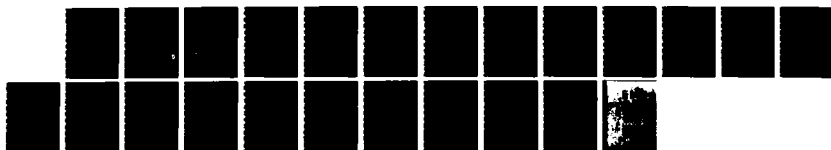


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# SOLID STATE ELECTRONICS LABORATORY

STANFORD ELECTRONICS LABORATORIES

DEPARTMENT OF ELECTRICAL ENGINEERING

STANFORD UNIVERSITY · STANFORD, CA 94305



STUDIES OF SURFACES AND INTERFACES ON III-V COMPOUNDS USING UV AND SOFT  
X-RAY EXCITATION

Final Technical Progress Report

1 December, 1974 through 30 September, 1982

Principal Investigators:

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Arlington, Virginia 22217

Contract No. N00014-75-C-0289

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ONR contract No. N00014-75-C-0289

Final Report

December 1, 1974 through September 30, 1982

"Studies of Surfaces and Interfaces on III-V Compound  
Semiconductors Using Ultraviolet and Soft X-ray Photoemission"

Professor W. E. Spicer and

Professor I. Lindau, Co-principal Investigators

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## I. Introduction

The work performed over the four year span of this contract comprises a large body of research. Its results are summarized in this document. The volume of work that has been done is significant: it has resulted in 94 publications in the scientific literature, and 8 students at Stanford University receiving their Ph.D. degrees, all under the direction of Professors W. E. Spicer and I. Lindau. The reader is directed to the papers referenced in the "List of Publications" in this report for further detailed information, as well as to the proposals of this contract.

The technical problem was to study the surfaces and interfaces of the III-V compound semiconductors. The semiconductors were selected for their technological as well as fundamental importance. The III-V compound semiconductors GaAs, InP, and GaSb were emphasized. The predominant methodology used was laboratory experimentation: photoemission spectroscopy excited by synchrotron radiation was utilized heavily, along with angle-resolved photoemission, photoemission excited by conventional ultraviolet and x-ray illumination, low energy electron diffraction, Auger electron spectroscopy, contact potential difference (Kelvin probe) measurements, as well as other techniques which are detailed in the publications. Although our approach was usually fundamental, we were guided by both fundamental and applied questions. In many cases we made important connections between the fundamental and applied. Where possible, we have utilized this knowledge to advance the development of electronic and opto-electronic devices. Experimental studies were often complemented with theoretical researches, typically by collaboration with leading theoreticians in those fields. Important collaborations which have been stimulated by this research are listed elsewhere in this document.

## II. Summary of technical results

- Schottky barrier formation on the III-V semiconductors. In contrast to the large amount of theoretical work attempting to explain this in terms of interactions at ideal metal-semiconductor interfaces, we now understand that Schottky barrier formation on the III-V semiconductors is due to Fermi level pinning by defects formed in the semiconductor at the metal-semiconductor interface by the metal deposition. The driving force is the heat of condensation of the metal. In fact, this same mechanism generates interface states at the oxide-GaAs or other insulator-GaAs interface. This Unified Defect Model, which we developed, is now quite widely accepted. It has proven important in III-V semiconductor integrated circuit development. The intrinsic (dangling bond) surface states are moved out of the bandgap of the (110) surfaces of GaAs, InP, and GaSb by atomic rearrangement at the surface. New levels due to atomic defects are created during oxidation or metal deposition. These defect levels influence Fermi level pinning at these metal-semiconductor and insulator-semiconductor interfaces.

- Attempts to develop GaAs MOS devices on an empirical basis have been expensive and unsuccessful. Based upon our work we now: (1) can understand why the MOS structure has been more successful on InP and the MES structure has been more successful on GaAs, (2) can correlate the success and failure of MOS and MES technologies on different III-V semiconductor alloys with the alloy composition, and (3) can guide future work with scientific engineering rather than empiricism.

