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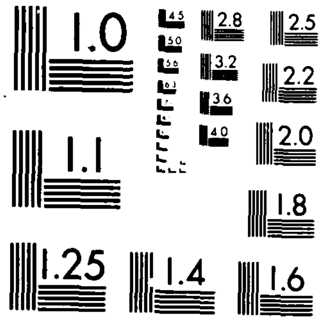
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This document is being submitted as the final report for a scientific program that was initiated in 1983 (see Item 11). The work completed under this award is summarized and a new program, based on the work supported by this contract, is described. The title of the program just completed was, "Synthesis and Characterization of Thermodynamically Stable Metal Contacts for III-V Compound Semiconductors." We have produced 21 research papers, covering the work conducted during this contract period, cited where applicable in the report.

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FINAL REPORT

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October 1, 1986

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FINAL REPORT

This document is being submitted to ONR as the final report for a scientific program that was initiated in 1983 with the award of contract N00014-83-K-0612. The work completed under the previous award will be summarized briefly. This research has prepared the foundation for our future work, which has been funded by the ONR on the basis of a new proposal. The new program will be broader in scope in that many different types of materials systems will be examined.

The title of the program just completed was "Synthesis and Characterization of Thermodynamically Stable Metal Contacts for III-V Compound Semiconductors". The goals of this program were highly specific and directed toward: 1) the study of the bulk thermodynamics of metal/compound semiconductor systems, 2) the identification of materials that were chemically stable when in contact with the compound semiconductors, 3) growing thin films of these metals on semiconductor substrates, and 4) the characterization of the resulting thermodynamically stabilized systems to see if interfacial chemical reactions could be controlled and if they might be of use in contacting technology.

These studies were motivated by the observations of many workers that strong chemical interactions occur at nearly all the metal/compound semiconductor interfaces that have been studied. The rationale behind the research was that no one could possibly hope to understand or control the processes that occur at an interface without first understanding the chemistry of the bulk materials.

After two and a half years of work in this area, all the original goals of the program have been attained, and the first attempts at using thermodynamically stable contacts in device structures are in progress at Hughes Research Laboratories. However, the many different unanticipated results and insights gained during this program have revealed new ways of thinking about the synthesis and characterization of materials. These discoveries have made this research extremely valuable and exciting from a basic scientific viewpoint. The major conclusion drawn from this work is that simple bulk thermodynamics, when properly applied, accounts for the vast majority of results that have been reported in the literature for chemical interactions between thin metal films and compound-semiconductor substrates.

In many ways, this realization is a bitter disappointment. These systems have been studied for well over a decade by hundreds of researchers all over the world, and the most sophisticated research tools have been used to examine them. However, no one had looked carefully enough at metal/compound-semiconductor systems to see if the simplest and most direct cause for interfacial chemistry, namely a reaction of the bulk materials to form thermodynamically more stable products, was the dominant factor. The implicit assumption has always been that some special interface effects were dominant. The primary reasons why simple thermodynamics have been ignored until now are: 1) very few chemists, trained to think about the energetics of reactions, are working in this area, and 2) the necessary experiments involved very low-level technology and therefore were not as exciting to do as extremely sophisticated surface science experiments, which unfortunately did not provide much direct and relevant information about the *chemistry* of the materials studied.

Of course, more has been established by the completed research project than the fact that thermodynamics is still valid. The specific results of these studies have been published or are presently being written up, as described below. They include determinations of electronic structure, measurements of transport properties, studies of epitaxial growth, and applications of bulk thermochemistry and phase diagrams to thin films and interfaces.

II. COMPLETED RESEARCH

One question that arises in the study of metal/semiconductor contacts is that of the nature of the electronic states at the interface. A large amount of effort has been invested in building up the necessary experimental and computational facilities to study the band structures of complex materials, such as bulk intermetallic compounds, thin films, and surfaces. Angle-resolved photoelectron spectroscopy and electron energy-loss spectroscopy were used to examine the E vs. k dispersions in the valence bands and critical points in the conduction bands, respectively. In addition, the mixed-basis band structure interpolation scheme, originally developed by N.V. Smith and co-workers (eg., Phys.Rev.B **9**, 1365 (1974)) for fcc d-band metals, has been extended to handle compounds with rock-salt, fluorite, and zinc-blende structures. By this method, it has been possible to calculate charge densities and to determine orbital-projected densities of states from a Hamiltonian that was determined by fitting to experimental results. These developments have been described in detail in the following:

