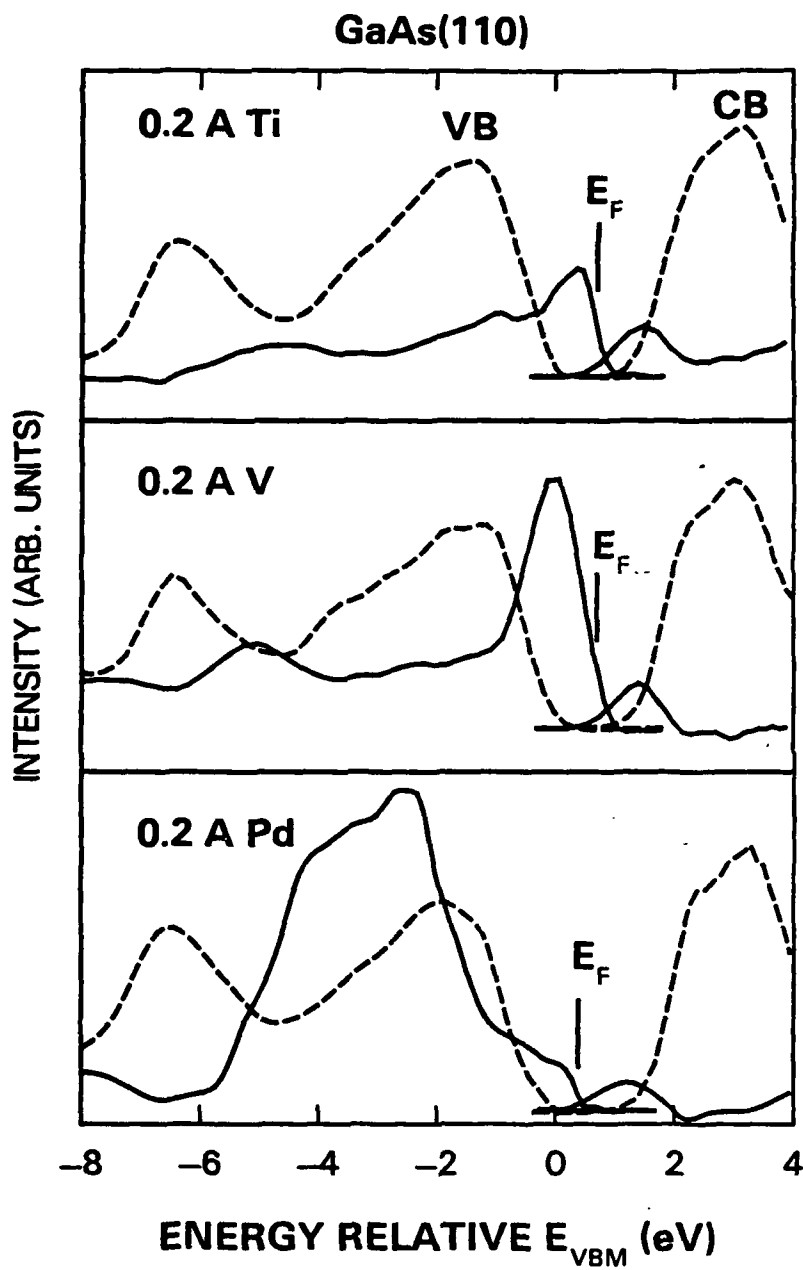


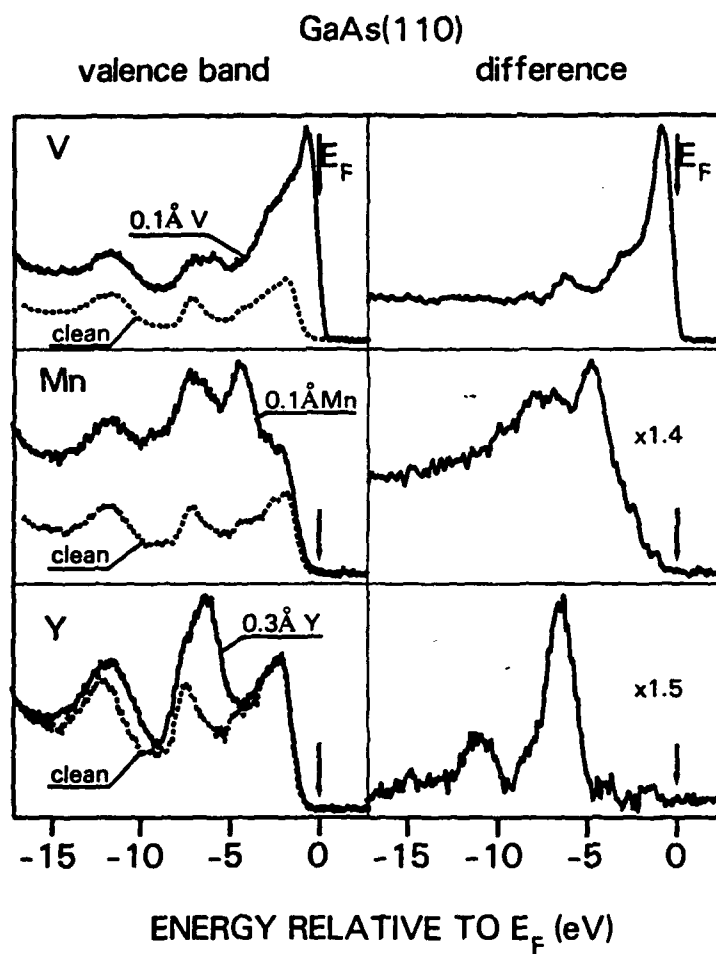
581

FJ 4 B





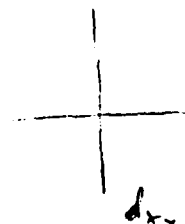
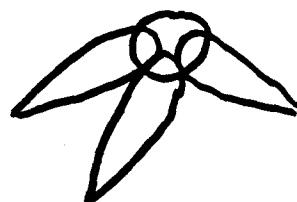
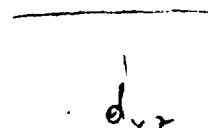
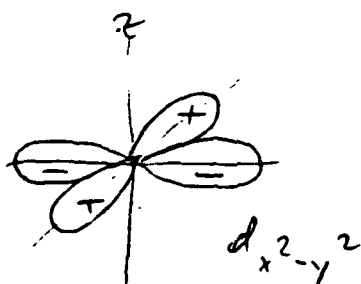
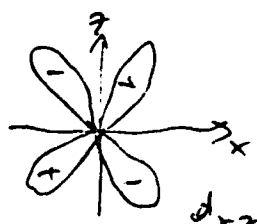
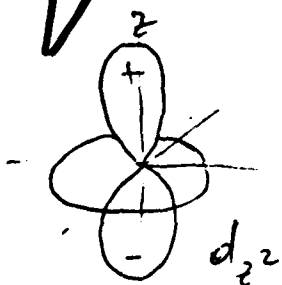
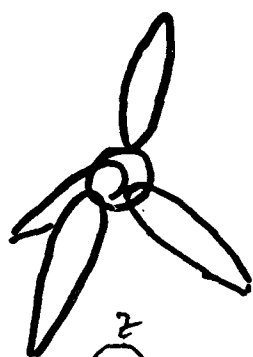
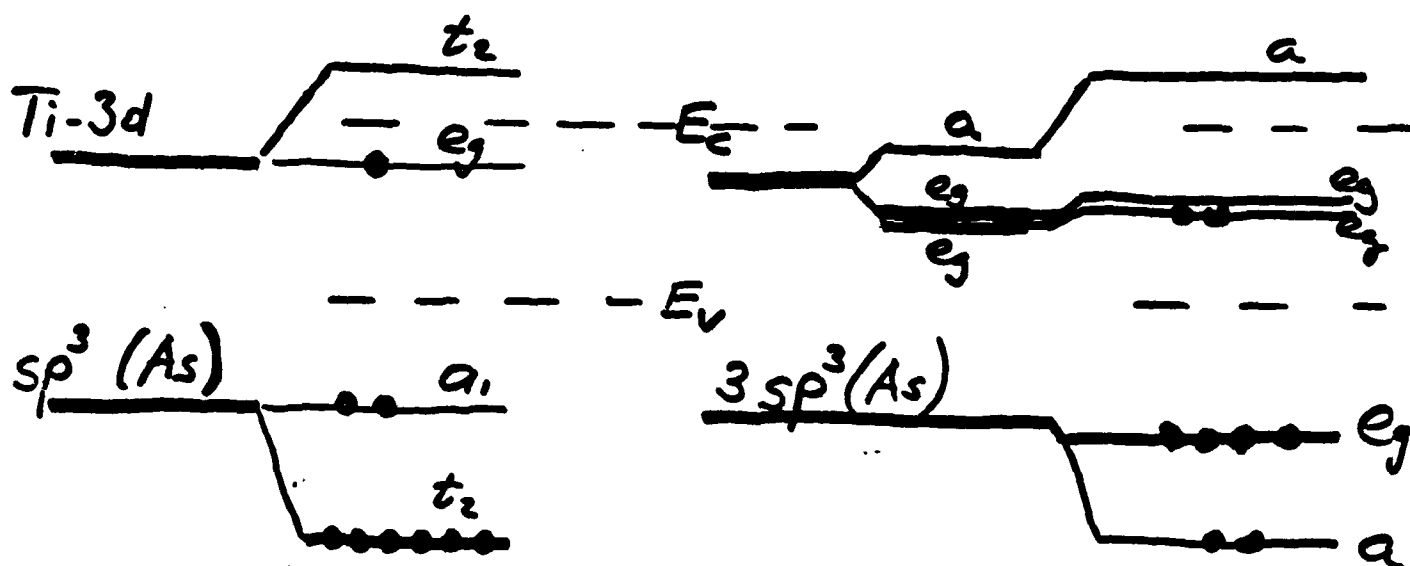




Bulk
 T_d

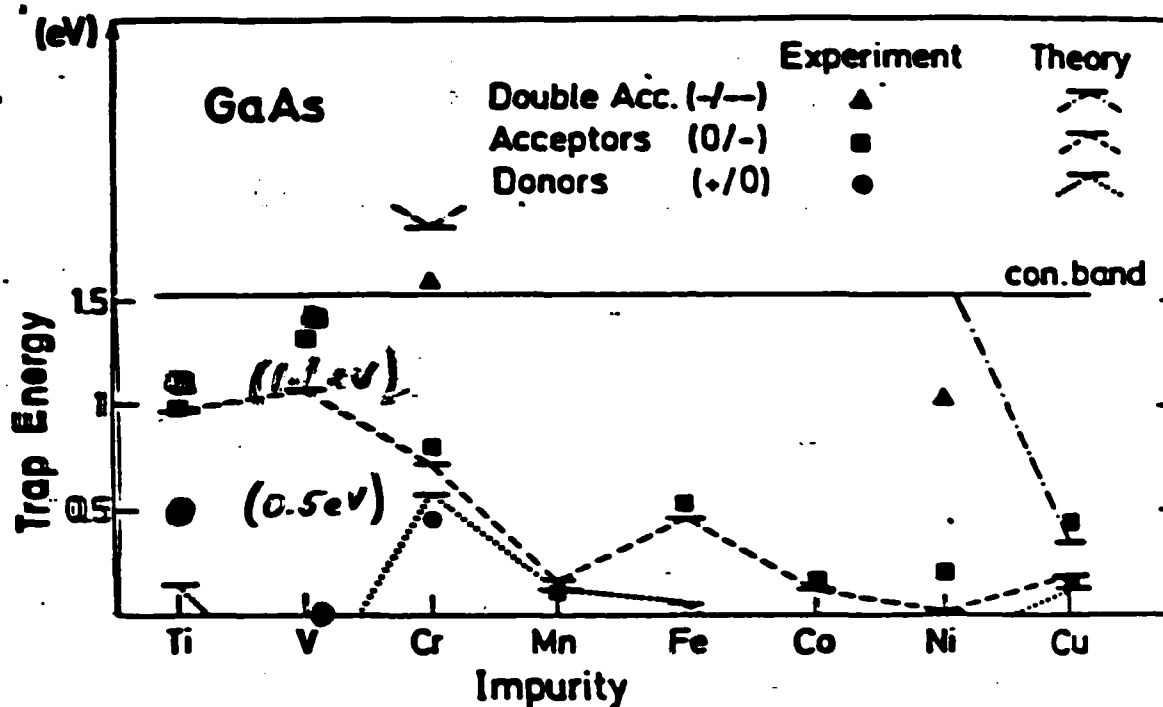
GaAs

Surface
 $\sim C_{3v}$



586

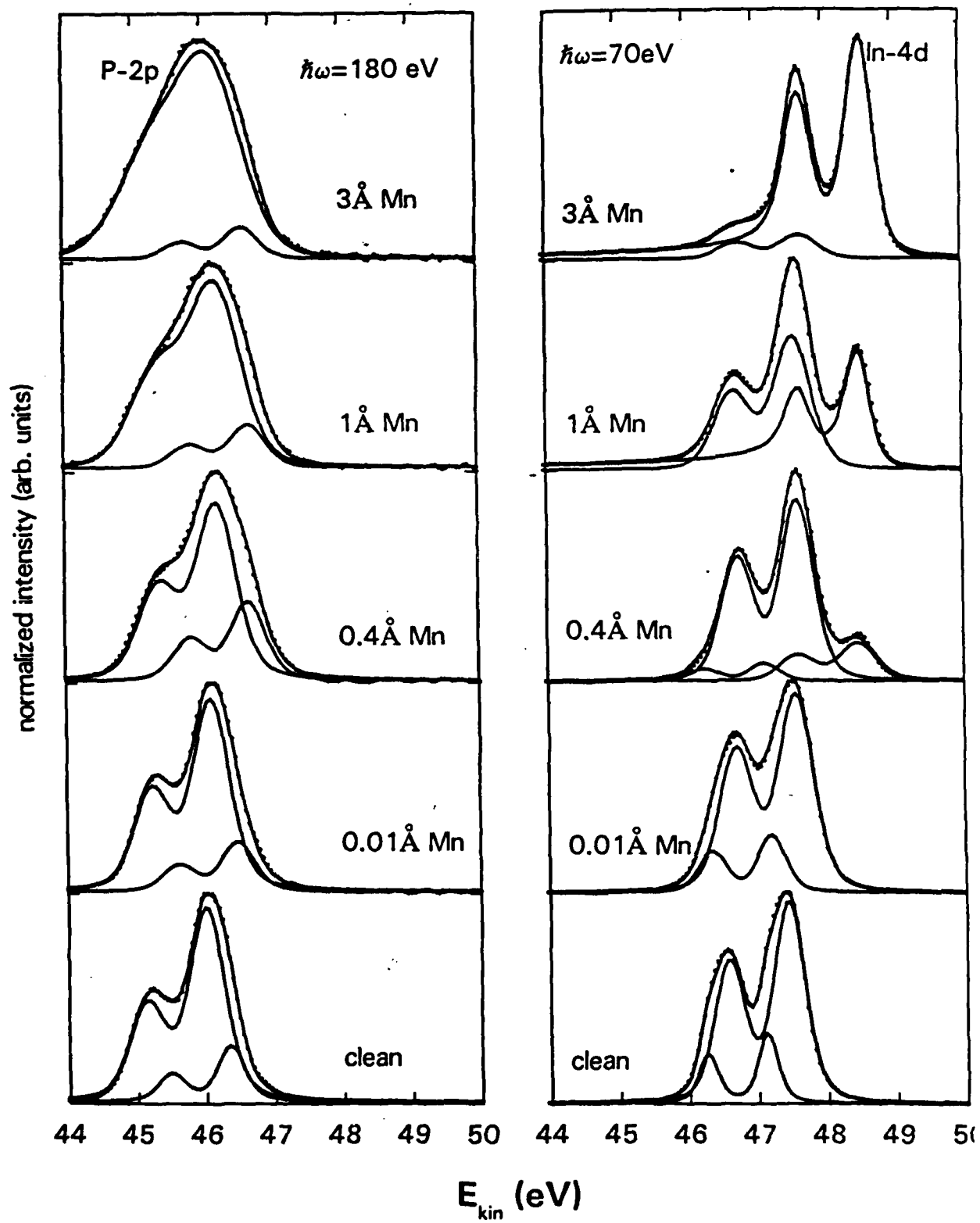
40 15



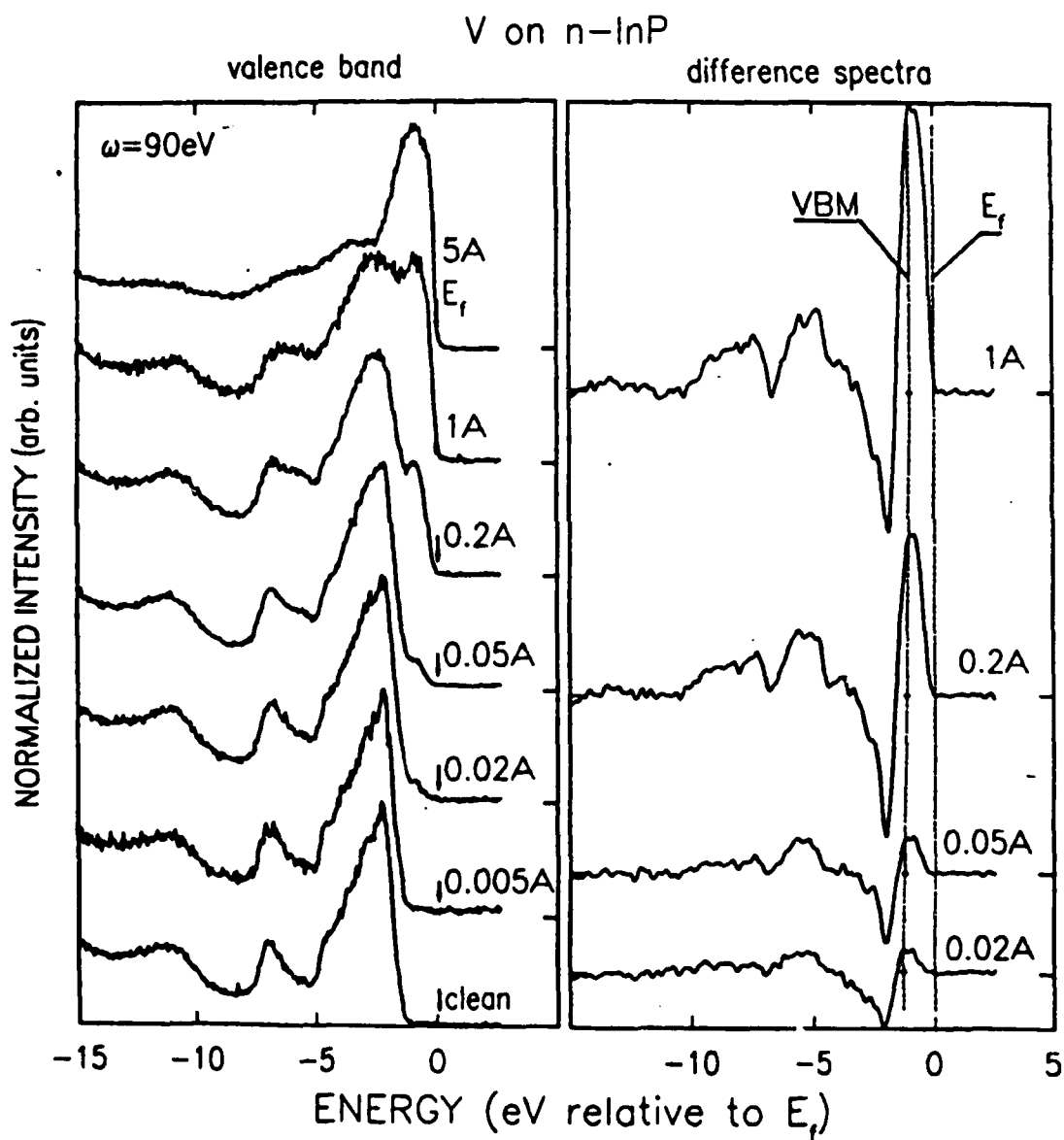
● (A. Hennel, unpublished)

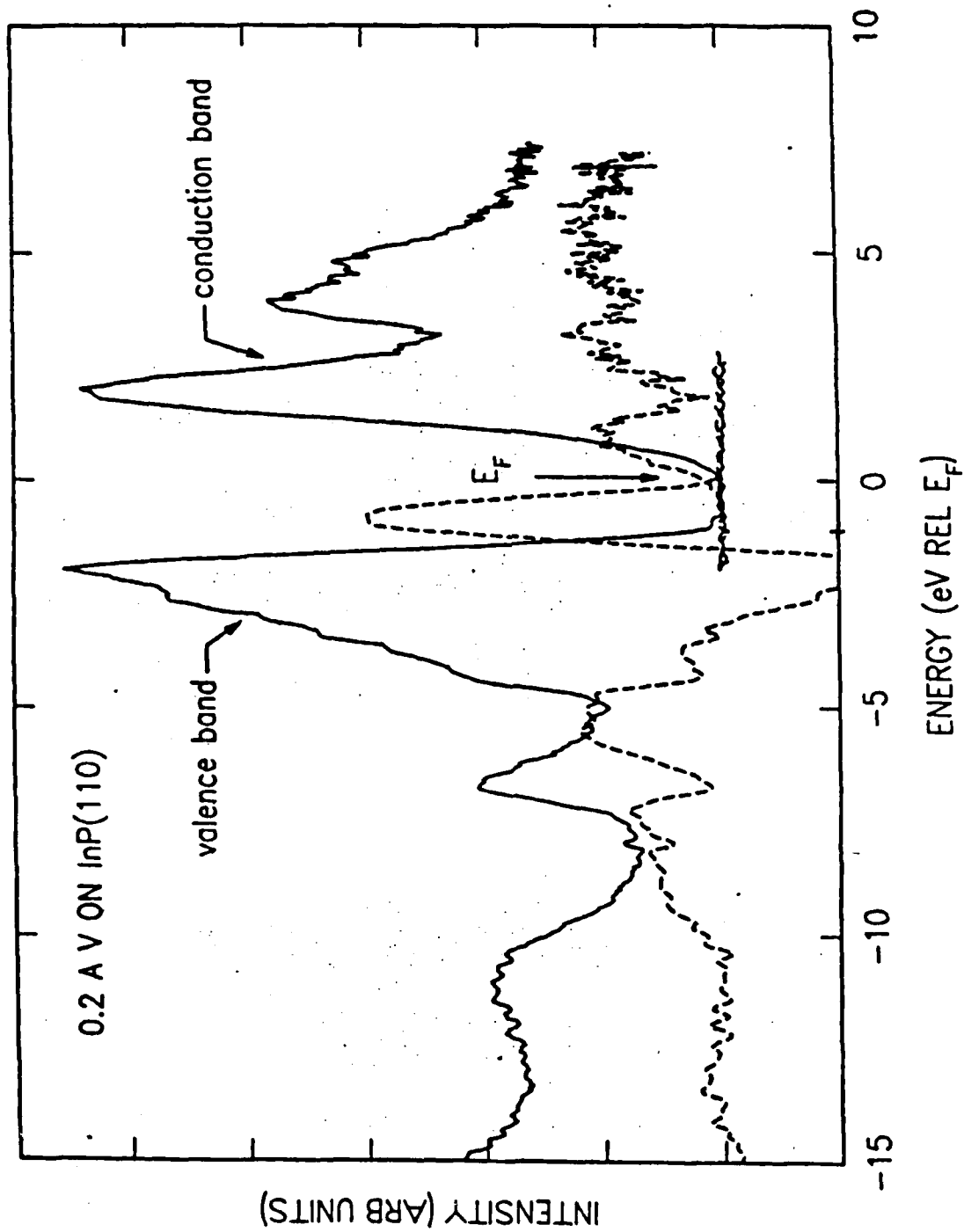
Energy levels of transition-metal impurities in GaAs as calculated by Vogl and Baranowski compared with experimental data. From Ref. 87.