- Bonding of column III and V metals on the III-V's. Ga and Al form metallic bonds to the surface, thus these elements form two-dimensional

"rafts" which are randomly oriented with respect to the semiconductor surface lattice. Sb forms a directional bond, and an ordered overlayer. This work has implications for understanding epitaxial III-V semiconductor crystal growth. Dynamical LEED intensity calculations were done by A. Kahn of Princeton University. A bonding model was developed based upon the tight-binding calculations of W. Harrison of Stanford University.

Prior to our work it was widely assumed (and predicted by theory) that Al or Ga atoms were bonded to the GaAs (110) surface via As lone pair electrons, or by bridging between As and Ga surface atoms. This sort of bonding, if present, would lead to a large change in surface lattice reconstruction and a distinctive valence band electronic structure. Neither of these effects were observed. Our data shows that there is no major change in the semiconductor surface lattice, and that Al or Ga metallic-like states appear even at submonolayer coverages.

➤ Preliminary angle-resolved photoemission measurements of the column III and column V metals on GaAs (110). These results helped us in specifying an angle-resolved system for purchase.

➤ Noble metals (Cu,Ag,Au) on GaAs and InP. (This work was supported for a time by DOE, as well as DARPA and ONR. The DOE support has now been terminated.) Significant intermixing has been found between the metal and semiconductor, even at room temperature. Differences have been found between the different metals and the different semiconductors. In general, the results are not explained by bulk thermodynamics, and we are developing an understanding of surface thermodynamics.

➤ Engineered Schottky barriers. As one result of the Unified Defect Model, we suggested that we might modify the Schottky barrier height by fabricating



diodes with heavily doped semiconductor layers at the metal-semiconductor interface. MBE (molecular beam epitaxy) was used for the device fabrication because it provided good control over the thin, heavily doped semiconductor layers, and because it allowed for in situ metallization which minimized interfacial contaminants.

Al metal was used on n-type GaAs. The unmodified barrier height was 0.80 eV. p<sup>+</sup> interfacial layers allowed us to controllably increase the barrier height up to 1.33 eV (compare  $E_{\text{gap}} = 1.42$  eV), and n<sup>+</sup> interfacial layers allowed us to reduce the barrier height all the way to ohmic behavior. In all cases there was only minimal degradation of the diode electrical characteristics.

- Oxygen chemisorption on GaAs(110). This is important for both fundamental and practical reasons. We are attempting to understand the effect of interfacial oxides which are always present in practical devices. We have developed a new valence band measurement which is sensitive to < 0.001 monolayer of oxygen. The chemisorbed state of oxygen on the GaAs (110) surface consists of an oxygen atom bonded to a surface As as well as an oxygen atom bridging between the As and a neighboring Ga. With unexcited oxygen we observe a 2.9 eV shift of the As 3d core level and an asymmetric broadening of the Ga 3d core level with a shift of no more than 0.7 eV. The first of these corresponds to the theoretical predictions of the Goddard group for an oxygen attached to a surface As without breaking any back bonds (J. Vac. Sci. Technol. 16, 1178 (1979)). In contrast, we have presented definitive evidence that the model of Brundle et al. which assumes As<sub>2</sub>O<sub>3</sub> plus Ga<sub>2</sub>O<sub>3</sub> clusters is incorrect (J. Vac. Sci. Technol. 16, 1186 (1979)). Our work has included a new high sensitivity valence band spectroscopy, studies of As<sub>2</sub>O<sub>3</sub> valence bands, thermal desorption, and

oxygen adsorption on sputtered (disordered, Ga rich) GaAs (110).

