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

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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

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

Chairman: Thomas C. McGill, CALTECH

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

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For Dr. Larry Cooper, ONR/Code 1114
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 Krentz  Rockwell International/
            Walter Harrison, Stanford
            "Effects on Schottky Barriers of Metat Substitution in Semiconductors"

4:40 - 4:45  Questions

4:45 - 5:05  Giorgio Marperisanto  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 Palmstrøm
Rutgers University

"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 these papers of this session

10:35 - 10:50 Coffee

Chairman: Paul Ha, 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 Kasch
IBM - Yorktown Heights

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

11:35 - 11:40 Questions

11:40 - 12:00
Bruce Bastian
Northwestern 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 Lunch, Duraad 450
**Tuesday, November 4th**

**Chairman: Ron Grant, Rockwell International**

<table>
<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:30 - 1:50</td>
<td>Harry Wieder</td>
<td>&quot;Composition Dependence of Metal In	extsubscript{X}Al	extsubscript{1-X}As Barrier Height and Its Applications&quot;</td>
</tr>
<tr>
<td>1:50 - 1:55</td>
<td>Questions</td>
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<tr>
<td>1:55 - 2:15</td>
<td>Steven Wright</td>
<td>&quot;In-situ Contacts to GaAs Based on InAs&quot;</td>
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<tr>
<td>2:15 - 2:20</td>
<td>Questions</td>
<td></td>
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<tr>
<td>2:20 - 2:40</td>
<td>Jerry Tersoff</td>
<td>&quot;Intrinsic Mechanisms for Fermi-level Pinning at Surfaces and Interfaces&quot;</td>
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<tr>
<td>2:40 - 2:45</td>
<td>Questions</td>
<td></td>
</tr>
<tr>
<td>2:45 - 3:10</td>
<td>General discussion of preceding papers</td>
<td></td>
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<tr>
<td>3:10 - 3:30</td>
<td>Coffee</td>
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**Chairman: Jorgoff Lindas, Stanford University**

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<tr>
<th>Time</th>
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<th>Title</th>
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<tbody>
<tr>
<td>3:30 - 3:50</td>
<td>Leonard J. Brillson</td>
<td>&quot;Recent Photoemission and Cathodoluminescence Spectroscopy Studies of III-V Semiconductor-Metal Interfaces&quot;</td>
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<tr>
<td>3:50 - 3:55</td>
<td>Questions</td>
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<tr>
<td>3:55 - 4:15</td>
<td>Jack Dow</td>
<td>&quot;Antisite Defects and Schottky Barriers&quot;</td>
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<tr>
<td>4:15 - 4:20</td>
<td>Questions</td>
<td></td>
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<tr>
<td>4:20 - 4:40</td>
<td>Paul Ho</td>
<td>&quot;Direct Measurements of Electronic States at Metal/GaAs Interfaces&quot;</td>
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<tr>
<td>4:40 - 4:45</td>
<td>Questions</td>
<td></td>
</tr>
<tr>
<td>4:45 - 5:05</td>
<td>Discussion of preceding papers</td>
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<tr>
<td>5:05 - 5:45</td>
<td>General discussion of all papers presented at meeting</td>
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<tr>
<td>6:00 - 7:00</td>
<td>Stanford Faculty Club - no host cocktail party</td>
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<td>7:00</td>
<td>Dinner - Stanford Faculty Club</td>
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**Wednesday, November 5th**

**Chairman: Harry Wieder, U.C. San Diego**

<table>
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<th>Time</th>
<th>Event</th>
<th>Speaker/Institution</th>
<th>Topic</th>
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<tbody>
<tr>
<td>8:00 - 8:30</td>
<td>Continental breakfast</td>
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<tr>
<td>8:30 - 8:50</td>
<td>Rudolf Ludeke, IBM-Yorktown Heights</td>
<td>&quot;The Role of Transition Metal Impurity States in Schottky Barrier Formation&quot;</td>
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<tr>
<td>8:50 - 8:55</td>
<td>Questions</td>
<td></td>
<td></td>
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<tr>
<td>8:55 - 9:15</td>
<td>Walter Harrison, Stanford University</td>
<td>&quot;Effects of Coverages, Relaxation, and Screening at Interfaces&quot;</td>
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<tr>
<td>9:15 - 9:20</td>
<td>Questions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9:20 - 9:40</td>
<td>Jerry M. Woodall, IBM-Yorktown Heights</td>
<td>&quot;Unpinned GaAs Surfaces by Photochemistry&quot;</td>
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<tr>
<td>9:40 - 9:45</td>
<td>Questions</td>
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<tr>
<td>9:45 - 10:05</td>
<td>Discussion of preceding papers</td>
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<tr>
<td>10:05 - 10:25</td>
<td>Coffee</td>
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**Chairman: Ferro Pianetta, Stanford University**

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<th>Topic</th>
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</thead>
<tbody>
<tr>
<td>10:25 - 10:45</td>
<td>Antoine Kahn, Princeton University</td>
<td>&quot;Kinetics of Schottky Barrier Formation: Metals on Low Temperature GaAs (110)&quot;</td>
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<tr>
<td>10:45 - 10:50</td>
<td>Questions</td>
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<tr>
<td>10:50 - 11:10</td>
<td>Sab Dosiush, Stanford</td>
<td>&quot;Microscopic Metal Clusters and Schottky Barrier Formation&quot;</td>
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<tr>
<td>11:10 - 11:15</td>
<td>Questions</td>
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<tr>
<td>11:15 - 11:35</td>
<td>Discussion of papers of this day</td>
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<tr>
<td>11:35 - 12:15</td>
<td>General discussion of workshop</td>
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</table>
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</tbody>
</table>

**Notes:**
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- Helms, Dr. C. Robert
- Harrison, Dr. Walter
- Kim, Mr. Ki Bum
- Deal, Dr. Mike
- Sands, Dr. Tim
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If it quacks, it's a duck.

I thought I saw a duck.

Just a bit more jack.

Antisite?!
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

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?

NO!
PREVIOUS WORK

Many investigators have calculated the change in enthalpy (\( \Delta H \)) 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.

Enthalpy of formation vs. Au mole fraction

Au-Ga Compounds

\[ \Delta H^\circ_{298} \] (kcal/g-atom)

0

Mole Fraction of Au


Meidema, et al., CALPHAD 1, 391 (1997)
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/GeA
- Summarize
Minimize Mass Transport

Rough

Abrupt

Minimize G
Experimental Determination of Bulk Phase Diagrams

Sealed Capsule (Nearly Ideal Closed Thermodynamic System)
Open System:

ie. mass is not necessarily constant
DISSOCIATION OF GaAs AND Ga0.7Al0.3As DURING ALLOYING OF GOLD CONTACT FILMS

K. Km. 1P. K. Gallager 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.a. As starts to appear at ~230°C and reaches a maximum rate of evolution at 420°C. Investigated Ga0.7Al0.3As shows an As peak at ~420°C.
Gibbs Free Energy of Reaction

\[ P_{\text{As}_4} = 10^{-8} \text{ torr} \]

\[
\begin{align*}
\Delta G_R (\text{kal/mole}) \\
(1) \quad \text{GaAs}_4 &\rightarrow \text{Ga}_1 + (1/4) \text{As}_4 (g) \\
(2) \quad \text{Au}_1 + \text{GaAs}_4 &\rightarrow \text{AuGa}_1 + \text{As}_4 (g) \\
(3) \quad \text{Au}_1 + \text{GaAs}_4 &\rightarrow \text{AuGa}_1 + (1/4) \text{As}_4 (g) \\
\end{align*}
\]

Temperature (K)

Reaction Sequence

\[ 7 \text{Au} + 2 \text{GaAs} \xrightarrow{800^\circ \text{C}} \text{Au}_7 \text{Ga}_2 + \text{As}_2 \uparrow \]

\[ \text{Au}_7 \text{Ga}_2 + \text{GaAs} \xrightarrow{1000^\circ \text{C}} \text{Au}_7 \text{Ga}_3 + \frac{1}{2} \text{As}_2 \uparrow \]

\[ \text{Au}_7 \text{Ga}_3 + 4 \text{GaAs} \xrightarrow{800^\circ \text{C}} 7 \text{Au} \text{Ga} + 2 \text{As}_2 \uparrow \]

\[ \text{AuGa} + \text{GaAs} \xrightarrow{575^\circ \text{C}} \text{AuGa}_2 + \frac{1}{2} \text{As}_2 \uparrow \]

for all reactions, \( \Delta H > 0 \)

but \( \Delta G < 0 \)!
Au + Ga on GaAs

GaAs Substrate

Au beam

Ga beam

2000Å Au on GaAs

Room Temp.

500°C
AuGa$_2$ on GaAs

a) 300°C

b) 480°C

c) 500°C

FIG. 2
Electrical Properties of Metal Contacts on GaAs
Leung, Yoshie, Bauer, and Milnes

<table>
<thead>
<tr>
<th>Material</th>
<th>As deposited</th>
<th>350°C Anneal</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>( \phi ) (eV)</td>
<td>( V_b ) (volts)</td>
</tr>
<tr>
<td>Au</td>
<td>0.95</td>
<td>1.05</td>
</tr>
<tr>
<td>AuGa(_2)</td>
<td>0.68</td>
<td>1.05</td>
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</tbody>
</table>
Predict
$8Au + 3InP \rightarrow 3Au_2In + Au_2P_3$
550 Å Au on InP(001)
Annealed under 1 Atm. Dry N₂

a) R.T. 35 days

b) 365 °C 1h0 min

initial reaction stage
continuous film
α phase

Intermediate
β₂ + Au₂P₃

AuIn₂

AuIn

Au

Au₂P₃

InP

P

closed system equil.
islants
γ + Au₂P₃
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)

*Present address: IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120-6099
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.
1. 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, Deal17, 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. 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 MGax and one MAsy binary compound exist.
2. Assume no MGaxAsy 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 MGax-MAsy 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, MGax, MAsy, and M are all stable with respect to new compound formation when in contact with GaAs.

Type II: MGax dominant. The key feature of this diagram is the MGax-As tie-line (Fig. 1b). From the Gibbs phase rule, the presence of the MGax-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 M(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-GroupV 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.\textsuperscript{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,\textsuperscript{30} an inert capping layer can be deposited over the wafer,\textsuperscript{31} or rapid thermal annealing can replace conventional furnace annealing.\textsuperscript{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\textsubscript{2}, and As\textsubscript{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.\textsuperscript{34} For example, for the M\textsubscript{Ga-x}M\textsubscript{As-y}-GaAs three-phase region in Fig. 1d, the reaction is

\[
x \text{GaAs} + M\text{As}_y = M\text{Ga}_x + (x+y)/n \text{As}_n
\]

the As\textsubscript{n} partial pressure is given by

\[
P_{\text{As}_n} = \exp[-\Delta G^*_\text{rxn} n/(x+y)RT]
\]
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 MGax 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.\textsuperscript{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.

\textbf{A. Type I}

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

Tsai and Williams\textsuperscript{21} 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 ($\sim 10\%$) and some arsenic ($<1\%$) at a processing temperature of $300^\circ$C.\textsuperscript{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.\textsuperscript{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 \textit{et al.}\textsuperscript{26} and Williams \textit{et al.}\textsuperscript{20} respectively.
The simplified Ag-Ge-As diagram shown in Fig. 4b can be derived from Panish's work.

The 2 phase is stable only in the temperature range 446-582°C.

Tungsten forms two compounds with arsenic — W₂As₃ and WAs₂ — but none with gallium. From available thermochemical data, it can be shown that the W-GaAs tie-line is favored over the Ga-W₂As₃ 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 study of SiO₂-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 W₂As₃ occurred at 900°C. However, greater gallium solubility in tungsten at higher temperatures and selective gallium loss through the SiO₂ 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-W₂As₃-GaAs three-phase region.

For completeness, we note that the semiconductors silicon, germanium, and tin also have Type I diagrams, as determined by Panish. 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, Kavanagh et al. 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 Eizenberg 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.

48

12
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.\textsuperscript{47, 48} If "metallic" gallium corresponds to elemental gallium, then these metals also have MA\textsubscript{3} dominant Type III diagrams. On the other hand, if "metallic" gallium corresponds to MGa\textsubscript{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.\textsuperscript{19} have shown that the Ga-As-O diagram is basically of this type (Fig. 5).

\textbf{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,\textsuperscript{13} the chromium diagram from an X-ray analysis by Deal,\textsuperscript{17} and the platinum diagram from thin film studies.\textsuperscript{49-52}

The Pd-Ga-As diagram determined by El-Boragy and Schubers\textsuperscript{53} (Fig. 7) can be used to explain several recent studies of Pd-GaAs thin-film diffusion couples.\textsuperscript{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, PdAs\textsubscript{2}, 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.,\textsuperscript{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 PdAs\textsubscript{2} formed at 600°C.\textsuperscript{58} The crystal structure, lattice parameters, and stoichiometry of Phase I
hexagonal, $a_0 \approx 0.67 \text{ nm}$ and $c_0 \approx 0.37 \text{ nm}$. $\sim \text{Pd}_{2.4}\text{GaAs}$ — matches those of the ternary phase designated $\text{Pd}_2\text{GaNAs}_{1-N}$ by El-Borgy and Schubert.\textsuperscript{59} Similarly, Phase II — hexagonal, $a_0 \approx 0.9 \text{ nm}$ and $c_0 \approx 0.34 \text{ 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-Borgy and Schubert.\textsuperscript{53}

Type V diagrams that have a ternary phase with the stoichiometry $M_x\text{GaAs}$ might be regarded as a subset of Type IV since the ternary phase usually transforms to a mixture of $M\text{Ga}_x$ and $M\text{As}_y$ after high-temperature annealing. Whether these ternary phases are metastable intermediates in $M$-$\text{GaAs}$ diffusion couples or are stable, low-temperature phases with tie-lines to $\text{GaAs}$ remains to be determined. Metals in this category include nickel\textsuperscript{60,61} and perhaps cobalt.\textsuperscript{62} 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 $\text{GaAs}$ 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.\textsuperscript{63,64}

Photoemission studies of aluminum monolayer reactions with $\text{GaAs}$ substrates are consistent with aluminum having a Type VI diagram. These studies\textsuperscript{65-68} have found that aluminum replaces gallium in the top layers of the $\text{GaAs}$ 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.\textsuperscript{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, MGaₓ, and MAsᵧ 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. It has been found that the silicide used on GaAs need not be the most silicon-rich silicide. 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. 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 WSi₂ and W₅Si₃ 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.

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References

44. S.K. Cheung, K.-M. Yu, T. Sands, N.W. Cheung, J.M. Jaklevic, and
Spring Meeting, 1986 (in press).

45. K.L. Kavanagh, J.W. Mayer, C.W. Magee, J. Sheets, J. Tong, P.D. Kirchner,


(1982).


54. P. Oelhafen, J.L. Freeouf, T.S. Kuan, T.N. Jackson, and P.E. Batson, J. Vac.

(1985).