Mn on n-InP



588





540

Fig. 22

#82

Comparison of spectral peaks + substitutional impurity levels

		<u>Present data</u>			
		bulk impurity levels			
		GaAs		InP	
Ti	A	1.30 *	<u>1.40</u>		
	D	0.50	<u>0.45</u>		
V	A	1.30	<u>1.39</u>	in CB	
	D	0	<u>0</u>	0.21	<u>0.20</u>
Mn	A	-	-		
	D	(-1)	<u>-4</u>		

* energies referred to VBM

CONCLUSIONS AND SUMMARY

- Observation of interface states:
 - filled and empty states in bandgap
 - states determine Fermi level
 - derived from d-electrons of transition metal
- Chemical evidence and spectroscopic signature suggests a substitutional impurity
- Limitations and issues
 - not applicable to all transition metals
 - single defect oversimplified
 - independent corroboration required
 - role of chemistry at interface
 - relevance to thick coverage not known

Effects of Coverages, Relaxation, and
Screening at Interfaces

Walter Harrison
Stanford University

WALT HARRISON

TIGHT-BINDING THEORY

Every thing understandable

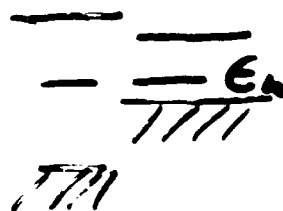
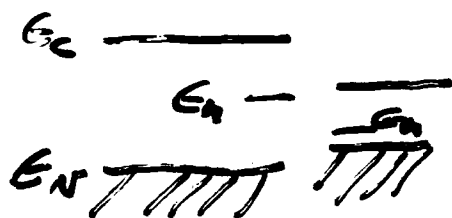
Sometimes predictable

Background: heterojunctions

$$E_N = \frac{E_P^+ + E_P^-}{2} - \sqrt{\left(\frac{E_P^+ - E_P^-}{2}\right)^2 + \left(\frac{1.28 \hbar^2}{2m d^2}\right)^2}$$

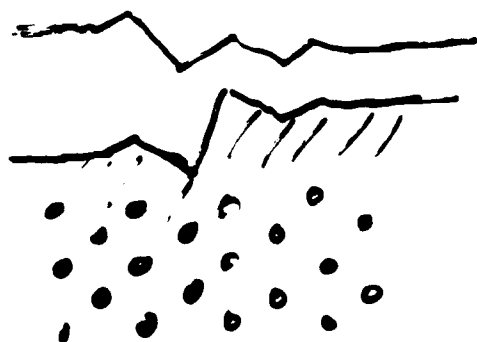
Natural band lineups

Neutral point



Really $\Delta E_h + \Delta E_c$ is

Dipole from 1st planes cross section



Direction of cross

Not seen

AD-A183 158

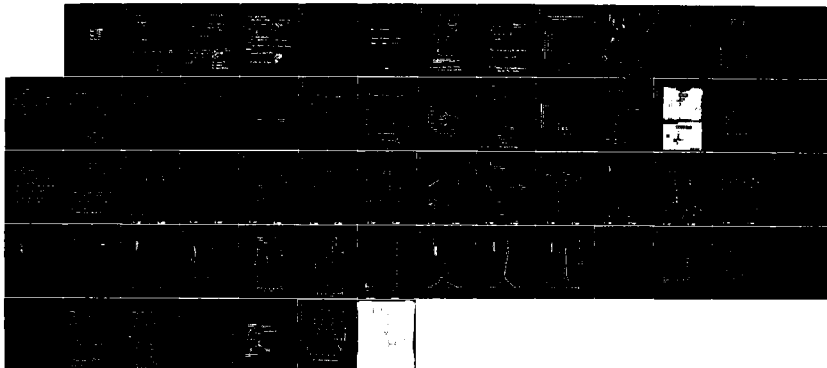
A WORKSHOP ON 3-5 SEMICONDUCTOR: METAL INTERFACIAL
CHEMISTRY AND ITS EFFECTS (U) STANFORD UNIV CA
W E SPICER ET AL. 05 NOV 86 N00014-87-G-0038

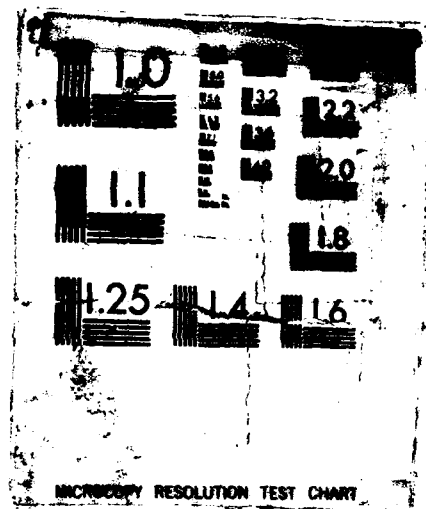
7/7

UNCLASSIFIED

F/G 20/12

NL





Alternate views:

van-de-Walle-Martin, Andersen

no dipole

Tight-binding: True if measure ϵ_r from $\bar{\epsilon}_h$

They found $\bar{\epsilon}_h$

Approximates $\epsilon(0) \approx \infty$. Ignores local effect

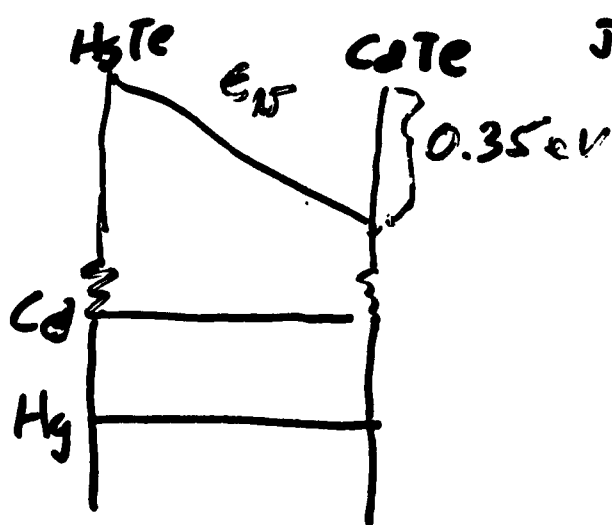
Launoo:

no charge: requires $\Delta \bar{\epsilon}_h = 0$

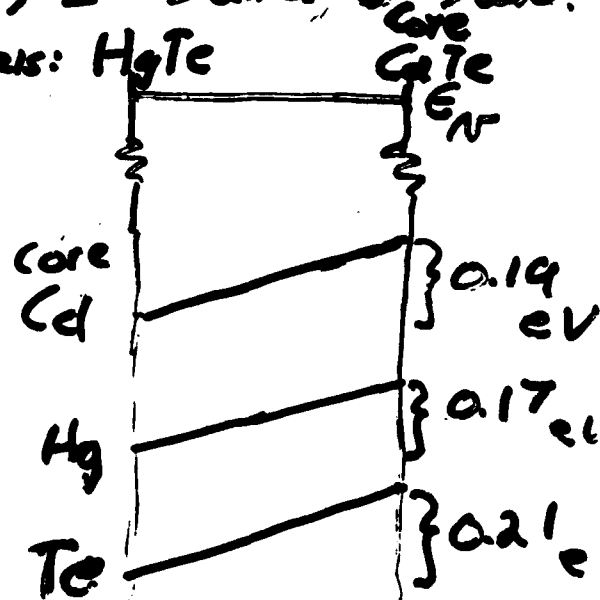
Core-shifts

Shih: Hg cores in Hg-Cd-Te

All HgTe bonds, Z^* same, ϵ same?

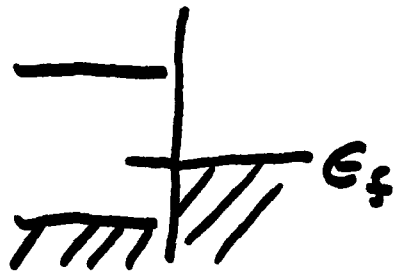


$$\Delta \epsilon_r = 0.35 \text{ eV} \quad 595$$



$$\Delta \epsilon_r = 0.29 \text{ eV}$$

SCHOTTKY BARRIERS

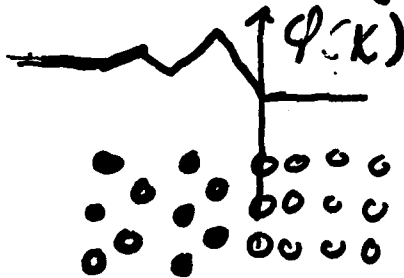


Reasonable accord

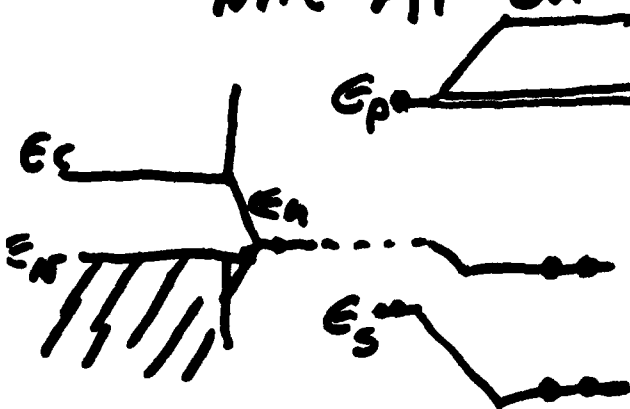
Really $\rightarrow \frac{E_h - E_f}{E(0)}$ & semi.

$$S = 1/E(0)$$

Should fluctuate



Partial coverage: Ideal geometry
One Al on Si:

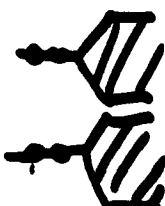


In this geometry
No charge
No band bending

Multiple atoms

No local charge till bands cross E_F

E_F  Width $\approx 2\sqrt{n \frac{V_{ppr}^2 + V_{pr}^2}{2}}$

π/π  $\approx \pi 3eV$

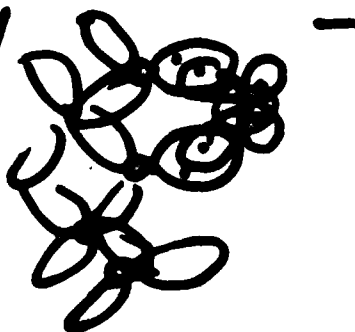
No band bending

But dipoles arise to shift metallic levels.

Once bands cross E_F , band-bending begins.

Depends on geometry

Favored for n-type.



**Unpinned GaAs Surfaces by
Photochemistry**

Jerry M. Woodall

IBM - Yorktown Heights

OXIDE/III-V INTERFACES

P. Kirchner, A. Warren, S. Offsey,
J. Baker, J. Tsang, S. Wright

IBM

T.E. Kazior et al. J Appl. Phys. 54 2533 (1983)

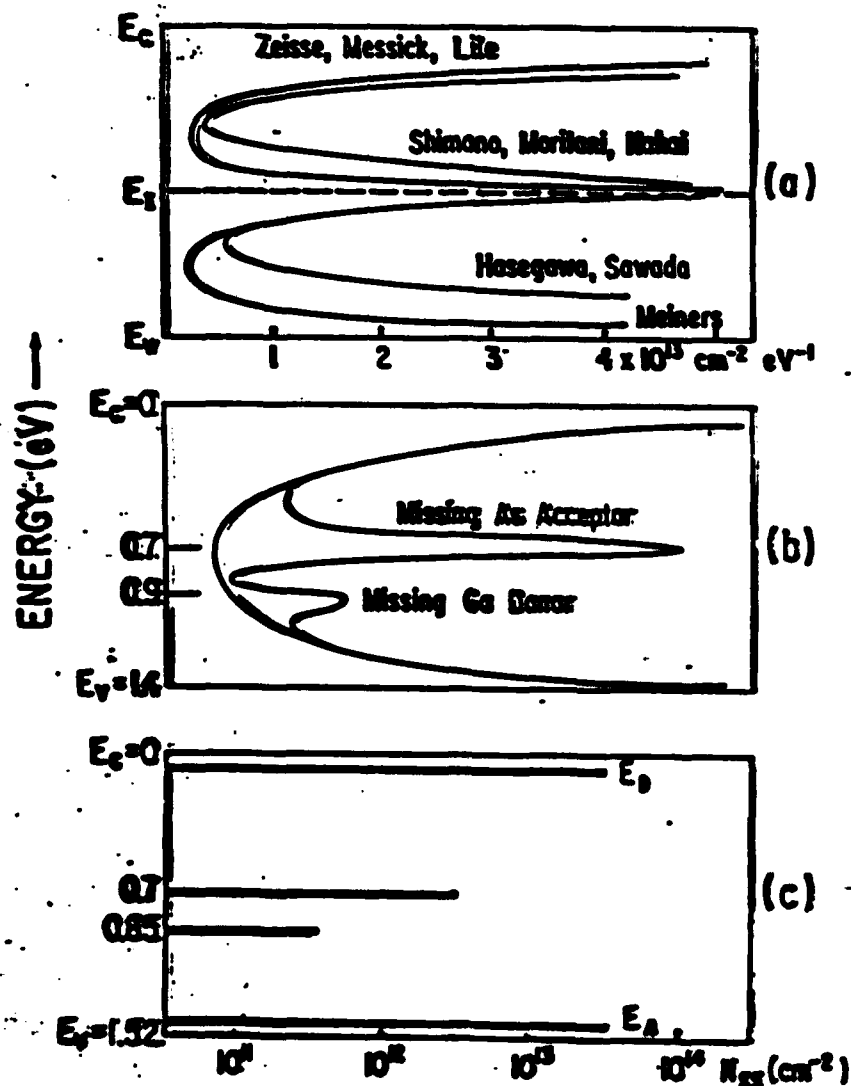
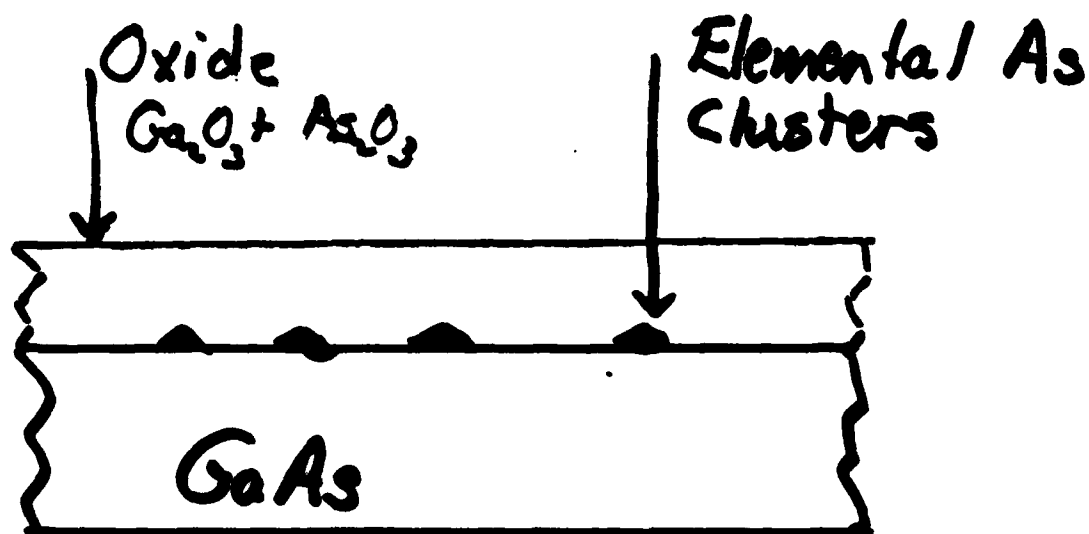
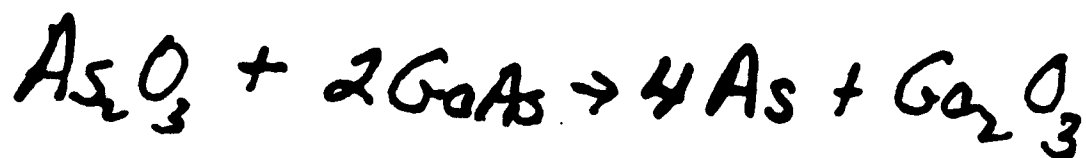


FIG. 1. GaAs interface state models: (a) U-shaped distributions obtained from capacitance measurements (Ref. 1-4); (b) unified defect model (Ref. 10); (c) our model derived from photoionization discharge current analysis (Ref. 15-21).

*Evidence for Fermi Level Pinning
at GaAs/Oxide Interfaces*



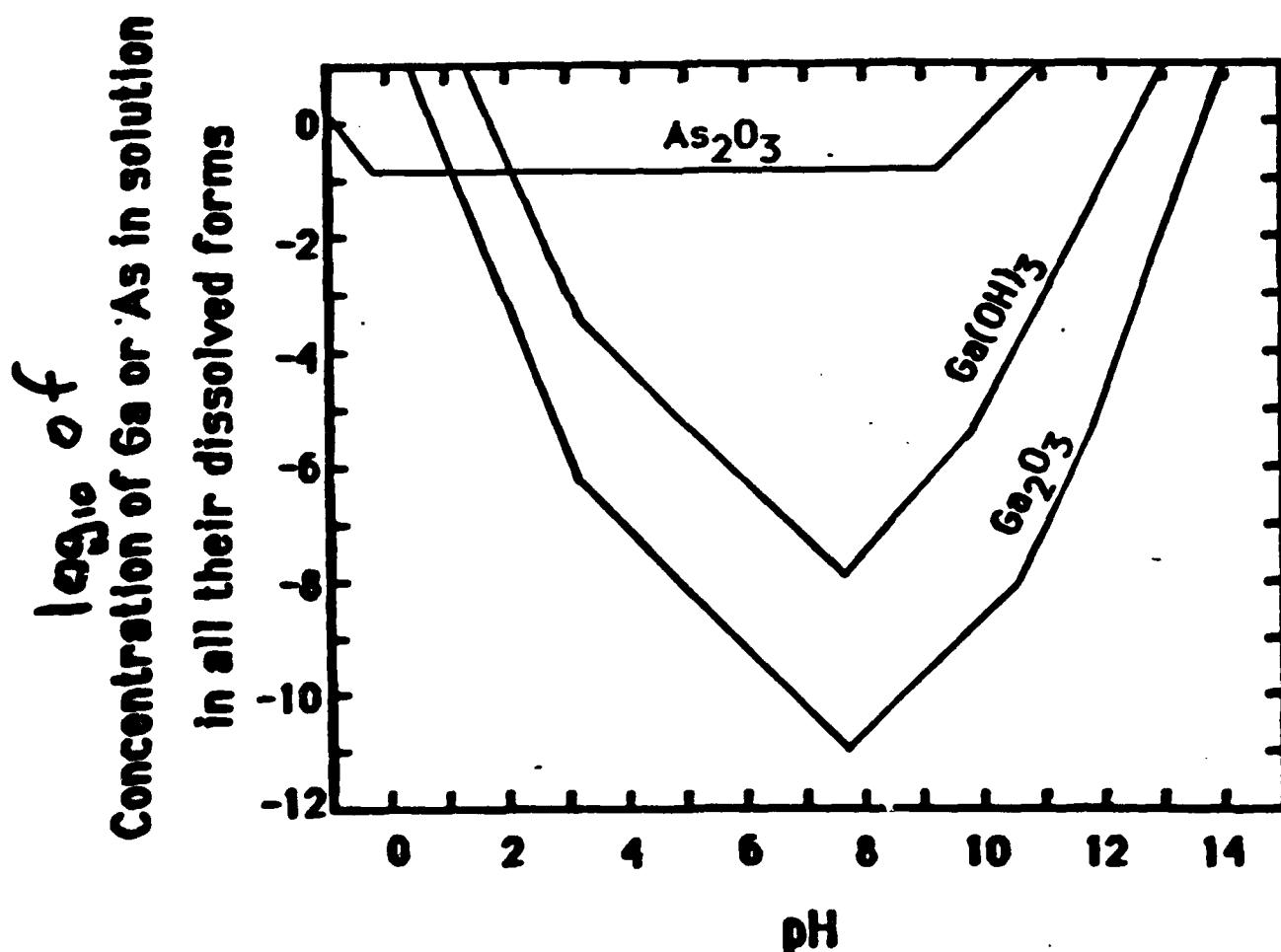
The Oxidized GaAs Surface



$$\Delta F < 0$$

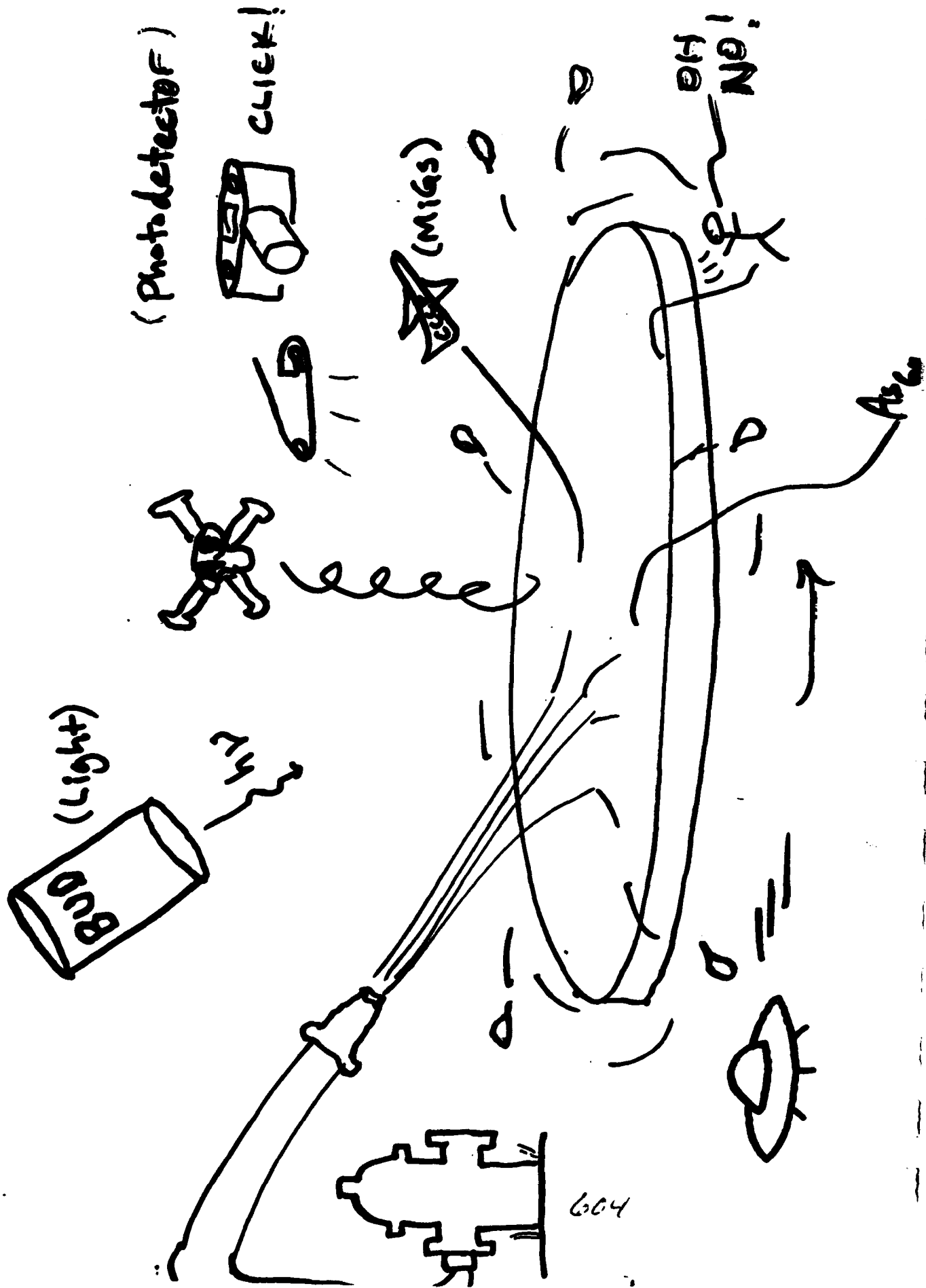
" E_F Pinning" (i.e. Schottky Barrier)
Due to As Clusters