- Room temperature oxidation of As and Ga. Oxygen exposure on amorphous As results in an oxidized phase having an electronic structure similar to both that of isolated (gas phase)  $\text{As}_4\text{O}_6$  molecules and that of crystalline  $\text{As}_2\text{O}_3$ . We have reported an analysis of the bonding in As oxides. The oxidation of Ga resulted in the formation of  $\text{Ga}_2\text{O}_3$ . We studied the valence band electronic structure, chemical shifts in the Ga 3d, and bonding in the oxide.
- Oxygen on GaAs(110). This work is important for understanding III-V semiconductor passivation. We collaborated with P. Mark of Princeton University on LEED and UPS studies of the order and disorder of the GaAs(110) surface during oxygen exposure. A small amount of oxygen ( $< 0.1$  monolayer) pins the surface Fermi level and disorders the valence band electronic structure. The same pinning energy is observed as for the metals.
- Oxygen on GaAs versus InP. The GaAs oxides are unstable, contributing to problems with GaAs MOSFET's. The InP oxide is stable, as only a surface oxide is formed and the InP is not "torn-up". This result, along with our Unified Defect Model, explains the success on InP MOSFET's and GaAs MESFET's, and the failure of GaAs MOSFET's. This work also allows us to understand dark-line defects and device failure in AlGaAs LED's and lasers, and the longer lifetimes of InGaAsP LED's and lasers.
- Laser enhanced oxidation of GaAs. In addition to its importance for understanding the oxidation and passivation of semiconductors, our laser enhanced oxidation work has implications for understanding the lifetimes and failure of practical LED's and semiconductor lasers. Our work was the

first demonstration of laser enhanced chemisorption of oxygen on a semiconductor surface (GaAs(110)). We observed an increase of the oxygen sticking coefficient of several orders of magnitude under low intensity laser illumination (3 watts/cm<sup>2</sup>, 514.5 nm). Our work indicates that this enhancement is due to an increase in the free electron and hole densities at the surface, due to the recombination of photo generated carriers. Prior work showed that the break-up of the O<sub>2</sub> molecule was the rate limiting step. Electrons and holes excited by the laser in GaAs may facilitate O<sub>2</sub> break-up and chemisorption. We found the same oxygen surface chemistry with or without laser irradiation, however the laser enhanced results have forced a modification of what we had previously interpreted as the saturated oxygen coverage.

The above summary touches on only the highlights of a large and diverse research program. As mentioned earlier, interested readers will find much more information in the publications listed elsewhere in this document, as well as in the proposals of this contract. Only a few of our beneficial collaborations were mentioned above. They are also listed elsewhere in this document.

Many of the experiments described herein were performed at the Stanford Synchrotron Radiation Laboratory which is supported by the National Science Foundation under Grant No. DMR77-27489 in cooperation with the Stanford Linear Accelerator Center and the Department of Energy.

### III. Implications for further research

The work performed under this contract raises new questions, and suggests new areas of investigations which are likely to be profitable in both applied and basic fields. Some of these topics are already receiving attention under current funding of our contract no. N00014-83-K-0073 (DARPA and ONR), which is essentially a combination and continuation of contract no. N00014-79-C-0072 (DARPA through ONR) and contract no. N00014-75-C-0289 (ONR).

- The question of the mechanisms by which Schottky barrier heights to the III-V semiconductors are determined has been advanced considerably during the last five years by the introduction, application, and development of our group's Unified Defect Model. This model, far better than any other, explains all the available data on surfaces and practical devices. Very few groups presently take issue with the Unified Defect Model. Most work is now devoted to exploring just how extensive its range of validity is, calculating second-order effects which modify slightly the proposed pinning positions, applying the model to practical devices (either their design or detailed modeling), etc. We are looking into the influences of different metals, different metal deposition conditions, the presence of contaminants, and different semiconductor surfaces and surface treatments. Some of the debate which persists deals with the relative effects of band bending and changes in electron affinity and work function. We intend to use photoemission spectroscopy and contact potential difference measurements to obtain additional information on these subjects, and incorporate what we learn into our theories of Schottky barrier formation.