(1985).

57. T. Sands, V.G. Keramidas, A.J. Yu, K.-M. Yu, R. Gronsky, and J. Washburn,


61. T. Sands, V.G. Keramidas, J. Washburn, and R. Gronsky, Appl. Phys. Lett. 48,
402 (1986).

934 (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 MGaₓ and/or MAₓᵧ compound exists. "X" marks the three-phase region the system will be in when equilibrium is reached. "Ø" 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 work indicates that the Cu₃As-Cu₉Ga₄ tie-line exists at ~600°C, but the Cu₉As-GaAs tie-line may exist at lower temperatures (~400°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. T = 600°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.
Fig. 1
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Fig. 4
Type II

Ga-As-O

Fig. 5
Pd-Ga-As

Fig. 7
Ni-Ga-As

Co-Ga-As

Fig. 8
Fig. 9
Phase Equilibria in Metal-Gallium-Arsenic Systems:
Thermodynamic Considerations for Metallization Materials

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Outline

Thermodynamics

Simplest Cases - idealized systems

Complicating Factors - real systems

Applications

Conclusions
Simplest Cases
Complicating Factors
Type II

Ga-As-O

Ga₂O₃
As₂O₃
GaAs
Ga
As

Diagram showing the Ga-As-O system with Ga₂O₃, As₂O₃, and GaAs phases.
Type I: GaAs dominant

Type II: MgAs dominant

Type III: MgAs dominant

Type IV: no phase dominant
Type IV:

Cr-Ge-As

Cu-Ge-As

Pi-Ge-As

\( \text{Cu}_n \text{Ge}_m \text{As}_p \)
\[
\begin{array}{c|c|c}
\text{Pd} & \text{GaAs} & \text{PdGa + PdAs}_2 \\
\hline
\text{Pd}_2 & \text{GaAs} & \text{Pd}_3 \text{Ga}_9 \text{As}_{0.3} \\
\hline
\hline
\end{array}
\]

200°C \quad \rightarrow \quad \rightarrow \quad 600°C
Type V: Ternary phase

\[ M \quad MG_a \quad M_{x}GaAs \quad MAs_y \quad Ga \quad GaAs \quad As \]
Applications
Conclusions

Type I: GaAs dominant

Type II: MGa_x dominant

Type III: MAs_y dominant

Type IV: no phase dominant

Type V: Ternary phase

Type VI: Solid Solubility

Type VII: Solid Solubility
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.
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) $\text{H}_2\text{SO}_4: \text{H}_2\text{O}_2: \text{H}_2\text{O}(5:1:1)$

(b) $\text{NH}_4\text{OH}: \text{H}_2\text{O}_2: \text{H}_2\text{O}(1:1:10)$

(c) $\text{HCl}: \text{H}_2\text{O}(1:1)$

(d) $\text{NH}_4\text{OH}: \text{H}_2\text{O}(1:10)$

$\phi_B = 0.71 \text{eV}$
Effect of Surface Clean on GaAs Surface
SCHOTTKY BARRIER HEIGHT OF Tl: GaAs INTERFACES VERSUS ANNEALING TEMPERATURE

*MEASUREMENTS DONE IN SPICER/HELM'S ELECTRICAL CHARACTERIZATION FACILITIES
EFFECT OF ANNEALING ON W:Ti:GaAs LAYERED STRUCTURE

*Auguster Sputter Profiling performed in system partially obtained with CMR funds

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PRELIMINARY Ti-Ga-As PHASE DIAGRAM

(KIM, SINCLAIR)
"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)
   - Al + GaAs -> Al_xGa_{1-x}As + Ga_yAl
   - 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
Is "Chemistry" on deposition of metals in agreement with bulk thermodynamics?

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

No ideal way to examine experimentally.

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

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, 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 Å, intensity of As becomes increasingly larger than that of Ga.

2. For coverages greater than 1.3 Å 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.


\[
\Delta E_A(x) = E(A; A_xB_{1-x}) - E(A+1; A_xB_{1-x}) + E(A+1; A)
\]

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

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
Due to alloying

\[ \Delta E = G \Delta S \]

\[ \Delta E \text{ with respect to Ga in GaAs} \]

<table>
<thead>
<tr>
<th>Metal</th>
<th>( \Delta E_{\text{exp}} ) (eV)</th>
<th>( \Delta E_{\text{cal}} ) (eV)</th>
<th>PES evidence of Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>-0.4</td>
<td>-0.38</td>
<td>Strong disruption of GaAs As surface segregation?</td>
</tr>
<tr>
<td>Cu</td>
<td>-0.8</td>
<td>-0.83</td>
<td>Strong disruption of GaAs</td>
</tr>
<tr>
<td>Ag</td>
<td>----</td>
<td>-0.79</td>
<td>No GaAs disruption No alloying No reaction</td>
</tr>
<tr>
<td>Ni</td>
<td>-0.7</td>
<td>-0.60</td>
<td>Strong disruption of GaAs As outdiffusion Ni/Ga/As phase?</td>
</tr>
<tr>
<td>Pd</td>
<td>-0.7</td>
<td>-0.30</td>
<td>B.E. still decreasing at 50Å Pd As surface segregation, arsenide formation</td>
</tr>
<tr>
<td>Cr</td>
<td>-1.25</td>
<td>-1.05</td>
<td>Strong disruption of GaAs, Strong As out-diffusion</td>
</tr>
<tr>
<td>Ti</td>
<td>-1.8</td>
<td>-1.43</td>
<td>Strong disruption of GaAs</td>
</tr>
</tbody>
</table>
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 example:

- If reactions go to completion
  For example:
  \[ \text{GaAs} + \text{Au} \rightarrow \text{GaAu}_3 + \text{As} \]

- So that all Au converted uniformly to GaAs
  Thermodynamics tend to favor

- However, many interfacial reactions appear to be kinetically or thermodynamically

  For example:
  \[ \text{Al} + \text{GaAs} \rightarrow \text{Al}_x \text{Ga}_{1-x} \]

- Which can't be calculated
See "Chemistry" of various types, using PES.

What effect on Electrical Properties:

1) Seen via PES (Very Thin Films)

2) Seen via electrical measurements on "thick" (~1000Å) films

For example, have different chemistry on deposition for Au, Cu, 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 after 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


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 (~25-50Å) 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
Anneal
\[ \text{Al} + \text{GaAs} \rightarrow \text{Al}_{x}\text{Ga}_{1-x}\text{As} + \text{Ga} \]

Show PES results

SBH increases 0.8 \( \rightarrow \) 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 \( \Sigma \) 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 are important.

4. Much more to be done.
In on GaAs gives Schottky barrier
room temperature SBH = 0.76 eV

Anneal, etc - "ohmic"
In + GaAs \rightarrow In_xGaAs_{1-x} + xGa

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

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Coworkers
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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

Adatoms

photon energy

emitted

synchrotron radiation

reacting interface

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:

ordered epitaxial growth - Fe/gaAs
Co/gaAs

cluster formation and disruption
- Cr/gaAs

disruption and compound formation - self-limiting intermixing giving rise to heterogeneous, metastable interface
Photoemission: photons in, electrons out
Auger electrons in, electrons out
LEED electrons in, spots
Inverse photoemission: electrons in, photons out
(STM)
Co/GaAs $\rightarrow$ Excellent lattice match
Fe/GaAs $\rightarrow$

Q: Can epitaxial layers be grown?
Yes. Prime 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

Cobalt $\rightarrow$ photoelectrons

GaAs $\rightarrow$ h$\nu$
XPS Fe/GaAs (100)

$\nu = 1486 \text{ eV}$

Modest resolution

Fe/GaAs (001) - c(8x2)

$\gamma = 15^\circ$

RELATIVE BINDING ENERGY (eV)

PHOTOELECTRON INTENSITY (arb. units)

Fig. 6
Co/GaAs (110)

Ga$_3$d

Ga 3d
60 eV

PHOTOEMISSION INTENSITY (arb. units)

RELATIVE BINDI

Substrate

Reaction Product
Co-Ga
Co/GaAs (110)

Conclusion: there is reaction and intermixing

Q: Is there epitaxy?
Angle-resolved Auger electron diffraction:
(Structural probe)
Conclusion: Excellent epitaxy.
So far:

1. Surface sensitive photoemissin shows copious amounts of As at and near vacuum surface $\Rightarrow$ disruption of GaAs by Co

2. Auger diffractim 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

$\theta$ = probe depth $\sim \lambda \sin \theta$
Polar-angle-dependent XPS
Co/GaAs (100)

Intensity normalized to clean surface

NORMALIZED INTENSITY

POLAR ANGLE (degrees)

grazing emission
normal emission

⇒ 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*

ideal epitaxy without disruption

epitaxy with limited exchange
What if solubility is very low?

thin overlayer

$\Rightarrow$

thick overlayer

surf. cs

solubility
Photoemission intensity of element A detected at an angle \( \theta \) wrt surface is

\[
I_A(\theta) = \sigma_A I_o(\theta) S \int_0^\infty \rho_A(z) e^{-\frac{z}{\lambda \sin \theta}} \, dz
\]

\( \sigma_A \) - photoemission clean spot density \( f^2 \) of element A
\( I_o(\theta) \) - unknown
\( S \) - surface area
Atom Profiles:
Co/GaAs (100)

Co/GaAs (100)

exp. Ga decay into Co layer

Substrate Yc ~ 3 Å

Co coverage 45 Å
How abrupt are interfaces?

As 3d
hv = 85 eV

Ga 3d
hv = 60 eV

REDUCED INTENSITY

METAL OVERLAYER COVERAGE (ML)

Au, Cu, Ti, Co, Fe, V, Sm
Similar picture for Au/GaAs

\( \frac{1}{e} \) values \( \sim 3 \) Å

\( \rho^{501} \sim 0.2 \text{ at.\%} \)

Segregated Ga and As (amount depends on surface)

For GaAs (100), \( \sim 2 \) ML of disruption then \( \sim \) Au layer

For GaAs (110), As signal rises for coverages \( \geq 10 \) 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) $\ h\nu = 112\text{eV}$

![Graph showing photoemission intensity vs. relative binding energy for Ti/Si(111) with varying Ti coverage.]

Rel. Binding Energy (eV)

$2p_{3/2}$

$2p_{3/2}$

complex reaction products

Fig. 3
Ti/Si(111)

Ultra thin transition region

Ti-Si reaction product

Si in solution in Ti

Fig. 5
Metastable Ti/Si interface

Ti-Si acts to regulate its own growth through kinetics.

Modeling gives stoichiometry. Temp dependences give $D_0$ and activation energy.
Interface Evolution

1. Heterogeneous formation of reaction products (islands)

2. Onset of mixed phase growth

3. Both reaction products grow as overlayer thickness increases

4. Complete coverage by final reaction product

5. Metal overlayer growth on a complex, multiphase system

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).

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
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).
a) Cu ON n-InP (110) Coverages in Monolayers

P 2p

\( h\nu = 185 \text{ eV} \)

Clean

1.0

4.4

9.5

19

45

In 4d

\( h\nu = 80 \text{ eV} \)

Clean

1.0

4.4

9.5

19

45

b) Ag ON n-InP (110) Coverages in Monolayers

P 2p

\( h\nu = 185 \text{ eV} \)

Clean

0.74

3.7

7.5

22

36

In 4d

\( h\nu = 80 \text{ eV} \)

Clean

0.74

3.7

7.5

22

36

c) Au ON n-InP (110) Coverages in Monolayers

P 2p

\( h\nu = 185 \text{ eV} \)

Clean

1.4

4.1

8.0

22

37

In 4d

\( h\nu = 80 \text{ eV} \)

Clean

1.4

4.1

8.0

22

37

KINETIC ENERGY (eV)
P2p
$\nu = 185\,\text{eV}$

Ni OnpInP (110)
Coverages in Å

In 4d
$\nu = 80\,\text{eV}$

INTENSITY (arbitrary units)

KINETIC ENERGY (eV)

reacted (single phase)
Ti on n-InP(110)

Ti coverage in Å:
- 42.0
- 30.0
- 18.0
- 12.0
- 7.0
- 4.0
- 2.0
- 0.5
- 0

In 4d 70 eV

NORMALIZED INTENSITY (a.u.)

KINETIC ENERGY (eV)

150
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)

<table>
<thead>
<tr>
<th>Metal</th>
<th>I-V Measurements</th>
<th>Fermi Level Pinning from PES*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Our Data</td>
<td>Our Data</td>
</tr>
<tr>
<td></td>
<td>Barrier Height (eV)</td>
<td>Ideality Factor</td>
</tr>
<tr>
<td>Ag</td>
<td>0.54</td>
<td>1.02±0.02</td>
</tr>
<tr>
<td>Cr</td>
<td>0.45</td>
<td>1.10±0.10</td>
</tr>
<tr>
<td>Cu</td>
<td>0.42</td>
<td>1.03±0.05</td>
</tr>
<tr>
<td>Au</td>
<td>0.42</td>
<td>1.03±0.03</td>
</tr>
<tr>
<td>Pd</td>
<td>0.41</td>
<td>1.03±0.07</td>
</tr>
<tr>
<td>Mn</td>
<td>0.35</td>
<td>1.1±0.3</td>
</tr>
<tr>
<td>Sn</td>
<td>0.35</td>
<td>1.0±0.15</td>
</tr>
<tr>
<td>Al</td>
<td>0.33</td>
<td>1.0±0.4</td>
</tr>
<tr>
<td>Ni</td>
<td>0.32</td>
<td>1.0±0.3</td>
</tr>
</tbody>
</table>

*Pinning established from original data for coverages below 10Å
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.
Eg = 1.35 eV

After Brillson et al.
+ After Zhao et al.
△ (▲), ○ (●), □ (■) our data from shifts of In 4d, P 2p and -6.20 eV VB peaks for n(p) type substrates

Coverage (Å)
Pd on InP(110)

- From In4d
- From P2p

Pd COVERAGE (Å)

$E_p - E_v (\text{eV})$
STABLE PHASES AT INTERFACES
REACTIVE METAL COMPOUND SEMICONDUCTOR

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Motivation for M/AB studies

Application of bulk equilibrium M-A-B phase diagrams to M/AB reactions:

- In/GaAs, a "success"
- Pd/GaAs, a "failure"

An example of uncharted territory: the Ni/InP reaction

Conclusions
Electron microscope studies of an alloyed Au/Ni/Au-Ge ohmic contact to GaAs  

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![Graph showing temperature vs. annealing time](image)

![Images A, B, and C depicting cross-sections of the contact layers](images)
Why study M/AB reactions?

