SESSION A25 DMP:
THEORY OF MATERIALS I:
LARGE-SCALE APPROACHES
Monday morning, 20 March 1995
Regency Ballroom I, Fairmont Hotel, at 8:00
N. Trouiller. presiding

'*Invited paper*

8:00

A251 **Electronic** Structure **of 1000 Atom Semiconductor Quamtum Structures via Pseudopotential Calcula-**

National Renewable Energy Laboratory, Golden, CO,80401

We have developed an approach which uses screened pseudopotentials and a plane wave basis to calculate the electronic structure for semiconductor thousand atom nanoscale quantum systems. A screened spherical pseudopotential is first fitted to a few first principle bulk total potentials, then is modifed to fit the experimental band structure. This produces a pseudopotential which is accurate for its wavefunctions and band energies, and is transferable to different crystal structures and unit cell volumes. Using such pseudopotentials, we can construct nonselfconsistently the total potential of a large system. To find the electronic structure **for such a** system for the given potential, we have developed three methods: (1) the "folded spectrum" method' , which finds the band edge states (e.g, the valence band maximum and conduction band minimum) without calculating all states below them and which scales linearly with the number of atom N at (2) the "generalized moments" methods which calculates the density of states and optical absorption spectrum, and whose computing time is roughly independent of N at (3) the Lanczos method' which can calculate all occupied states and scales roughly as the square of N at These methods are much faster than the widely used preconditioning conjugate gradient method, making possible calculations for thousand atom systems in one or two Cray-90 YMP CPU hours. The current approach has been used in the study of Si quantum dots' with a local pseudopotential and CdSe quantum dots with nonlocal pseudopotentials and spin-orbit coupling. The band gap, radiative lifetime, density of states and dielectric constants are studied as functions of quantum dot size and shape. This relatively sophisticated calculation has been used to judge the accuracy of other simpler calculations and models.

'L.W. Wang and A. Zunger, J. Chem. Phys. 100, 2394 (1994).
[2] L.W. Wang, Phys. Rev. B 49, 10154 (1994).
[3] L.W. Wang and A. Zunger, Comp. Mat. Sci. 2,326 (1994).
[4] L.W. Wang and A. Zunger, J. Phys. Chem. 98, 2158 (1994); Phys. Rev. Lett. 73, 1039 (1994).

SESSION C4: GeSi: FROM MATERIALS RESEARCH TO DEVICES AND TECHNOLOGY. SYMPOSIUM OF THE COMMITTEE ON APPLICATIONS OF PHYSICS

Monday afternoon, 21 March 1994; Room South 2 at 14:30: L. Rubin, presiding

14:30

C4 1 An Overview **of GeSi Materials: Structural Stability, Band Offsets, and Electronic Structure.** *A l e x Z u n g e r National Renewable Energy Laboratory.*

Thi bask properties of GeSi materials will be reviewed. The main focus will be on electronic properties of alloys and short period superlattices as a function of composition, substrate composition, and substrate orientation. Band-gap bowing' and band offsets[2] will be discussed. Brillouin zone folding, which in short period superlattices can lead to quasidirect band-gaps and greatly enhanced optical transitions, will be described. Finally, structural stability of alloys and superlattices will be addressed.

[1] J. F. Morar and P. E. Batson, J. Vac. Sci. Technol. B **10**, 2022 (1992).

[2] E. T. Yu et al., J. Vac. Sci. Technol. B 8,908 (1990); W.-X. Ni and G. V. Hansson, Phys. Rev. B 42, 3030 (1990).

[3] T. P. Pearsall et al., Phys. Rev. Lett., 58,729 (1987); S. Froyen, D. M. Wood, and A. Zunger, Phys. Rev. B **36**, **4547** (I 987); Phys. Rev. Lett. 62, 975 (1989); Appl. Phys. Lett. 54, 2435 (1989); Thin Solid Films 183, 33 (1989); M. S. Hybertson, and M. Schlüter, Phys. Rev. B **36**, **9683** (1987); S. Satpathy, R. M. Martin, and C. G. Van de Walle, Phys. Rev. B 38, 13237 (1988); U. Menczigar et al., Phys. Rev. B 47.4099 (1993) and references therein.

[4] A. Ourmazd and J. C. Bean, Phys. Rev. Lett., 55, 765 (1985); J. E. Bernard and A. Zunger, Phys. Rev. B 44, 1663, (1991); E. Müller et al., Phil. Mag. Lett. 64, 183 (1991); J. E. Jesson et al., Phys. Rev. Lett., 70, 2293 (1993); F. K. LeGoues et al., Phys. Rev. B 47. 10012 (1993).