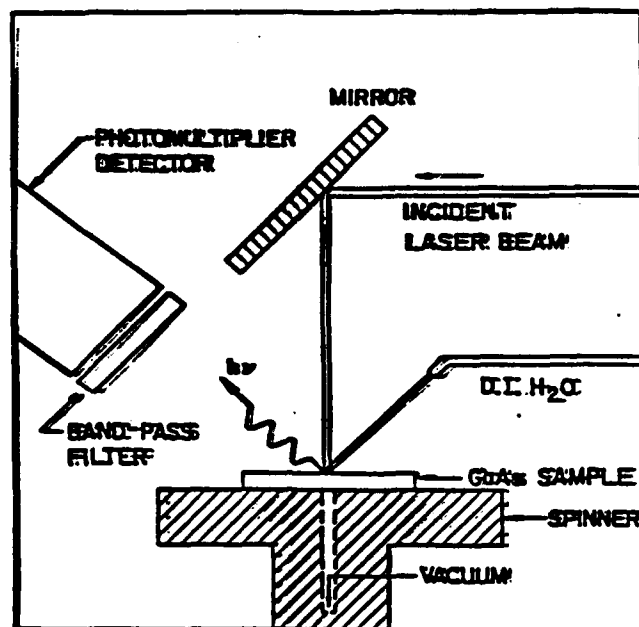
Influence of pH on the solubility of Ga and As oxidation products



After M. Pourbaix, Atlas of Equilibria in Aqueous Solutions

Courtesy of D. Podlesnik, Columbia U.

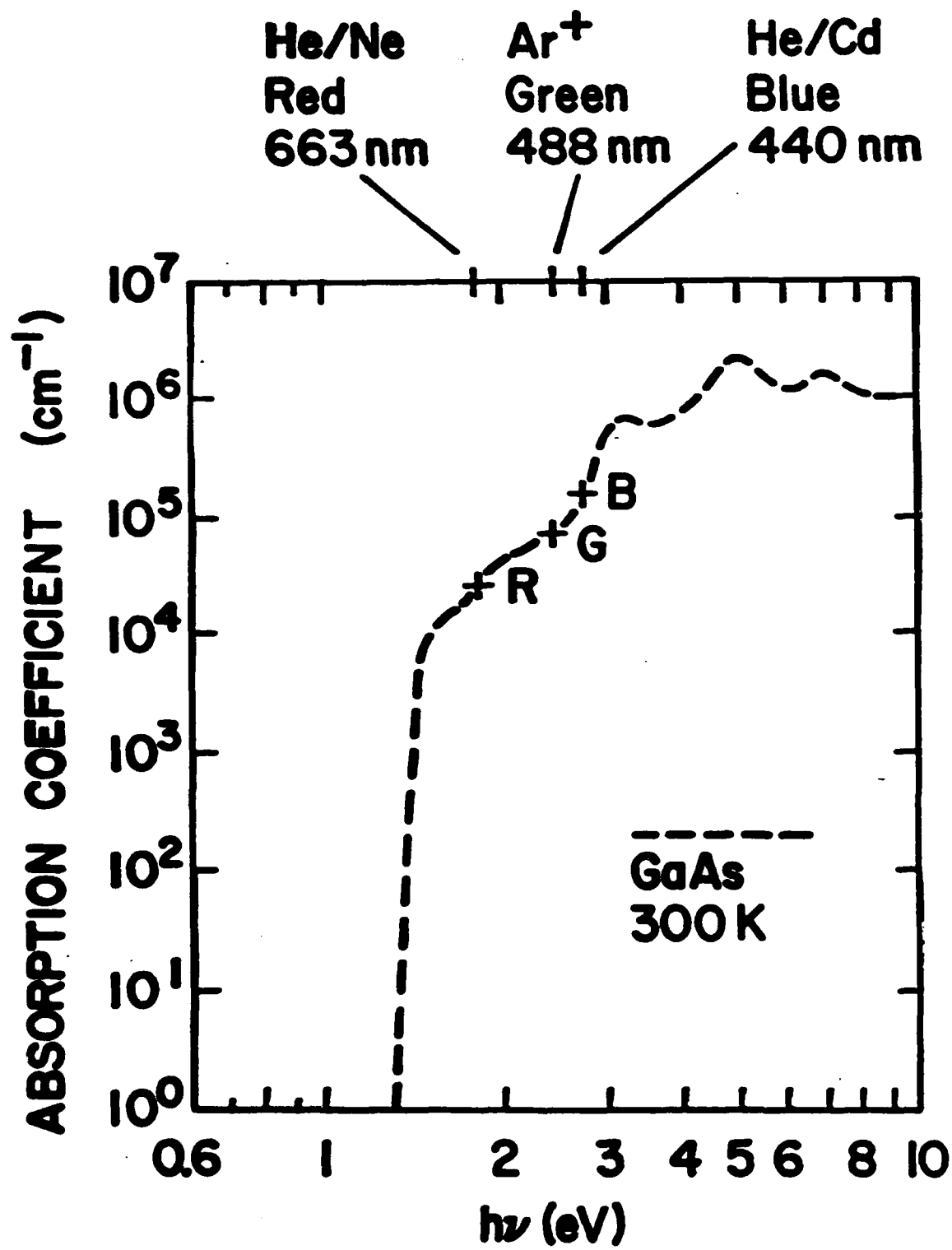




Experimental Setup

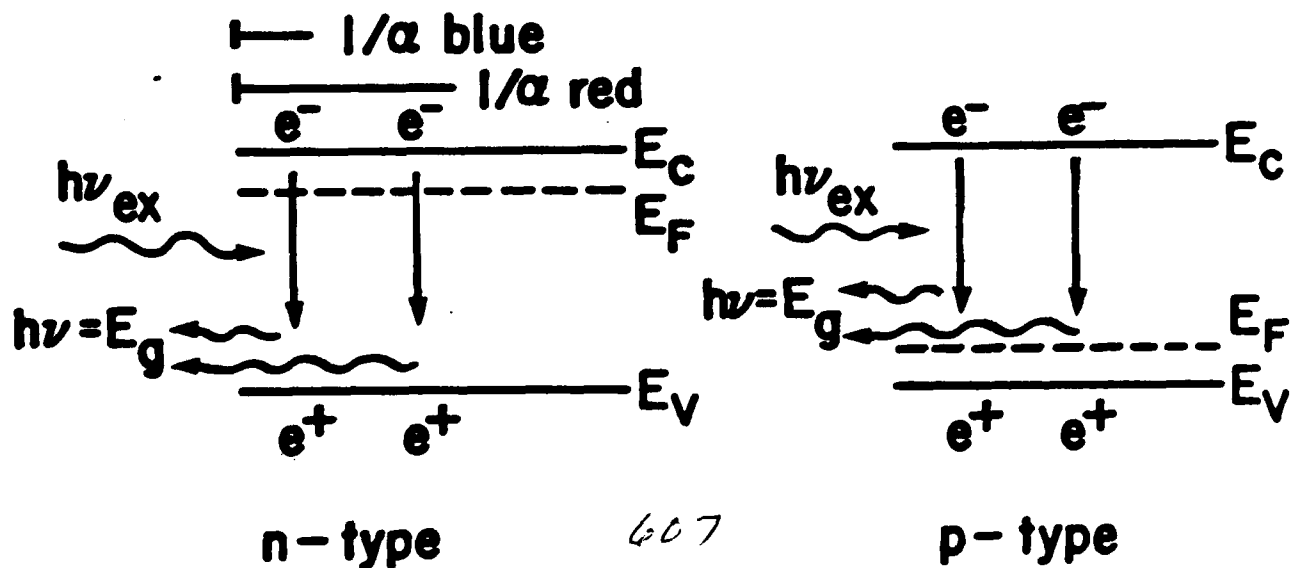
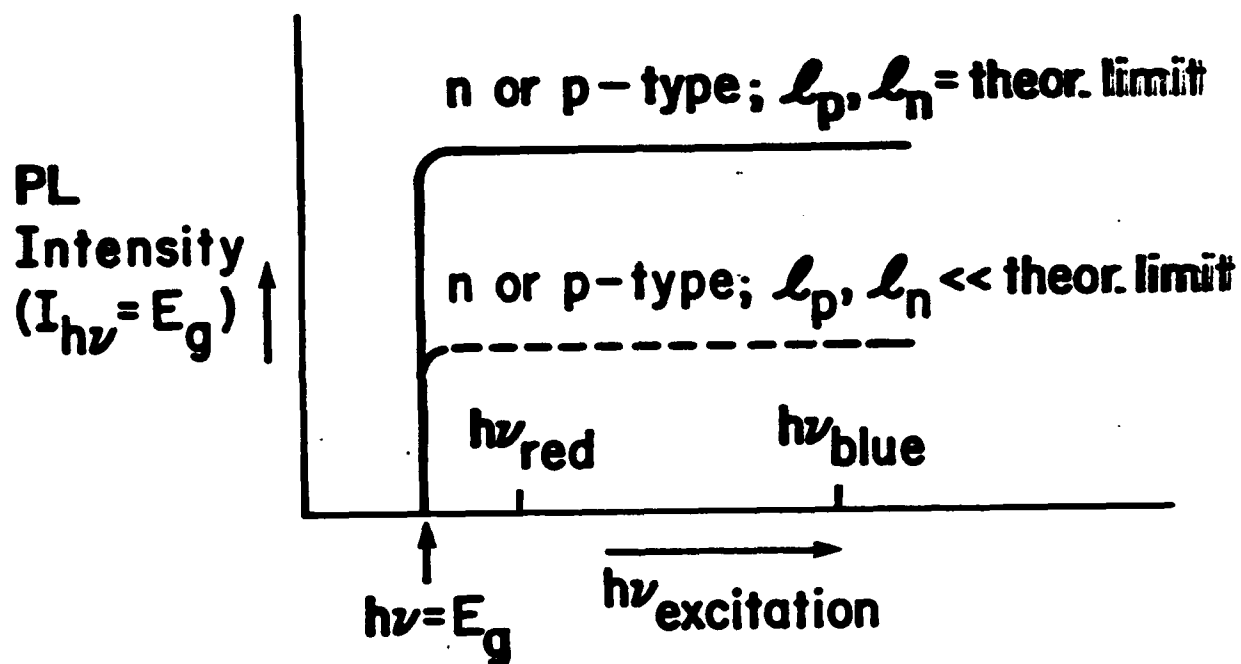
Verification of the Unpinned Surface

- **Band edge photoluminescence of n and p-type GaAs versus excitation energy shows a nearly flat response indicating substantial decrease in both surface band bending and surface recombination velocity**
- **Raman Spectroscopy shows a reduced LO phonon intensity and an enhanced plasmon intensity indicating a reduced surface depletion region**
- **C-V measurements of Hg/PMMA/GaAs MOS capacitors are consistent with low interface state density**



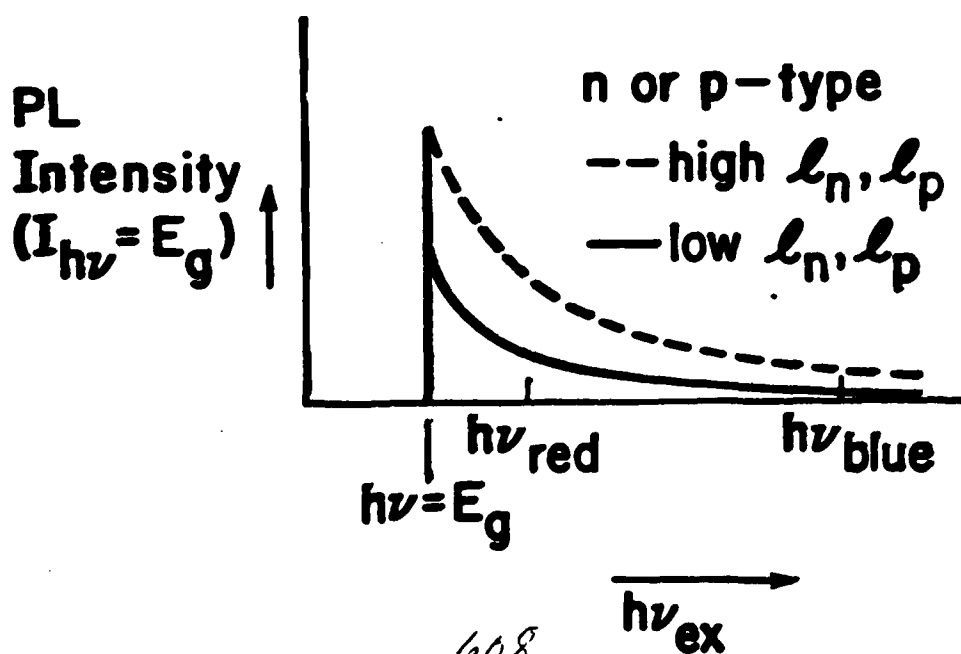
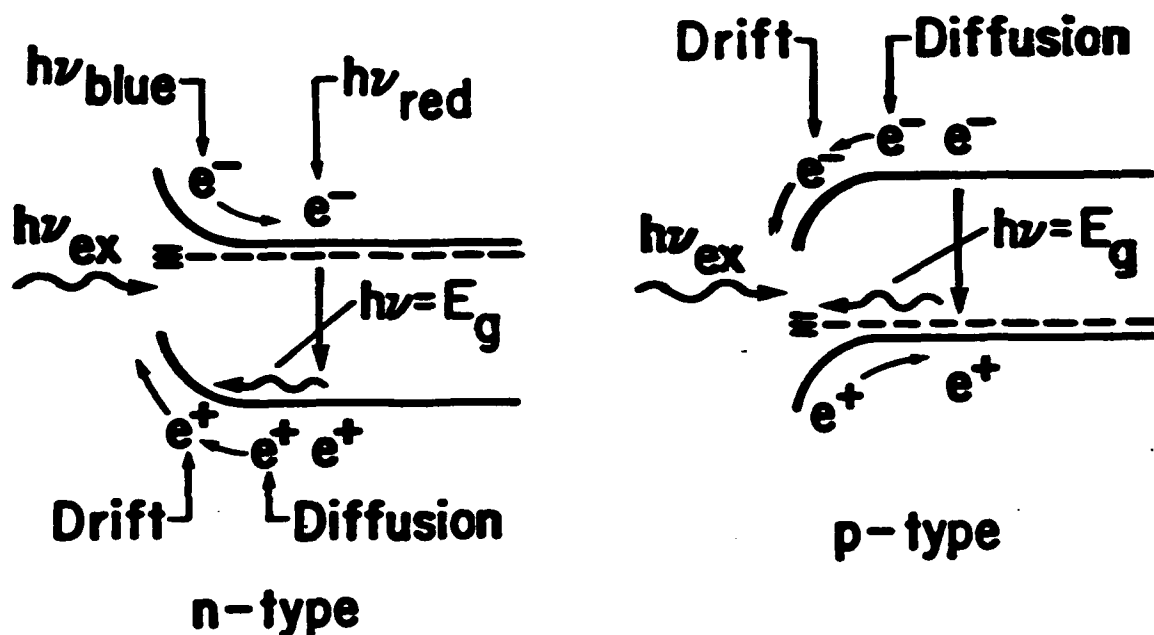
PHOTOLUMINESCENCE (PL) SPECTROSCOPY

CASE I: NO PINNING, i.e. flat band



PHOTOLUMINESCENCE SPECTROSCOPY

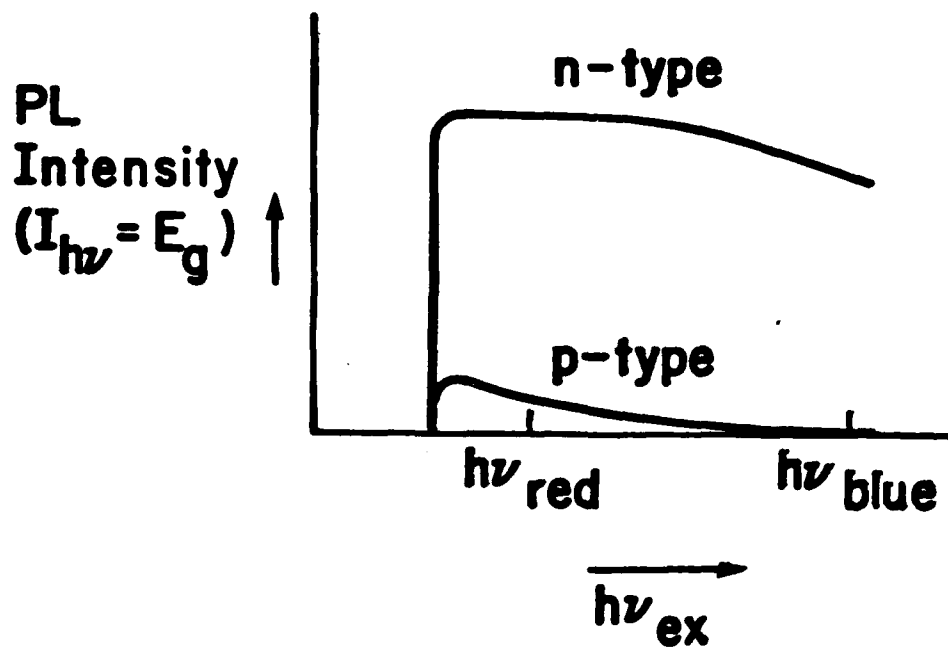
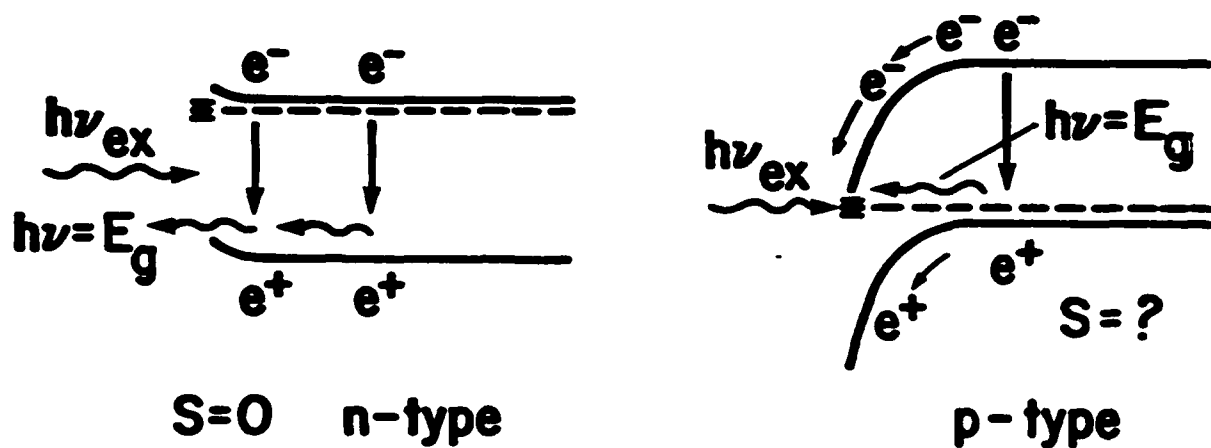
CASE II: MID-GAP PINNING