Au-Ni-Ge/n-GaAs:  
- low $r_c$, but  
- difficult to reproduce  
- not stable at moderate $T$  
- 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.
In-Ga(2)

InAs

Ga

GaAs

As

T < Tc
50 nm In/GaAs

No. of precipitates

x in In$_{1-x}$Ga$_x$As

650°C

500°C

350°C

XBL 868-3109
60nm Pd/GaAs, 500°C, 10 min, SiO₂ cap

- PdGa
- PdAs₂
- GaAs

Δ200
Δ400
Δ400
Δ321
Δ400

2θ°

Intensity
Ni$_{2.7}$InP amorphous
mono. Ni$_2$InP

1 $\mu$m
Conclusion

- 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:
  - Surface and interface contributions to the free energy may be significant (e.g. Pd/GaAs)
  - An M/AB system cannot be assumed to be a closed system (e.g. Pd/GaAs, Ni/InP, ...)
- 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

<table>
<thead>
<tr>
<th>System</th>
<th>Intermediate</th>
<th>Stable*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/GaAs</td>
<td>Co$_2$GaAs ?</td>
<td>CoGa, CoAs</td>
</tr>
<tr>
<td>Rh/GaAs</td>
<td>RhAs</td>
<td>RhGa, RhAs$_2$</td>
</tr>
<tr>
<td>Ir/GaAs</td>
<td>IrGa</td>
<td>Ir$_3$Ga$_5$, IrAs$_2$</td>
</tr>
<tr>
<td>Ni/GaAs</td>
<td>Ni$_3$GaAs</td>
<td>NiGa, NiAs</td>
</tr>
<tr>
<td>Pd/GaAs (60nm)</td>
<td>Pd$_x$GaAs (I and II)</td>
<td>PdGa, PdAs$_2$</td>
</tr>
<tr>
<td>Pd/GaAs (12nm)</td>
<td>Pd$_x$GaAs (I)</td>
<td></td>
</tr>
<tr>
<td>Pt/GaAs</td>
<td>Pt$_3$Ga</td>
<td>PtGa, PtAs$_2$</td>
</tr>
<tr>
<td>Ni/InP</td>
<td>Ni$_2$InP (amor.) Ni$_x$InP (hex.)</td>
<td>Ni$_2$InP (mono.)</td>
</tr>
</tbody>
</table>

*e-gun deposited on (100) GaAs, capped with SiO$_2$. 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
   - MoGaInW 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
AaNiGe Ohmic Contacts

typical as-deposited sample

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>50 nm</td>
</tr>
<tr>
<td>Ni</td>
<td>30 nm</td>
</tr>
<tr>
<td>Au-Ge</td>
<td>100 nm</td>
</tr>
<tr>
<td>Ni</td>
<td>5 nm</td>
</tr>
</tbody>
</table>

GaAs

Si peak doping: $1 \times 10^{18}$/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"
"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
- \( \beta\)-AuGa phase \( (T_m = 360^\circ C) \) 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\(^\circ\)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 2 min annealing
(b) Thermal stability at 400°C annealing

- Electrical resistance measurement

![Graph showing electrical resistance measurement over annealing time at 400°C.]

Grain growth and phase transformation of \( \beta \)-AuGa at 400°C

**Before 400°C Anneal**

- \( \beta \)-AuGa

**After 400°C Anneal**

- \( \beta \)-AuGa

- NiAs (Au)

- GaAs
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 \( \sim 800^\circ C \)
- Expected to be thermally stable at \( 400^\circ C \) after contact formation

Focus of Present Research

(a) Search process (composition-temperature) window to form
   \( R_c < 0.5 \, \Omega \cdot \text{mm} \)

(b) Investigate thermal stability at \( 400^\circ C \) 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

![Graph showing contact resistance vs. temperature for 53% Mo - 47% Ge]
Search Process Window for $R_c < 0.5 \Omega$-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
(2) Indium Transport To Contact During Annealing

<table>
<thead>
<tr>
<th>W</th>
<th>50 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_e$</td>
<td>6 nm</td>
</tr>
<tr>
<td>$H_e$</td>
<td>13 nm</td>
</tr>
<tr>
<td>$d_c$</td>
<td>4 nm</td>
</tr>
</tbody>
</table>

- Annealed in InAs over pressure atmosphere

![Diagram of indium transport during annealing](image)

![Graph showing depth profile with different temperatures](image)

IBM

M. Murakami 1/28/86
(1) Direct Deposition of Indium

capped by 100nm thick Si₃N₄ layer
annealed at 800°C for 10 min in Ar/H₂ gas
Microstructure Which Produces Low Contact Resistance

<table>
<thead>
<tr>
<th>Before Anneal</th>
<th>750°C Anneal</th>
</tr>
</thead>
<tbody>
<tr>
<td>W 40 nm</td>
<td>W, Ge 40 nm</td>
</tr>
<tr>
<td>Mo 12 nm</td>
<td>Mo₅As₄ 25 nm (Mo₅Ge₂)</td>
</tr>
<tr>
<td>In 4 nm</td>
<td>In GaAs 10 nm</td>
</tr>
<tr>
<td>Ge 10 nm</td>
<td>GaAs</td>
</tr>
</tbody>
</table>
(c) Present Understanding

InGaAs layer could contribute to the barrier height reduction.

- Energy (eV)
- Composition of In$_x$Ga$_{1-x}$As

(Kajiyama, 1973)

In$_{x}$Ga$_{1-x}$As
Summary

II. AuNiGe ohmic contacts
   - Low contact resistance (~ 0.2 Ω-mm)
   - Deterioration of edge profiles
   - Thermally unstable at 400°C

III. MoGeW ohmic contacts (InAs overpressure annealing)
   - Thermally stable at 400°C
   - $R_c \sim 0.3$ Ω-mm
   - Poor run-to-run reproducibility

III. MoGeInW ohmic contact
   - Good reproducibility
   - No visible morphological change
   - Wide application (short diffusion distance)
   - $R_c \sim 0.8$ Ω-mm

Focus of Future Study for MoGeInW Ohmic Contacts:

"Reduction of $R_c < 0.2$ Ω-mm"
OHMIC CONTACTS

by

T.C. McGill + W.J. Baudinelle

California Institute of Technology

The LORD created so-called ohmic contacts to give solid-state types (especially the onsets) 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

\[ S_c = \text{specific contact resistance} \cdot \frac{A}{R} \]

\[ R_c \equiv \text{contact resistance} \approx \frac{S_c}{d} \]

\[ R_{SD} \equiv \text{Source-Drain Resistance} \approx \frac{l_{\text{bulk-channel}}}{wd} \]

Condition for neglecting \( R_{SD} > R_c \)

or

\( \{ S_c < l_{\text{bulk-channel}} \} \)
Numerical Considerations

\[ S_{\text{bulk}} \approx 4 \times 10^{-2} \Omega \text{-cm.} \]

\[ l \sim 1 \mu m. \]

\[ S_c < 4 \times 10^{-6} \Omega \text{-cm}^2 \]

Future

\[ S_c < 4 \times 10^{-6} \Omega \text{-cm}^2 \left( \frac{l}{1 \mu m} \right) \]
OUTLINE

A. SIMPLE MODEL OF OHMIC CONTACT

B. FLUCTUATIONS IN POTENTIAL ⇒ FLUCTUATIONS IN CONDUCTANCE

C. POSSIBLE WAYS OF SUPPRESSING FLUCTUATIONS

D. SUMMARY

E. FUTURE
SIMPLE CONTINUUM MODEL

I. FIRST THEORY
CHANG, FANG, AND SZE, SSE (1971).
• VERY SIMPLE MODEL OF SCHOTTKY BARRIER
• \( \Gamma(N(E)) \sim \sqrt{2m_0^* E} \)

II. IMPROVED THEORY
• USE TWO BAND MODEL
  OF COMPLEX BAND STRUCTURE
**Barrier Model**

\[ \phi(x) = \phi_0 + \frac{N_0 e^2}{2 \epsilon_0 \epsilon_s} (x^2 - 2x_0 x) - \frac{e^2}{8\pi\epsilon_0 \epsilon_s x} \]

\[ -\frac{N_0 e^2 d}{\epsilon_0 \epsilon_s} e^{-x/d} \]

\[ X_D = \sqrt{\frac{2 \epsilon_0 \epsilon_s}{N_0 e^2} \left[ \phi_0 + V_A - V_D \right]} \]
TWO BAND VS ONE BAND MODEL

(Energy (eV))

(Imaginary Part of $k)^2 (\xi^{-2}$)

1-Band Model

2-Band Model
CURRENT

\[ J_{\text{NET}} = J_{L \rightarrow R} - J_{R \rightarrow L} \]

\[ = 2e \int \frac{d^2k_y}{(2\pi)^2} \int_{0}^{\infty} \frac{dk_{\perp}}{2\pi} \frac{\hbar k_{\perp}}{m^2} T(E_{\perp}) \left[ f_L(E) - f_R(E) \right] \]

\[ T(E_{\perp}) = \text{Transmission coefficient} \]

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

\[ f_L(E), f_R(E) = \text{Fermi functions}. \]
CONDUCTANCE

AND

RESISTANCE.

\[ G \left( \frac{S}{m^2} \right) = \frac{1}{R \left( \Omega \cdot m^2 \right)} = \left( \frac{\partial J}{\partial V} \right)_{V=0} \]

\[ G = \frac{1}{R} = \frac{m^*e^2}{2\pi^2\hbar^3} \int dE_i \frac{T(E_i)}{e^{(E_i-E_F)/kT}+1} \]

\[ G(E) = \frac{m^*e^2}{2\pi^2\hbar^3} \frac{T(E_i)}{e^{(E_i-E_F)/kT}+1} \]
CALCULATIONS

$\Phi_0 = 0.80 \text{ eV}$

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

$\varepsilon_S = 13.18$

$m^*_n = 0.065 m_e$

$T = 300^\circ K$

$E_{F_n-L} = 0.28 \text{ eV}$

$m^*_L = 0.55 m_e$

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

$d = 5 \text{ Å}$

DOPING = ?
DISTRIBUTION OF CONDUCTANCE

$\log_{10}(G) \quad \rightarrow 10^{-5} \rightarrow 10^{0}$

Energy $0.5 \ V_{th}$

$N_0 = 10^{17} \ cm^{-3}$
DISTRIBUTION OF CONDUCTANCE

\[ \log(GG) \]

\[ \approx 1 \text{ } 5 \text{ } 16 \]

\[ N_D = 10^{18} \text{ } \text{cm}^{-3} \]
DISTRIBUTION OF CONDUCTANCE

\[ N_D = 10^{19} \text{cm}^{-3} \]
Small-Signal Resistance vs. Doping

- nonparabolic
- parabolic
- \( N_s = 5 \times 10^{14} \text{ cm}^{-2} \),
  \( d = 5 \text{ Å} \)
- Chang, Fang
  and Sze

\( \Phi_0 = 0.8 \text{ eV} \)
\( T = 300 \text{ K} \)
INHOMOGENEOUS MODEL

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

where \( G(x,y) = \text{conductance/area at } (x,y) \).

- REGIONS OF HIGH \( G \) DOMINATE
SPATIAL INHOMOGENEITY DUE TO DISCRETE DOPANTS.

- Dopant atoms discrete.
  ⇒ Potential inhomogeneous

- Use "REM0" techniques to simulate effect.
Contributions to the Potential

(-x, y, z)

metal

(x, y, z)

depletion region

(x_d, y_d, z_d)

n-GaAs
Small-Signal Resistance vs. Doping

- nonparabolic
- Monte Carlo
- Chang, Fang
  and Sze

\[ \phi = 0.6 \text{eV} \]

\[ T = 300 \text{K} \]
Small-Signal Resistance vs. Doping

- nonparabolic
- Monte Carlo
- \langle 100 \rangle
- Chang, Fang, and Sze

\[ \phi = 0.8 \text{eV} \]
\[ T = 300 \text{K} \]
Small-Signal Resistance vs. Doping

- nonparabolic
- Monte Carlo
- Chang, Fang
- and Sze

$\Phi = 1.0 \text{eV}$

$T = 300K$
metal

\[ \text{volume of ionised dopants} \]

bulk n-GaAs

\[ n_i \quad n_j \]

\[ X_i \quad X \]

\[ X_d \]
\( l = 100 \text{Å} \quad x = 49.5 \text{Å} \)

\[ T = 300 \text{K} \quad \Phi = 0.8 \text{eV} \]

\( 10^{19} \text{cm}^{-3} \)

\[ 10^{18} \text{cm}^{-3} \]
2 Lattice Planes

\[ l = 100\text{A} \quad x = 49.5\text{A}, 74.9\text{A} \]

- \( \times \) 10^{18}\text{cm}^{-3}
- \( \circ \) 10^{19}\text{cm}^{-3}

\begin{align*}
\log_{10} R_0 (\text{Ohm}\cdot\text{cm}) & \\
\log_{10} \text{doping (cm}^{-3}) & \\
\end{align*}

\<100\> T = 300K \phi = 0.8eV

mean

1 sigma
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 \( \rho_c \)?

B. HOW DOES \( \rho_c \) 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?
Non-alloyed ohmic contact by Solid State Reactions

U.C.S.D. IBM Cornell
Eric Marshall T. F. Kuech K. Kavanagh
Bei Zhang
L. C. Wang
S. S. Lau
We concentrate on:

$$\text{Ge/Pd/n - GaAs}$$

and

$$\text{Si/Pd/n - GaAs}$$

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

A. K. Sinha et al 1975


<table>
<thead>
<tr>
<th>n-GaAs</th>
<th>Ge</th>
<th>Pd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2 x 10^{16}</td>
<td>500 Å</td>
<td>500 Å</td>
</tr>
</tbody>
</table>

500 - 600 °C
3 - 4 x 10^{17} cm^{-2}
Surface very rough

The contact deposition scheme is inverted in our case appears to make a big difference
Solid State Reactions:
Configuration (schematical):

<table>
<thead>
<tr>
<th>GaAs &lt;100&gt;</th>
<th>Pd</th>
<th>Ge (a)</th>
<th>\text{Anneal}</th>
<th>GaAs</th>
<th>Ge</th>
<th>PdGe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>275-400°C</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

The idea is to simulate this

\[
\begin{align*}
\text{metal} & \quad \text{Ge} \\
& \quad n = 1.4 \times 10^{19} \text{cm}^{-3} \\
& \quad \text{thickness} = 250 \text{Å} \\
& \quad \phi = 0.5 \text{eV} \\
& \quad E_g - E_C = 0.4 \text{eV} \\
& \quad 60 \text{meV} - \Delta E_C \\
& \quad E_g - E_C = 0.06 \text{eV} \\
\end{align*}
\]

R. Stoll, C. E. C. Wood, K. Board, and L. F. Eastman,

\[ R_C \leq 10^{-7} \frac{\Omega}{\text{cm}^2} \] or less

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As-Deposited
GaAs <100> Pd Ge
325°C 30 min.

Annealed
GaAs <100> Ge PdGe

YIELD (ARB. UNITS)

CHANNEL NUMBER

350 400 450 500

Random
<100> Aligned
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 \rho_c; \quad Pd/Ge/GaAs \rightarrow high \rho_c)

2) Ge is necessary
   (Pd/n-GaAs \rightarrow high \rho_c \quad or \quad non-\Omega.)

3) Complete transport of Ge generally leads to
   lower \rho_c and better thermal stability.
How does the Ge/Pd system work?