Invited Papers

8:00
Q14.1 Spontaneous Ordering in Semiconductor Alloys.'
ALEX ZUNGER,[+] *National Renewable Energy Laboratory.*

Vapor-phase (MOCVD, MBE, ALE) growth of many $A_{1-x}B_xC$ semiconductor alloys results in spontaneous long-range order, most often in the form of monolayer-alternation $(AC)_1/(BC)_1$ superlattices along the (111) direction (the "CuPt" structure). At the same time, it is known theoretically that: (i) the lowest energy state of **bulk** alloys is phase-separation into AC + BC, and that (ii) the lowest energy state of **epitaxial** alloys is the ABC, chalcopyrite structure. A combination of first-principles total energy calculations and lattice-gas thermodynamic models [1] clarifies that: (i) phase-separation is inhibited by the epitaxial coherence with the substrate, (ii) the chalcopyrite structure is surface-unstable relative to the CuPt structure. and (iii) dimerization, buckling and tilting of surface cations stabilizes even at $T \sim 900K$ a special variant ("CuPt-B") of the CuPt structure. Spontaneous ordering changes profoundly the band structure of the alloy [2], leading to (a) bandgap reduction, and (b) splitting of the degeneracy of the valence band maximum. These reflect L-point zone folding and crystal-field effects, respectively. I will discuss the electronic structure of random, ordered and partially-ordered alloys, demonstrating new opportunities for alloy bandgap engineering at fixed composition, including the possibility [3] of attaining far-IR bandgaps of **ordered** III-Vs.

[1] Froyen. zunger, Phys. Rev. Lett. **66, 2132** (1991); Bernard, Froyen. Zunger, Phys. rev. B 44, 11178 (1991); Osorio, Bernard. Froyen and zunger, **ibid 45**, 11173 (1992)
[2] Wei and Zunger, Appl. Phys. Lett. 56, 662 (1990); Laks, Wei and Zunger, Phys. Rev. Lett, (December 24, 1992)
[3] Wei and Zunger, Appl. Phys. Lett. 58, **2684** (1991).

SESSION E17: DCMP: ELECTRONIC STRUCTURE: METALS AND ALLOYS
Tuesday morning, 23 March 1993; Room 606 at 8:OO; 0. Johnson, presiding

Invited Paper

8:OO
E17 1 Predicting Stable Structures of Intermetallic Compounds.*
ZHU WEI L U National Renewable Energy Laboratory.

The voluminous catalogues of phase-diagrams of intermetallic compounds testify to the great structural diversity in these systems. Attempts have previously been made at explaining this type of selectivity by contrasting the self-consistently calculated total energies of a few ordered structures. Such calculations select but a small, $O(l0)$ set of "intuitive structures" out of the 2N possible configurations of two types of atoms on a fixed lattice with N sites, searching for the lowest energy. Clearly, the potential for omitting unsuspected, yet stable structures, is great. We use instead first-principles calculations of the total energies of $O(l0)$ structures to define a multi-spin Ising Hamiltonian, whose ground state structures can be systematically searched using methods of lattice theories. This is illustrated here for the intermetallic compounds AlNi, CuRh, CuPd, CuPt, CuAu, PtAu, PtPd, PtRh, PtNi, and PdRh, [1,2] for which the correct ground states are identified out of N 65,000 configurations. This establishes a direct and systematic link between the electronic structure and phase stability. The analysis reveals intriguing cases such as relativity-induced long-range order (NiPt) and phase separation (PtAu).3 Combined with simulated annealing, such an Ising expansion yields thermodynamic quantities, and short range order parameters which can be compared with experiment.

'2. W. Lu, S.-H. Wei, A. Zunger, Phys. Rev. Lett. 88, 1973 (1991); ibid 68, 1961 (1992).
2Z. W. Lu, S.-H. Wei, A. Zunger, S. Frota-Pessoa, and L. G. Ferreira, Phys. Rev. B 44, 512 (1991).
3Z. W. Lu, S.-H. Wei, A. Zunger, Euro. Phys. Lett. to be published.

SESSION J13: DMP: THEORY OF MATERIALS
Wednesday morning, 24 March 1993; Room 211 at 11:00 G. Baraff, presiding

11:00
J13 1 Chemical-Potential Dependence of Impurity and Defect-Formation Energies in GaAs.*
SHENG BAI ZHANG, National Renewable Energy Laboratory.