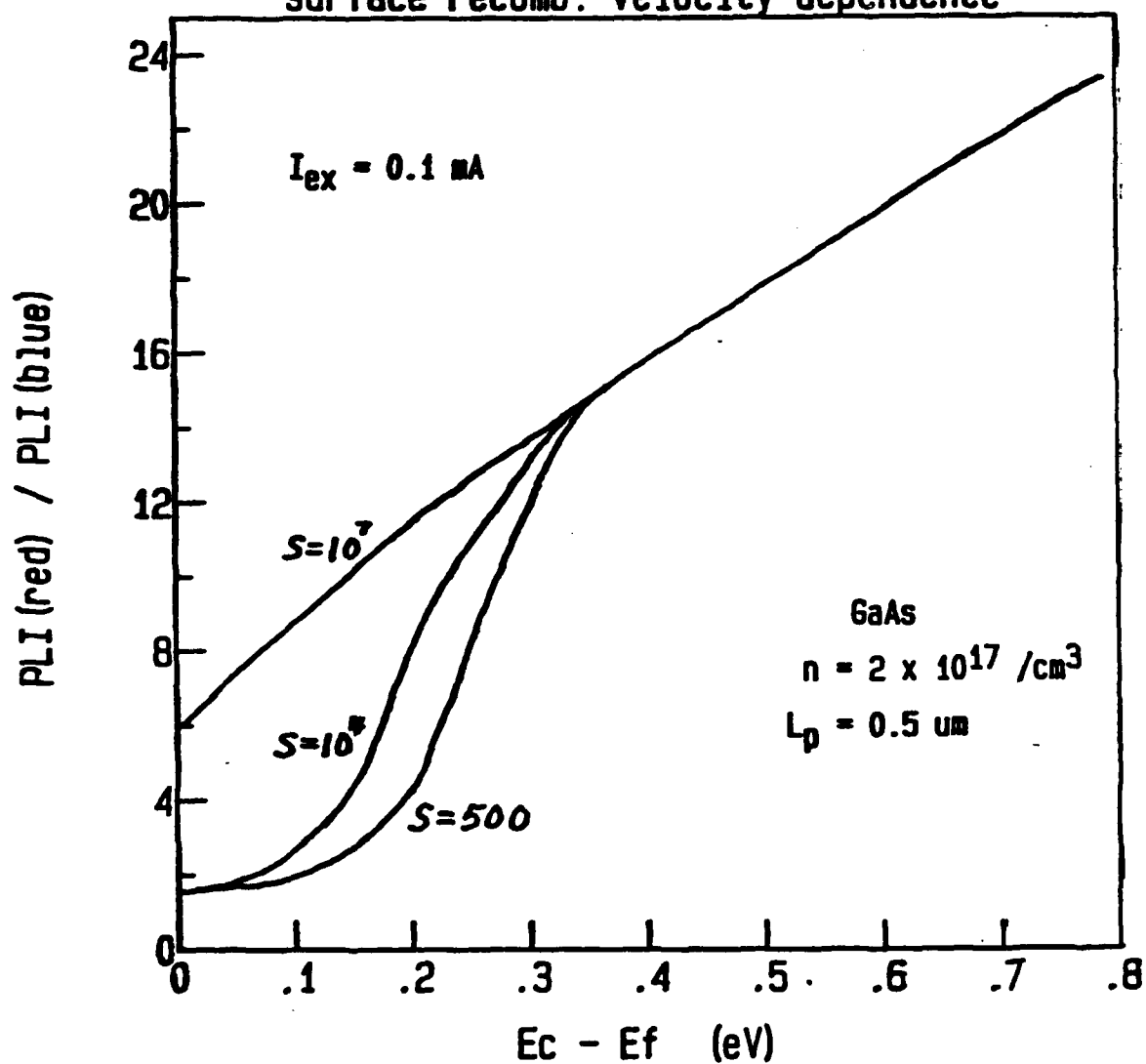
PHOTOLUMINESCENCE SPECTROSCOPY

CASE III: PINNING NEAR A BAND EDGE

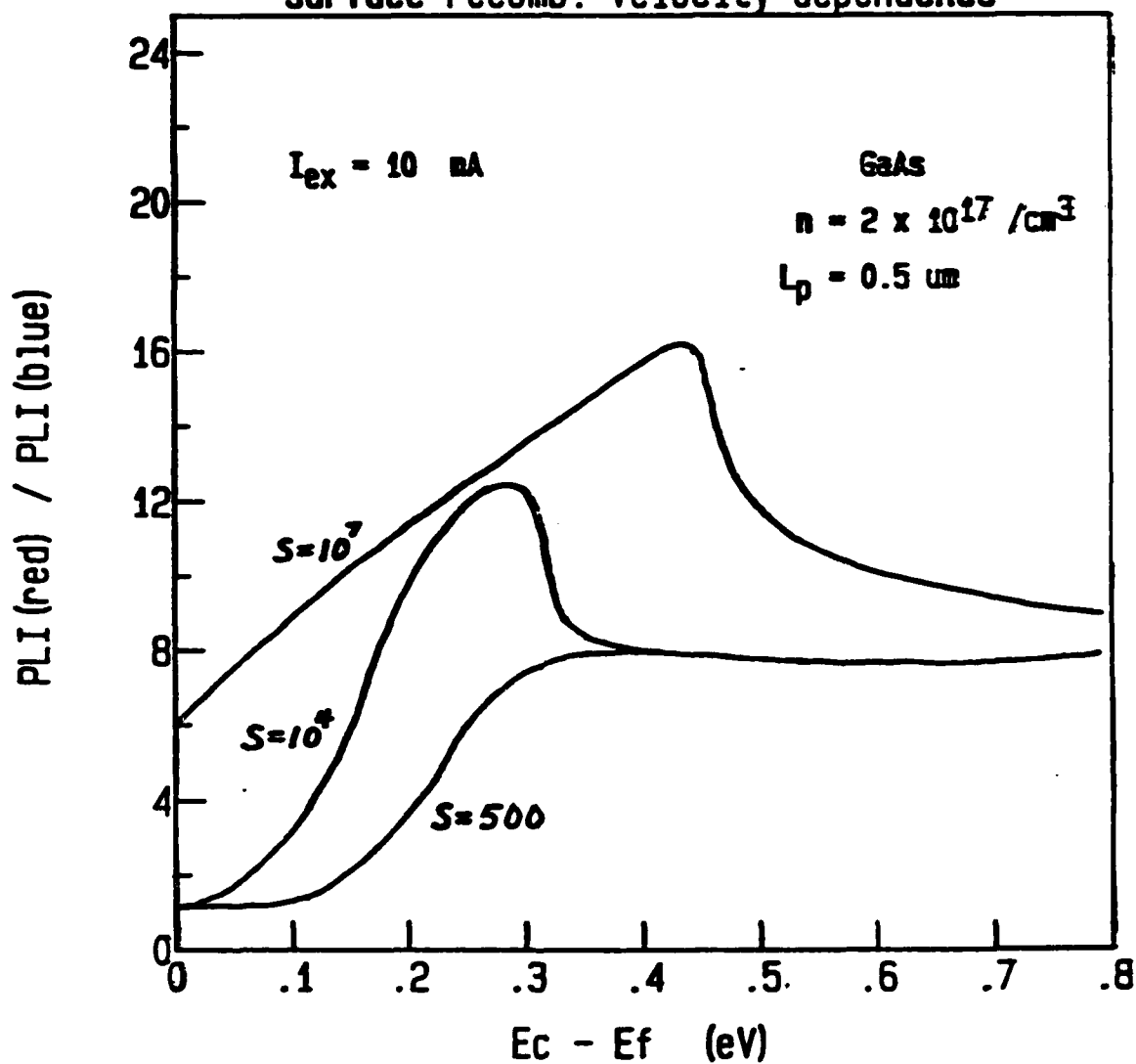
e.g. InP



PL Quantum Yield vs. Band Bending surface recomb. velocity dependence



PL Quantum Yield vs. Band Bending
surface recomb. velocity dependence



Photoluminescence Results

PL Intensity:

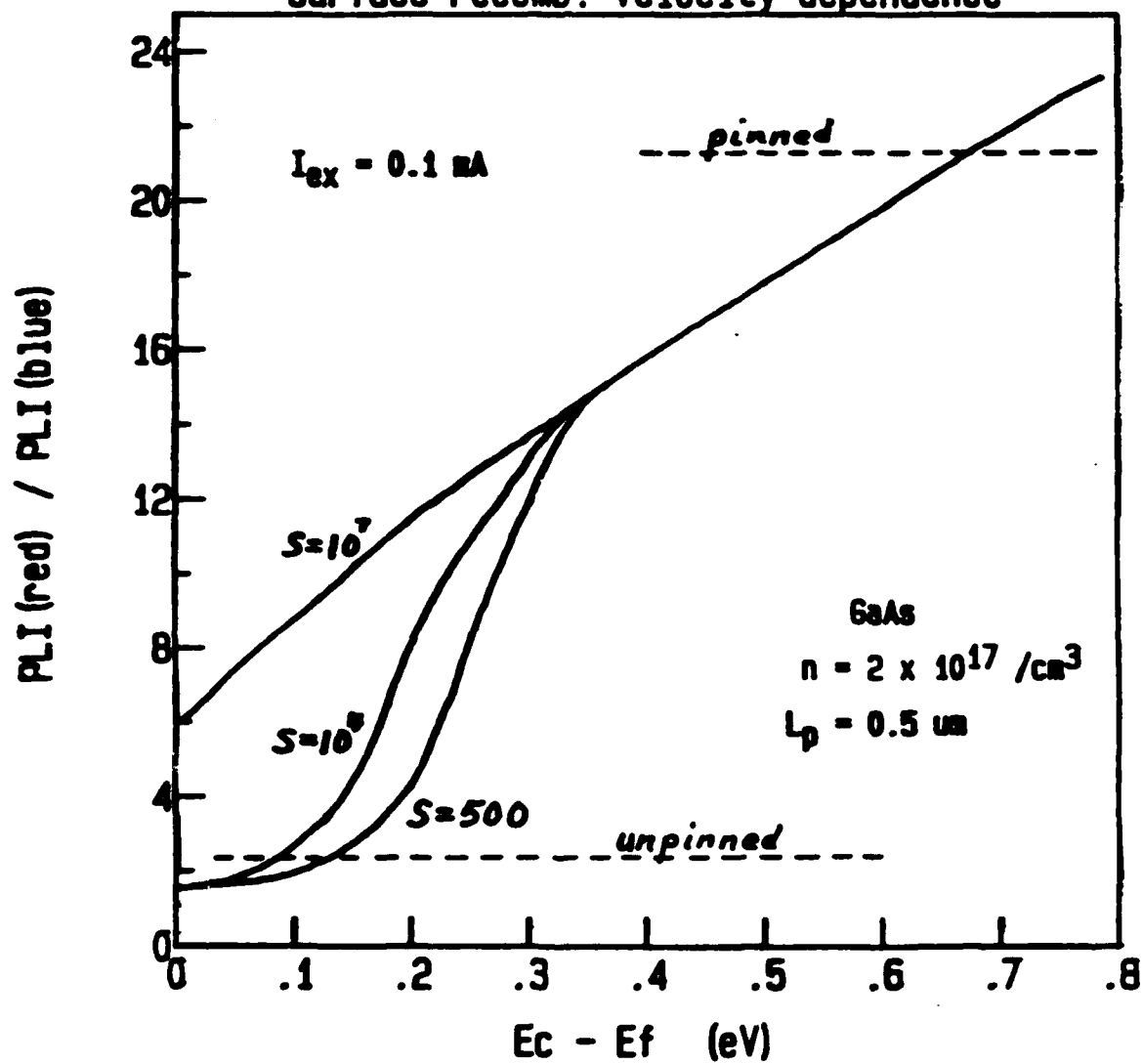
	<u>Before</u>		<u>After</u>	
	blue	red/blue	blue	red/blue
n-type	1	20	15	-2
p-type	10	4	80	~2

Analysis: Woodall et al. JVST 16(5)1389
(1979)
n-type GaAs
 $N_D = 2 \times 10^{17} / \text{cm}^3$
 $L_p = 0.5 \mu\text{m}$ from EBIC

$$\text{red/blue} = 20 \Rightarrow \begin{aligned} V_B &= 0.8 \text{ volts} \\ v_s &= 10^7 \text{ cm/sec} \end{aligned}$$

$$\text{red/blue} = 2 \Rightarrow \begin{aligned} V_B &= 0.1 \text{ volts} \\ v_s &= 10^4 \text{ cm/sec} \end{aligned}$$

PL Quantum Yield vs. Band Bending surface recomb. velocity dependence



Plasmon - Phonon Coupling

Courtesy F. Pollak, Brooklyn College

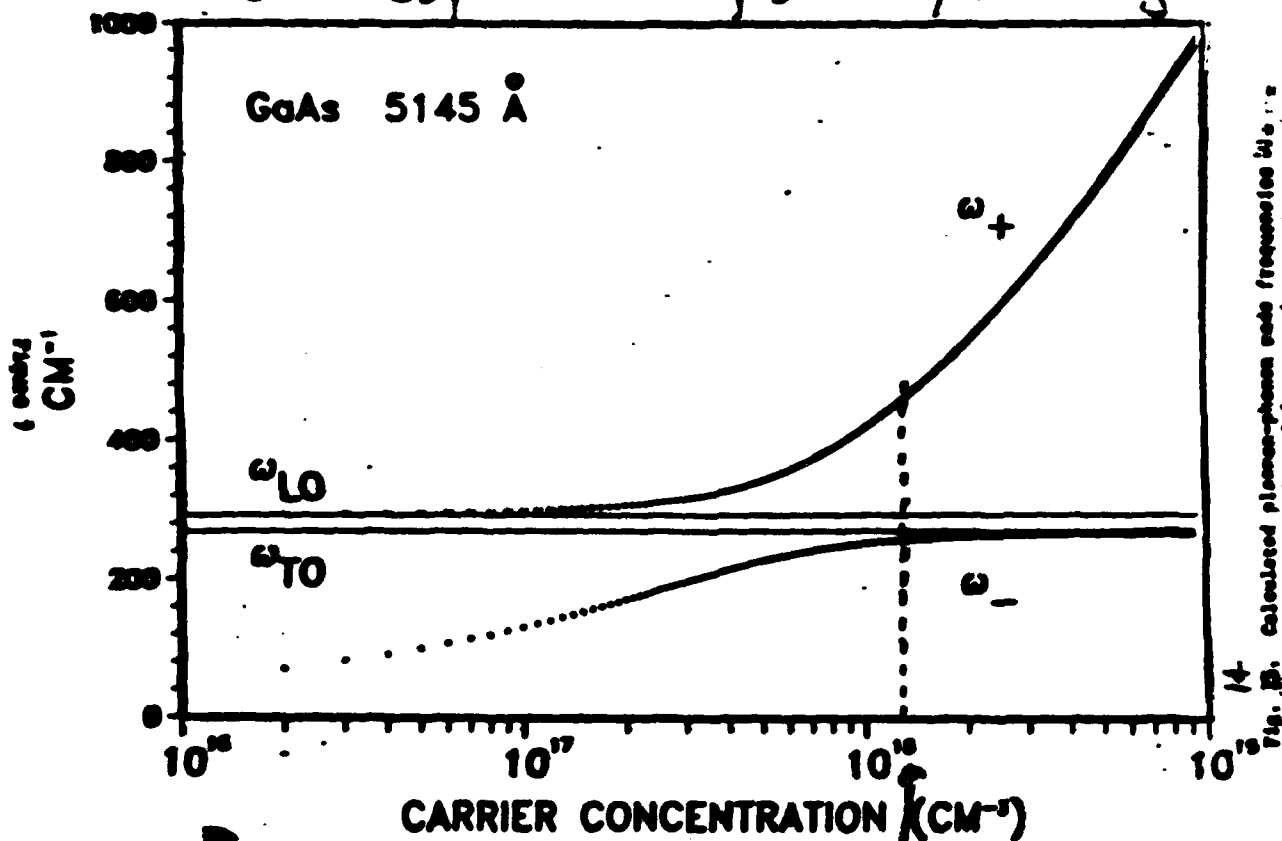
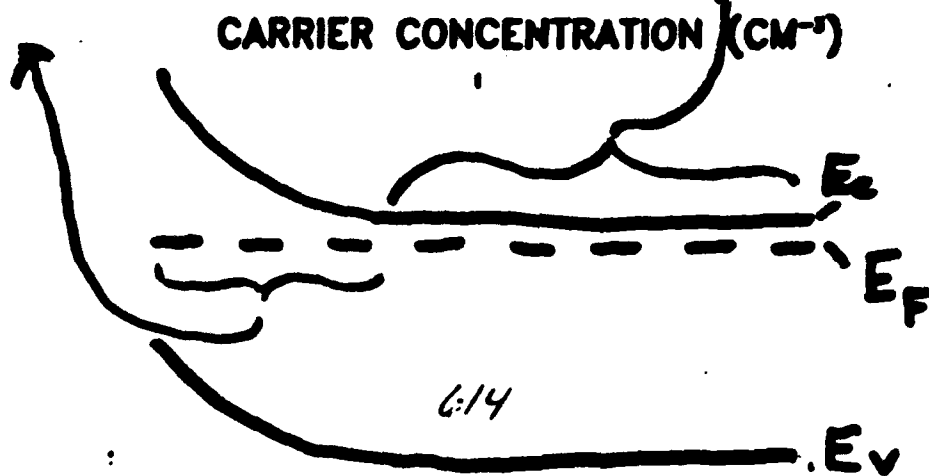
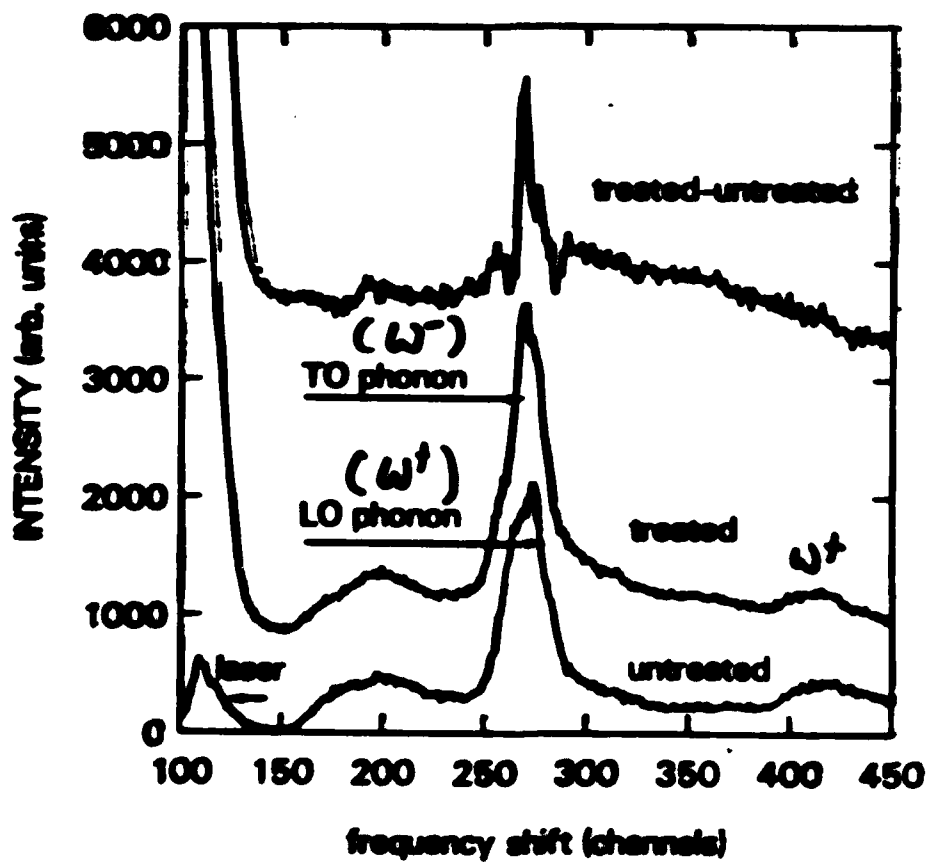
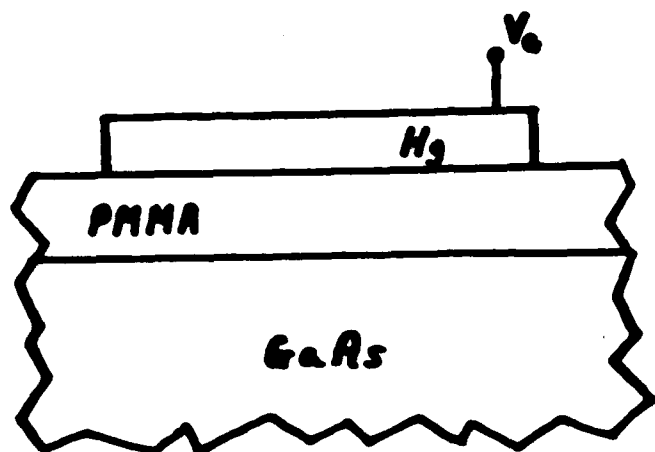


Fig. 14. Calculated plasmon-phonon mode frequencies $\omega_{\pm}$ as a function of free carrier concentration for GaAs. The solid lines correspond to the bulk LO and TO modes. The calculations have been corrected for finite carrier concentration effects.