It is proposed:

Formation of PdGa (or PdGa$_{3}$As$_{2}$) → 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 $\rho_c$ for p type GaAs!
a) — 40 nm

Ge

Pd

Pd \_xGa\_yAs

GaAs

Pd

Pd \_xGa\_yAs

GaAs

b) — 4 nm
specific contact resistivity $\rho_c$ ($\Omega \cdot \text{cm}^2$) vs. thickness $x$ (Å)

- $\Delta$: $\text{Ge}(1.54x + 500Å)/\text{Pd}(xÅ)/\text{GaAs}(n)$
- $\circ$: $\text{Pd}(500-xÅ)/\text{Ge}(1265Å)/\text{Pd}(xÅ)/\text{GaAs}(n)$
Experimentally:

(1) For n-type GaAs.
Ge/Pd yields low $\rho_c$ from $4 \times 10^{16}$ to $2 \times 10^{18}$/cm$^3$
(N$_c = 4.7 \times 10^{17}$)
Pd alone does not work well.

(2) For p-type GaAs,
Ge/Pd yields low $\rho_c$ from $> 1 \times 10^{19}$/cm$^3$
(N$_v = 7 \times 10^{18}$/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 ~400 °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 $E_F$ 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 Fermi Energy $E_F^i$ and Chemistry
- I-V and C-V Electrical Measurements for $\phi_B$

![Diagram of GaAs energy levels with Fermi level, $E_F$, and interface energy $E_F^i$](image)

$E_{cl}$ measured at interface

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

$$\Delta E_{cl} = \Delta E_{cl} \text{ ev}$$

$$\phi_B = 1.43 - E_F^i \text{ eV}$$
CHANGE IN $E_F$ FOR OXIDE AND METAL SURFACE TREATMENTS (GRANT ET AL. 1981)

GaAs (100)

$\text{Ga}_2\text{O}_3 + 25L H_2O$ gas

$\sim 0.7\text{eV}$

(SAME BASIC BEHAVIOR ON 110 SURFACE)
DEPOSITION OF METALS ON Ga₂O₃ SURFACE

ΔE_{Ga3d} = ΔE_F

KOWALCZYK, et al

Ga 3d core level

(1) INITIAL Ga₂O₃ SURFACE (LOW BAND BENDING)

(2) AFTER DEPOSITION OF SEVERAL MONOLAYERS METAL

INCREASE IN Ga3d B.E. IN EACH CASE INDICATES INCREASE OF E_F WITH METAL DEPOSITION
- low band bending, $E_F \sim 1.2$ eV, observed for $\text{Ga}_2\text{O}_3(\text{H}_2\text{O})$ covered 100 surfaces


- low band bending condition eliminated after metal deposition onto $\text{Ga}_2\text{O}_3$

- up to $\sim 0.7$ eV shift in $E_F$ 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 EF ~0.15 eV to EF(chalcogen) = ~0.85 eV. Chalcogen exposure alone does not account for low φ_B
- S and Se form ~5Å reacted region, Te is nonreactive
- Additional EF shift occurs with metal deposition onto chalcogenide surface
- Reactive metals (Al, Mn) increase EF upon metal-chalcogen reaction; nonreactive metals (Au, Ag, Pd) decrease EF
- Final EF is after metal deposition
- XPS observed range in EF is >0.5 eV
Representative I-V data for a selection of GaAs Schottky barrier contacts
Area = 5.07 x 10^{-4} cm^2
I-V data consistent with XPS E_F observations
Nonreactive metal-chalcogen contacts have higher \( \phi_b \) than reactive metal-chalcogen contacts

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# Table I

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

<table>
<thead>
<tr>
<th>Metal</th>
<th>Interface</th>
<th>n</th>
<th>$\Phi_V$ (eV)</th>
<th>$\Phi_B$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>S</td>
<td>1.05</td>
<td>0.52</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>1.5A Se</td>
<td>1.03</td>
<td>0.53</td>
<td>0.52</td>
</tr>
<tr>
<td></td>
<td>4A Se</td>
<td>--</td>
<td>~ 0.35</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>21A Se</td>
<td>1.19</td>
<td>0.48</td>
<td>0.39</td>
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<tr>
<td></td>
<td>3A Te</td>
<td>1.04</td>
<td>0.51</td>
<td>0.53</td>
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<tr>
<td></td>
<td>7A Te</td>
<td>1.06</td>
<td>0.44</td>
<td>0.40</td>
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<tr>
<td></td>
<td>22A Te</td>
<td>1.06</td>
<td>0.52</td>
<td>0.50</td>
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<tr>
<td></td>
<td>ideal</td>
<td>1.04</td>
<td>0.74</td>
<td>0.75</td>
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<td>ideal$^a$</td>
<td>1.07</td>
<td>0.85</td>
<td>0.84</td>
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<tr>
<td>Mn</td>
<td>7A Se</td>
<td>1.08</td>
<td>0.51</td>
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<tr>
<td></td>
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<td>1.03</td>
<td>0.82</td>
<td>0.82</td>
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<tr>
<td>Ti</td>
<td>11A Te</td>
<td>1.02</td>
<td>0.72</td>
<td>0.72</td>
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<tr>
<td></td>
<td>ideal$^a$</td>
<td>1.03</td>
<td>0.83</td>
<td>0.83</td>
</tr>
<tr>
<td>Au</td>
<td>$^b$</td>
<td>1.03</td>
<td>1.00</td>
<td>1.02</td>
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<td>20A Se$^b$</td>
<td>1.08</td>
<td>0.97</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>0.5A Te</td>
<td>1.03</td>
<td>0.89</td>
<td>0.87</td>
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<tr>
<td></td>
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<td>1.03</td>
<td>0.83</td>
<td>0.81</td>
</tr>
<tr>
<td></td>
<td>~ 100A Te</td>
<td>1.02</td>
<td>0.79</td>
<td>0.78</td>
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<td>ideal$^a,b$</td>
<td>1.03</td>
<td>0.69</td>
<td>0.89</td>
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<tr>
<td>Ag</td>
<td>$^b$</td>
<td>1.05</td>
<td>0.96</td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>3A Te</td>
<td>1.04</td>
<td>0.84</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>ideal$^a,b$</td>
<td>1.03</td>
<td>0.90</td>
<td>0.89</td>
</tr>
<tr>
<td>Pd</td>
<td>$^b$</td>
<td>1.04</td>
<td>0.93</td>
<td>0.94</td>
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<tr>
<td></td>
<td>ideal$^a$</td>
<td>1.03</td>
<td>0.91</td>
<td>0.93</td>
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</table>

$I-V$ and $C-V$

$\Phi_B$ range is ~0.35 eV to 1.0 eV

268 ($\sim 0.65$ 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 $\phi_B$

- XPS for $E_F$ measurement and composition analysis

- $\phi_B$ measured on thick contacts by I-V (XPS characterized interfaces)

- high temperature nonalloyed ohmic contact applications
$E_F^i$ FOR THIN (~10Å) Ge OVERLAYER ON CLEAN GaAs (100)

MAX $E_F^i$ VARIATION IS 0.75 eV

MAXIMUM $E_F^i$ IS ~1.2 eV
Representative I-V data for a selection of contacts that have a variety of structures (area = $5.07 \times 10^{-4}$ cm$^2$)

Multilayered contacts are shown on right.

For contacts with Ge interlayer, $E_F = 1.0 - 1.2$ eV before subsequent depositions.

XPS $E_F$ measurements for deposition on Ge overlayer consistent with I-V $\phi_B$ measurements.
- Low $\phi_B$ 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 $\phi_B$ ranged from 0.23 to 0.89 eV (~0.65 eV range).
Summary

- $E_F$ of $\sim 1.0 - 1.2$ eV can be obtained with Ga$_2$O$_3$(H$_2$O) overlayers, Ge(As) overlayers, and metal-chalcogen reactions.

- $\phi_B (E_F)$ variations $> 0.6$ eV can occur with interfaces that have a wide variety of compositions.

- $E_F$ 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

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Effects on Schottky Barriers of Metal Substitution in Semiconductors
E. A. Kraut\textsuperscript{1} and W. A. Harrison\textsuperscript{2}

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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.
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 substitution \(^1\)–\(^3\) and the recent Harrison-Tersoff tables of band lineups.\(^1\)

3.) E. A. Kraut and W. A. Harrison, to be published
III-V Interfaces: Schottky Barriers vs. Heterojunctions

Giorgio Margaritondo

University of Wisconsin
HETEROJUNCTION BAND LINEUPS
VS.
SCHOTTKY BARRIER HEIGHTS

What can we learn from their correlation?
Photoemission measurements of band lineups
ZnSe-Ge

$N(E)$

$E(\text{eV})$

$\Delta E_v$

a, b, c
CORRELATION BETWEEN SCHOTTKY BARRIERS AND HETEROJUNCTION BAND DISCONTINUITIES

(A NAÏVE PICTURE)
**Correlation Between Schottky Barriers & Heterojunction Band Discontinuities**

![Graph showing correlation between Trial and Error](image)

- Theory vs. Experiment
- $\Delta E_v (eV)$
- Slope $1$

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CORRELATION BETWEEN
HETEROJUNCTION BAND LINEUPS
AND SCHOTTKY BARRIER HEIGHTS
(ERENBERG, HEIBLUM, NATHAN & BRESLAIU)
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

\[ X = h\nu - D - E_g \]

\[ E_g \]

DOS

E_V  E_C

VL  Edge

Energy

EDC

hv

X

D
BREAKDOWN OF THE ELECTRON AFFINITY RULE

The Rule Predicts:

$$\Delta E_v = D_1 - D_2$$

Experimental Reality (ZnSe-Ge):

$$D_1 - D_2 = 2.21 \pm 0.46 \text{ eV}$$
$$\Delta E_v = 1.44^{+0.08}_{-0.15} \text{ eV}$$
Figure showing the energy distribution of electrons (N(E)) as a function of energy (E) for different materials. The graph includes curves for ZnSe, ZnSe+4ÅGe, ZnSe+8ÅGe, and Ge. The energy level hv=17 eV is also indicated. The inset shows a comparison of N(E) for ZnSe and Ge.
Midgap-Energy Approach
(J. Tersoff)

Semiconductor

$E_C$

$E_F$

$E_V$

Metal

$E_B$ (Midgap-Energy Point)

Metal-Induced Gap State (MIG's)

$E^1_B$

$\Delta E_V = E^1_B - E^2_B$

(Linear!)

Semiconductor-Semiconductor
HIGH-RESOLUTION ELECTRON ENERGY LOSS RESULTS:

$Si(100)7x7-Al$

(N. KELLY, G. MARGARITONDO, J. FRANKEL, G.J. LAPEYRE)

$Si(100)7x7$ is metallic; first Al adatoms make it non-metallic (GAP WIDENS)

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

$\rightarrow$ At $\approx$ 1.5 monolayer coverage:

- $E_F$ movement saturates (Schottky Barrier is formed)
- Metallic character is strong
* MIDGAP - ENERGY *

THEORY vs.  
EXPERIMENT ($\Delta E_V$)

$\Delta E_V$(eV)

Theory

Experiment

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DEFINITION OF "LINEAR" MODELS:

Band Discontinuity = \( T_i \)

\( T_i \) depends on semiconductor \( i \)

Examples:

- ELECTRON AFFINITY RULE  
  (Anderson, Duke-Mailhiot, Flores et al., etc.)

- MIDGAP-ENERGY APPROACH

- TIGHT-BINDING  
  (Harrison)

- PSEUDOPOTENTIAL  
  (Frensley-Kroemer)

- DEEP-IMPURITY APPROACH  
  (Zunger et al., Langer-Heinrich)

General Optimization: Katnani-Margaritondo
ALL THE GENERAL-PURPOSE HETEROJUNCTION DISCONTINUITY MODELS ARE

\[
\Delta E_{V}^{1,2} = T_1 - T_2
\]

(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.
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.)
MODIFICATION OF A BAND LINEUP BY A THIN INTRALAYER

\[ SiO_2 \text{ on Si (111)} \]

- Intensity

- Binding Energy, eV

- 

- Si valence edge

- SiO$_2$ valence edge

- (a) as oxidized

- (b) forming gas

- (c) chemisorption D

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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

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L. Dolittle and N. Thompson

RUMP' RES

Conven.
Metal/Si reactions

Si Ni → Si \(^{15}N\) Ni

Si \(\text{NiSi}^2\) → Si \(\text{NiSi}^2\) \(\text{Ni}^{15}\)
Energy (MeV)

Normalized Yield

3MeV He$^{++}$ 7° tilt

GaAs Co

experiment

simulation

Channel
3MeV He$^{++}$ 7° tilt

400°C 90min

Normalized Yield

Energy (MeV)

Channel

GaAs
Co

Ga
As

Co

experiment
simulation
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
Si

O impurity

Si

C.A. Crider et. al. JAP (1981)
Co/GaAs 390°C 1 hr

in-situ UHV

Concentration

Thickness (1E15 atms/cm²)
Co dominant diffusing species

Ga and As dominant diffusing species
\[
\begin{align*}
\text{Ni/GaAs} & \quad T \geq 200^\circ C & \quad \text{Ni}_{x}\text{Ga}_{2-y}\text{As}_y \\
\text{Ni}_{x}\text{Ga}_{2-y}\text{As}_y & \quad T \geq 300^\circ C & \quad \text{NiGa} + \text{NiAs} \\
& & y \approx 1
\end{align*}
\]

Lakshmi et al. (1984, 85, 86)  
Chen et al. (1985)  
T. Sando (1988)
Co/GaAs 500°C 1hr

Concentration

Depth (1E15 atms/cm²)
2 Nov 1986 12:14:44 FDIODE

-4
-5
-6
-7
-8
-9
-10
10
20
30
40
50
60
70
80
90
100
Vf (VOLT)

If (AMPS)

oJp075_15C Co/GaAs unann etched
oJp003_15C Co/GaAs 4h etched 285°C
oJp071_15B Co/GaAs 5h etched 390°C Qbm ~0.79eV n=1.04
oJp075_15A Co/GaAs 570°C 1h etched 455°C
Electrical study of Schottky diodes formed on clean cleaved III-V surfaces:

Implications to Theoretical Models

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

Stanford University

Z. Liliental-Weber and E. R. Weber

U.C. Berkeley
$I_{cm}$

A-GaAs

DOPING:

$5 \times 10^{16} / cm^3$

$n=1.05$

$V (mV)$

$I (A/cm^2)$
pinP (110)
Diodes fabricated and measured in UHV.

\( n = 1.04 \)
as

Internal Potential (eV)
Room Temp.