- Intermixing and interdiffusion of metals on semiconductors, especially the noble metals Cu, Ag, and Au. Included: temperature effects, Fermi level pinning, Schottky barrier and ohmic contact formation.
- Ohmic contacts.
- Studies of (100) and (111) surfaces (surfaces other than the cleavage surface). This will require us to develop new preparation and passivation techniques.
- Closer coupling with MBE (molecular beam epitaxy) and other novel materials synthesis techniques.
- Laser enhanced oxidation, including low temperatures, H<sub>2</sub>O oxidation, and the oxidation of new semiconductors. Goals include MOS structures, understanding oxygen chemistry on semiconductors, and investigating photon-semiconductor interactions.
- When high fluxes and improved energy resolution are available from the new DOD/Xerox/NSF beam line under construction at SSRL, we will study surface versus bulk chemical shifts, oxidation, and other projects.
- Hydrogen and halides on III-V semiconductor surfaces, with and without oxygen. Applications to practical MIS/MOS devices.
- Further investigations of column III and V elements on the III-V semiconductors, including angle-resolved photoemission, temperature effects, and column III and V elements simultaneously to learn about epitaxial growth mechanisms. Goals are an improved understanding of the fundamental physics and chemistry of III-V crystal growth, temperature dependences,

growth rates, and dopant incorporation.

- Angle-resolved photoemission and LEED (low energy electron diffraction) to investigate domain structures on cleaved surfaces. Many applications.
- SEXAFS (surface extended x-ray adsorption fine structure) on the new DOD/Xerox/NSF SSRL beam line to study the surface geometry of adsorbed species and reconstruction of the clean surface.
- Silicide program expanded to include additional metals V, Nb, Ta, In, Os, and contaminants. We will attempt to develop models and unify the data.
- Device measurements on metal-semiconductor contacts will be incorporated increasingly into our surface physics studies.
- Engineering of interfaces, including techniques to heal semiconductor defects, and the introduction of dopants to modify Fermi level pinning and study interface electrostatics.
- III-V ternary and quaternary semiconductor alloys.
- Interface states at III-V semiconductor heterojunctions.
- Surface chemistry and surface thermodynamics.

#### IV. Important collaborations fostered by this research

The researches described in this document have benefitted from collaborations with scientists throughout the world. In addition to the formal collaborations, our experimental work and modeling have stimulated much theory and some experiment in labs elsewhere. The following list includes only some of the groups with whom we have collaborated, or whose work has been stimulated (at least in part) by our own.

Professor W. Harrison, Stanford University

Professor L. Braicovich and group, Milan, Italy

Professor G. Ottaviani and group, Italy

IBM, E. Fishkill

Professors P. Mark (deceased) and A. Kahn, Princeton University

Xerox, Palo Alto Research Center

Professors McGill and Goddard, Cal Tech

Professor M. Cohen, U. C. Berkeley

Professor Joannopoulos, M.I.T.

Dr. A. Zunger, SERI

Professor Gatos and coworkers, MIT

Professor Monch and coworkers, University of Duisberg, West Germany

Naval Oceans Systems Center, San Diego

Professor J. Dow, University of Illinois

V. Graduate students who received Ph.D. degrees under this contract

The students listed here were specifically supported by this contract and received Ph.D. degrees during the period of this contract. However, there are several other students in Professors Spicer and Lindau's group at Stanford who were not doing thesis work on semiconductors, but benefitted from working closely with these students. This is most dramatically seen in the many students who did their thesis outside of the semiconductor field, but are nonetheless employed in leadership positions in the semiconductor and electronics industries today.

This is not an inclusive list of all who contributed to this work. Consult the list of publications for a complete list of contributors.

Dr. Chung-Yi Su

Dr. Patrick W. Chye

Dr. C. Michael Garner

Dr. Perry Skeath

Dr. Jeffrey N. Miller

Dr. Se-Jung Oh

Dr. Piero Pianetta

Dr. Paul E. Gregory



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