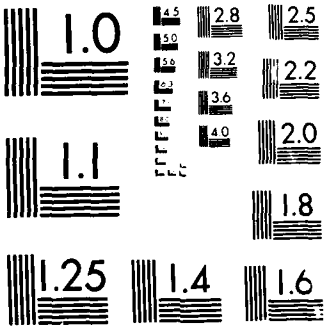
AD-A195 601 STRUCTURAL THEORY OF METASTABLE PSEUDOBINARY 1/1
SEMICONDUCTOR ALLOYS(U) SRI INTERNATIONAL MENLO PARK CA
M A BERDING ET AL. 06 MAY 88 N00014-85-K-0448
UNCLASSIFIED F/G 9/1 NL



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

4

STRUCTURAL THEORY OF METASTABLE PSEUDOBINARY SEMICONDUCTOR ALLOYS

Final Report

6 May 1988

By: M.A. Berding, Research Physicist
A. Sher, Associate Director
Physical Electronics Laboratory

A.-B. Chen, Physics Department
Auburn University

Prepared for:

Office of Naval Research
800 North Quincy Street
Arlington, Virginia 22217-5000
Attn: Dr. K.B. Hathaway
Scientific Program Officer

Contract N00014-85-K-0448

SRI Project 1010

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

SRI International
333 Ravenswood Avenue
Menlo Park, California 94025-3493
(415) 326-6200
Telex: 334486

CONTENTS

I INTRODUCTION

The objective of this program [ONR Contract N00014-85-K-0448 (SRI Project 1010)] has been to develop a structural theory of pseudobinary semiconductor alloys grown by nonequilibrium methods. Alloys prepared this way are metastable, but often have room temperature lifetimes against transitions to their equilibrium phases that are well in excess of those any operating device is likely to experience. Because of the great advantage of the tailorability of alloy electronic and structural properties, alloys grown by these methods have received great emphasis in recent years. This program has contributed to the development of a comprehensive phase theory of these nonequilibrium systems. (JES)

Section II of this final report is a summary of the work accomplished in the program. Section III contains an index of the publications, patents, presentations, and honors achieved under funding of this program.

II SUMMARY OF WORK ACCOMPLISHED

A. *Order/Disorder Theory*

We have devised a new statistical theory of order/disorder transitions of zincblende structured semiconductor alloys of the form $A_{1-x}B_xC$ that removes many of the former limitations.[1]

A cluster of n atoms is specified with the number of B atoms, $n_j(B)$; states of energy, ε_j; and degeneracy, g_j. If cluster/cluster interactions are neglected, then a simple argument replicates the number of possible combinations of the system calculated from the exact "Cluster Variation Method." A steepest-descents argument then proves that the cluster populations, $\overline{x}_j$, are grand canonical ensembles with chemical potential μ,

$$\overline{x}_j = g_j \, e^{+\left[\mu n_j(B) - \varepsilon_j\right] kT} / q \ ,$$

where q is the grand partition function, and μ is determined by the condition that the composition is properly given

$$nx = \sum_j n_j(B) \, \overline{x}_j \quad .$$

The combinatorial analysis then gives the proper mixing entropy, ΔS, and the mixing enthalpy, ΔE, is calculated from

$$\Delta E = \sum_j \varepsilon_j \, \overline{x}_j \quad ,$$

with the result that the mixing free energy and, consequently, the nature of the equilibrium phases and critical temperatures are determined once the sets $\{\varepsilon_j\}$ and $\{g_j\}$ are known.

A general theorem has been proven: If $\varepsilon_j = \varepsilon_0 + \Delta\varepsilon n_j(B)$ is a linear function of $n_j(B)$, and if $g_j = g_j^0 \equiv \left[\begin{matrix} n \\ n_j(B) \end{matrix}\right]$ is not split (so it is g_j^0 the cluster degeneracy of a random alloy), then

$$\overline{x}_j = x_j^0 = g_j^0 (1-x)^{n-n_j(B)} x^{n_j(B)}$$

is the population distribution of a random alloy. This theorem tells us that only those interactions that are nonlinear in the number of B atoms on the cluster or interactions that split the cluster states' degeneracies cause deviations from random alloys.