Au

GaAs

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

Anneal to 290°C

Au

GaAs

AuGa$_2$GeAs
$\phi_B = 0.8 \text{ eV}$

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

Au

GaAs

Still Schottky
$\phi_B = 0.8 \text{ eV}$

From Top

Au

"Flawed Au" "OHMIC"

Schottky

GaAs
Au - n GaAs ANNEALING STUDY

- 430°C
- 360°C

n-GaAs I-V

- Before Mesa Etch
- After Mesa Etch

V (mV)

I (amps)

10^-2
10^-3
10^-4
10^-5
10^-6
10^-7
10^-8
10^-9
10^-10

0 200 400 600 800

340
GaAs $\langle 110 \rangle$
Al + GaAs $\rightarrow$ Al$_x$Ga$_{1-x}$As + Ga

$\text{I} \text{ (amps)}$

$\text{V} \text{ (mV)}$

$10^{-10}$

$10^{-9}$

$10^{-8}$

$10^{-7}$

$10^{-6}$

$10^{-5}$

$10^{-4}$

$10^{-3}$

Room Temp to 800°C

$0.82\text{eV}$

$0.87\text{eV}$

$0.91\text{eV}$

$0.99\text{eV}$

$n = 1.05$
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. Ludake (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
Au dots

plan view sample

cross-section sample
Orientation relationship of Au planes with GaAs planes.
Sample cleaned in UHV with in situ Au deposition.
Annealing in \( N_2 \) for 10 min at 400 \(^\circ\)C.

\[
\begin{align*}
(\text{111})_{\text{GaAs}} &= 3.26 \text{ Å} \\
(\text{111})_{\text{Au}} &= 2.355 \text{ Å} \\
(\text{200})_{\text{GaAs}} &= 2.826 \text{ Å} \\
(\text{111})_{\text{Au}} &= 2.355 \text{ Å} \\
\end{align*}
\]

\[
5 \cdot 2.826 = 6 \cdot 2.355 = 14.13 \text{ Å}
\]
Trigonals formed in the film layer after annealing at 905°C.
Polycrystalline Au particles present inside triangular formed in Au after annealing at 401°C.
e beam parallel to [001]

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
(200) \( \text{SbAs} \) = 2.826 Å

400 \( \sigma \text{Ga}_2\text{O}_3 \) = 2.05Å \( \approx (200) \) \( \text{Rb} \) = 2.039 Å
\( \text{Rb} = 2.024 Å \)
\( \text{Ag} = 2.044 Å \)

T. Sands, J. Washburn and R. Gromby

(220) \( \text{SbAs} \) = 1.998 Å

4\( \sigma \text{Ga}_2\text{O}_3 \) = 1.45Å \( \times (022) \) = 1.442 Å
\( \text{Rb} \)
\( \text{Ag} = 1.431 \)

J.W. Evans and O.R. Monteiro

500°C to 30 Torr of oxygen
\( \text{SbAs} \rangle \text{epitaxial} \sigma \text{Ga}_2\text{O}_3 \rightarrow \text{polymer} \) \( \sigma \text{Ga}_2\text{O}_3 \rightarrow \text{polymer} / \beta \text{Ga}_2\text{O}_3 \)

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CONCLUSIONS

- SURFACE PREPARATION (PRESENCE OF OXYGEN) DETERMINED:
  - interface morphology
  - metal grain orientation-relationship with GaAs
  - formation of new phases

- CONTACT FORMATION MECHANISM:

  - Schottky contacts:
    * Au, Al and TiSi₂ 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)
SELF-ALIGNED ENHANCEMENT MODE GaAs MESFET
SIICON GATE NMOS
SELF—ALIGNED
GaAs MESFET

P—SILICON

SI GaAs
N+ IMPLANT

IMPLANT

ANNEAL CAP

ANNEAL

SELF-ALIGNED
SELF-ALIGNED ENHANCEMENT MODE GaAs MESFET

Surface Depletion
SOURCE GATE DRAIN

Gate Interaction

SI GaAs
Refractory Gate Self-Aligned MESFET

Need a gate material that:

- Can be patterned to small dimensions (< 1 μm).
- 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 ~ film thickness). Interacts strongly with GaAs above ~ 600° 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.
SIMS: Ti/W Film

As Deposited

Log_{10} Counts

Sputter Time (Seconds)

As Deposited

10/86 (T. Jackson)
SIMS: Ti/W Film

Annealed: 850° C, 15 min.
As deposited and after 850° C, 15 min. anneal
C-V: "Good" W/Si

As Deposited

Depth (µm)

Carrier Concentration (cm⁻³)

After Anneal

Depth (µm)

Carrier Concentration (cm⁻³)

Annealed: 850°C, 20 min.

~W₃Si
C-V: W Rich W/Si

Annealed: 850°C, 20 min.
C-V: Si Rich W/Si

Si Rich, After Anneal

Annealed: 850°C, 20 min.

10^18

5

2

10^17

0.0 0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16

Depth (μm)

Carrier Concentration (cm^-3)
C-V: Fe Contaminated W/Si

Approx. 1000 ppm Fe, After Anneal

Annealed: 850°C, 20 min.
**GRAPHICS PLOT**

**Variable1:**
- **VDS**: Ch2
- **Linear sweep**
- **Start**: 0.0000V
- **Stop**: 2.5000V
- **Step**: 0.0500V

**Variable2:**
- **VS**: Ch3
- **Start**: 0.0000V
- **Stop**: 0.8990V
- **Step**: 0.1000V

**Constants:**
- **VS**: Ch1 0.0000V
Short Channel Effects

![Graph showing the effect of nominal gate length on Vt for E-FET and D-FET. The graph displays a horizontal trend for both types of FETs as the gate length increases.]
"No-Channel" FET

SI GaAs
Vt for "No-channel" MESFETs

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

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<tr>
<th>Gate Length</th>
<th>Threshold Voltage</th>
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<tr>
<td>0.25 micron</td>
<td>-2.0 V</td>
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<tr>
<td>0.5 micron</td>
<td>+0.5 V</td>
</tr>
<tr>
<td>1.0 micron</td>
<td>+1.0 V</td>
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</tbody>
</table>

Companion structures with W/Si removed prior to anneal showed only small conduction even at 0.25 micron gate length.
***** GRAPHICS PLOT *****
2.2 2x10 NO CHANNEL

Variable 1:
- VDS - Ch2
  - Linear sweep
  - Start: 0.0000V
  - Stop: 2.0000V
  - Step: 0.0500V

Variable 2:
- VG - Ch3
  - Start: 0.0000V
  - Stop: -2.0000V
  - Step: -0.2000V

Constants:
- VS - Ch1: 0.0000V

4000A 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 ******

0.5x/10um  800°C-10' Anneal

4000 A  w/s:

<table>
<thead>
<tr>
<th>Variable1:</th>
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<tr>
<td>VDS - Ch2</td>
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<td>Start</td>
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<table>
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<td>Stop</td>
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<td>Step</td>
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<table>
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<tr>
<th>Constants:</th>
</tr>
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<tbody>
<tr>
<td>VS - Ch1</td>
</tr>
</tbody>
</table>

ID (mA)

1.000

.1000

.0000

397

VDS

1.2000 div (v)

.0000
**GRAPHICS PLOT**

0.5x10⁻⁶m 850°C - 6” Flash (Arsine)

4000Ω w/s:

**Variable 1:**
- VDS - Ch2
- Linear sweep
- Start: 0.0000V
- Stop: 2.0000V
- Step: 0.0500V

**Variable 2:**
- VG - Ch3
- Start: 0.0000V
- Stop: 1.0990V
- Step: 0.1000V

**Constants:**
- VS - Ch1: 0.0000V
Flash Anneal

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

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(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 W₅Si₃, not WSi₅. 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 workers¹,² 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 characteristic 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 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 ≈ 4 × 10¹⁷/cm³) by magnetron sputtering from Ti-W and Si targets. As can be seen, there is no significant change in barrier height or ideality 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 × 10¹⁷/cm² 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 As out of the GaAs 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 in ~ 4 × 10¹⁷/cm³, 15 min anneal.
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 $n \approx 2 \times 10^{17} \text{cm}^{-3}$. Some previous workers have had difficulty depositing a wide range of W-Si compositions because of stress (film failure) at some compositions. By using the 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 CF$_4$ + O$_2$ and then annealed in an anneal system that provides an arsenic overpressure to prevent GaAs decomposition.

**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 ($n = 4 \times 10^{17} \text{cm}^{-3}$).

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

**Fig. 4.** C-V carrier concentration profiling results for a W-Si film with composition near W$_x$Si on bulk-doped GaAs ($n = 2 \times 10^{17} \text{cm}^{-3}$) before and 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 $W_2Si$. Such films also show excellent $I-V$ characteristic stability, as expected. Other workers have found stable W-Si films with about 37.5–39 at. % Si ($W_2Si$). 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 $W_2Si$. We have used W-Si films with compositions near $W_2Si$ to fabricate GaAs MESFET 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 ($\sim 2 \times 10^{17} \text{cm}^{-3}$) 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 ($\sim 0.3$ 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.

It is also quite possible to have impurities present in W-Si films whose presence can have a large 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.
CONCLUSION

Stable refractory metal silicide films are important components of some high-performance self-aligned GaAs MESFET 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.

MOVPE GROWTH OF III-V MATERIALS AND INTERFACES

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Yorktown Heights, N.Y.

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

At Thermal Equilibrium

\[ \text{Ga}(v) + \frac{1}{4} \text{As}_4(v) \rightleftharpoons \text{GaAs} ; \Delta G_f \]

\[ K_{eq} = P_{Ga}^O P_{As_4}^{O \frac{1}{4}} \]

- 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.

\[ \frac{1}{P_{Ga}} \cdot \frac{1}{P_{As_4}} > \frac{1}{P_{Ga}^o} \cdot \frac{1}{P_{As_4}^o} \]

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

- Near Equilibrium - small supersaturation
  - fast reaction kinetics

  - Liquid Phase Epitaxy
    \( As(\text{solution}) + Ga(l) \rightleftharpoons GaAs(s) \)

  - Halide Growth
    \( GaCl(v) + \frac{1}{4} As_4(v) + \frac{1}{2} H_2 \rightleftharpoons GaAs(s) + HCl(v) \)

- Growth chemistry far from chemical equilibrium

  Metal-organic Vapor Phase Epitaxy
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**: $0.5 - 6.0 \mu$m/hr
- **Gas Composition**:
  - Metal-Organic: $X_{\text{MO}} \approx 10^{-3} - 10^{-4}$
  - Hydride: $X_{\text{hydride}} \approx 5 - 100X_{\text{MO}}$
- **Pressure**: $0.01 - 1$ atm
- **Growth Temperature**: 550-800°C
- **Carrier Gas**: H$_2$, N$_2$, ...

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10/86 (T.F. Keesch)
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

<table>
<thead>
<tr>
<th>Cation Source</th>
<th>Anion Source</th>
<th>Compound Semiconductor</th>
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<tbody>
<tr>
<td>Ga(CH₃)₃</td>
<td>AsH</td>
<td>GaAs</td>
</tr>
<tr>
<td>Ga(C₂H₅)₃</td>
<td>AsH(C₂H₅)₂</td>
<td>Al₂Ga₁₋ₓAs</td>
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<tr>
<td>Al(CH₃)</td>
<td>PH₃</td>
<td>GaAsₓP₁₋ₓ</td>
</tr>
<tr>
<td>Al(C₂H₅)₃</td>
<td>(CH₃)₂PH₂</td>
<td>AlₓGa₁₋ₓP</td>
</tr>
<tr>
<td>In(CH₃)</td>
<td>Sb(CH₃)</td>
<td>InₓGa₁₋ₓSb</td>
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Temperature Dependence

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

Phase Equilibrium

\[ \text{Ga(v)} + \left\{ \frac{1}{4} \text{As}_4 \text{ or } \frac{1}{2} \text{As}_2 \right\} \rightleftharpoons \text{GaAs(s)} \]

Chemical Equilibrium

\[ \text{Ga(CH}_3)_3 + \text{AsH}_3 \rightleftharpoons \text{GaAs(s)} + \text{CH}_4(v) \]

- 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

\[ \frac{1}{2} \text{As}_4(v) \rightleftharpoons \text{As}_\text{As} + \text{As}_\text{Ga} \]

\[ K_{eq} = [\text{As}_\text{Ga}]P_{\text{As}_4}^{-\frac{1}{2}} \]

\[ [\text{EL2}] = [\text{As}_\text{Ga}] \propto P_{\text{As}_4}^{-\frac{1}{2}} \]

Growth Environment Interactions

Hetero-interfaces

III-III'  V-V'

- residence time  • kinetics of hydride decomposition
- lattice matching  • thermodynamics
- large V partial pressures  • residence time
- lattice matching
Ill-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, $\tau$, of the reactants in the reactor
  - interface width, $\Delta w$
    $\Delta w = GR \times \tau$
  - growth interruption; impurity accumulation at the interface

- Lattice mis-matched systems
  - 3-D or island nucleation
  - dislocations
Al$_x$Ga$_{1-x}$As-GaAs Interfaces

Deep Level and Defects

$$xAl(v) + (1 - x)Ga(v) + \frac{1}{4}As_4(v) \rightleftharpoons Al_xGa_{1-x}As ; \Delta G_f$$

$$|\Delta G_f^0(ALAs)| > |\Delta G_f^0(GaAs)|$$

$$P_{Al}^0 P_{As_4}^0 \frac{1}{4} < P_{Ga}^0 P_{As_4}^0 \frac{1}{4}$$

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

V-V' Hetero-interfaces

Growth Environment

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

Heterojunction Formation

- Rapid switching of all components
- Interface width, $\Delta w$, is determined by the residence time of reactants:
  $$\Delta w \approx GR \times \tau$$
- Interface structure may reflect changes in the local activity of the group V components.
Thermodynamics

\[ G_2(T) + \frac{1-x}{4} P_4 + \frac{x}{4} As_4 \rightleftharpoons GaAs_xP_{1-x}; \Delta G_f(T) \]

\[ \frac{\frac{x}{P_{As_4}} \frac{1-x}{P_{P_4}}}{a_{GaAs_xP_{1-x}}} = K(T) \]

Kinetics at the Growth Surface

\[ 4AsH_3 \xrightarrow{k_A} As_4 + 6H_2 ; k_A(T) \]

\[ 4PH_3 \xrightarrow{k_P} P_4 + 6H_2 ; k_P(T) \]

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

$G_2(CH_3)_3 + x PH_3 + (1-x) AsH_3 \rightarrow G_2 As_{1-x} P_x$

Influence of Alloy Composition

→ Influences Decomposition Rate
→ Thermodynamic Influences

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**InGaAsP/InP Heterostructures**

**Multi-Quantum Wells**
M. Razeghi, J.P. Duchemin, J.C. Portal

**Shubnikov-de Haas Oscillations**
\[ n_{2D} = 4.2 \times 10^{11}\text{cm}^{-2} \]

**Growth Conditions**
- Low Growth Rate \( \sim 3 \text{ Å/sec} \)
- High Gas Velocity
- Continuous Growth
  - residence time of gases \( \sim 1\text{sec} \)

**IBM**

06/86 (T.F. Kuech)
GaAs$_y$Sb$_{1-y}$ - Metastable Compositions


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10/86 (T.F. Kuech)
Growth of GaAs$_y$Sb$_{1-y}$

Input Reactants Decomposed at the Growth Front

\[ P_{Ga(C_2H_5)_3} \approx P_{Ga}, P_{As(CH_3)_3} \approx P_{As}, P_{Sb(CH_3)_3} \approx P_{Sb_4}, \]

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

\[ \frac{a_{GaAs}^s}{P_{Ga}^o P_{As}^o \frac{1}{4}} = K_{GaAs} \]

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

\[ \frac{a_{GaSb}^s}{P_{Ga}^o P_{Sb_4}^o \frac{1}{4}} = K_{GaSb} \]

Composition:

\[ y = \frac{P_{As}^o - P_{As_4}}{(P_{As_4} - P_{As_4}^o) + (P_{Sb_4} - P_{Sb_4}^o)} \]

Stoichiometry:

\[ (P_{Ga} - P_{Ga}^o) = 4 (P_{As_4} - P_{As_4}^o) + 4 (P_{Sb_4}^o - P_{Sb_4}) \]

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4/2
Growth of GaAs from $\text{Ga(CH}_3\text{)}_3$ and $\text{AsH}_3$

$$\text{Ga(CH}_3\text{)}_3 + \text{AsH}_3 \rightarrow \text{GaAs} + 4\text{CH}_4$$

![Graph showing normalized intensity of C-peak (A.U.) against AsH$_3$ to TMG ratio.](image)

Normalized intensity of C-peak (A.U.)