Recent experiments and theoretical studies both point to the direction that the absolute formation energy and hence the equilibrium concentration of defects and impurities in GaAs depends strongly on the atomic chemical potentials of As and Ga as well as the electron chemical potential. For example, (1) ab initio calculations showed that the equilibrium Ga vacancy concentration changes by more than 10 orders of magnitude as the chemical potentials of As and **Ga vary** over the thermodynamically allowed range. This result indicates that the rate of Ga self-diffusion depends strongly on the surface-annealing conditions. (2) By calculating the formation energy of Si donors, acceptors and defect complexes, the equilibrium concentrations of native defects and Si-defect complexes as well as the total solubility of Si in GaAs were determined. The calculated solubiity limit is in good agreement with experiment. A Si-vacancy complex ($[Si_{Ga} - V_{Ga}]^{2-}$) occurs in relatively high concentration under As-rich conditions and may therefore mediate Si and **Ga** diffusion. This complex also provides an important mechanism for compensation in heavily doped GaAs.

11:36

J13 2 Calculations of the Doping limits in ZnSe
DAVID LAKS, IBM Thomas J. Watson Research Center.

ZnSe and other wide-band-gap semiconductors have always been plagued by doping problems, particularly for p-type material. We use first-principles density-functional-theory calculations to provide a comprehensive description of the semiconductor-dopant system, using ZnSe doped with Li, Na, or N acceptors as our examples. Calculations are performed for the' native point defects, the dopant atoms at different sites in the crystal, and for the bulk solid phases of the native and dopant atoms. By introducing the chemical potentials of the various atomic species, we address the issues of (I) compensation by native defects and its relation to the stoichiometry of the host crystal, (2) self-compensation reactions in which substitutional acceptors become donors by moving to interstitial sites, and (3) the salubility of the acceptor dopants. Our results show that native-defect compensation and self-compensation can be avoided by adjusting the growth conditions, while acceptor solubility poses a much more serious limit to acceptor-doping of ZnSe.

Invited Paper

14:30
C23 Stability of Semiconductor Superlattices and Their Alloys.' ALEX ZUNGER. *Solar Energy Research Institute*

Most theoretical research on semiconductor superlattices focused on their electronic properties. Here I will discuss the thermodynamic stability [I] of **a variety** of strained-layer superlattices [CaAs-GaSb, GAP-GaAs, CaP-InP, GaAs-InAs, AlP-InP, ZnTe-HgTe and ZnTe-CdTe] in different **orientations.** Artificial growth of ApBp superlattices (SL's) is based **on a series** of sequential **exposures of a substrate to** the pure compound A then **pure B,** etc., thus largely circumventing the thermodynamically controlled simultaneous reaction $xA+(1-x)B \rightleftarrows A_x B_{1-x}(\gamma)$ which could have produced a variety of structures y ranging from disordered alloys to phase separation. Rather than focus on simulation of **growth kinetics,** I ask here how stable is an already grown SL **with** respect to decomposition into its constituents or to disordering into **an** alloy and how does the repeat period p and orientation $\hat{G}$ affect the above. These questions are addressed by (i) first-principles (LAPW and psuedopotential) calculations of the total energies of ordered $A_p B_p$ SL's, and (ii) statistical mechanics (cluster-variation) calculations for the disordered $A_{0.5}B_{0.5}$ alloys (21. This shows: (i) the dominance of strain over charge transfer **iffectr** leads to the instability of all bult SL's with respect to **disproportionation, except** (ii) $(AlX)_2(InX)_2$ for X=P, and As where the opposite **is true in the chalcopyri te structure. (iii)** The stability order. **for Long $p \to \infty$ bulk SL's.** is **[001]>[201]>[110]>[111], reflecting the sequence of** the biaxial strain in the binaries. (iv) For small p's, there are "magic numbers" whereby **p=2[110]** and **[201] SL's** are the atablest, owing to an effective interfacial **relaxation (v) the 50%-50% random** alloy is stabler than **all SL's except those at the** "magic numbers", for which **spontaneous** Long range ordering of an alloy **is** possible, (vi) **the** stability of epitaxial **SL's** on a lattice matched substrate is greatly enhanced **relative to bulk** due to the destabilization **of the** decomposition products.

[1] R. C. Dandrea, J. **E.Bernard,** S.-B. **Wei** and A. **Zunger,** submitted to **Phys.** Rev. Letters.
[2] L. C. **Ferreira, S.-H. Wei** and A. Zunger, **Phys.** Rev. **B40, 3197(1989).**

9:12

A'2 1 Stabilization of **Epitaxial Structures.** DAVID M. WOOD, *SERI*.