The interactions that cause energies ε_j that vary nonlinearly with the number of B atoms on clusters can be grouped into three classes as follows:

- Those arising from strains resulting from the bond-length differences between the alloy constituents.
- Those caused by alloy modifications of the electron/ion interactions (chemical-bonding terms).
- Those due to electron/electron Coulomb interactions,[2] including Madelung modifications and driven by polarity differences between the constituents.

For most alloys, the strain terms dominate, and the others interject smaller, but often significant modifications. A few alloys (e.g. $Ga_{1-x}Al_xAs$ and $Hg_{1-x}Cd_xTe$) are bond-length-matched; in these, the weaker terms are all that remain.[3,4]

Interactions that split the degeneracies, g_j^0, include long-range coherent strain fields such as those found in an epitaxial layer grown on a lattice-mismatched substrate or those caused by temperature gradients behind the growth front in a Bridgeman process. The ordered $Si_{0.5}Ge_{0.5}$ material grown on a silicon substrate by MOCVD is an example of this effect in action.

A quantitative theory of ε_j due to strains and chemical terms has been completed, and a preliminary calculation of the electron/electron interactions has been done for $x = 0.5$ alloys. These interactions predict mixing enthalpies that agree with experiments for a number of materials. The deviations $\bar{x}_j - x_j^0$ in the cluster populations from those of a random alloy are approximately 5 percent for many alloys grown near their melting points, and can be much larger—approximately 15 percent—for alloys grown at lower temperatures.

Because many alloy phenomena are sensitive to short-range correlations, 5- to 15-percent deviations in majority species populations can have profound effects on growth,[1] structural,[5] and electronic properties.[6,7] Several are under investigation.

B. Elastic Constants

In a structure with tetrahedral symmetry, there are, in principle, three independent elastic constants. Yet, valence force-field models that contain only two constants are remarkably accurate, predicting a number of different phenomena in agreement with experiment. We have derived a simple relation between the three constants from Harrison's theory; this relation agrees with the experimental numbers for all Group IV, III-V, and II-VI compounds remarkably well, thereby providing a sound theoretical justification for the valence force-field theory.[8,9]

We have found a way to select parameters in the context of Harrison's theory to determine accurately the bond length, bond energies, and the three elastic constants of all the tetrahedrally coordinated semiconductors.[10] This is required as input to calculate structural and thermal properties of the alloys of these materials.

Calculations of alloy elastic constants are in progress, and our first results are being written for publication.

C. *Solidus Phase Diagrams*

We have formulated a theory for solidus phase diagrams from our order/disorder theory that agrees remarkably well with experimental curves in the cases tested ($Ga_{1-x}In_xAs$, $Ga_{1-x}In_xP$, and $GaP_{1-x}As_x$).[11] We are now extending these calculations to a variety of other materials. These results are sensitive to the $\{\varepsilon_j\}$ set and demonstrate the accuracy of our method.

D. *Vacancy-Formation Energies*

We have devised a new vacancy-formation theory that is sensitive to the local environment around the vacancy site.[12] The total energy of a cluster (as many as 176 bonds are needed to attain convergence) is calculated before and after the central atom is removed to a different environment. The cluster is coupled to the rest of the crystal through a perturbation (as done by Harrison); however, within the cluster, the tight-binding Hamiltonian is solved exactly. Because there are approximations in determining the Hamiltonian, improvements remain to be made. After the atom is removed, the cluster is permitted to relax; Coulomb energies resulting from charge redistribution and rebonding of the dangling hybrids around the vacant site are all taken into account. A variety of final states for the removed atom are treated. These include taking the atom to infinity (the removal energy), taking the atom to a surface (a Schottky defect vacancy-formation energy), and taking the atom to a metallic inclusion. We still have to treat interstitial final states (Frenkel defects).

The most interesting conclusions for compounds arise from trends in the difference between the cohesive energy and the extraction energy per bond. The low-cohesive-energy Group IV and III-V compound materials (e.g. tin and germanium) all have smaller extraction energies than cohesive energies; in the higher cohesive materials (e.g. diamond), the extraction energies are higher than the cohesive energy. As usual, silicon is well-behaved, and the extraction and cohesive energy are nearly equal. This effect helps to explain the relatively high dislocation densities found in bulk-grown, weakly bound materials, compared with those found in the more strongly bound materials. There are also informative trends in the relative ease of extracting anions and cations. This information is an essential ingredient to sticking coefficients and growth models.