AsH$_3$ TO TMG RATIO

$N_{\text{carbon}}$ increases with $T_{\text{growth}}$

- decreases with $P_{\text{arsine}}$
- increases with As surface site density


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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.
Ethyl Based MOVPE Growth

Possible Reaction Paths:

\[ 2C_A + \frac{5}{2}H_2 \]

\[ \text{Ga - } C_2H_3 \rightarrow + \text{AsH}_{3-x}(\text{ad}) \rightarrow C_2H_x^\dagger + \text{AsH}_{2-x}(\text{ad}) \]

\[ C_2H_x^\dagger + H(\text{ad}) \]

The use of larger hydrocarbon radicals:

1. weakens the metal-carbon bond

2. introduces new reaction paths for decomposition and carbon elimination.
Model of Carbon Incorporation for Methyl Based Growth of GaAs

1. Adsorption of CH\textsubscript{3} on As atoms

2. Adsorption of AsH\textsubscript{2-1} on Ga atoms

3. Hydrogen Transfer Reaction
\[ \text{CH}_3(\text{ad}) + \text{AsH}_2 \rightarrow \text{CH}_4(\text{ad}) + \text{AsH}_2(\text{ad}) \]

4. Desorption of CH\textsubscript{4}
\[ \text{CH}_4(\text{ad}) \rightarrow \text{CH}_4(\text{g}) \]

\[ \text{Ga} \text{(CH}_3 \text{)}_2 + \text{AsH}_3 \rightarrow \text{GaAs} + \text{CH}_4 \]
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.

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,

\[ J_{\text{dopant}} \propto J_{\text{Ga}} \rightarrow \Delta n \propto \Delta \left[ \frac{J_{\text{dopant}}}{J_{\text{Ga}}} \right] \]
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.
Studies of Buried Interfaces

using

Total External Reflection of X-Rays

and

Extended X-Ray Absorption Fine Structure

EXAFS

Bruce A. Bunker
Notre Dame
EXAFS
Extended X-Ray Absorption Fine Structure

Incident X Ray

Interference Modulates X-Ray Absorption Coefficient

Absorption Coefficient

Distance

# Neighbors, Types of Neighbors

Type of Atom

X-Ray Energy

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

43c
EXPERIMENTAL METHODS

(1) TRANSMISSION

![Diagram of transmission setup]

\[ \mu \sim \text{#Core Holes Produced as a Function of X-Ray Energy} \]
Creation & Decay of Core Holes

Absorption
Creation 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

- Tetrahedral Interstitial Site
- First Shell Expands 0.10±0.05Å
- Second Shell Contracts 0.07±.06Å

Precision measurement:
Beats in EXAFS Amplitude yield Distance Difference $R_2 - R_1$

If Undistorted: 0.35Å
We Find: 0.18±0.03Å

Excellent Agreement With Theory: Zunger, et al.: 0.17Å
--- agreement within 0.01Å!
Total External Reflection of X Rays...

Incident Beam  Reflected Beam

Sample

X-Ray Penetration Region

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

In X-ray region, index of refraction $n < 1$

$\rightarrow$ total external reflection possible for grazing incidence

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

--- Surface Sensitivity
Total External Reflection + Fluorescence Detection = Surface Sensitivity

Ion Chamber

Fluorescence Radiation -> Incident X-ray Beam

Reflected Beam

Probe Local Environment within ~10 Å of Surface

MUCH MORE SENSITIVE THAN "SEXAFS"

\( \rightarrow 0.01 - 0.001 \) MONOLAYER DETECTABLE
Low-Z Overlayers
e.g. Al on GaAs

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

-- Sensitive to As atoms within
~10Å of Buried Interface

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

GaAs, MBE GROWN
500 Å AL DEPOSITED IN-SITU

(1) 500°C DEPOSITION TEMP.
(2) 90°C

FRANK CHAMBERS
AMOCO RESEARCH LABS
NAPERVILLE, IL
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
  - 0.01 Monolayer
- Probe Buried Interfaces

Study Atomic Environment for Atoms Within \( \sim 10 \, \text{Å} \) of Interfaces

Around Each Species

- Types of Neighbors
- Number of Neighbors
- Bond Lengths
Composition Dependence of Metal In$_x$Al$_{1-x}$Al 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

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

$\Phi_{bn} = 0.8 \text{ eV}, \text{ C-V}$

$\Phi_{bn} = 0.6 \text{ eV}, \text{ internal photoemission}$

MBE grown, $T_s < 530^\circ \text{C} \sim \text{semi-insulating}$

445
CL peak energies as a function of In$_{1-x}$Al$_x$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.
Lattice Mismatch, $\Delta a/a_0$.

Lattice Matched to InP

$X$ values: 0.40, 0.50, 0.60.
Lattice Matched to InP
In$_x$Al$_{1-x}$As

$\Phi_{an} = 2.46 - 3.16 \times \ x \quad (x > 0.42)$

$\Phi_{an} (AlAs) = 1.2 \text{ eV} \quad \text{(measured)}$

$\Phi_{an} (x = 0.32) = 1.45 \text{ eV} \quad \text{(extrapolated)}$

$\Phi_{an} (x = 0.78) = 0$

$\Phi_{an} (x > 0.78) = \text{inverted surface}$
(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.
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

\[ \text{Al}_{x}\text{Ga}_{1-x}\text{As} \quad \text{n}^+ \text{GaAs} \quad \text{AuGeNi} \]

\[ \text{n}^+ \text{InAs} \quad \text{n}^+ \text{InAs} \quad \text{WSi}_x \]

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

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

![Non-Abrupt Interface Diagram]

abrupt junction: InAs/GaAs

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

![Graph showing $m^*$ versus doping concentration](image)

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

![Graph showing doping concentration versus electrically active concentration](image)
InAs bulk Fermi level

Fermi level (meV)

electron concentration (cm\(^{-3}\))
InAs/GaAs
300 K

\[ L_c = \left( \frac{\Delta E_c}{kT} \right) \cdot L_D \]

\[ \Delta E_c = 0.9 \text{ eV} \]

\[ \Delta E_c' \sim 50 \text{ meV} \]

\[ \Delta E_c = 0.5 \text{ eV} \]

eff. \( \phi_b = 2 \text{ kT} \)

\[ \Delta E_c' \sim 200 \text{ meV} \]

assuming
\[ \Delta E_c' \propto \frac{1}{L} \]
Transmission Line Structures
Resistance (ohms) vs. Gap Spacing (microns)

- W (µm) = 20
- R₀ (Ω/Ω) = 439 10
- R₁ (Ω-mm) = .25 .02
- L (µm) = .56 .04
- R₂ (Ω-cm²) = 1.37E-06 1.79E-07

Linear corr. coeff. = .99923

Note: The diagram includes a graph with data points and a legend indicating the materials used: VB44 200A etch, abrupt, Se17 GaAs, 1s 880 C anneal.
**Abrupt Structures: typical results**

<table>
<thead>
<tr>
<th>Sample</th>
<th>GaAs doping</th>
<th>$R_s$($\Omega$-mm)</th>
<th>$\rho_s$($\Omega$-cm$^2$)</th>
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<tbody>
<tr>
<td>V671</td>
<td>$2 \times 10^{17}$</td>
<td>0.47</td>
<td>$9 \times 10^{-6}$</td>
</tr>
<tr>
<td>300Å n+InAs</td>
<td>850°C, 3 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V844</td>
<td>$5 \times 10^{17}$</td>
<td>0.3</td>
<td>$1 \times 10^{-6}$</td>
</tr>
<tr>
<td>200Å n+InAs</td>
<td>880°C, 1 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V917</td>
<td>$1 \times 10^{18}$</td>
<td>0.17</td>
<td>$2.6 \times 10^{-6}$</td>
</tr>
<tr>
<td>300Å n+InAs</td>
<td>750°C, 5 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>850°C, 18 sec</td>
<td>0.23</td>
<td>$2.2 \times 10^{-6}$</td>
</tr>
</tbody>
</table>
V903 1B3
n+ InAs on pl
18s 850 C anneal

gap 2.1 2.6 3.7 4.6 5.7 6.7 ll .0
R 11.7 14.7 17.3 20.4 24.2 27.6 ll .0

1108 5-SEP-90

Resistance (ohms)

Gap Spacing (microns)

W (μm) = 30
R_b (Ω/Ω) = 102 2
R_l (Ω-mm) = .07 .00
L_l (μm) = .70 .04
R_c (Ω-cm²) = 5.07E-07 5.72E-08
lin. corr. coeff. .99941
**Metal/InAs interfacial contact resistance**

ex) V903: 500Å n+ InAs/π GaAs buffer

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>$R_s$(Ω-mm)</th>
<th>$\rho_c$(Ω-cm$^2$)</th>
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<tbody>
<tr>
<td>as-grown</td>
<td>0.07</td>
<td>3-5×10$^{-7}$</td>
</tr>
<tr>
<td>650°C, 5 min</td>
<td>0.06</td>
<td>3.6×10$^{-7}$</td>
</tr>
<tr>
<td>750°C, 5 min</td>
<td>0.06</td>
<td>3.3×10$^{-7}$</td>
</tr>
<tr>
<td>850°C, 5 min</td>
<td>0.09</td>
<td>2.3×10$^{-7}$</td>
</tr>
<tr>
<td>850°C, 18 sec</td>
<td>0.07</td>
<td>4.0×10$^{-7}$</td>
</tr>
</tbody>
</table>

- finite WSi/InAs interface resistance
  $\rho_c \leq 5 \times 10^{-7}$ Ω-cm$^2$

- NOT a limiting factor in most cases
Graded Structures: typical results

0.2μm $1 \times 10^{18}$ GaAs channel/ graded layer/ 200 Å n+ InAs

contact layer etched down to channel in gap regions.
5 min. 750 °C arsine anneal

<table>
<thead>
<tr>
<th>sample</th>
<th>$R_i(\Omega/\square)$</th>
<th>$R_i(\Omega$-mm)</th>
<th>$\rho_e(\Omega$-cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V914 as-grown</td>
<td>213</td>
<td>0.09</td>
<td>$4 \times 10^{-7}$</td>
</tr>
<tr>
<td>600Å grade</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V914 annealed</td>
<td>458</td>
<td>1.0</td>
<td>$2 \times 10^{-5}$</td>
</tr>
<tr>
<td>V907 as-grown</td>
<td>192</td>
<td>0.08</td>
<td>$3.5 \times 10^{-7}$</td>
</tr>
<tr>
<td>320Å grade</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V907 annealed</td>
<td>209</td>
<td>0.19</td>
<td>$1.7 \times 10^{-6}$</td>
</tr>
<tr>
<td>V905 as-grown</td>
<td>207</td>
<td>0.09</td>
<td>$4 \times 10^{-7}$</td>
</tr>
<tr>
<td>180Å grade</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V905 annealed</td>
<td>176</td>
<td>0.07</td>
<td>$3 \times 10^{-7}$</td>
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</tbody>
</table>
HBT characteristics

vertical npn structure on n+ substrate
25 µm diameter emitter
WSi/InAs self-aligned ohmic contact
p+ implant; 850 °C, 2-3 s anneal
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: $\Delta E_c$ (InAs/GaAs) $\sim$ 0.5-0.6 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: $\rho_c \sim 1-5 \times 10^{-5}$ $\Omega$-cm$^2$ (non-linear)
  annealed: $\rho_c \sim 1 \times 10^{-6}$ $\Omega$-cm$^2$, ($R_t \leq 0.3$ $\Omega$-mm)
- WSi/InAs interfacial resistance: $\rho_c \leq 5 \times 10^{-7}$ $\Omega$-cm$^2$
- as-grown graded structures have low contact resistance
  $\rho_c \leq 4 \times 10^{-7}$ $\Omega$-cm$^2$, $R_t \leq 0.1$ $\Omega$-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.
$E_F$

Metal

Semiconductor (n-type)

$\phi_n$

475
Schottky (1940)

\[ \Phi_b = \text{metal work function} \]
\[ - \text{semiconductor } e \text{ affinity} \]

Terrible

Fermi level "pinned"
BARDEEN (1947)

$E_F$

\[ d \rightarrow \infty \quad 10^{12} \text{ states/cm}^2 \text{ will pin } E_F \\
\]
\[ d \rightarrow 0 \quad \text{need } 10^{14} \]

Cf. true interface: "MIGS" etc.


HEINE (1965)  
LOUIS et al. (1976)  
TEJEDOR et al. (1977)  
TERSOFF (1984)
WHAT IS $\phi_0$? \implies WHAT IS $\varepsilon_{ss}$?

APPELBAUM + HAMANN (1974):
ROLE OF SELF-CONSISTENT DIPOLE
Real $k$  Imaginary $k$
SURFACE VS. INTERFACE

TEJEDOR & FLORES (1978)

SURFACE STATES AND INTERFACE STATES (HIGGS) BOTH MN E_F AT E_B
GENERALIZE TO 3-D, HETEROPOlar

\[ \phi_{b_p} + \phi_{b_m} = E_g - E_g^s \]

FOR BARE SURFACE,

ADDING METAL BROADENS STATES (MIGS).