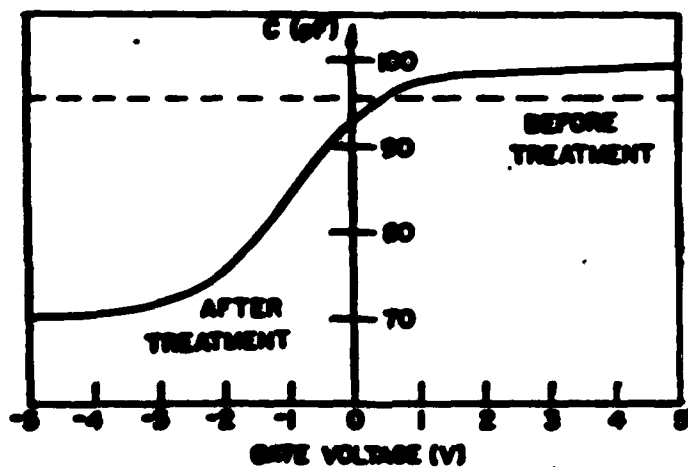




Capacitor Structures

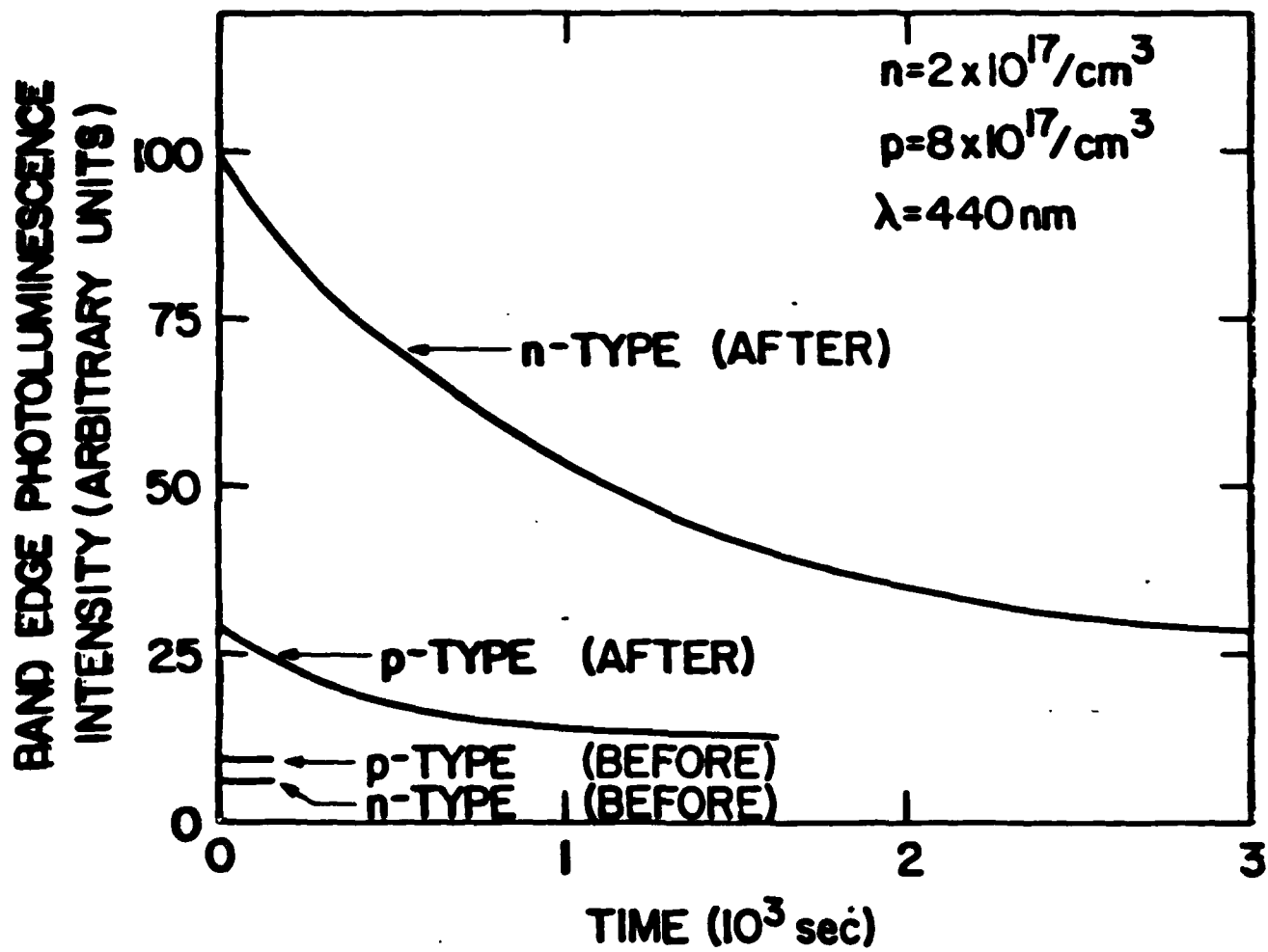


0.1 μm of PMMA on treated or untreated GaAs

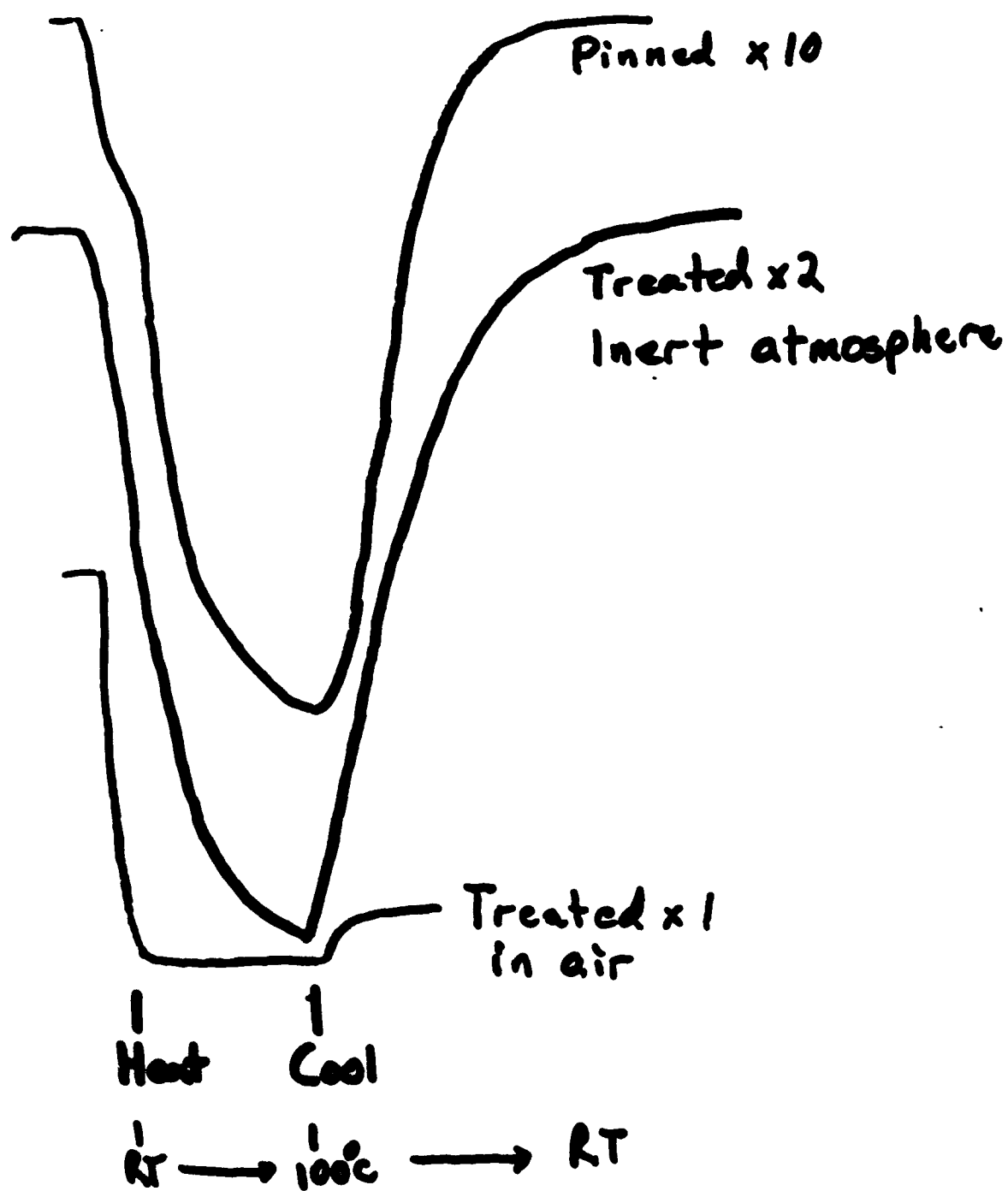


(20 KHz)

High frequency C-V, n-type GaAs
from Offsey, et al., APL 48(7) 475 (1986)
616



PL vs Time



Auger Data

Photo-Rinsed

Etched, Rinsed, Air Exposed

C

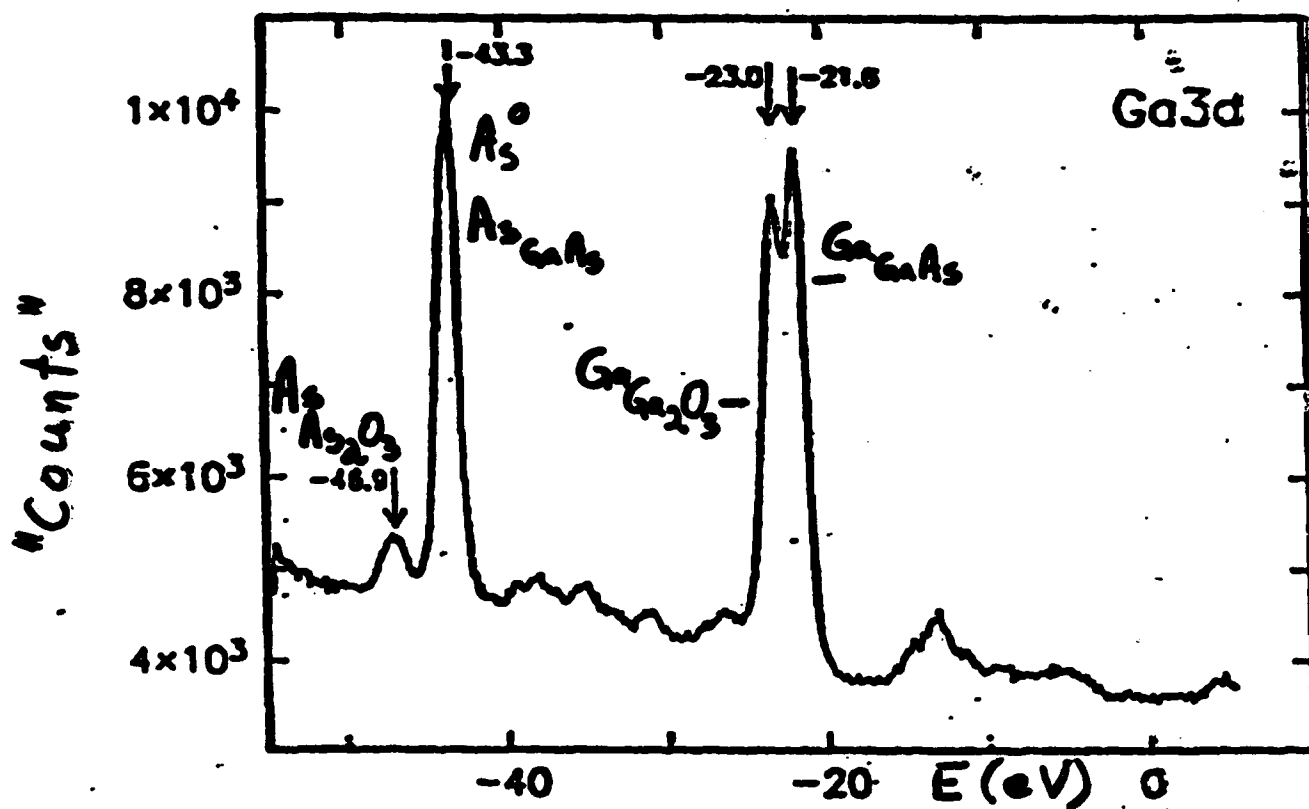
O

Ga.

As

619

XPS Data - J. Baker



$\Rightarrow 13 \text{ \AA } \text{Ga}_2\text{O}_3 (90\%)$

Characteristics of the Treated (Unpinned) Surface

- Repins in air ($\tau \cong 1$ h) and on heating in air ($\tau < 1$ m, $T \cong 100^\circ\text{C}$)
- Repins in acid and base solutions and vapors ($\tau \cong 1$ s)
- Stable in vacuum and inert ambients even on heating ($T \cong 100^\circ\text{C}$)
- Stable in desiccated air at room temperature
- Auger electron spectroscopy of thick oxide layers shows oxide consists of $> 98\%$ Ga oxide and $< 2\%$ As oxide (detection limit). Untreated surface shows about equal parts of Ga and As oxides
- XPS of thinner oxides shows oxide species to be predominantly Ga_2O_3

Chemistry

1. Band-bending sweeps $h\nu$ -generated minority carriers to surface, speeding oxidation
2. $\text{GaAs} \rightarrow \text{Ga}_2\text{O}_3, \text{As}_2\text{O}_3, \dots, \text{As}^\circ$
3. H_2O removes As_2O_3 & As°
(Massies & Contour JAP 58 (1985) 806)
4. Ga_2O_3 passivates GaAs surface
5. residual band-bending drives further oxidation

Conclusions

- Unpinned GaAs in air
- Detection by CV, PL, Raman
- Ga_2O_3 layer
 - OK passivation
 - Lousy insulator
- Behavior supports EWF model where As° is culprit
- Simple, inexpensive process

⇒ STILL A LONG WAY
FROM GaAs MOSFETs

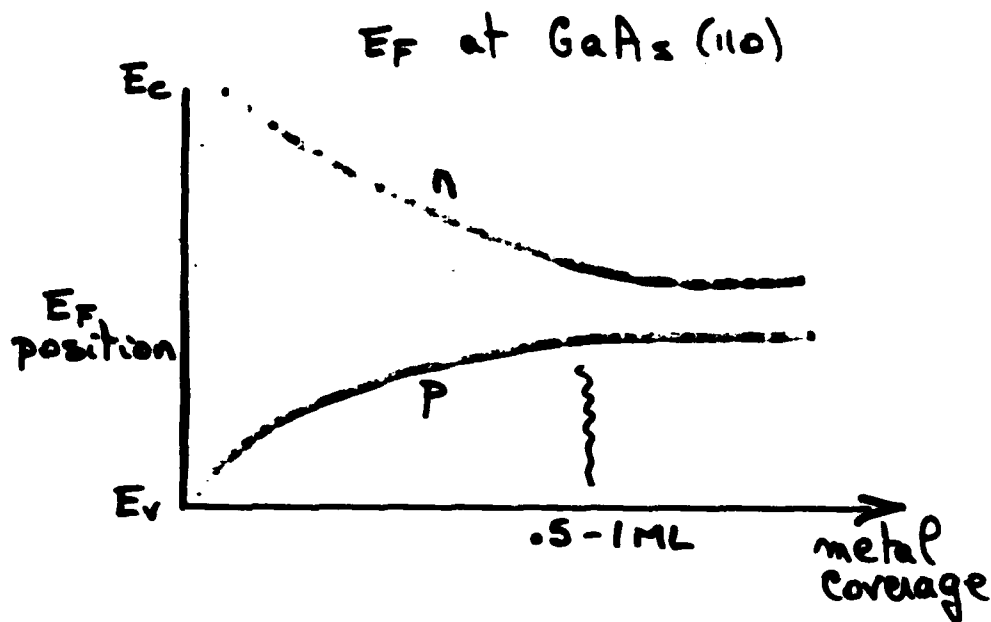
Kinetics of Initial Stages of Schottky Barrier Formation*

K. Stiles and A. Kahn
Dept. of EE, Princeton Univ.

D. Kilday and J. Margaritondo
SRC, Univ. of Wisconsin

* Partially supported by NSF (DMR-84-06820)

1. Motivation for low temperature (LT) experiments.
2. Experiments (LEED, AES, EELS, SXPS).
3. Morphology of interfaces formed at LT Al, In and Au on GaAs(110).
4. Effect of temperature on initial pinning at GaAs interfaces with Al, Au, In, Ag and Sn : multi-mechanism picture?
5. Conclusions.



Metal-induced defects

- Origin of defects?
- Nature of defects?
- homogeneity of pinning?
- role of structure?

Metal-induced gap states

- pinning at ultra-low coverage? (metal?)
- homogeneity of pinning

Rapid and quasi-symmetric initial pinning on n- and p- substrates at RT could result from simultaneity of various "interface phenomena"

Experiment

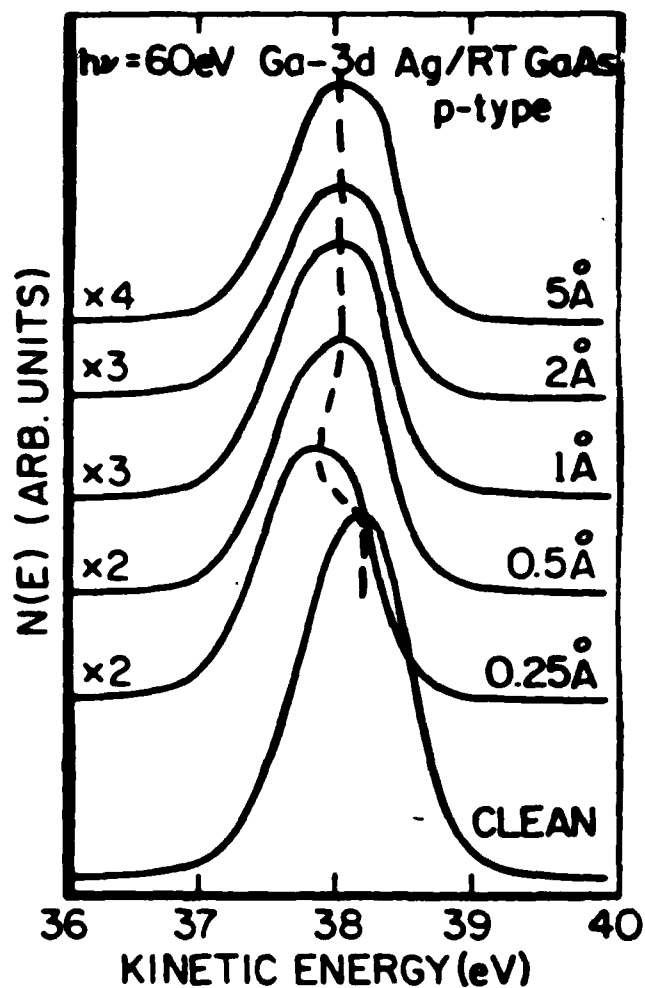
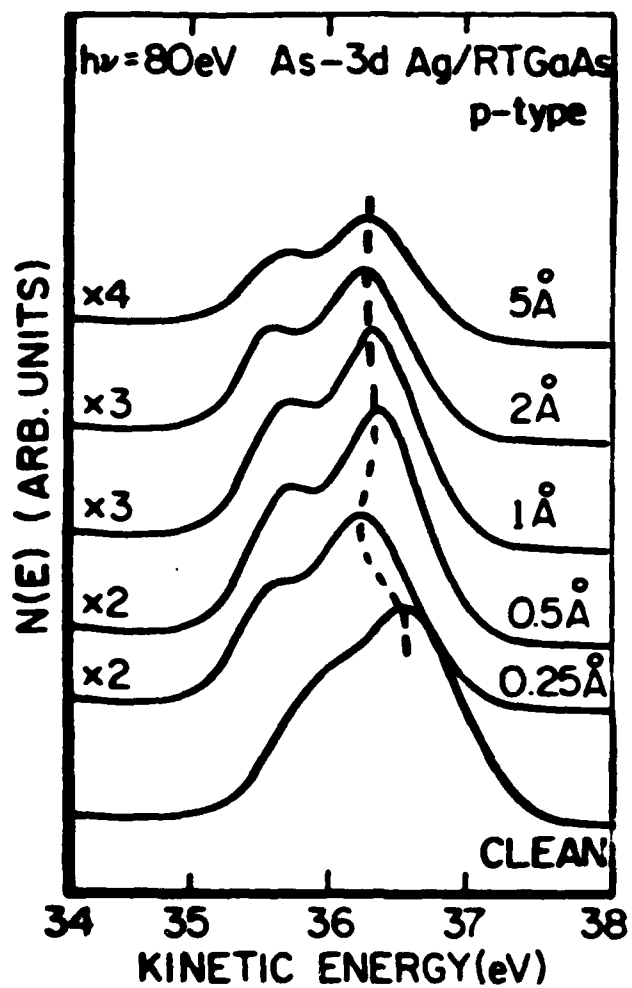
Soft X-ray Photoemission Spectroscopy:
band bending measured from Ga-3d and As-3d
core level shifts.

n-type ($4-7 \times 10^{17} \text{ cm}^{-3}$) and p-type ($1 \times 10^{18} \text{ cm}^{-3}$)
GaAs substrates.

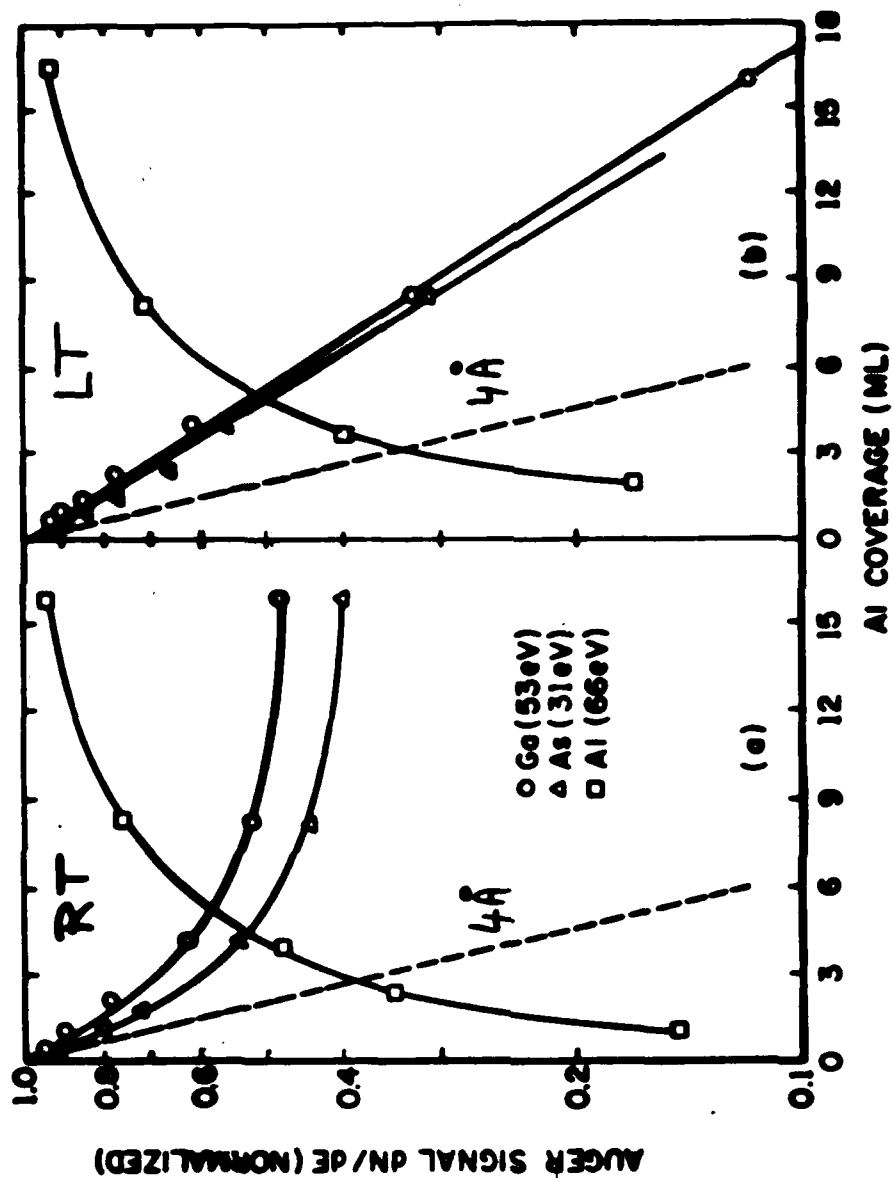
metal deposited on room temperature (RT) and
 80° K (LT) surfaces.

