STRUCTURAL THEORY
OF METASTABLE PSEUDOBINARY SEMICONDUCTOR ALLOYS

Final Report

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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.

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.\footnote{\textsuperscript{1}}

A cluster of $n$ atoms is specified with the number of $B$ atoms, $n_j(B)$; states of energy, $\varepsilon_j$; 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, $x_j$, are grand canonical ensembles with chemical potential $\mu_j$,

$$x_j = g_j e^{\left[\mu_j(B) - \varepsilon_j\right]/kT} / q,$$

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

$$n_x = \sum_j n_j(B) x_j.$$

The combinatorial analysis then gives the proper mixing entropy, $\Delta S$, and the mixing enthalpy, $\Delta E$, is calculated from

$$\Delta E = \sum_j \varepsilon_j x_j,$$

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 $g_j = g_j^0 \equiv \left[\begin{array}{c} n \\ n_j(B) \end{array}\right]$ is not split (so it is $g_j^0$ the cluster degeneracy of a random alloy), then

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

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 $e_j$ 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, 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$_x$As and Hg$_{1-x}$Cd$_x$Te) 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 $e_j$ 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, structural, 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\textsubscript{1−x}In\textsubscript{x}As, Ga\textsubscript{1−x}In\textsubscript{x}P, and GaP\textsubscript{1−x}As\textsubscript{x}).\textsuperscript{11} We are now extending these calculations to a variety of other materials. These results are sensitive to the \{ε\} 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.\textsuperscript{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.\textsuperscript{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


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


**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


H. Contributed Papers


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).


I. Honors/Awards/Prizes

None.

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

None.

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REFERENCES


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