In alloys, we find that the various vacancy-formation energies are quite sensitive to the local environment from which an atom is removed.[13] This means that diffusion coefficients, sticking coefficients, and other properties that depend on these formation energies will exhibit multiple activation energy behavior. Any attempt to devise a computer-aided fabrication design of devices built on alloys without including this information will almost certainly fail. On the other hand, control of the cluster populations provides an opportunity to engineer materials to a purpose.

III PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS

If other contracts have provided partial support to any of the following publications, the contract number is noted in parentheses at the end of the listing.

A. *Papers Submitted to Referred Journals*

Chen, A.-B., A. Sher, and M.A. Berding, "Semiconductor Alloy Theory: Internal Strain Energy and Bulk Modulus," submitted to *Physical Review B* (AFOSR Contract F49620-85-K-0023).

Patrick, R.S., A.-B. Chen, A. Sher, and M.A. Berding, "Phase Diagrams and Microscopic Structures of (Hg,Cd)Te, (Hg,Zn)Te and (Cd,Zn)Te Alloys," submitted to *Journal of Vacuum Science and Technology A* (AFOSR Contract F49620-85-K-0023, NASA Grant NAG-1-708 and NAS1-18232).

B. *Papers Published in Referred Journals*

Shih, C.K., W.E. Spicer, W.A. Harrison, and A. Sher, 1985: "Bond-Length Relaxation in Pseudobinary Alloys," *Phys. Rev. B*, Vol. 31, No. 2, p. 1139 (January) (DARPA Contract 800989-B8).

Chen, A.-B., and A. Sher, 1985: "Semiconductor Alloys: Local Bond Lengths, Mixing Enthalpies, and Microclusters," *Proc. Mat. Res. Soc. Symp.*, Vol. 46, p. 137 (AFOSR-84-0284, and DARPA MDA-903-83-C-0108).

Sher, A., A.-B. Chen, and M. van Schilfgaarde, 1986: "Correlations in Pseudobinary Alloys," *J. Vac. Sci. Technol.*, Vol. A4, p. 1965 (AFOSR-84-0284, and DARPA MDA-903-83-C-0108).

van Schilfgaarde, M., A.-B. Chen, and A. Sher, 1986: "Coulomb Energy in Pseudobinary Alloys," Phys. Rev. Lett., Vol. 57, p. 1149 (AFOSR Contract F49620-85-K-0023).

Berding, M.A., A.-B. Chen, and A. Sher, 1987: "HgCdTe versus HgZnTe: Electronic Properties and Vacancy Formation Energies," *Mat. Res. Symp. Proc.*, Vol. 90, p.127 (NASA and NV&EOC Contract NAS1-12232, and AFOSR Contract F49620-85-K-0023).

Sher, A., M. van Schilfgaarde, A.-B. Chen, and W. Chen, 1987: "Quasichemical Approximation in Binary Alloys," *Phys. Rev. B*, Vol. 36, No. 8, p. 4279 (September) (AFOSR Contract F49620-85-K-0023).

Sher, A., A.-B.Chen, M. van Schilfgaarde, and M.A. Berding, 1987: "Semiconductor Alloys, Structural Property Engineering," *Proc. 1st International SAMPE Electronics Conference, Sunnyvale, California*, p. 323 (23-25 June) (AFOSR Contract F49620-85-K-0023, and NASA Contract NAS1-18232).

Sher, A., M.A. Berding, S. Krishnamurthy, M. van Schilfgaarde, and A.-B. Chen, 1987: "Structure-Property Relationships in Semiconductor Alloys," *Mat. Res. Soc. Symp. Proc.*, Vol. 90, p. 91 (NASA Contract NAS1-18232, and AFOSR Contract F49620-85-K-0023).