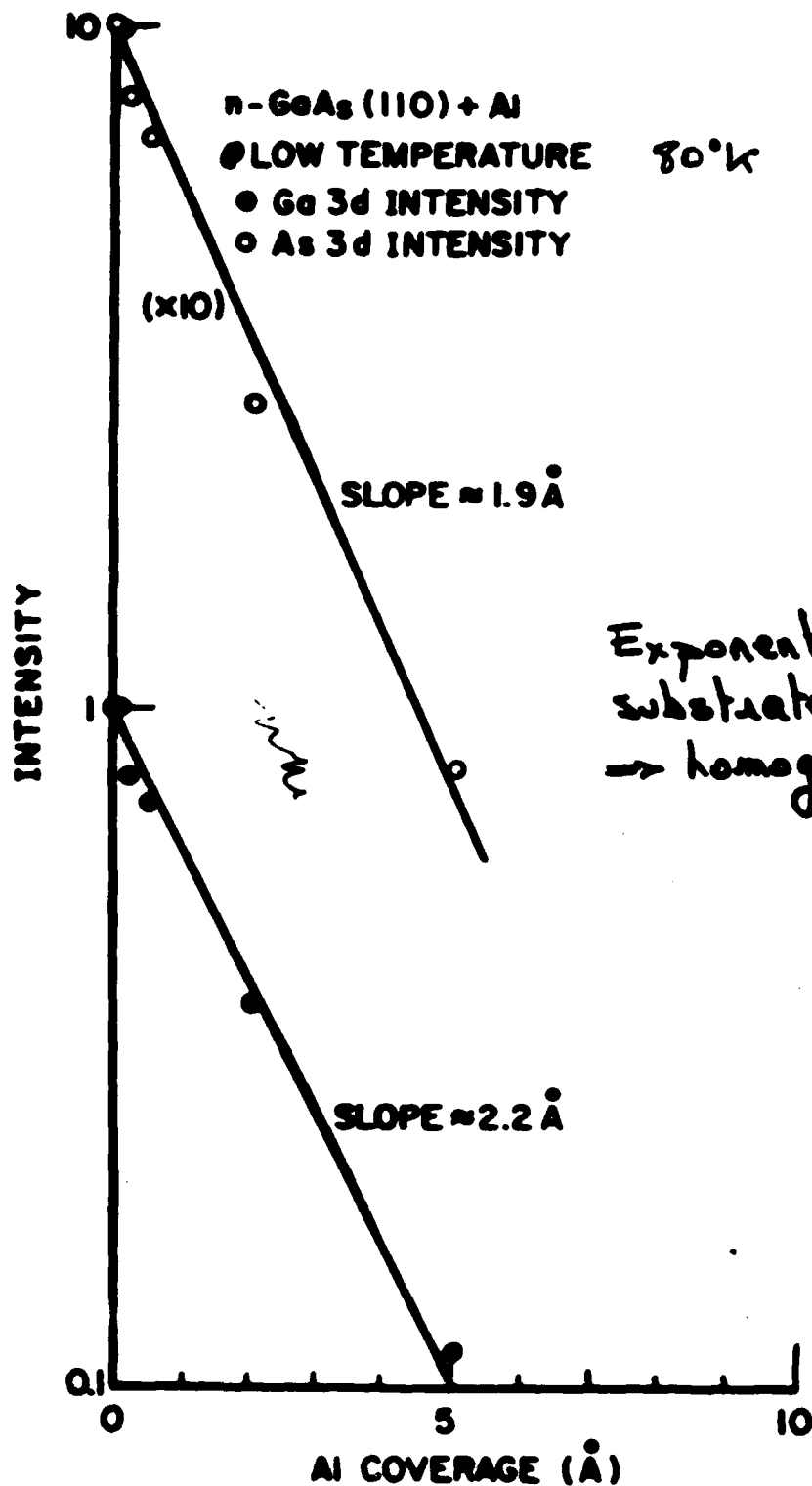
coverage ranges : $0.05 - 20 \text{ \AA}$

Other measurements :	LEED	Al, In / GaAs
	AES	Al, In, Au / GaAs
	EELS	Al, In, Au / GaAs
	CPD	Al,



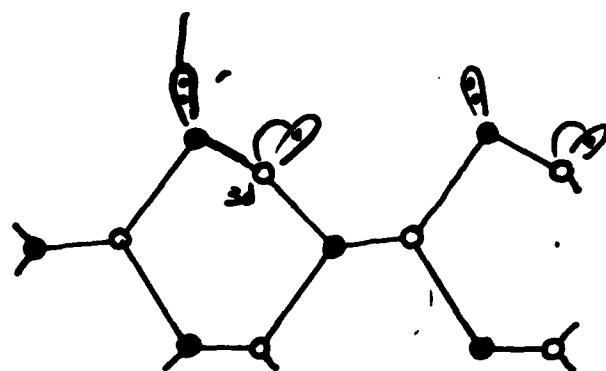
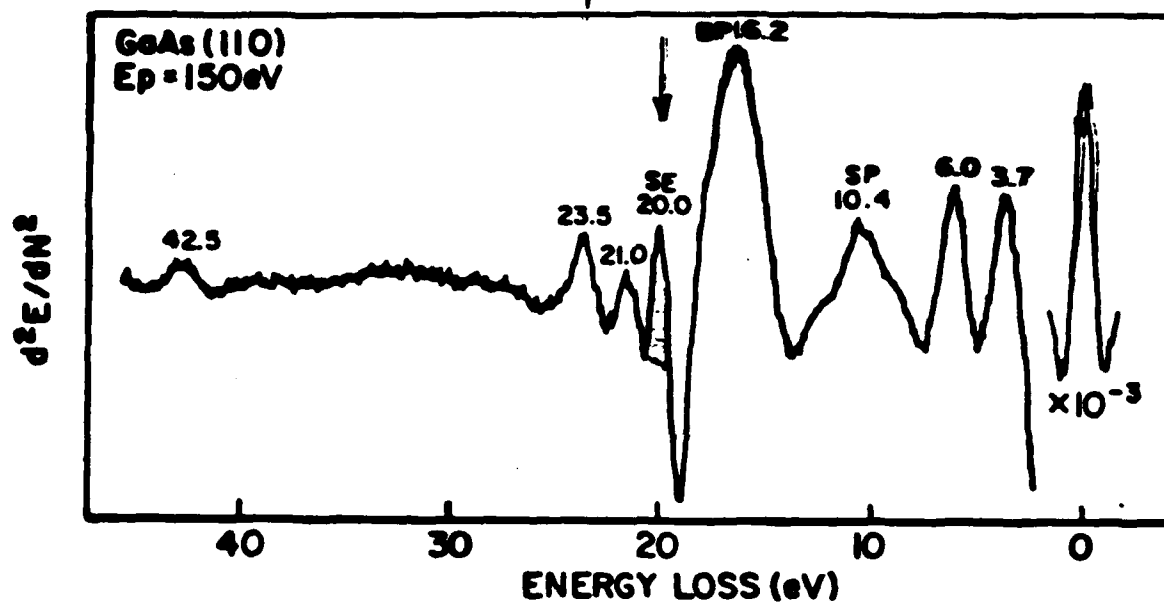
Al on GaAs(110) (110°K)





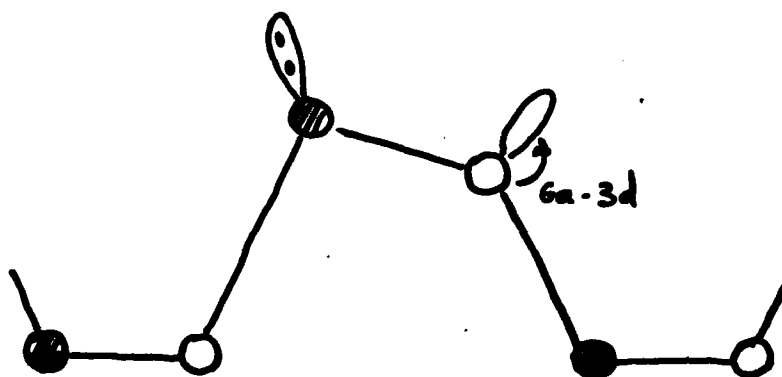
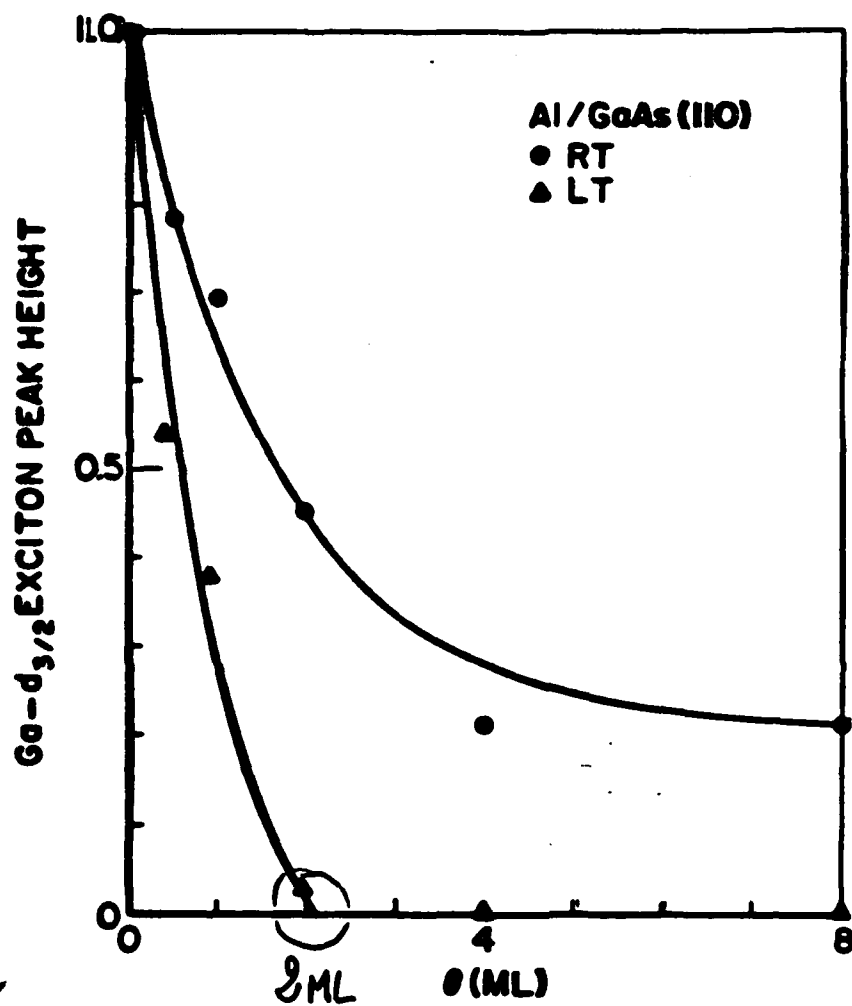
EELS SPECTRUM FROM GaAs(110)

surface Exciton

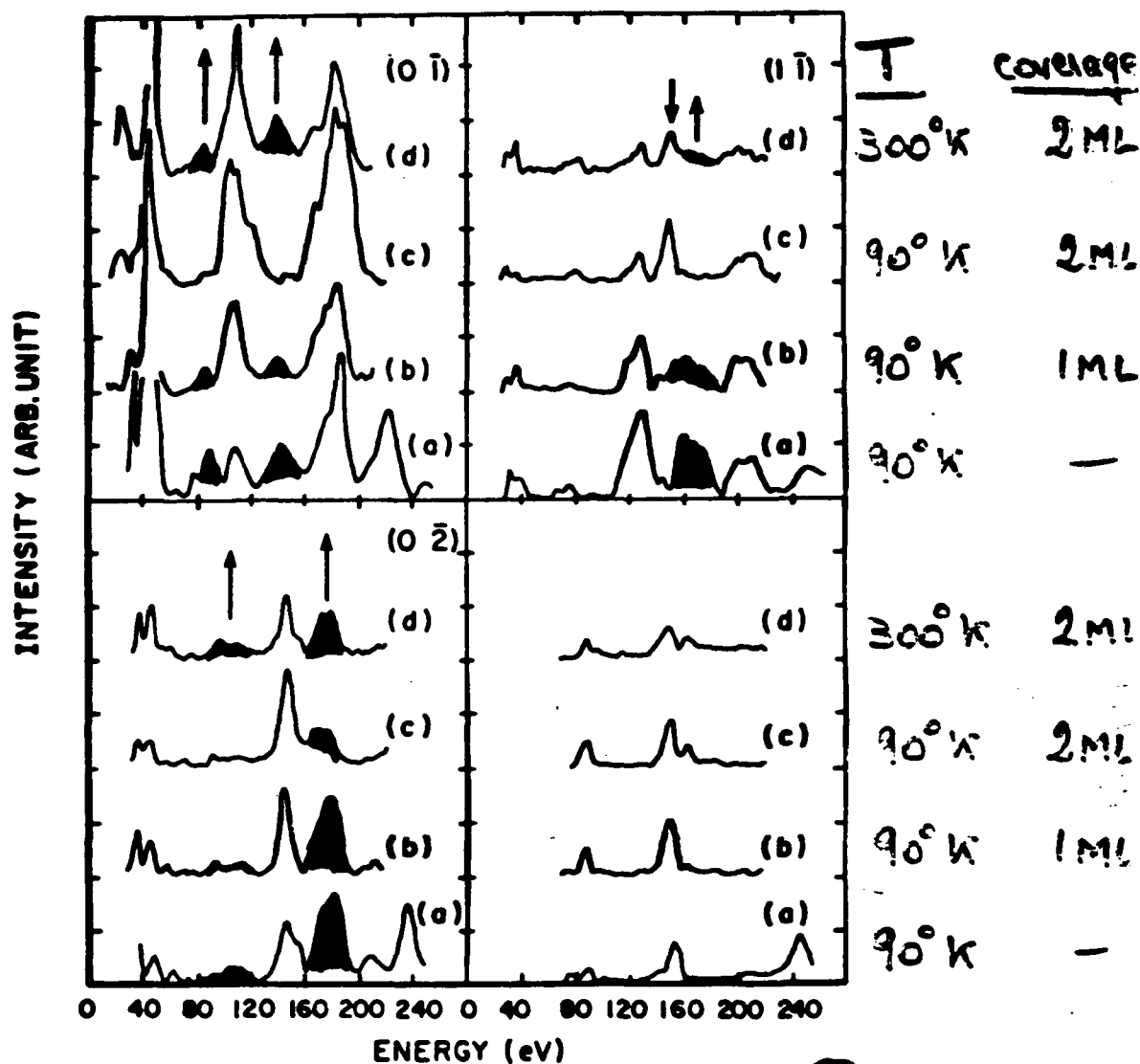


● As
 ○ Ga

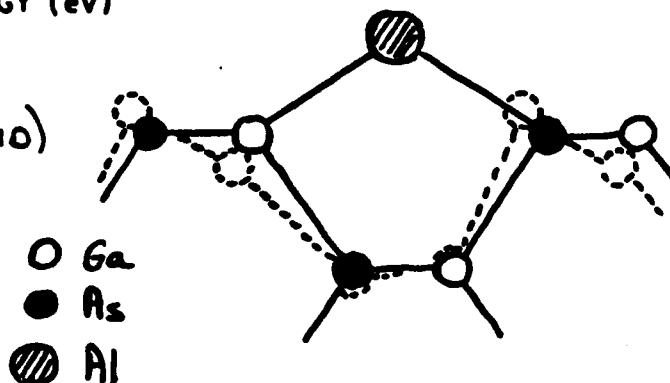
20 eV SE peak characteristic of sp^2 like Ga



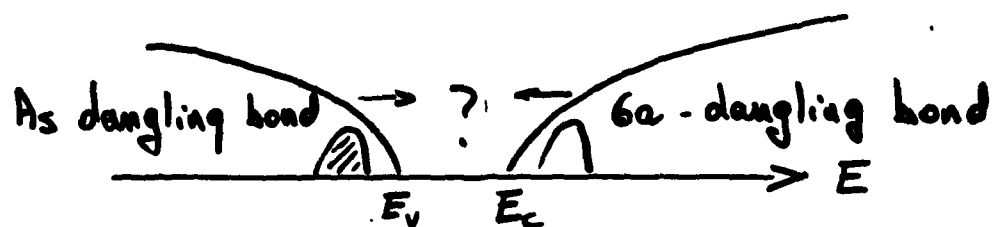
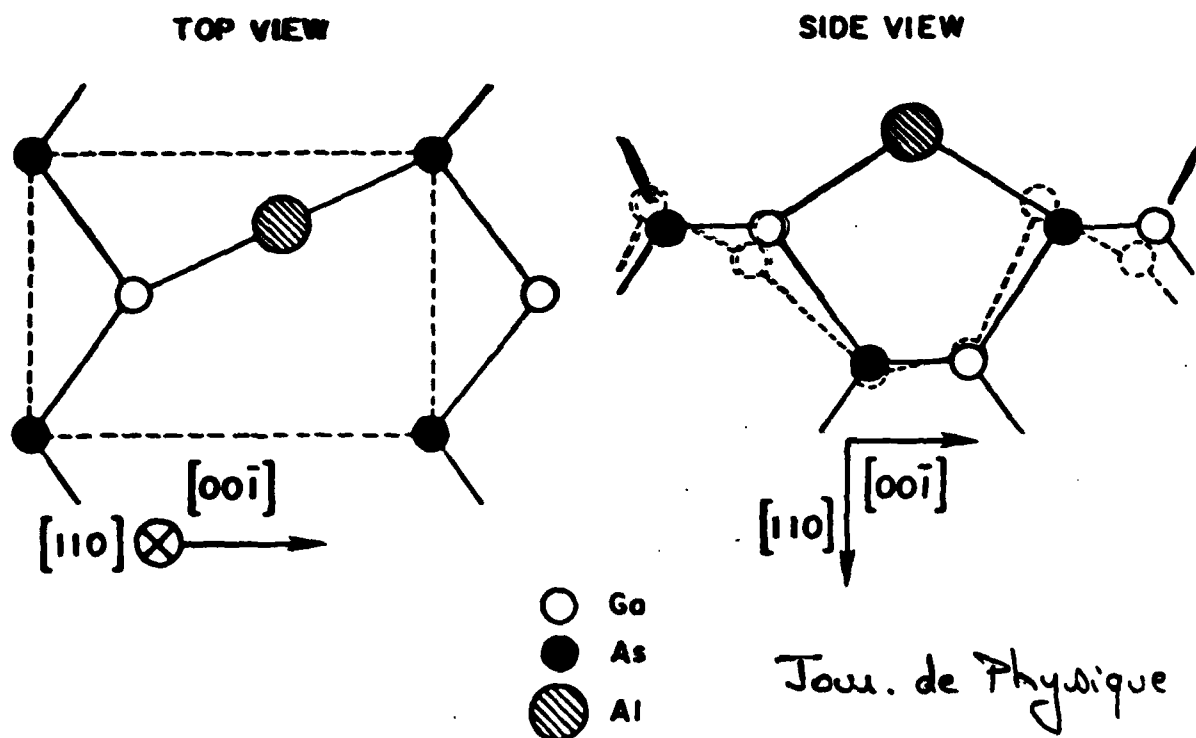
GaAs LEED intensities for Al deposited at LT

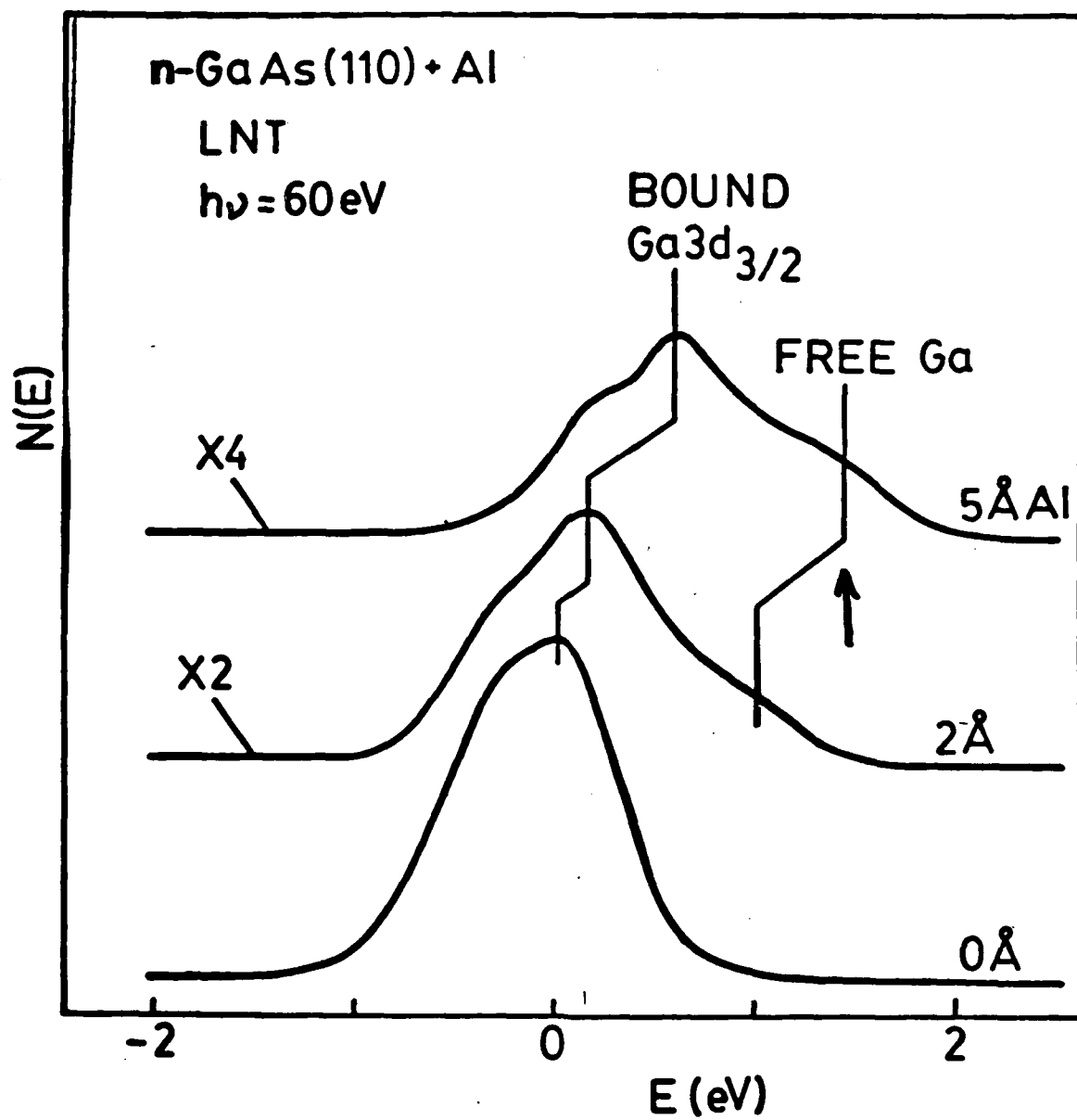


Reversible Al-induced
cancellation of the GaAs (110)
surface relaxation
(detected at LT)



Reversible Al-induced cancellation of the GaAs (110) surface relaxation (detected at LT)