THEN \( E_g^s \to 0 \), \( E_F \) PINNED MIDWAY,

\[ E_F \to E_x \]
POSSIBLE INTERPRETATION OF STANFORD EXPERIMENTS

GaAs (110)

UNBUCKLED

METALLIZED
PREDICTING SCHOTTKY BARRIERS

- At bare surface, surface state pin $E_F$ around effective gap center $E_g$ (Bardeen, Appelbaum & Hamann)

- At metal-semiconductor interface, surface states hybridize with metal states, become "migs"; $E_F$ still pinned near $E_g$

- Calculate $E_g$
Generalize to three dimensions

\[ G(\vec{r}, E) = \int d^3 r \sum_{nk} \frac{\psi^*(\vec{r}) \psi(\vec{r} + \vec{R})}{E - E_{nk}} \]

\[ = \sum_{nk} \frac{e^{i\vec{k} \cdot \vec{R}}}{E - E_{nk}} \]

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
REAL SEMICONDUCTOR

LINE UP "CENTER" OF GAP

WHERE IS CENTER?
Effective gap center

\[ E_0 = \frac{(\bar{E}_v + \bar{E}_c)}{2} \]
\[ \bar{E}_v = E_v - \Delta/3 \]
\[ \bar{E}_c = E_v + E_g^i \]
\[ \bar{E}_b = E_0 - E_v = \frac{1}{2}(E_v - \Delta/3 + E_v + E_g^i) - E_v \]
\[ = \frac{1}{2}(E_g^i - \Delta/3) \]

need some adjustable parameter

\[ \Rightarrow E_b = \frac{1}{2}(E_g^i - \Delta/3) + \delta_m \]
\[ \delta_m = -0.20 \text{ eV} \]
\[ \text{rms} = 0.07 \text{ eV} \]
\[ \max = 0.13 \text{ eV} \]
\[ S = \frac{d\phi_{bm}}{d\gamma_m} \]
\[ \bar{S} = S/A \quad A \approx 2.8 \text{eV} \]
\[ \Delta \phi_{bm} = S \Delta \gamma_m = A \Delta \gamma_m / \epsilon_{\text{eff}} \]
\[ \Rightarrow \bar{S} = \frac{1}{\epsilon_{\text{eff}}} \]
\[ 0 \leq \bar{S} \leq \frac{1}{\epsilon_{\text{oo}}} \quad \text{guess} \quad \bar{S} = \frac{1}{\epsilon_{\text{oo}}} \]
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.
  [SCHRODINGER 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!

\[
E_F \quad \text{METAL} \quad n\text{-GaAs} \quad 300\AA
\]

IDEAL INTERFACE: \( \Phi_b \to \text{TRANSPORT} \)
OTHER POSSIBILITIES.
SIMPLE EXAMPLES

\[ p^+ \quad n \quad \phi_b \quad \phi_{\text{exp}} \]

\[ n^+ \quad \phi_b \quad \text{CHMIC} \]
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.

\[ \Delta E_v = \Delta E_B = 1 \text{ eV}. \]
SUMMARY

- INTRINSIC SURFACE OR INTERFACE STATES PIN $E_F$ NEAR $E_B$
- EXCELLENT AGREEMENT WITH EXP
- $E_B \sim \frac{1}{2} E_0$
- METAL DEPENDENCE: $S \sim \frac{1}{2}E_0$
- DIRECT CONNECTION WITH BAND LINEUPS
- EVIDENCE AGAINST EXTRINSIC MECHANISM

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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
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</tr>
</tbody>
</table>
TRANSPORT IN SCHOTTKY BARRIER FORMATION WITH CHEMICAL REACTIVITY

![Graph showing barrier formation with chemical reactivity]

- SAME TRANSITION FOR IONIC AND COVALENT SEMICONDUCTORS
- TRANSITION AT EXPERIMENTALLY DETERMINED $\Delta H_R$

L.J. Brillson
STOICHIOMETRY OF OUTDIFFUSION

vs

SCHOTTKY BARRIER HEIGHT

STRENGTH OF INTERFACE CHEMICAL BONDING
DETERMINES ELECTRICITY - ACTIVE SITES (III-V's)
Thermal Cleaning of As-"Capped"

$\text{In}_x\text{Ga}_{1-x}\text{As}(100)$

As "Cap"

0.75 $\mu$m

$\text{InGaAs:Si}$ $5 \times 10^{16} \text{ cm}^{-3}$

$\text{InGaAs:Si}$ $1 \times 10^{19} \text{ cm}^{-3}$

$\text{GaAs:Si}$ $1 \times 10^{19} \text{ cm}^{-3}$

$\text{GaAs:n}^+$

Woodall, Pettit, Kirchner, & 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 UHV
Interface Dissociation

Interface Dissociation

\[ \text{In}_{0.75}\text{Ga}_{0.25}\text{As}(100) + \text{Au} \]

- 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

In\textsubscript{0.75}Ga\textsubscript{0.25}As(100) + Al

- Al replaces In in In\textsubscript{2}As Lattice
- No Ga dissociation
- \( \varepsilon_F \) 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

\( \Rightarrow \text{KINETIC LIMITATION TO REPLACEMENT REACTION} \)

- Higher proportion of Surface As
Metal–Semiconductor Interface Composition

\[ \text{Au} \quad \text{As-Deficient} \leftarrow \text{As-Rich} \]
\[ \varnothing \sim \varnothing_{\text{Au}} \quad \varnothing \sim \varnothing_{\text{As}} \]

\[ \text{In} \quad \text{As-Rich} \leftarrow \text{As-Deficient} \]
\[ \varnothing \sim \varnothing_{\text{As}} \quad \varnothing \sim \varnothing_{\text{In}} \]

\[ \text{Al} \quad \text{As-Rich} \leftarrow \text{As-Deficient} \]
\[ \varnothing \sim \varnothing_{\text{As}} \quad \varnothing \sim \varnothing_{\text{Al}} \]

\[ \text{InAs} \quad \text{In}_{x}\text{Ga}_{1-x}\text{As} \quad \text{GaAs} \]

509
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"  
  \textbf{45}, 1458 (1984)

- Regular Trends Across Alloy Series

- Tracking With Conduction Band

- Air-Exposed Surfaces: Different
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

AIR-EXPOSED InAs (100) + Au

- 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 ($h\nu > 0.6eV$)
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

- 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

<table>
<thead>
<tr>
<th>Metal</th>
<th>Schottky Barrier</th>
<th>( E_G - h\nu_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au, Cu</td>
<td>(~ 0.5 \text{eV})</td>
<td>(0.57 \text{ eV})</td>
</tr>
<tr>
<td>Al</td>
<td>(0-0.25 \text{eV})</td>
<td>(0, 0.2-0.5 \text{ eV})</td>
</tr>
</tbody>
</table>

GaAs (110) n-type

<table>
<thead>
<tr>
<th>Metal</th>
<th>( E_G - h\nu_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>(0.8-0.9 \text{eV})</td>
</tr>
</tbody>
</table>
CONCLUSIONS

- Metal dependent chemical trends across In$_x$Ga$_{1-x}$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

Antisites
Vacancies
Dangling bonds
Extrinsic
MIGS
Fermi-level pinning
Defects

R.E. Allen
O.F. Sankey

ND
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
- O.F. Sankey
Dependence on contact
Surface Fermi Energy (eV)

Conduction

In contact
Al contact
Au contact

AlAs GaAs
Alloy composition
GaAs

\[ \text{Ga}_{\text{As}} \quad \text{As}_{\text{Ga}} \quad \text{DATA} \]
Explanations:

1. # Donors ≈ # Acceptors (Mönch)
   \[ \text{or} \]
   \[ \# \text{Ga}_{\text{As}} \approx \# \text{As}_{\text{Ga}} \]

2. Chemisorption defect ≠ cleavage defect (Mönch)
   \[ \text{Ga}_{\text{As}} ≠ \text{As}_{\text{Ga}} \]

3. Abrupt change of barrier at \( T_{\text{anneal}} \) (antisite); (Mönch)
   a) p-barrier --- \( \text{As}_{\text{Ga}} \)
   b) n-barrier remains --- \( \text{Ga}_{\text{As}} \)

4. Surface levels ≠ bulk levels
All impurities produce
a) $\infty$ 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

$\begin{align*}
T_2(p) \\
A_1(s)
\end{align*}$

DEEP IMPURITY

$\begin{align*}
T_2(p)
\end{align*}$
Surface levels ≠ bulk levels
Surface Ga site: Doping anomaly

\[ \text{Al, Si, P, S, Cl, O} \]

Accepter!
PART II:
Si/Transition-metal silicide
Schottky barriers

O.F. Sankey, R.E. Allen, + J.D. Dow

FACTS:

(A) On \( \sim \) 1 eV scale, barrier is independent of
i) transition metal (Ni, Pt, Pd)
ii) crystal structure (NiSi, NiSi\(_2\), NiSi\(_3\))
iii) Si surface
iv) stoichiometry

(B) On \( \sim \) 0.1 eV scale barrier depends on
i) transition metal (\( \sim \) \( e_{\text{atomic}} \))
ii) crystal structure

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

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

(E) Si is similar to III-V's.
No crossing makes level independent of Ni, etc.
CONDUCTION

\[ V_{s_i}(T_2) \]

VALENCE

\[ V_{s_i}(A_i) \]
Schottky barriers in silicides

(Si$_2$Ni)
Silicide

Missing Si bridge

$Ni -$ = Si + V
Si/T-metal silicide Schottky barriers $\phi$

1. $\phi$ independent of T-metal on 1 eV scale ($\text{Ni, Pt, Pd}$)
2. $\phi$: chemical trends with T-metal on 0.1 eV scale
3. < 1 monolayer of T-metal gives $\phi$
4. $\phi$: independent of crystal structure (on > 0.1 eV scale): $\text{NiSi, NiSi}_2, \text{Ni}_2\text{Si}$
5. $\phi$: independent of stoichiometry, Si surface (on > 0.1 eV scale)
6. $\phi_n + \phi_p \approx E_{\text{gap}}$
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
Direct Measurements of Electronic States at Metal/GaAs Interfaces

Paul Ho
IBM - Yorktown Heights
SCHEMATIC PRESENTATION OF 
Al/Pd$_2$Si/Si REACTION

a) INITIAL STAGE

b) INTERMEDIATE STAGE

c) FINAL STAGE
Fig. 7. Comparison of the rates of Pd$_2$Si dissociation in Al/Pd$_2$Si/Si contacts for polycrystalline Pd$_2$Si 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$_2$Si. 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.

MgGaAs 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
PHOTOEMISSION FROM LASER EXCITED INTERFACES AND SURFACES
PM41E AV 0.5 - 1 PICOSECOND
IOILN CRYSTAL 0.2-5 ow
GRTMNU6 TLI IESOLVD £Im AMLYSIGI SGI AV GEEATO

PULSED LASER
TIME RESOLVED
PHOTOEMISSION SYSTEM

DYE AMPLIFIER
VARIABLE DELAY
0.2-5 ev
PER PHOTON
DOUBLING CRYSTAL
8-15 ev
PER PHOTON
XUV GENERATION CHAMBER
SAMPLE
TIME OF FLIGHT
ELECTRON SPECTROMETER
UHV ANALYSIS CHAMBER

5.57
1.0
0.8
0.6
0.4
0.2
0.0

ENERGY (eV)
0.0 0.5 1.0 1.5 2.0

EMISSION INTENSITY (RELATIVE UNITS)

VBM
CBM
Clean
photocreated
(a)
0.1 ml Au
(b)
photocreated
0.35 ml Au
(c)
photocreated
0.1 ml Au
unexcited
(d)
R. HAINIT
J. Chem.
PRL
SCL 2846 (786)
In depth distribution — freq.

Interface — optical discontinuity

Experimental Arrangement and Physical Principle
of Photothermal Displacement Spectroscopy
Sources of Optical Heating

Non-Radiative Processes:

- Carrier thermalization $\rightarrow$ lattice heating
  - Employed to measure minute optical absorption ($\alpha L \sim 10^{-7} - 10^{-8}$)

- Non-radiative carrier recombination
  yields carrier mobility and lifetime; dynamics
Spatially-Resolved Photothermal Probing of Carrier Transport

Signal = Thermal term + minority carrier term
        ↓                  ↓
        dominant         dominant
        at low frequencies at high frequencies

Can measure minority carrier lifetime and diffusion length (on the μm scale)
Photothermal Scans of GaAs Wafer
Showing Arsenic Inclusions
SILICIDE n-SILICON

ELECTRON

FORWARD BIAS V

HOLE

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.

![Graph showing capacitance vs voltage for Ni/n-Si diodes at different temperatures: TYPE B 250°C and TYPE B 450°C.](image)
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. Schäffler
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
- m-s interface

$$(2q\varepsilon N_d V)^{\frac{1}{2}} \leq Q_i \leq \frac{\varepsilon V}{4\pi d}$$

$$10^{12} \leq Q_i \leq 10^{14} \text{ e cm}^{-2}$$

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
  - \( \phi \) (anion) is relevant parameter
  - presence of anion clusters at interface

- Metal Induced Gapstates
  - metal independent
  - requires delocalized states (metal)
If $N(E)$ represents the photoemission spectrum, with core levels and $E_F$ indicating the Fermi level. The relationship $E = KE - h\nu$ is also shown, where $h\nu$ represents the energy of the incident photon.
I.