Berding, M.A., A. Sher, and A.-B. Chen, 1987: "Vacancy Formation Energies in II-IV Semiconductors," *J. Vac. Sci. Technol.*, Vol. 5, p. 3009 (NASA and NV&EOC Contract NAS1-12232, and AFOSR Contract F49620-85-K-0023).

Sher, A., M. Berding, M. van Schilfgaarde, A.-B. Chen, and R. Patrick, 1987: "Modeling of Mechanical Properties of II-VI Materials," *J. Cryst. Growth*, Vol. 86, p. 15 (AFOSR Contract F49620-85-K-0023, and NASA Contract NAS1-18232).

Patrick, R.S., A.-B. Chen, and A. Sher, 1987: "Phase Diagram and Local Correlations in Pseudobinary Alloys," *Phys. Rev. B*, Vol. 36, p. 6585 (AFOSR Contract F49620-85-K-0023, and NASA Grants NAG-1-708 and NAS1-18232).

Berding, M.A., A. Sher, and A.-B. Chen, 1987: "Polarity in Semiconductor Compounds," *Phys. Rev. B*, Vol. 36, p. 7433 (AFOSR Contract F49620-85-K-0023 and NASA Contract NAS1-12232).

van Schilfgaarde, M., and A. Sher, 1987: "Tight-Binding Theory and Elastic Constants," *Phys. Rev. B*, Vol. 36, No. 8, p. 4375 (September) (AFOSR Contract F49620-85-K-0023).

van Schilfgaarde, M., and A. Sher, 1987: "Tight-Binding Theory of Force Constant Models," *Appl. Phys. Lett.*, Vol. 51, No. 3, p. 175 (July) (AFOSR Contract F49620-85-K-0023).

C. Books Submitted for Publication

None.

D. Books Published

None.

E. Patents Filed

None.

F. Patents Granted

None.

G. Invited Presentations at Topical or Scientific/Technical Society Conferences

Sher, A., A.-B. Chen, and M. van Schilfgaarde, 1985: "Correlations in Pseudobinary Alloys," 1985 U.S. Workshop on the Physics and Chemistry of Mercury Cadmium Telluride, San Diego, California (8-10 October).

Sher, A., M.A. Berding, S. Krishnamurthy, M. van Schilfgaarde, A.-B. Chen, and W. Chen, 1986: "Structure Property Relationships in Semiconductor Alloys," 1986 Fall Meeting MRS, Boston, Massachusetts (1-6 December) (NASA Contract NAS1-18232, and AFOSR Contract F49620-85-K-0023).

Sher, A., A.-B. Chen, M. van Schilfgaarde, and M.A. Berding, 1987: "Semiconductor Alloys: Structural Property Engineering," presented at 1st International SAMPE Electronics Conference, Sunnyvale, California (June).

Sher, A., M.A. Berding, M. van Schilfgaarde, A.-B. Chen, and R.S. Patrick, 1987: "Modeling of Mechanical Properties of II-VI Materials," presented at the 7th American Conference on Crystal Growth in Conjunction with II-VI-87, Monterey, California (12-17 July).

H. Contributed Papers

Chen, A.-B., M. van Schilfgaarde, and A. Sher, 1986: "Formation Energies of Semiconductor Alloys: Dipolar Contributions," APS Meeting, Las Vegas, Nevada (March).

van Schilfgaarde, M., A. Sher, and A.-B. Chen, 1986: "Atomic Correlations in Pseudobinary Semiconductor Alloys," APS Meeting, Las Vegas, Nevada (March).

Berding, M.A., S. Krishnamurthy, and A. Sher, 1986: "Electronic Structure of HgCdTe and HgZnTe," 1986 Fall Meeting MRS, Boston, Massachusetts (1-6 December). (NASA Contract NAS1-18232, and DARPA Contract F49620-85-C-0103).

Tsau, G.-H., A. Sher, M. Madou, J.A. Wilson, V.A. Cotton, and C.E. Jones, 1985: "State Characterization of the Hg1-xCdxTe/Photox SiO2 Interface," 1985 U.S. Workshop on the Physics and Chemistry of Mercury Cadmium Telluride, San Diego, California (8-10 October).