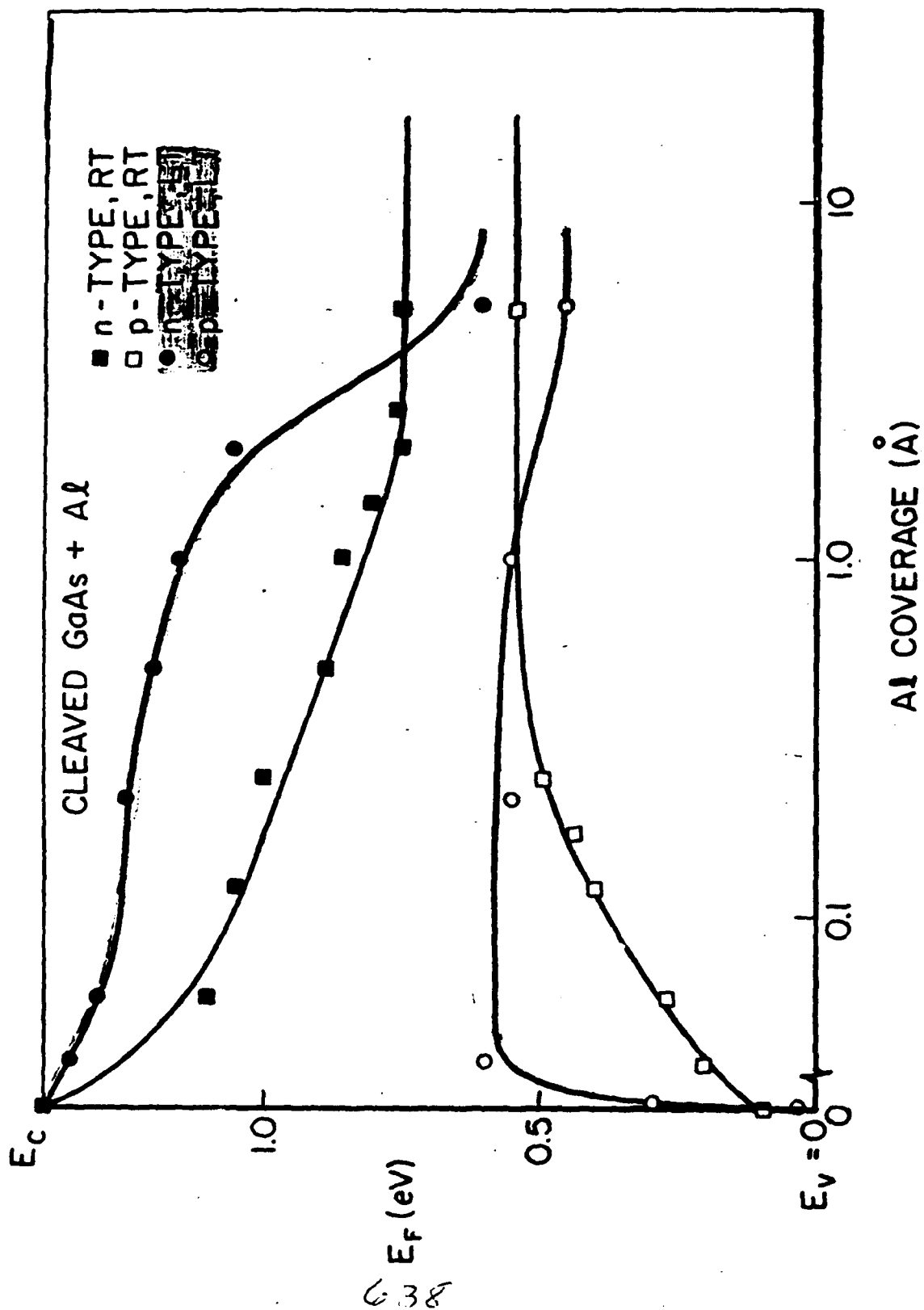


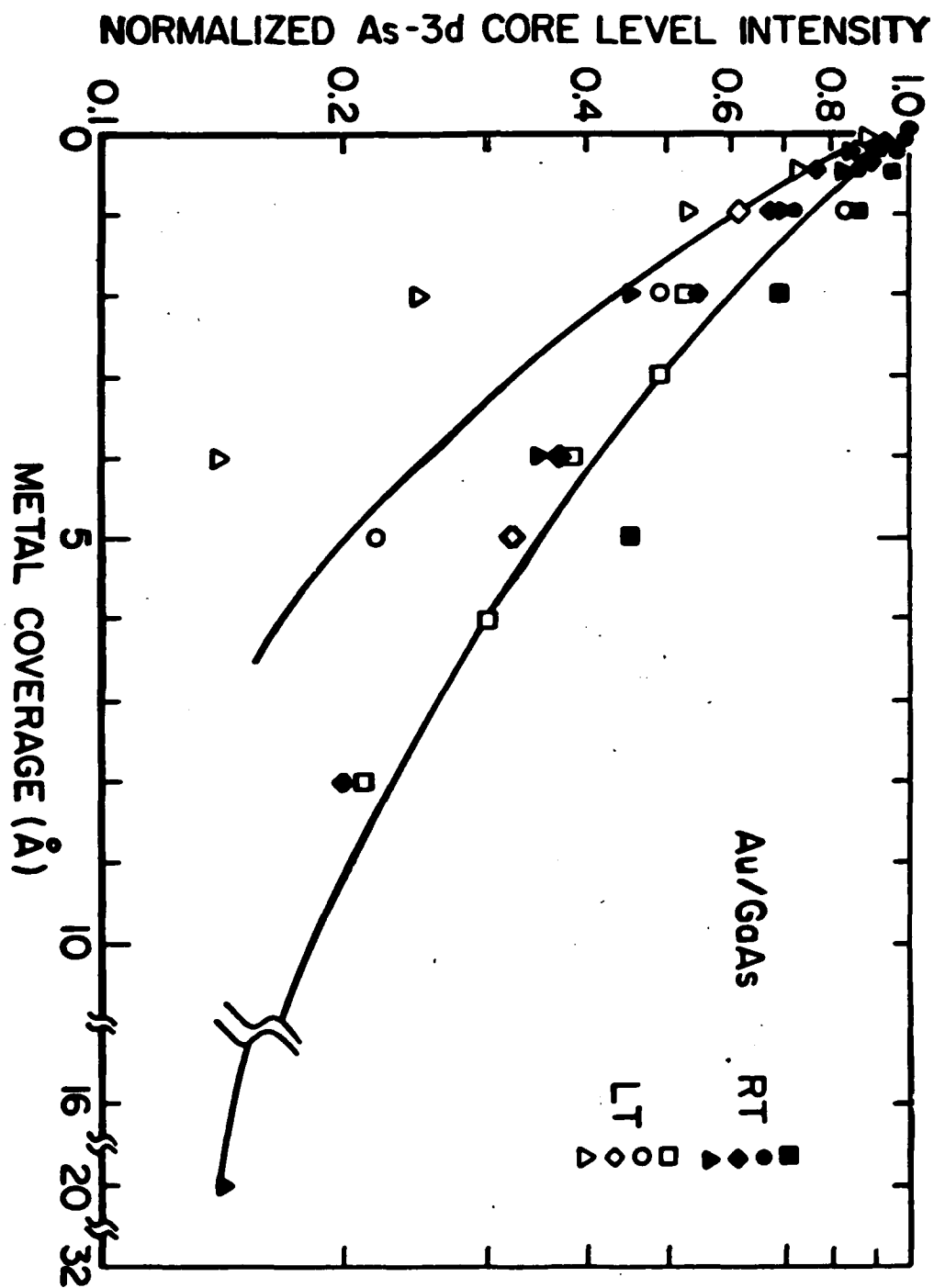
Reduced Al - Ga exchange reaction

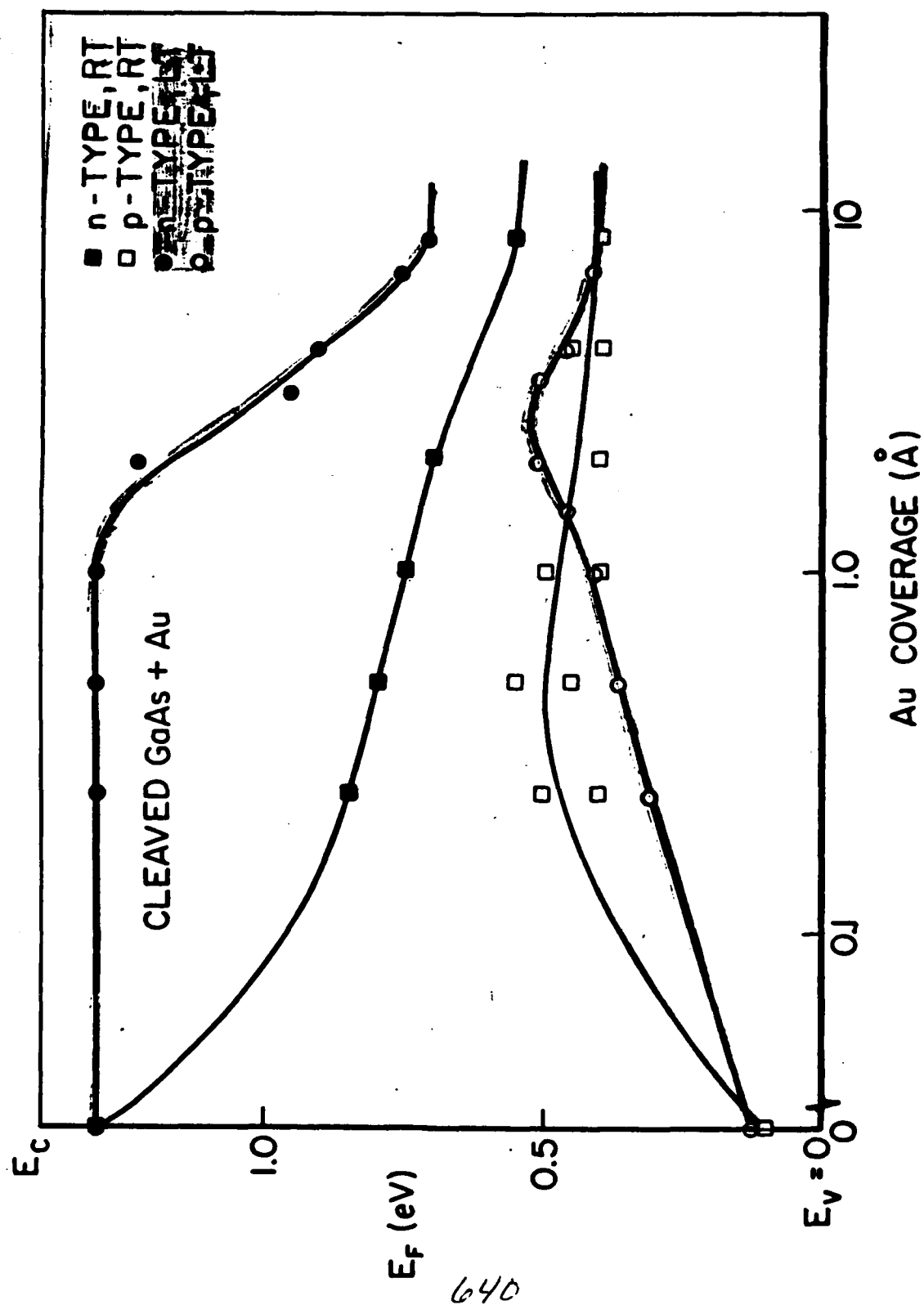
Solid State Communications

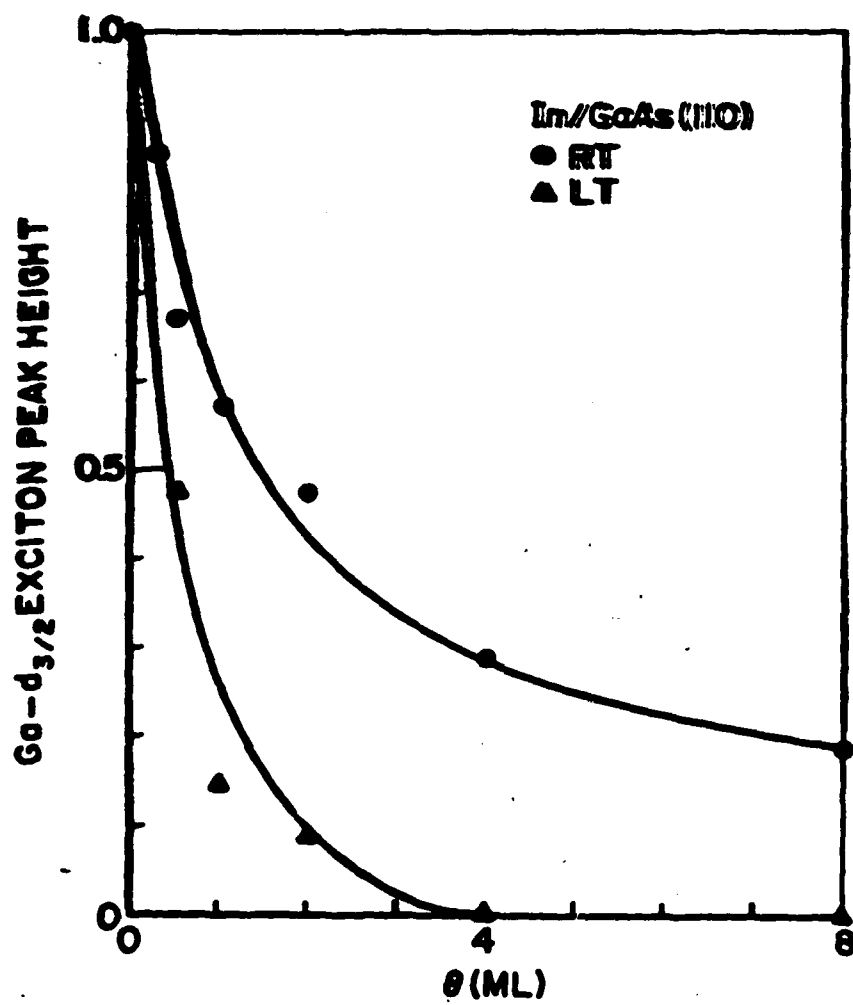
637

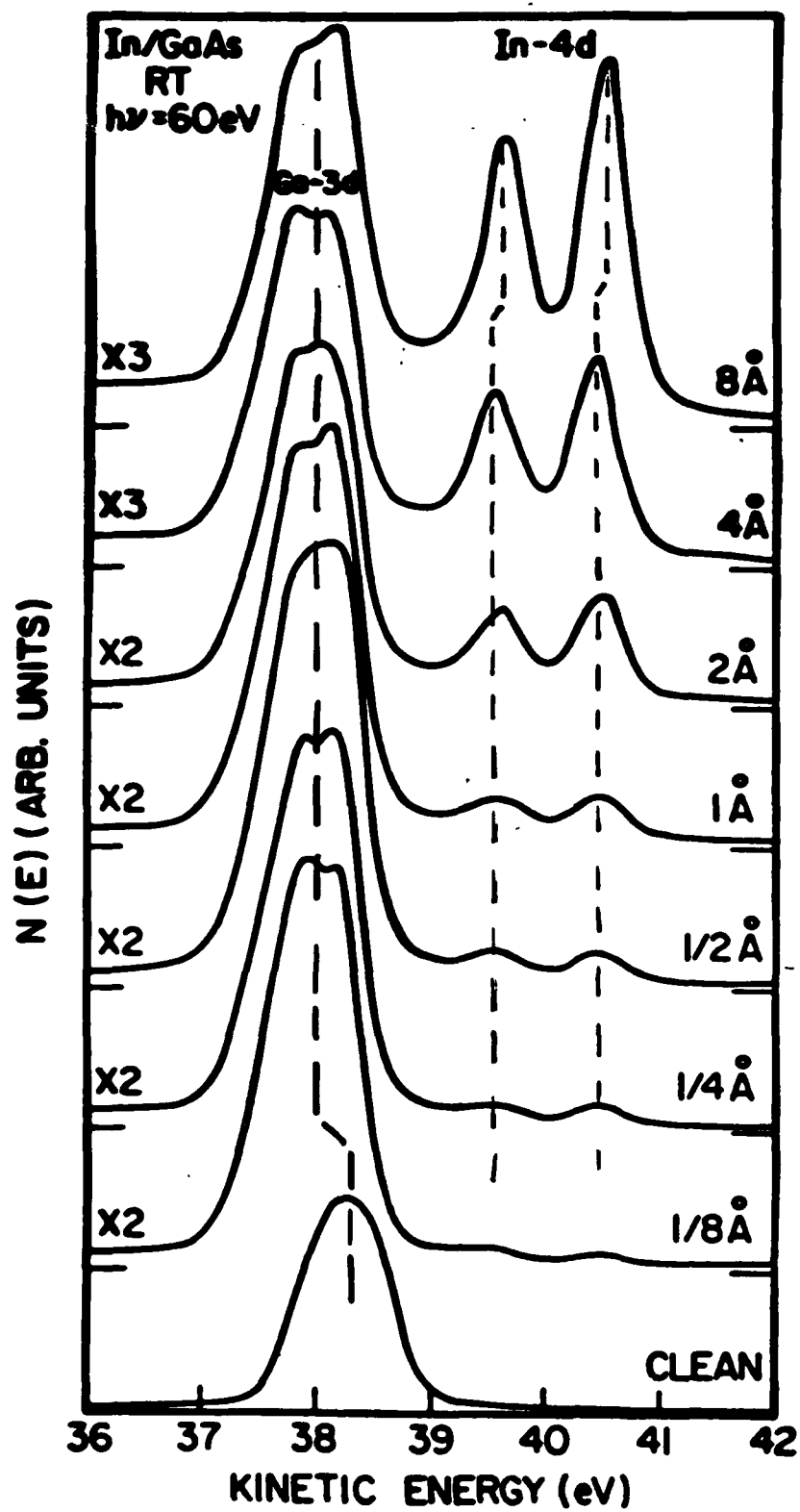
1986

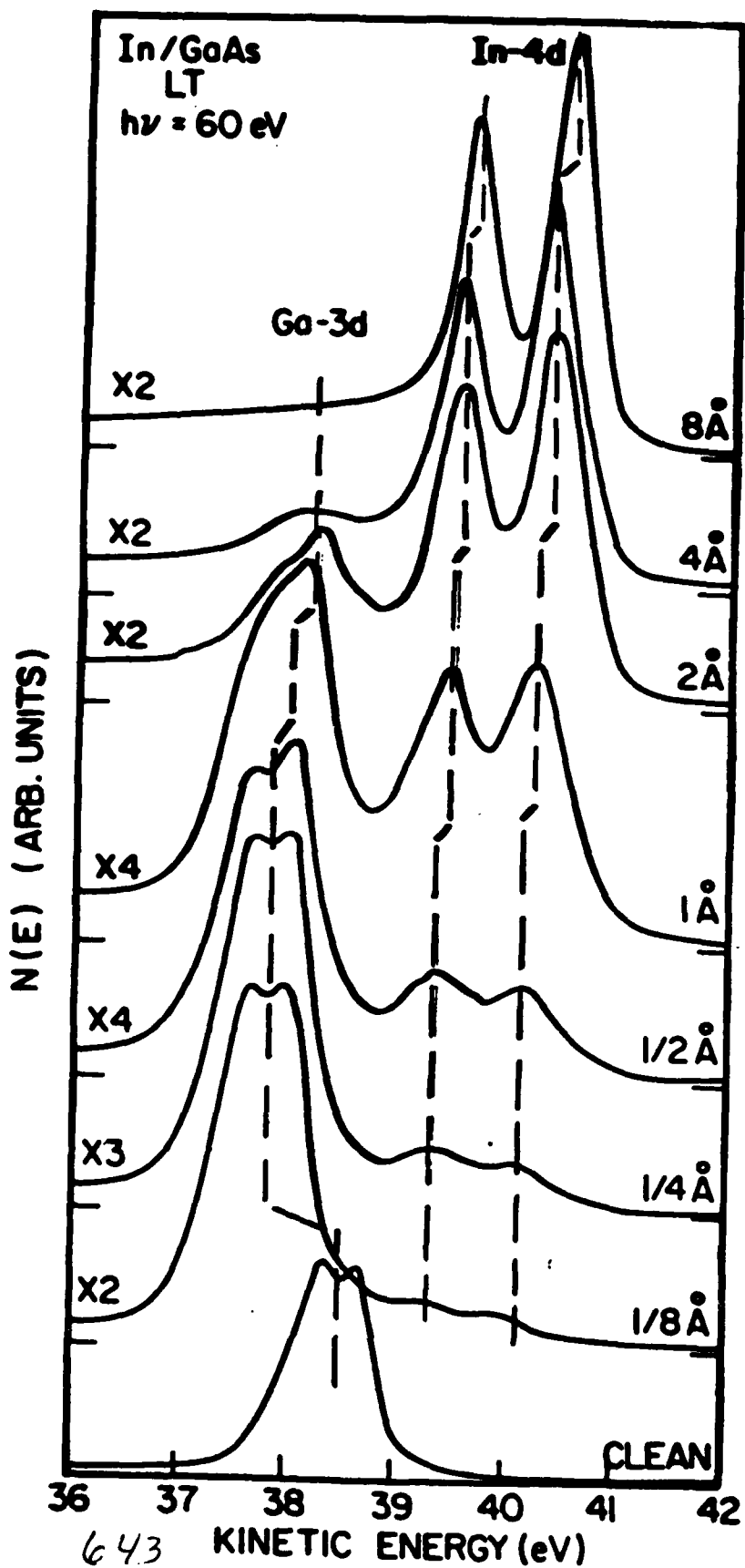


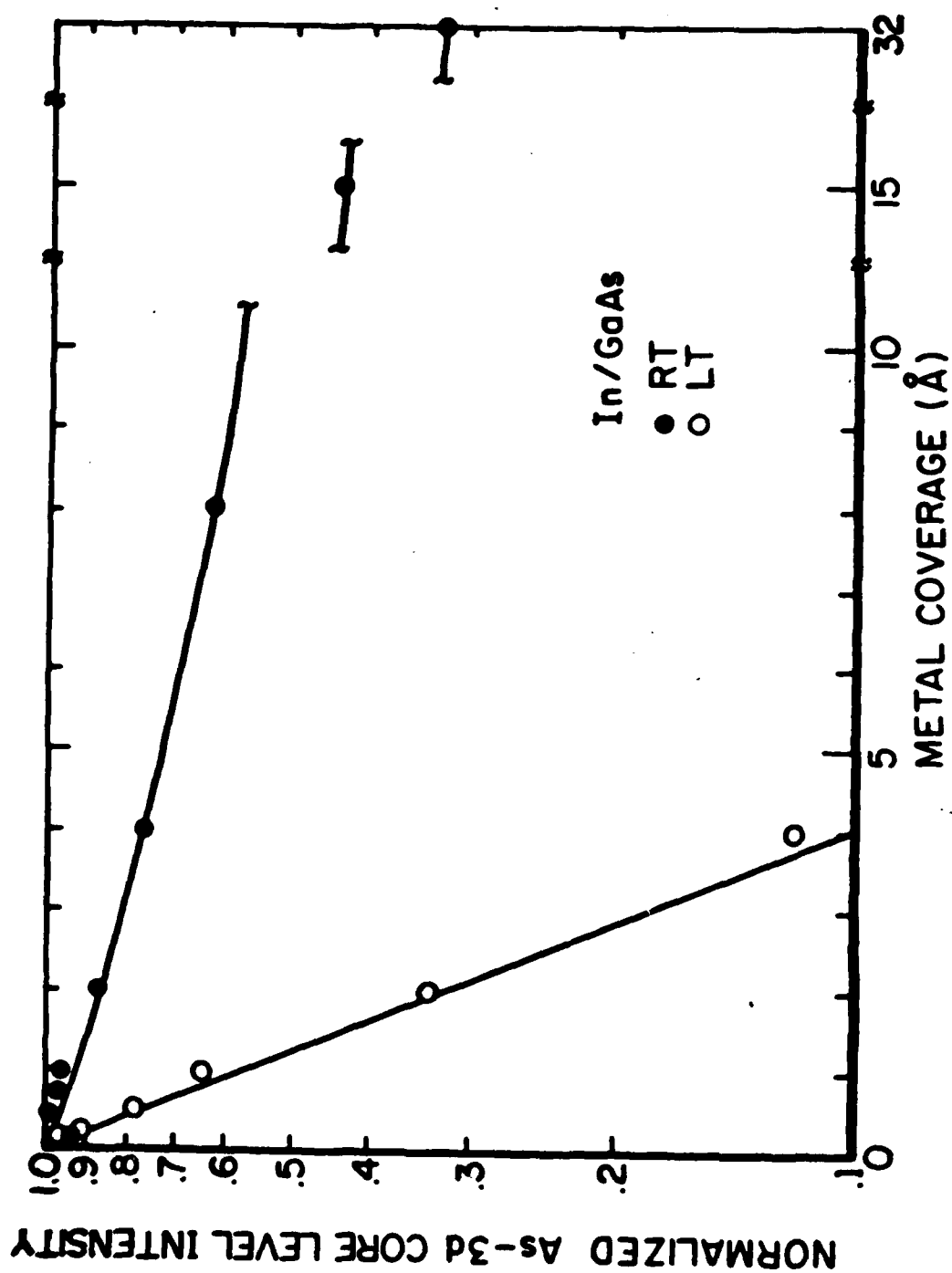


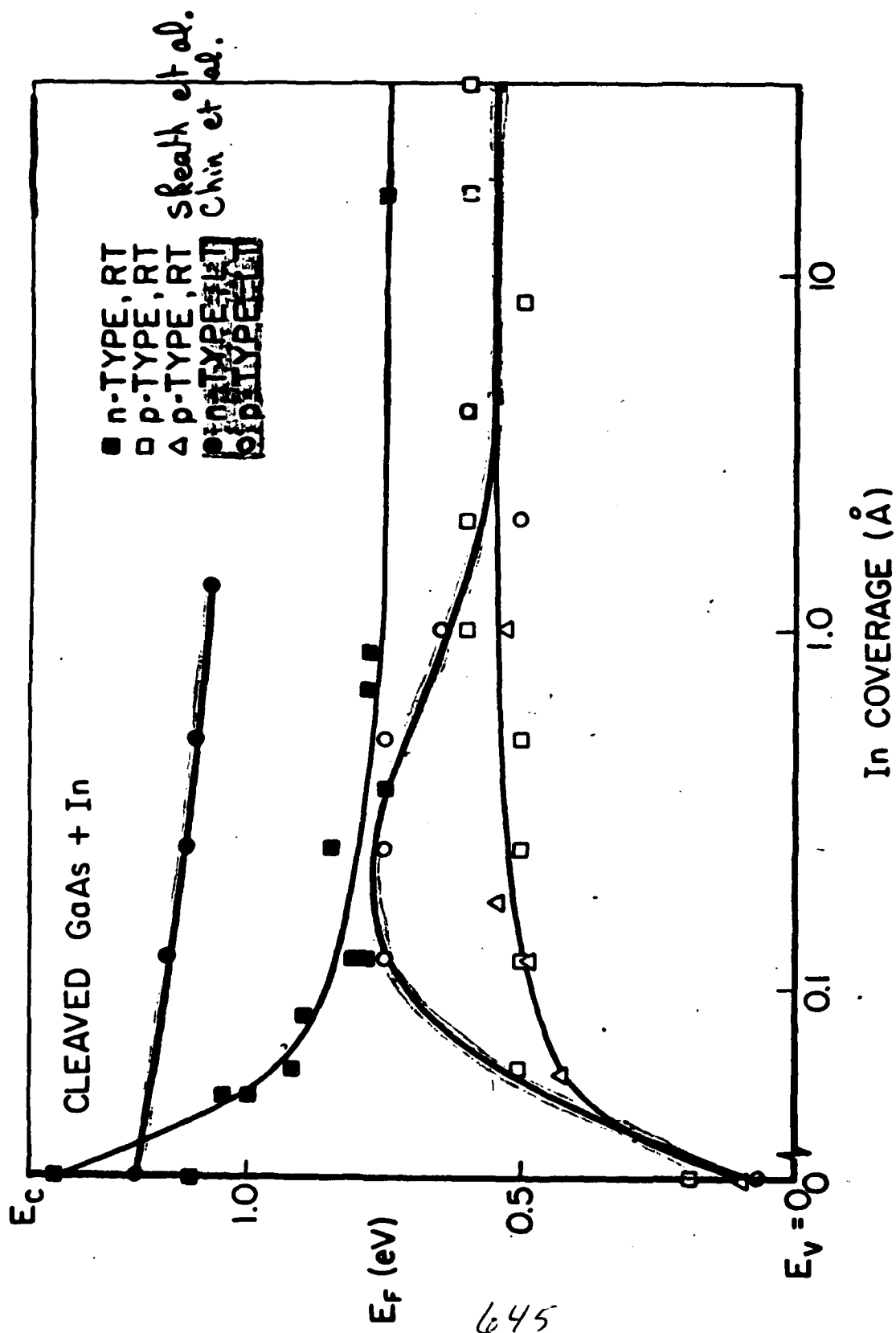


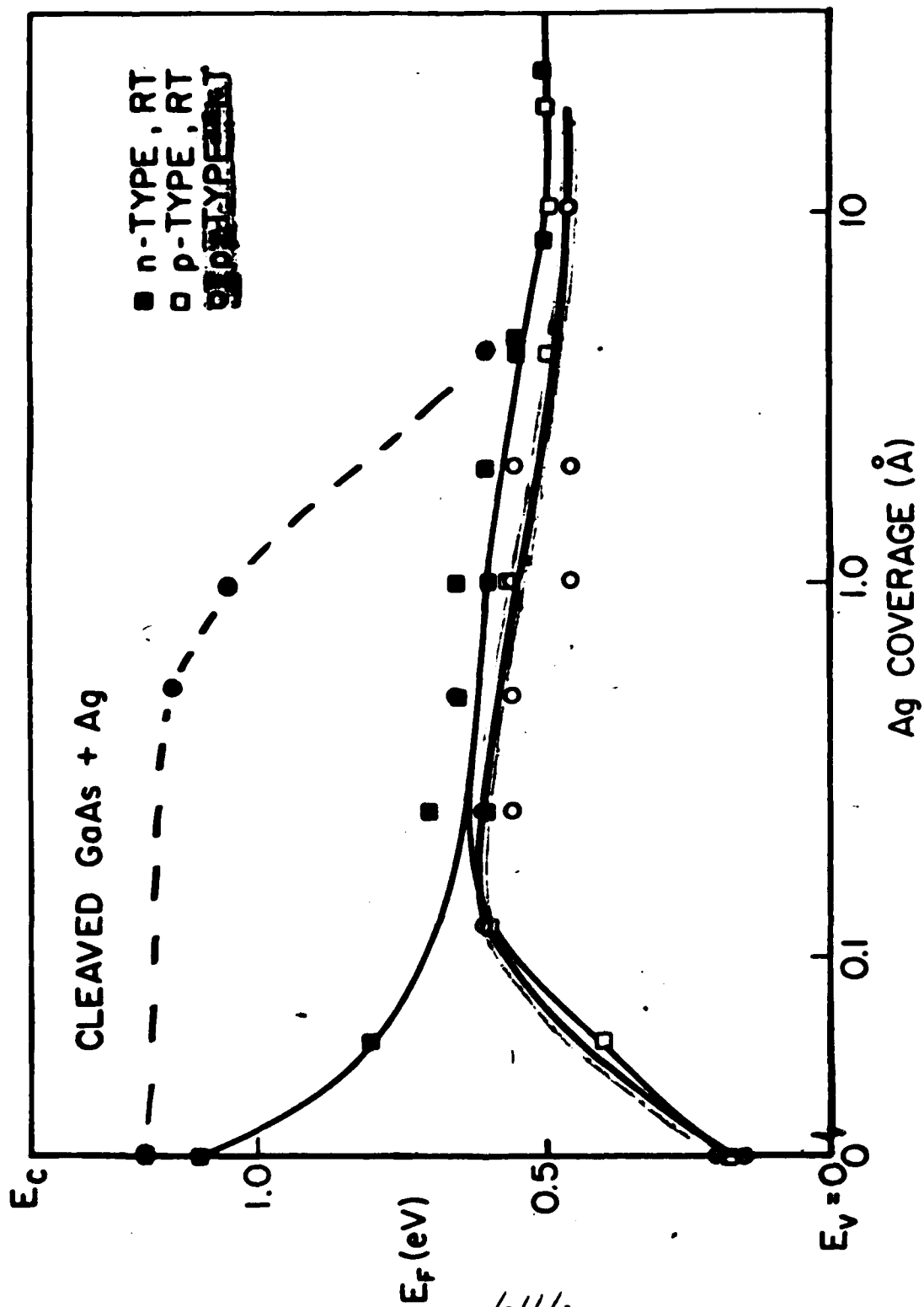


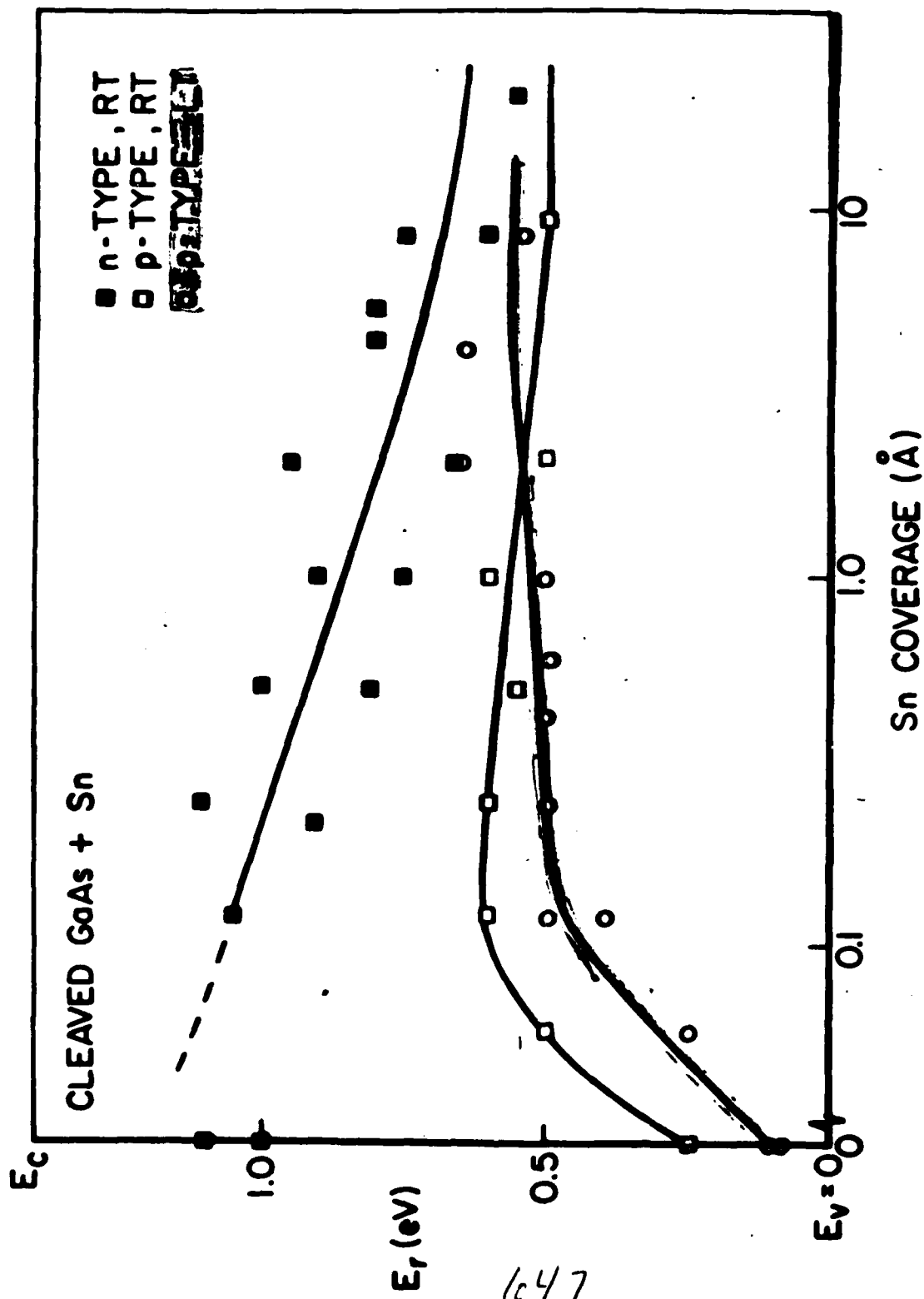












Overlayer Morphology

- ① Deposition at AT generally involves substantial clustering, chemical reaction or interdiffusion
- ② Deposition at LT enhances overlayer homogeneity: lower surface mobility and reduced clustering. (residual clustering with thermal evaporation)

Interdiffusion and reactions are slowed down.

Atomic reconstruction induced by the metal at the SC surface can be detected (Al / GaAs)

Initial E_F pinning rates at RT and LT.

Metal	n- GaAs		p- GaAs	
	RT	LT	RT	LT
Al	fast	slow	fast	fast
Au	fast	slow	fast	fast
In	fast	slow	fast	fast
Ag	fast	(slow)	fast	fast
Sn			fast	fast

Slow pinning at LT on n- GaAs consistent with reduced clustering, defect formation, chemical reaction.

Fast pinning at LT on p- GaAs requires a different mechanism.

Initial pinning rates

- * The deposition temperature affects the kinetics of Schottky barrier formation: rate of EF pinning different at 80°K.
 - * The strong asymmetry in pinning rates on LT n- and p- GaAs results from the partial inhibition of some interface phenomena. It makes it impossible to explain the Schottky formation process with a single mechanism.
 - * From the point of view of defects:
 - need a substantial complication of model:
 - ex As_{Ga} (double donor) + compensating defect
- ← different kinetics →
- Or
- entirely different model
 - ex acceptors activated by formation of clusters or chemical reaction
 - + donors linked to reconstruction or interface bonds.

Conclusions.

1. LT deposition simplifies the overlayer system by reducing interactions (except structural) with the semiconductor.
