DOE/ER/45061--6

DE90 008430

DOE/ER/45061-76

THEORETICAL AND EXPERIMENTAL STUDY OF SOLID PHASE MISCIBILITY GAPS IN III/V QUATERNARY ALLOYS

Progress Report
for Period April 1, 1987 - June 2, 1989

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June 2, 1989

Prepared for
THE U.S. DEPARTMENT OF ENERGY
AGREEMENT NO. DE-FG02-84ER45061

TABLE OF CONTENTS

I. PROJECT SUMMARY

The first 8 years of this DOE supported research was directed toward understanding, for the first time, the thermodynamics of miscibility gaps and ordering in III/V alloys. This research has led to the publication of 32 papers in technical journals as well as 17 *invited* papers and national and international conferences. In addition, this work led directly to the invitation to organize the "Joint US/Japan Workshop on Alloy Semiconductor Physics and Electronics" held October 1988 in Hawaii. The Workshop was co-organized by myself and Professor A. Sasaki of Kyoto University. The proceedings will be published later this year as a book, as well as a special issue of the Journal of Crystal Growth.

The continuity of DOE funding has led to a research effort resulting in major advances in our understanding of III/V alloy semiconductors. It has opened-up the possibility of producing a number of alloys previously impossible to grow due to the existence of regions of solid immiscibility. In addition, it has led to the discovery and characterization of spontaneous, atomic-scale ordering in a number of III/V alloys.

The major accomplishments of the last 3 years (2 1/4 years in reality, beginning April 1, 1987) are briefly summarized below:

1) The effects of growth parameters, such as temperature, growth rate, and substrate orientation, on ordering in $GaAs_{0.5}Sb_{0.5}$ have been systematically studied. The two ordered structures $L1_0$ and $E1_1$ can be made to appear and disappear, somewhat independently, by changing the temperature, growth rate, and substrate orientation.
2) Ordering has been observed in the 3:1 alloy $GaAs_{0.25}Sb_{0.75}$ with alternating {100} planes on the anion sublattice composed of Sb and a 50/50 As-Sb mixture (the $L1_3$ or Cu_3Pt structure).
3) The quaternary alloy $Ga_{0.63}In_{0.37}As_{0.98}Sb_{0.02}$ has been grown and found to order with the $L1_0$ and $E1_1$ structures found for $GaAs_{0.5}Sb_{0.5}$.
4) The binary alloy GaPSb, with a critical temperature of 1996°K, has been grown for the first time. We have also completed a study of the effects of the OMVPE growth parameters on the quality and properties of GaPSb.

5) The first layers of the metastable alloy InPSb, with a critical temperature of 1319°K, produced by any technique, were grown by OMVPE.
6) The energy band gap and phonon spectra for both GaPSb and InPSb alloys have been investigated throughout the range of solid composition.
7) Ordering phenomena in these two alloys, GaPSb and InPSb, as well as InAsSb, GaAsP, and GaInP, have been studied.
8) We are just completing an investigation of the OMVPE growth of the quaternary alloy GaInPSb. Needless to say, this is also the first time these alloys have been grown and studied. The optical properties and ordering in these materials are currently under investigation. These studies will be completed before the March 31, 1990 end of the current grant.

The results of these experiments are described more fully in the papers listed below. This list includes the papers and invited lectures based on the DOE supported research since the beginning of *the last 3 year period (April 1, 1987 - present).* Preprints of unpublished papers are attached as an appendix to this proposal.

I. Papers

1) Long-Wavelength Lattice Dynamics of GaInAsSb Quaternary Alloys, (with D.H. Jaw and Y.T. Cherng), J. Appl. Phys. (accepted for publication).

2) Organometallic Vapor Phase Epitaxyial Growth Studies of GaPSb and InPSb (with M.J. Jou), J. Crystal Growth (accepted for publication).

3) Organometallic Vapor Phase Epitaxy for Metastable and Natural and Artificially Structured Materials, Section in Proceedings of Workshop on "Materials Science of Epitaxial Heterostructures", (to be published).

4) Long Range [111] Ordering in GaAsP (with H.R. Jen and D.S. Cao), Applied Physics Letters 54 1890 (1989).

