Final Technical Report

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Title:

Electronic and Total Energy Properties of Ternary and Quaternary Semiconductor Compounds, Alloys and Superlattices

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1 Introduction

This proposal was mainly concerned with the theoretical study of semiconductor compounds, alloys and superlattices of interest for photovoltaic applications. In the last year (1991) a study was devoted to metal/graphite bonding in relation to use of graphite fiber reinforcement of Cu for high thermal conductivity applications.

Below, we briefly describe the main research topics addressed during the full period of the grant, organized as follows.

1. Studies of the In-Ga-As ternary system
2. Band-offsets at common anion and InAs/GaSb InAs/AlSb heterojunctions
3. Alloy theory (cluster variation method)
4. Cu/graphite bonding

Most of the work in points 1-3 has been described more extensively in previous yearly reports and renewal applications and in publications. The last topic is described more fully in a separate report attached herewith. A list of publications resulting directly from this grant or from other grants but related to this work and of conference presentations is given at the end.

2 Technical Description of Research Activity

2.1 In-Ga-As system

During the December 1988-January 1991, we mainly studied the energy of formation and electronic structure of the $In_xGa_{1-x}As$ system. The general approach taken was to calculate total energies of the ordered compounds formed in the $L1_2$ (25 % and 75 %) and $L1_0$ (50 %) superlaticces of the cation fcc sublattice. The energy of disordered alloys is described by means of a cluster expansion in terms of tetrahedral clusters of the cation sublattice. The energies of the basic tetrahedra A_4, A_3B, A_2B_2, AB_3 and B_4 are obtained from the above mentioned ordered compounds and the binary semiconductors

A and B. Combined with the mixing entropy, the resulting free energy as a function of composition and temperature forms the basis for a study of the phase diagram.

Total energy calculations were carried out using the density functional theory in the local density approximation and the linear muffin-tin orbital method in the ASA approximation. The position of the common anion sublattice must be relaxed with respect to the cation sublattice in order to allow local bond length relaxation. This relaxation was studied by means of the Keating model. It was found necessary to adjust the spring constants α of the Keating model to the elastic properties obtained from first-principles (i.e. the bulk modulus) in order to obtain accurate results. The effects of various treatments of the shallow core electrons (Ga 3d and In 4d) on the energy of mixing was investigated. Also, the relativistic effects on the energies of formation were investigated. We found fair agreement for the formation energies with previous work of Boguslavski and Baldereschi,[1] (hereafter referred to as BB), when the band-dispersion of shallow core states was not included and relativistic effects were included. Values about twice as large, however were obtained when core-state dispersion was included. Also, our results did not agree with BB's work as to the decomposition of the energy of formation in contributions due to elastic hydrostatic deformation of the starting compounds, mixing enthalpy at constant volume and bond relaxation. We note that our work gave better agreement with experimental lattice constants than theirs and thus describes the volume effects more accurately. This work was presented at the APS March meeting in 1990. Further work using full-potential LMTO for the relaxations and two panel treatment of the d-partial waves was deemed necessary before this project could be finished with a publication.

2.2 Band-offsets

A second topic of study during this period (1988-1991) was the band-offsets at semiconductor heterojunctions. After developing a general theory of band-offsets, the so-called *self-consistent dipole theory* in the context of other grants, we applied it to the study of the orientation dependence of band-

[1] P. Boguslavski and A. Baldereschi, *Solid State Communic.* 66, 679 (1988)

offsets with partial support from this NASA grant. [2] This study was devoted to the common anion systems AlP/GaP, AlAs/GaAs, AlSb/GaSb and CdTe/HgTe. We found the band-offsets to be largely interface independent as a result of the important screening. A slightly larger dependence was found for the non-common anion systems InAs/GaSb and InAs/AlSb.