Chen, A.-B., M. van Schilfgaarde, S. Krishnamurthy, M.A. Berding, and A. Sher, 1986: "Alloy Electronic Structure and Statistics," 7th Conference on Ternary and Multinary Compounds, Snowmass, Colorado (9-12 September) (AFOSR Contract F49620-85-K-0023, and NASA Contract NAS1-18232).

van Schilfgaarde, M., A.-B. Chen, and A. Sher, 1986: "Configuration Dependence of Coulomb Interactions in Pseudobinary Alloys," 7th Conference on Ternary and Multinary Compounds, Snowmass, Colorado (10-12 September) (AFOSR Contract F49620-85-K-0023).

Berding, M.A., A. Sher, and A.-B. Chen, 1986: "Vacancy Formation Energies in II-VI Semiconductors," presented at the 1986 U.S. Workshop on the Physics and Chemistry of Mercury Cadmium Telluride, Dallas, Texas (7-9 October).

Berding, M.A., A.-B. Chen, and A. Sher, 1986: "HgCdTe versus HgZnTe: Electronic Properties and Vacancy Formation Energies," presented at Fall Meeting of MRS, Boston, Massachusetts (1-6 December).

Chen, A.-B., R.S. Patrick, A. Sher, and M. van Schilfgaarde, 1987: "Microclustering in Pseudobinary Semiconductor Alloys," presented at the March Meeting of the American Physical Society, New York, New York (16-20 March) (AFOSR Contract F49620-85-K-0023, and NASA Contract NAS1-18232).

I. *Honors/Awards/Prizes*

None.

J. *Graduate Students and Postdoctorals Supported Under the CRP for the Year Ending 1 October 1987*

None.

REFERENCES

1. Sher, A., M. van Schilfgaarde, A.-B. Chen, and W. Chen, 1987: "Quasichemical Approximation in Binary Alloys," *Phys. Rev. B*, Vol. 36, p. 4279.

2. Sher, A., M. Berding, M. van Schilfgaarde, A.-B. Chen, and R. Patrick, 1987: "Modelling of Mechanical Properties of II-VI Materials," J. Crys. Growth, Vol. 86, p. 15.

3. Sher, A., A.-B. Chen, and M. van Schilfgaarde, 1986: "Correlations in Pseudobinary Alloys," *J. Vac. Sci. Technol. A*, Vol. 4, p. 1965.

4. van Schilfgaarde, M., A.-B. Chen, and A. Sher, 1986: "Coulomb Energies in Pseudobinary Alloys," *Phys. Rev. Lett.*,Vol. 57, p. 1149.

5. Berding, M.A., A. Sher, and A.-B. Chen, 1987: "Vacancy Formation Energies in II-VI Semiconductors," *J. Vac. Sci. Technol. A*, Vol. 5, p. 3009.

6. Chen, A.-B., M. van Schilfgaarde, S. Krishnamurthy, M.A. Berding, and A. Sher, 1986: "Alloy Electronic Structure and Statistics," Seventh International Conference on Ternary and Multinary Compounds, Snowmass, Colorado (10-12 September).

7. Berding, M.A., S. Krishnamurthy, A. Sher, and A.-B. Chen, 1987: "Electronic and Transport Properties of HgCdTe and HgZnTe," *J. Vac. Sci. and Technol. A*, Vol. 5, p. 3014.

8. van Schilfgaarde, M., and A. Sher, 1987: "Tight-Binding Theory of Force Constant Models," *Appl. Phys. Lett.*, Vol. 51, p. 175.

9. van Schilfgaarde, M., and A. Sher, 1987: "Tight-Binding Theory and Elastic Constants," *Phys. Rev. B.*, Vol. 36, p. 4375.

10. Chen, A.-B., unpublished.

11. Patrick, R., A.-B. Chen, and A. Sher, 1987: "Phase Diagrams and Local Correlations in Pseudobinary Alloys," *Phys. Rev. B*, Vol. 36, p. 6585.

12. Berding, M.A., A. Sher, and A.-B. Chen, "Vacancy Formation Energies in Semiconductor Compounds," submitted to *Physical Review B*.

13. Berding, M.A., A. Sher, and A.-B. Chen, "Vacancy Formation Energies in Semiconductor Alloys" (in preparation).

END
DATE
FILMED
9-88
DTIC