5) Ordered Structures and Metastable Alloys Grown by OMVPE, Journal of Crystal Growth, co/published as a book chapter in

Proceedings of US/Japan Seminar on Alloy Semiconductor Physics and Electronics, (invited paper, accepted for publication).

6) Long Range Order in InAsSb (with H.R. Jen and K.Y. Ma), Appl. Phys. Lett. 54 1154 (1989).

7) Lattice Vibration Spectra of GaPSb and InPSb, (with Y.T. Cherng, D.H. Jaw, and M.J. Jou), J. Appl. Phys. 65 3285 (1989).

8) OMVPE Growth of the New Semiconductor Alloys GaPSb and InPSb, (with M.J. Jou, Y.T. Cherng, and H.R. Jen), J. Crystal Growth 93 15 (1988).

9) OMVPE Growth and Characterization of the Metastable Alloy - InPSb, (with M.J. Jou and Y.T. Cherng), J. Appl Phys. 64 1472 (1988).

10) Raman Scattering in $GaP_{1-x}Sb_x$, (with Y.T. Cherng, M.J. Jou, and H.R. Jen), J. Appl. Phys. 63 5444 (1988).

11) OMVPE Growth of a New Semiconductor Alloy - GaPSb, (with M.J. Jou, Y.T. Cherng and H.R. Jen), Appl. Phys. Lett. 52, 549 (1988).

12) The Kinetics of Ordering in GaAsSb Grown by Organometallic Vapor Phase Epitaxy, (with H.R. Jen, M.J. Jou, and Y.T. Cherng), J. Crystal Growth 85 175 (1987).

13) Ordered Structures in OMVPE Grown GaAsSb and GaInAsSb Alloys, (with H.R. Jen, M.J. Cherng, and M.J. Jou), *GaAs and Related Compounds, 1986*(Institute of Physics, London, 1987) Vol. 83, 159.

14) Ordered Structures In $GaAs_{1-x}Sb_x$ Grown by Organometallic Vapor Phase Epitaxy, (with H.R. Jen, M.J. Cherng, and M.J. Jou), Ternary and Multinary Compounds, ed. S.K. Deb and A. Zunger (Materials Research Society, Pittsburg, 1987), p. 353-8.

15) Thermodynamics, Kinetics and Mechanisms of OMVPE, in *Processing of Electronic Materials*, ed C.G. Law and R. Pollard (The American Institute of Chemical Engineers, New York, 1987), pp. 114-133.

II. Invited Lectures

1) *Ordered Structures in Alloys Grown by OMVPE*, Electronic Materials Conference, Boston, June 1989.

2) *Epitaxial Growth of Metastable Structures*, American Physical Society Meeting, St. Louis, March, 1989.

3) *OMVPE for Metastable Alloys and Natural and Artificially Structured Materials*, DOE Workshop on Materials Science of Epitaxial Heterostructures, Monterey, Ca, January 9-14, 1989.

4) *Ordered Structures and Metastable Alloys Grown by OMVPE*, Joint US/Japan Seminar on Alloy Semiconductor Physics and Electronics, Hawaii, October 1988.

5) *Miscibility Gaps and Ordering in III/V Alloys*, Workshop on the Physical and Mechanical Properties of Alloys: Semiconductors and Beyond, Dayton, September, 1987.

II. STUDENTS SUPPORTED and GRADUATED

Two PhD students in the Department of Materials Science and Engineering have been supported by this research project. H.R. Jen does the electron microscopy and electron microprobe analysis and M.J. Jou does the OMVPE growth and optical and electrical characterization of the material. Mr. Jou is also involved in thermochemical calculations related to the OMVPE growth of meastable alloys. The students work under the direct supervision of Professor G.B. Stringfellow. H.R. Jen will graduate with a PhD degree in Materials Science and Engineering from the University of Utah during the Autumn quarter of the 1989-90 academic year. Mr. Jen, a US citizen, will work in the Poloroid research laboratories after graduation.

III. INTERACTIONS WITH OTHER DOE SUPPORTED LABORATORIES

An informal collaborative effort continues with Dr. Z. Liliantal-Weber at U.C. Berkeley. This has involved mainly sending samples to Dr. Liliantal-Weber to examine using the more sophisticated electron microscopes at

Berkeley. We no longer use the Berkeley ion mill, since we have recently obtained our own which operates satisfactorily.

APPENDICES (Preprints of DOE Supported Research)

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