II

III

V

on GaAs(110) As-3d

X2.5

10 A

X1.5

3.0 A

1.0 A

0.05 A

Clean

INTENSITY (ARBITRARY UNITS)

KINETIC ENERGY (eV)

575
Pd ON GaAs(110)

3-d CORE LEVEL SHIFTS

CHANGE IN KINETIC ENERGY (eV)

Pd THICKNESS (ANGSTROMS)

Ga-3d
As-3d
GaAs
GALLIUM
ARSENIDE

BULK SENS.
SURF. SENS.
Mn on n-GaAs(110)

Ga-3d
As-3d

E_{kin} (eV)

0.5 Å
1 Å
3 Å

It=70eV
hw=90eV
1.4

1.2 Mn on GaAs(110)

V on GaAs(110)

Ga-peak(n)

Ga-peak(p)

0.6

0.4

0.2

0.0

ENERGY ABOVE VBM (eV)

10^{-3} 10^{-2} 10^{-1} 1

V COVERAGE (Angstroms)

Mn on GaAs(110)

Ga-bulk peak(n)

Ga-surf peak(n)

Ga-bulk peak(p)

Ga-surf peak(p)

10^{-3} 10^{-2} 10^{-1} 1 10

Mn COVERAGE (Angstroms)
FERMI LEVEL AT GaAs(110) INTERFACE

METAL COVERAGE (Å)

ENERGY (eV)

CB

VB

10^{-3}  10^{-2}  10^{-1}  10^0  10^1  10^2

1.2  1.0  0.8  0.6  0.4  0.2

Ti  Pd  Ag  Y  V  Mn  Ag  Pd  chemistry
0.24 Å Ti on GaAs(110) A

Emission intensity (arb. units)

Energy relative $E_{VBM}$ (eV)

bonding  non-bonding  anti-bonding
GaAs(110) + V

$E_i = 15.25$ eV

$k \parallel = 0$

NORMALIZED PHOTON INTENSITY (ARBITRARY UNITS)

ENERGY (eV relative to $E_{VBM}$)

Clean

6.3 A

2.5 A

1.6 A

0.8 A

0.23 A

0.05 A
NORMAIZED PHOTON INTENSITY (ARBITRARY UNITS)

ENERGY (eV relative to $E_{\text{vac}}$)

-2
0
5
10
15
20
25

0.05 A
0.23 A
0.8 A

clean

EF

1.39 eV

GaAs(110) + V
GaAs(110)

0.2 A Ti  VB  CB  $E_F$

0.2 A V

0.2 A Pd

ENERGY RELATIVE $E_{VBM}$ (eV)

INTENSITY (ARB. UNITS)
GaAs(110) valence band difference

\[ E_F \]

ENERGY RELATIVE TO \( E_F \) (eV)
Bulk  
\text{Td}  

\begin{align*}
\text{Ti-3d} & \quad t_2^2 \\
\text{sp}^3 (\text{As}) & \quad a_1 \\
\end{align*}

\begin{align*}
E_g & \quad a \\
E_v & \quad 3 \text{sp}^3 (\text{As}) \\
\end{align*}

GaAs  

\begin{align*}
E_g & \quad a \\
\end{align*}

Surface  
\sim \text{C}_{3v}
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

\[ \hbar \omega = 180 \text{ eV} \]

\[ \hbar \omega = 70 \text{ eV} \]

\[ 3 \text{Å Mn} \]

\[ 1 \text{Å Mn} \]

\[ 0.4 \text{Å Mn} \]

\[ 0.01 \text{Å Mn} \]

\[ \text{clean} \]

\[ E_{\text{kin}} \text{ (eV)} \]

588
V on n-InP

Valence band difference spectra

\( \omega = 90 \text{eV} \)

Normalized intensity (arb. units)

ENERGY (eV relative to \( E_f \))

\( VBM \)

\( E_f \)

\( 0.2 \text{A} \)

\( 0.05 \text{A} \)

\( 0.02 \text{A} \)

\( 0.005 \text{A} \)

\( \text{clean} \)
Comparison of spectral peaks + substitutional impurity levels

Present data

<table>
<thead>
<tr>
<th>bulk impurity levels</th>
<th>GaAs</th>
<th>InP</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.30</td>
<td>1.40</td>
</tr>
<tr>
<td>Ti</td>
<td>0.50</td>
<td>0.45</td>
</tr>
</tbody>
</table>

V

| D  | 0   | 0   |

Mn

| D  | (-1) | -4  |

* 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
TIGHT-BINDING THEORY

Every thing understandable
Sometimes predictable

Background: heterojunctions

$$\epsilon_n = \frac{e^+ + e^-}{2} - \sqrt{\left(\frac{e^+ - e^-}{2}\right)^2 + \left(\frac{1.28\times10^{-2}}{\text{md}^2}\right)^2}$$

Natural band lineups

Neutral point

Dipole from 1st planes exist ...
Alternate views:
van-de-Walle-Martín, Andersen
no dipole
Tight-bind: true if measure $E_0$ from $E_n$
They found $E_n$
Approximates $E(0) \approx 00$. Ignores local effect

Landoo:
no charge: requires $\Delta E_n = 0$
Core-shifts
Shih: Hg cores in Hg-Cd-Te
All HgTe bonds, $Z^+$ same, $E_-$ same?

J. Kreps: HgTe

\[ \Delta E_{\sigma} = 0.35 \text{eV} \]

\[ \Delta E_{\sigma} = 0.29 \text{eV} \]
**SCHOTTKY BARRIERS**

Reasonable accord
Really \( \frac{E_g - E_f}{E(0)} \) < semi.
\[ S = \frac{1}{E(0)} \]

Should fluctuate

Partial coverage: One Al on Si:

Ideal geometry

In this geometry
No charge
No bond breaking
Multiple atoms
No local charge till bands cross $E_F$

$\frac{\hbar^2}{2m} \text{ width } \approx 2\sqrt{n \nu_{pp} r + \frac{1}{2\pi}}$

$T \approx 3eV$

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
Evidence for Fermi Level Pinning at GaAs/Oxide Interfaces
The oxidized GaAs surface

\[ \text{As}_2\text{O}_3 + 2\text{GaAs} \rightarrow 4\text{As} + \text{Ga}_2\text{O}_3 \]

\[ \Delta F < 0 \]

"\( E_F \) 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
He/Ne
Red
663 nm

Ar
Green
488 nm

He/Cd
Blue
440 nm

GaAs
300 K

hν (eV)

ABSORPTION COEFFICIENT (cm⁻¹)

10⁷
10⁶
10⁵
10⁴
10³
10²
10¹
10⁰
0.6 1 2 3 4 5 6 8 10
PHOTOLUMINESCENCE (PL) SPECTROSCOPY

CASE 1: NO PINNING, i.e. flat band

![Diagram of PL intensity vs. excitation energy](image)

- n or p-type; $L_p, L_n = \text{theor. limit}$
- n or p-type; $L_p, L_n << \text{theor. limit}$

$\nu_{\text{red}}$ $\nu_{\text{blue}}$

$\nu = E_g$ $\nu_{\text{excitation}}$

$\frac{1}{\alpha} = \text{blue}$

$h\nu = E_g$ $h\nu_{\text{ex}}$

$n$-type $p$-type
PHOTOLUMINESCENCE SPECTROSCOPY

CASE II: MID-GAP PINNING

n-type

p-type

PL Intensity ($I_{h\nu = E_g}$)
PHOTOLUMINESCENCE SPECTROSCOPY

CASE III: PINNING NEAR A BAND EDGE

e.g. InP

\[ h_{\text{ex}} \]

\[ h_{\nu} = E_g \]

\[ e^- \quad e^- \quad e^- \quad e^- \]

\[ e^+ \quad e^+ \quad e^+ \quad e^+ \]

\[ S = 0 \quad \text{n-type} \]

\[ \text{p-type} \]

PL Intensity

(\( I_{h\nu} = E_g \))

\[ h_{\nu} \quad \text{red} \quad h_{\nu} \quad \text{blue} \]

\[ h_{\text{ex}} \]

609
PL Quantum Yield vs. Band Bending
surface recomb. velocity dependence

$I_{ex} = 0.1 \text{ mA}$

$S=10^7$
$S=10^8$
$S=500$

GaAs
$n = 2 \times 10^{17} / \text{cm}^3$
$L_p = 0.5 \text{ um}$
PL Quantum Yield vs. Band Bending

surface recomb. velocity dependence

I = 10 mA

GaAs
n = 2 x 10^17 /cm^3
L_p = 0.5 um

Ec - Ef (eV)

PLI(red) / PLI(blue)
Photoluminescence

Results

PL Intensity:

<table>
<thead>
<tr>
<th></th>
<th>Before</th>
<th>After</th>
</tr>
</thead>
<tbody>
<tr>
<td>blue</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td>red/blue</td>
<td>1</td>
<td>-2</td>
</tr>
<tr>
<td>n-type</td>
<td>1</td>
<td>15</td>
</tr>
<tr>
<td>p-type</td>
<td>4</td>
<td>-2</td>
</tr>
</tbody>
</table>

Analysis: \[ *Woodall et al. JVST 16(5)1389* (1999) \]

\[
\begin{align*}
n-type \text{ GaAs} & \\
N_0 &= 2 \times 10^{17} \text{ cm}^{-3} \\
L_p &= 0.5 \mu m \text{ from EBIC}
\end{align*}
\]

\[
\begin{align*}
\text{red/blue} &= 20 \Rightarrow V_b = 0.8 \text{ volts} \\
&\quad v_e = 10^7 \text{ cm/sec}
\end{align*}
\]

\[
\begin{align*}
\text{red/blue} &= 2 \Rightarrow V_b = 0.1 \text{ volts} \\
&\quad v_e = 10^4 \text{ cm/sec}
\end{align*}
\]
PL Quantum Yield vs. Band Bending
surface recomb. velocity dependence

I_ex = 0.1 mA

GaAs
n = 2 \times 10^{17} / \text{cm}^3
L_p = 0.5 \text{ um}

S=10^7
S=10^8
S=500
Plasmon - Phonon Coupling

Courtesy F. Pollak, Brooklyn College

GaAs 5145 Å

Carrier Concentration (cm⁻²)
Capacitor Structures

0.1 μm of PMMA on treated or untreated GaAs

(30 KHz)
High frequency C-V, n-type GaAs
from Offsey, et al., APL 48(7) 475 (1986)
Band edge photoluminescence intensity (arbitrary units)

- n-TYPE (AFTER)
- p-TYPE (AFTER)
- p-TYPE (BEFORE)
- n-TYPE (BEFORE)

Parameters:
- \( n = 2 \times 10^{17} \text{ /cm}^3 \)
- \( p = 8 \times 10^{17} \text{ /cm}^3 \)
- \( \lambda = 440 \text{ nm} \)
PL vs Time

- Pinned x 10
- Treated x 2
- Inert atmosphere

Heat → 100°C → RT

Treated x 1

In air
Auger Data

Etched, Rinsed, Air Exposed

Ga, As
XPS Data - J. Baker

\[ \Rightarrow 13\text{Å} \text{ Ga}_2\text{O}_3 \text{ (90\%)} \]
Characteristics of the Treated (Unpinned) Surface

- Repins in air (τ ≈ 1 h) and on heating in air (τ < 1 m, T≈ 100°C)
- Repins in acid and base solutions and vapors (τ ≈ 1 s)
- Stable in vacuum and inert ambients even on heating (T≈ 100°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$_2$O$_3$
Chemistry

1. Band-bending sweeps hy-generated minority carriers to surface, speeding oxidation

2. GaAs $\rightarrow$ Ga$_2$O$_3$, As$_2$O$_3$, ..., As$^\circ$

3. H$_2$O removes As$_2$O$_3$ & As$^\circ$
   (Massies & Contour JAP 58 (1985) 806)

4. Ga$_2$O$_3$ passivates GaAs surface

5. residual band-bending drives further oxidation
Conclusions

- Unpinned GaAs in air
- Detection by CV, PL, Raman
- Ga$_2$O$_3$ layer
  - OK passivation
  - Lousy insulator
- Behavior supports EWF model where As is culprit
- Simple, inexpensive process

$\Rightarrow$ 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 Å

**Other measurements:**

- **LEED**
  - Al, In / GaAs
- **AES**
  - Al, In, Au / GaAs
- **EELS**
  - Al, In, Au / GaAs
- **CPD**
  - Al,
n-Ge$_x$As$_{1-x}$ (110) + Al

Low temperature 80 K

• Ga 3d INTENSITY
• As 3d INTENSITY

(×10)

SLOPE = 1.9 Å

Intensities

Exponential decay of substrate core levels

Homogeneous layer

Al COVERAGE (Å)

SLOPE = 2.2 Å
EELS SPECTRUM FROM GaAs(110)

surface Exciton

GaAs (110)
Ep = 150 eV

\[ \frac{dE}{dE} \]

ENERGY LOSS (eV)

20, 30, 40, 50, 60

23.5, 20.0, 21.0, 816.2

80 w SE peak characteristic of sp²-like Ga
Al/GaAs (110)

- RT
- LT

Ga-d, s, 2 EXCITON PEAK HEIGHT vs. ML

0 ML 4 ML 8 ML
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)

As dangling bond → ? → 6a-dangling bond

\[ E_v \quad E_c \quad E \]
n-GaAs(110) + Al
LNT
hv = 60 eV

BOUND
Ga3d3/2
FREE Ga

Reduced Al - Ga exchange reaction

Solid State Communications
637
1986
CLEAVED GaAs + Al

$E_C \rightarrow 1.0 \rightarrow 0.5 \rightarrow E_V = 0$

$E_F$ (ev)

AL COVERAGE (Å)
NORMALIZED As-3d CORE LEVEL INTENSITY

METAL COVERAGE (Å)

Au/GaAs

LT
RT

0.1 0.2 0.4 0.6 0.8 1.0
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.

<table>
<thead>
<tr>
<th>Metal</th>
<th>n-GaAs</th>
<th></th>
<th>p-GaAs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>RT</td>
<td>LT</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>fast</td>
<td>slow</td>
<td>fast</td>
</tr>
<tr>
<td>Au</td>
<td>fast</td>
<td>slow</td>
<td>fast</td>
</tr>
<tr>
<td>In</td>
<td>fast</td>
<td>slow</td>
<td>fast</td>
</tr>
<tr>
<td>Ag</td>
<td>fast</td>
<td>(slow)</td>
<td>fast</td>
</tr>
<tr>
<td>Sn</td>
<td>fast</td>
<td>fast</td>
<td>fast</td>
</tr>
</tbody>
</table>

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°C.

* 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:
    - As$_{Ga}$ (double donor) + compensating defect
  - entirely different model
    - acceptors activated by formation of clusters or chemical reaction
    + donors linked to reconstruction or interface bonds.
Conclusions.

1. LT deposition simplifies the overlay 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:**
\[ \phi_b = -\frac{\phi_d^2}{2n_de} \]
- Band bending
- Charge transferred
  - Number of defects/area
- Donor density

Saturates when
\[ \mu_{\text{defect}} = \mu_{\text{semicond}} + \phi_b \]
- Defect electron affinity
- Bulk semiconductor Fermi level

**Cluster charging model:**
\[ \mu_{\text{cluster-complex}} = \frac{\partial E_{\text{complex}}}{\partial n} \]
- Coulomb energy
- Effective capacitance
\[ E_{\text{complex}} = n \epsilon_c + n^2 \frac{U}{C(R)} \]
- # of electrons transferred
Clustering model assumptions

\[ C(R) \propto R \propto N^{1/3} \]

Effective capacitance

Coverage = \( N_c \cdot N \)  
(number of atoms per cluster varying)

(number of clusters) held fixed

**Equilibrium condition:**

\[ \varepsilon_c + n \frac{U}{C(R)} = -n^2 \left( \frac{N_c}{N_{sat}} \right)^2 (\varepsilon_c - \varepsilon_s) + \varepsilon_s \]

\( \varepsilon_c \) - \( \varepsilon_s \), \( \alpha = \frac{U/C_1}{\varepsilon_c - \varepsilon_s} \), \( \beta = \left( \frac{N_c}{N_{sat}} \right)^2 \)

Fit data in terms of parameters

empirically \( \beta = \beta_0 \alpha^{3.3} \)
Fig. 3. The n-GaAs (TTO) surface band bending as the function of the effective noble metal coverage or the ideally cleaved n-GaAs (TTO) 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.

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Single Donor/Single Acceptor (SD/SA)

SCREENING CHARGE

INTERFACE STATES

SEMICONDUCTOR

METAL

TRAPPED CHARGE

UNCOMPENSATED CHARGE

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data: Kuan Ken Chin

- Ag - RT
  - $\varepsilon_c = 0.7 \text{ eV}$
  - $U = -2 \text{ eV}$

- Al - LT
  - $\varepsilon_c = 1.1 \text{ eV}$
  - $U = 1.3 \text{ eV}$

- Al - RT
  - $\varepsilon_c = 0.6 \text{ eV}$