2. It reveals fundamental differences in the initial pinning on n- and p- substrates, marked by fast interactions at RT
3. If 2. holds true, it requires re-thinking of initial pinning mechanisms.

**Microscopic Metal Clusters and Schottky
Barrier Formation**

S. Doniach

**Applied Physics
Stanford University**

Effect of clustering on Surface Fermi level pinning

Single defect model:

$$\phi_b = - \frac{Q^2}{2 n_d e}$$

← charge transferred
 $\propto$ number of defects/area
 ← donor density
 → band bending

Saturates when

$$\mu_{\text{defect}} = \mu_{\text{semicond}} + \phi_b$$

→ defect electron affinity
 ← bulk semiconductor Fermi level

Cluster charging model:

$$\mu_{\text{cluster-complex}} = \frac{\partial E_{\text{complex}}}{\partial n}$$

← electron affinity
 ← Coulomb's energy
 $E_{\text{complex}} = n \epsilon_c + n^2 \frac{U}{C(R)}$
 → # of electrons transferred
 ← effective capacitance (6.54)

Clustering model assumptions

$$C(R) \propto R \propto N^{1/3}$$

effective capacitance

$$\text{Coverage} = N_c \cdot N$$

number of clusters ← held Fixed

number of atoms per cluster varying

Equilibrium condition :

$$E_c + n \frac{U}{C(R)} = -n^2 \left(\frac{N_c}{N_{\text{sat}}} \right)^2 (E_c - E_s) + E_s$$

average electron number per cluster

cluster density

single defect saturation density

Fit data in terms of parameters

$$E_c - E_s, \quad \alpha = \frac{U/C_1}{E_c - E_s}, \quad \beta = \left(\frac{N_c}{N_{\text{sat}}} \right)^2$$

$$\text{empirically } \beta = \beta_0 \alpha^{3.3 \pm 0.55}$$

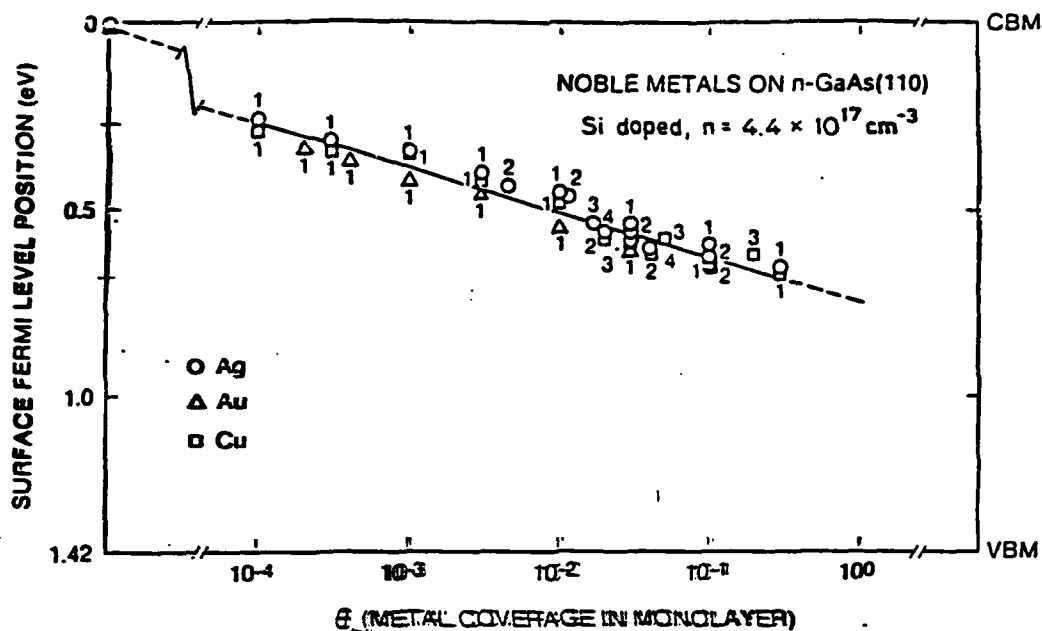
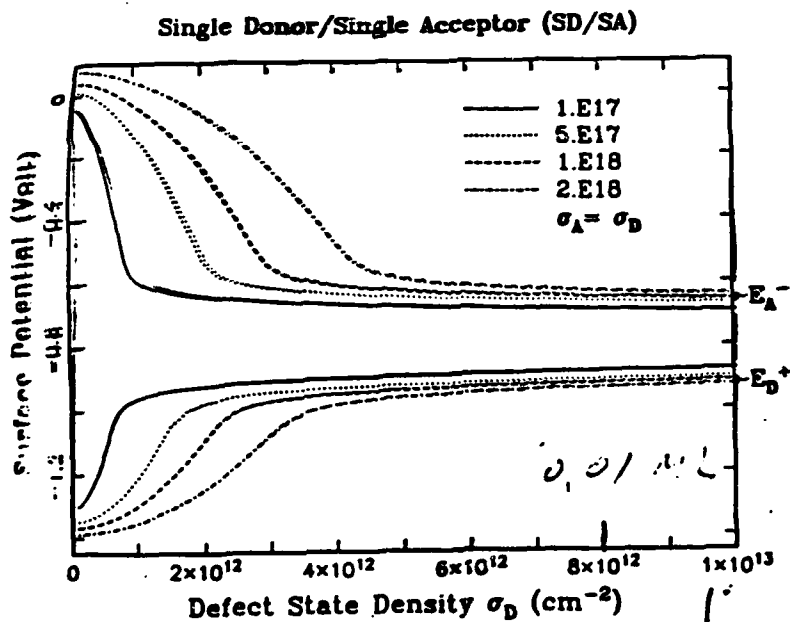


Fig. 3. The n-GaAs (110) surface band bending as the function of the effective noble metal coverage or the ideally cleaved n-GaAs (110) surface band bending as the function of the noble metal coverage. The numbers in the mark refer to the sample numbers as shown in Fig. 2.

K.K.Chin, R.Cao, K.Hiyang, C.E. McCants, I.Lindan + W.E Spicer

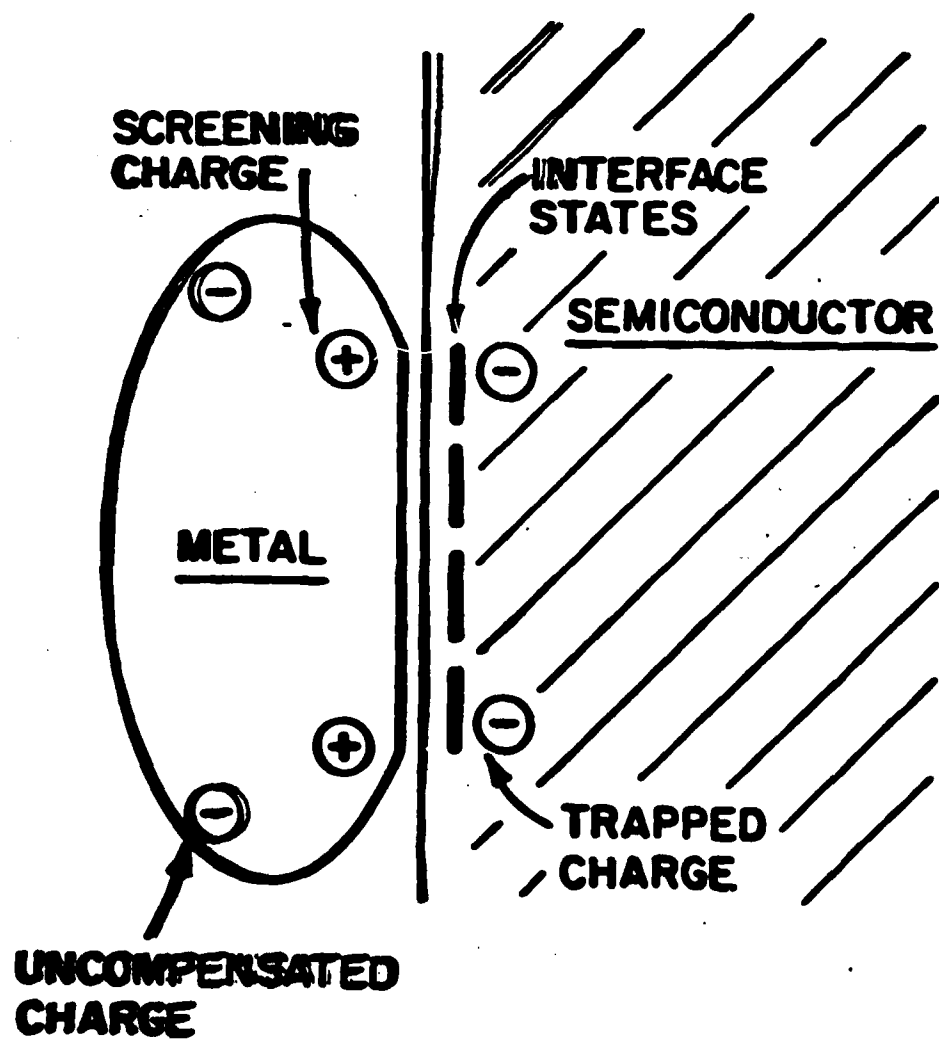


Tang + Freeouf

654

J Vac Sci Tech

B2 459 (84)



data: Kuau Kén Chin