1. J.G. Nelson, W.J. Gignac, J.R. Lince, and R.S. Williams : "Characterization of the Surface Net and Electronic Structure of $AuGa_2$(100)," J.Vac.Sci.Technol.A **2**, 534 (1984). *(Tech.Rep.#2)*

2. S. Kim, J.G. Nelson and R.S. Williams: "A Mixed-Basis Band Structure Interpolation Scheme Applied to the Fluorite Structure Compounds $NiSi_2$, $AuAl_2$, $AuGa_2$ and $AuIn_2$," Phys.Rev.B **31**, 3460 (1985). *(Tech.Rep.#6)*

3. J.G. Nelson, W.J. Gignac, J.R. Lince, S. Kim and R.S. Williams: "Angle-Resolved Photoemission Study of $AuGa_2$ and $AuIn_2$ Intermetallic Compounds," Phys.Rev.B **31**, 3469 (1985). *(Tech.Rep.#5)*

4. W.J. Gignac, R.S. Williams, and S.P. Kowalczyk: "The Valence and Conduction Band Structure of the Sapphire $(1\bar{1}\bar{0}1)$ Surface," Phys.Rev.B **32**, 1237 (1985). *(Tech.Rep.#4)*

5. J.G. Nelson, S. Kim, W.J. Gignac, R.S. Williams, J.G. Tobin, S.W. Robey and D.A. Shirley: "High-Resolution Angle-Resolved Photoemission Study of the Ag Band Structure along Λ ," Phys.Rev.B **32**, 3465 (1985). *(Tech.Rep.#9)*

6. S. Kim and R.S. Williams: "Analysis of Chemical Bonding in TiC, TiN and TiO by use of Second-Principles Band Structures from Photoemission Data," J.Vac.Sci.Technol.A **4**, 1603 (1986). *(Tech.Rep.#10)*

7. S. Kim and R.S. Williams: "A Mixed-Basis Band Structure Interpolation Scheme Applied to the Rock-Salt Compounds TiC, TiN, and TiO," Phys.Rev.B, submitted. *(Tech.Rep.#15)*

8. S. Kim and R.S. Williams: "Semi-Empirical Band Structure and Partial Density of States of CuCl," Phys.Rev.B, submitted.

A study of the transport properties of a one-monolayer film of Ag on a Ge(001) surface led to a very exciting and controversial result. The resistance of many different one-monolayer films as a function of temperature was studied, and most of the films displayed weak localization of the charge carriers. These experiments were extremely difficult, and the materials were highly intractable. Nevertheless, two of the samples displayed the onset of a superconducting transition, which was completely unexpected. This result was not caused by any contamination of the film, and is still not understood completely, although the possibility of a superconducting transition in this system has been supported by the theoretical work of K. Johnson (private communication). This experiment was described in the following:

9. M.J. Burns, J.R. Lince, R.S. Williams and P.M. Chaikin: "Electron Localization and Superconductivity in Very Thin Epitaxially Grown Ag Films on Ge(001)", Sol.State Commun. **51**, 865 (1984). *(Tech.Rep. #3)*

A topic closely related to the chemical nature of a thin film is its atomic structure. The simplest type of thin film, and therefore the easiest to characterize, is an epitaxial overlayer. In metal/semiconductor systems, growing epitaxial layers also provides a more uniform contact, minimizes diffusion through the film, and makes it possible to fabricate various hot-electron devices. Epitaxial $NiSi_2$ on Si(001) was examined in order to gain some experience with such structures, and epitaxial $AuGa_2$ on GaSb(001) was grown as a demonstration of a thermodynamically stable and epitaxial metal/compound-semiconductor interface, as reported in the following:

10. W.J. Gignac, S. Kim, and R.S. Williams: "Electronic Structure Investigation of Epitaxial Nickel Silicides on Si(001)," J.Vac.Sci.Technol.A **2**, 269 (1984). *(Tech.Rep. #1)*

11. J.R. Lince and R.S. Williams: "$AuGa_2$ on GaSb(001): An Epitaxial, Thermodynamically Stabilized Metal/III-V Compound-Semiconductor Interface," J.Vac.Sci.Technol.A **3**, 1217 (1985). *(Tech.Rep. #7)*

The thermochemistry of metal/compound semiconductors has been studied in detail. The ternary phase diagrams for all of the Au-III-V (III=Al,Ga,In; V=P,As,Sb) ternaries, shown in Fig.1, have been determined with combined experimental measurements (x-ray powder diffractometry of equilibrium systems) and calculations that used literature values for enthalpies and entropies of formation, when available. Using the existing thermochemical data, augmented by observations reported in the literature, it was possible to determine the ternary phase diagrams of nearly all the ternaries formed with the metals Pt, Ag, Cu, Ni, and Co with the group-III and group-V elements. These phase diagrams provide a basis for understanding chemical reactions between metals and semiconductors; they also show which metals are thermodynamically stable. Thus, the study of the interfacial chemistry of these systems has been made much more quantitative.