2.3 Alloy Theory

During 1990-1991, we continued the development of alloy theory with the aim of calculating phase diagrams using the cluster variation method and extensions of the Connolly-Williams approach. The programs for this were developed in our group by Carlos Amador with partial support from this grant. The main application of this work has been to a metallic alloy system Ni_xPt_{1-x}. A new approach for inclusion of the relaxations was developed. It is based on effective local volume renormalization of the nearest neighbor interactions. The preparation of a publication of this work for Phys. Rev. Letters is in progress.

We also used the developments of alloy theory in the context of other grants (mainly related to diamond and other wide band gap semiconductors such as SiC, AlN and c-BN). These deal with pure ternary and quaternary systems although they can still be treated as pseudobinary because of the local stoichiometry requirements.

2.4 Cu-Graphite bonding

As mentioned earlier, the topic of research was changed in 1991 to a study of Cu to graphite bonding. This change was made because of an interest arising in this subject in the Materials Brach at NASA LeRC (Dr. Stephen Pepper). We successfully explained the electronic reasons for weak bonding in this system and made a critical evaluation of the exisiting literature values for surface energies of Cu and graphite and their application to the wetting studies of metals on graphite. We also found a small charge transfer to take place in this system consistent with known results on other metal/graphite systems.

[2] W. R. L. Lambrecht and B. Segall, *Phys. Rev. B* **41**, 8353 (1990).

3 Publications and Presentations

3.1 Publications directly resulting from this grant and acknowledging NASA support.

1. Interface dependence of band offsets in lattice-matched isovalent heterojunctions, by Walter R. L. Lambrecht and Benjamin Segall, *Phys. Rev. B* **41**, 8353-7 (1990).

2. Temperature composition phase diagram of Ni–Pt alloys based on first-principles energetics, by Carlos Amador, Walter R. L. Lambrecht, Benjamin Segall and Mark Van Schilfgaarde, in preparation for Phys. Rev. Lett. (1992)

3.2 Presentations at Conferences

1. Interface-orientation Dependence of Band-offsets, by W. R. L. Lambrecht and B. Segall, APS March Meeting in St. Louis, 1989, *Bull. Am. Phys. Soc.* **34**, 878 (Abstract N14.9) (1989).

2. Energetics of $In_xGa_{1-x}As$ ordered compounds and superlattices, by C. H. Lee, W. R. L. Lambrecht, B. Segall, and M. Van Schilfgaarde, APS March Meeting in Anaheim 1990 *Bull. Am. Phys. Soc.* **35**, 305 (Abstract C23.7) (1990).

3. Interface dependence of band offsets in isovalent heterojunctions, B. Segall and W. R. L. Lambrecht, APS March Meeting in Anaheim 1990, *Bull. Am. Phys. Soc.* **35**, 417 (Abstract G7.11) (1990).

4. First-principles calculation of the phase diagram of NiPt, C. Amador, W. R. L. Lambrecht and B. Segall, APS March Meeting in Indianapolis 1991, *Bull. Am. Phys. Soc.* **37**, 496 (Abstract K25.1) (1990).

3.3 Other related publications

1. Self-consistent-dipole theory of heterojunction band-offsets, by W. R. L. Lambrecht, B. Segall and O. K. Andersen, *Phys. Rev. B* **41**, 2813-31 (1990).

2. Interface-bond-polarity model for heterojunction band-offsets, by W. R. L. Lambrecht and B. Segall, *Phys. Rev. B* **41**, 2832-18 (1990)

3. Electronic structure and bonding at SiC/AlN and SiC/BP interfaces, by W. R. L. Lambrecht and B. Segall, *Phys. Rev. B* **43** 7070-85 (1991).

4. Phase diagram of Ni-Pt from linear muffin-tin orbitals total energy calculations, by C. Amador, W. R. L. Lambrecht, B. Segall, in *Application of Multiple Scattering Theory to Materials Science*, edited by W. H. Butler, A. Gonis, P. H. Dederichs, R. L. Weaver, Mater. Res. Soc. Symp. Proc., Vol. 253 (MRS, Pittsburgh 1992), p. 297-302.