Phenomena peculiar to coherent epitaxial growth of alloys include: (i) ordered compounds not present in the bulk phase diagram; (ii) constituents insoluble in bulk below a miscibility temperature T G become epitaxially soluble even 1200 "C lower; (iii) the pinning of the measured composition x of an **epitaxlx** alloy near where the alloy is lattice matched to the substrate ('lattice latching' or pulling'), while the composition x of a **bulk** alloy grown under identical conditions varies widely. A simple picture of epitaxial energetics makes clear the origin of these effects. A cluster-based theoretical description permits prediction and quantitative comparison of bulk and epitaxial (x,T) phase diagrams for the same system. It also places the common phenomenological treatment of an alloy as an elastic continuum on a microscopic footing (and highlights its inadequacies!). Results will be given for (a) $cu_{1-x}Au_x$, a typical 'ordering' alloy (with stable stoichiometric compounds in bulk) and (b) the isovalent semiconductor $GaAs_xSb_{1-x}$, a typical Phase separating' alloy (insoluble until entropy dominates above T_{MG}). All of the effects above emerge naturally from our treatment; we trace them to the lattice mismatch between the alloy constituents, not to mismatch with the substrate. A simple expression relates the degree of composition pinning to the epitaxial suppression of the miscibility temperature . Using an epitaxial generalization of a recent thermodynamic treatment of bulk molecular beam epitaxy growth of $A_{1-x}B_xC$ isovalent semiconductors[3] we demonstrate that composition pinning should be observabfe here as well. Substrate orientation and film thickness effects will also be discussed.

[1] D. M. Wood and Alex Zunger, Phys. Rev. Lett. 61, 1501 (1988).
[2] D. M. Wood and Alex Zunger, Phys. Rev. **B38** (in press).
[3] I. Seki and A, Koukitu, J. Cryst. Growth 78, 342 (1986).

**SESSION PAa: SYMPOSIUM OF THE DIVISION OF CONDENSED MATTER PHYSICS:
METASTABLE STRUCTURES AND ORDERING IN SEMICONDUCTORS**
Friday morning 20 March 1987; Grand Ballroom East at 8:00; C. B. Stringfellow, presiding

8:00
PAa 1 ,Stability, Ordering, and **Metastability of Semiconductor Alloys.'** ALEX ZUNGER, *Solar Energy Research Institute.*

Bulk phase diagrams of all isovaLent semiconductor alloys appear to differ profoundly from those of metallic alloys: the former did not exhibit any compound formation and were invariably associated with positive mixing enthalpies $A_n(n)(x) > n$, suggesting disproportionation of the disordered (n) alloy $A_x B_{1-x} C$ into its constituents AC and RC at a sufficiently low temperature. These classic observations motivated previous models of semiconductor alloys to postulate a revulsive interaction $\Delta E^{(n)} > 0$ (analogous to ferromagnetism) of each of the "building blocks" $A_n B_{4-n} C_4$ (0<n<4) with respect to its end-point constituents nAC + (4-n)RC. Applying first-prin ciples self-consistent total energy calculations to the ordered $A_n B_{4-n} C_4$ phases, we find that $\Delta E^{(n)}(V)$ represents a competition between destabilizing strain effects and potentialLy stabilizing "chemical" (or "spin-, flip") effects, such as charge transfer and polarization. Furthermore, the abiltty of the common atom C to utilize its cell-internal structural degrees of freedom (resulting in generally dissimilar A-C and R-C bond lengths) can substantially stabilize such ordered structures. As a result, some systems can have $\Delta E^{(n)} < 0$ (e.g., SI-C, CdTe-MnTe) and others (e.g. GaAs-AlAs, Si-Ce) have $\Delta E^{(n)} > 0$. Using these volume (V)- dependent~interactton energies $\{\Delta E^{(n)}(V)\}$ in an approximate solution (through the Cluster Variation Method) of the appropriate spin 1/2 f.c.c. Ising model (including up to four-body interactions), we calculate the alloy phase diagrams as well as $AH(D)(x)$. We predict that: (i) Ordered stoichiomctric phases and disproportionation can coexist in the same phase diagram, (ii) strain stabilize ordered phases when chemical interactions are attractive, but otherwise (iii) strain Leads to metastahle ordered phases, and (iv) the interactions $\Delta E^{(n)}(V)$ can lead either to clustering or anti-clustering. Our predictions will be compared to unprecedented subsequent experimental observations of long-range order in semiconductor alloys reported recently.

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