One of our primary accomplishments was to demonstrate the importance of entropy in the chemistry of compound semiconductors. Since all the group-V elements are highly volatile, any reaction that can release gas-phase species will be favored at a high enough temperature. Even if the reaction is endothermic, the enormous increase in entropy of the system, as the group-V element sublimes, will drive the Gibbs Free Energy of Reaction G_R negative. In all cases, the most stable metal, containing any particular element in contact with a III-V material, will be the intermetallic compound containing the largest percentage of the group-III element, eg., $AuGa_2$ onGaSb and GaAs.

Thin films of $AuGa_2$ have been grown on both GaSb and GaAs substrates, and their behavior as a function of annealing temperature has been studied. These systems essentially form interfaces that are atomically abrupt, and are completely inert even if the systems are heated above the melting point of $AuGa_2$. The Schottky barrier height of $AuGa_2$ on GaAs is independent of annealing up to at least 350°C, whereas elemental Au contacts react chemically and turn ohmic. The intermetallic compound also grows epitaxially on both substrates, although the lattice mismatch with GaAs is ~7.5%. These results have been described in the following:

12. T.C. Tsai and R.S. Williams:
"Solid Phase Equilibria in the Au-Ga-As, Au-Ga-Sb, Au-In-As, and Au-In-Sb Ternaries," J.Mater.Res. **1**, 352 (1986). *(Tech.Rep.#12)*

13. J.H. Pugh and R.S. Williams:
"Entropy-Driven Loss of Gas-Phase Group V Species from Au/III-V Compound Semiconductor Systems,"
J.Mater.Res. **1,** 343 (1986). *(Tech.Rep.#11)*

14. R.S. Williams, J.R. Lince, C.T. Tsai, and J.H. Pugh:
"Thermodynamically Stable Metal III/V Compound Semiconductor Interfaces," Mat.Res.Soc.Symp.Proc. **54,** 335 (1986). (*Tech.Rep.13)*

15. J.R. Lince and R.S. Williams:
"Comparison of Reactive and Nonreactive Metal Films on III-V Compound Semiconductors: Au and $AuGa_2$ on GaSb(001),"
Thin Solid Films, **137,** 251 (1986). *(Tech.Rep.8)*

16. J.R. Lince, C.T. Tsai, and R.S. Williams:
"The Growth of AuGa`{W! Thin Films on GaAs(001) to Form Chemically Unreactive Interfaces,"
J.Mats.Res. **1,** 537 (1986). *(Tech.Rep.#14)*

17. C.T. Tsai and R.S. Williams:
"Chemical Reactions at the Au/InP Interface,"
Submitted to J.Mats.Res. *(Tech.Rep.#16)*

18. R.S. Williams:
"The Thermodynamic Stabilization of Metal/Compound-Semiconductor Interfaces," submitted to Thin Solid Films.

19. T.C. Tsai, J.H. Pugh, and R.S. Williams:
"Solid Phase Equilibria in the Au-III-V Ternaries and Their Relation to Thin Film Chemistry,"
in preparation.

20. T.C. Tsai and R.S. Williams:
"Solid Phase Equilibria in the Pt-Ga-As and Pt-Ga-Sb Ternaries,"
in preparation.

21. J.H. Pugh and R.S. Williams:
"Solid Phase Equilibria of M-III-V Ternaries (M=Co,Ni,Cu; III=Al,Ga,In, V=P,As,Sb),"
in preparation.

A large number of possible systems still remain to be studied, such as other transition metals with III-V, II-VI, and IV-VI compounds. However, now that the basic ideas of thermodynamic stabilization of metal/compound-semiconductor interfaces have been formulated, such investigations essentially take the form of development, rather than research. Thus, upon completing the present experiments supported by the ONR contract, the study of thermodynamic stabilization of metal/

compound-semiconductor interfaces, in order to apply them to devices, will be performed in collaboration with investigators at Hughes Research Labs. Future funding from ONR will be used to support new areas of research.

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3. Mr. Elliot Ecklund
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