

Comments

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Validity of the recursion method for calculating the energy gap of $(\text{GaAs})_{1-x}\text{Ge}_{2x}$: Comments on a paper by Gu, Newman, and Fedders

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(Received 5 August 1987; revised manuscript received 14 December 1987)

We have shown previously that the energy gap of $(\text{GaAs})_{1-x}\text{Ge}_{2x}$, as calculated by the recursion method, is sensitive to the presence of As-As nearest-neighbor pairs. When significant concentrations of such As-As bonds are incorporated into alloys with near-midrange compositions the gap decreases from about 0.5 eV, in agreement with optical-absorption data, to zero, in clear disagreement with experiment. This provides a strong reason for rejecting the Newman-Dow (ND) thermodynamic model of the alloy, which predicts large concentrations of As—As bonds. In a recent paper Gu, Newman, and Fedders claimed that the recursion calculations, upon which our rejection of the ND model is based, are invalidated by an elementary error. We demonstrate that this assertion is unfounded.

The physics underlying the structural and electronic properties of the metastable semiconductor alloys $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ and $(\text{GaSb})_{1-x}\text{Ge}_{2x}$ has been discussed previously by us and by others.¹⁻⁶ The main properties to be explained are the composition dependences of the energy gap of $(\text{GaAs})_{1-x}\text{Ge}_{2x}$, which is deeply bowed, and of the long-range order of $(\text{GaSb})_{1-x}\text{Ge}_{2x}$, which exhibits a transition from zinc-blende to diamond symmetry above a critical Ge content, i.e., with $x > x_c \approx 0.3$ (for specimens grown in a $\langle 100 \rangle$ direction). There has been extensive debate about the relative merits of two types of model that are based upon quite distinct assumptions about the phenomena that determine the atomic arrangements in these alloys.

In the thermodynamic model first proposed by Newman and Dow^{1,2} (ND) the ordering of group-III and group-V atoms onto their respective sublattices occurred in response to a local minimum in the free energy of the bulk crystalline phase. In application of the theory the value of the critical composition was not derived, but was chosen to make the theory fit $x_c = 0.3$. A feature of the thermodynamic model is the occurrence of large concentrations of wrong bonds (i.e., As—As and Ga—Ga) at midrange alloy compositions. (The concentrations are somewhat reduced in later variations of the thermodynamic model with more adjustable parameters, but the conclusions reached here still apply in such cases.)

In the alternative class of growth models that has been proposed by us³⁻⁵ and by Kim and Stern⁶ the atomic arrangements are assumed to arise from random placement of atoms on lattice sites subject to some nearest-neighbor

restrictions. As first pointed out by Kim and Stern, such a process can arise from the selection of energetically favorable sites during incorporation of constituents that arrive randomly at a growing surface. A striking feature of the growth models is the absence of any continuously adjustable parameters. We have found that the critical composition, $x_c \approx 0.3$, for $\langle 100 \rangle$ growth is obtained with a model that is quite insensitive to details of these rules for growth.⁴ Unlike the thermodynamic model, the growth models prohibit the occurrence of significant concentrations of wrong bonds.

Controversy has arisen from a difference between the energy gap calculated by ND (Refs. 1 and 2) for $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ with their postulated structure and that obtained by us with the same structural assumptions.³ Calculations of the energy gap that were made using the recursion method^{3,4} show that the As—As wrong bonds of the thermodynamic model give zero energy gap towards the middle of the composition range. This is in sharp contrast to the growth model, whose structures without wrong bonds gave a minimum energy gap of about 0.5 eV, in accord with experiment. The gap-closing effect of the wrong bonds arises from alloy scattering, which is inherently not treatable with the virtual-crystal approximation (VCA) that was used by ND. Thus, if our recursion calculations for the ND structure are correct, then the ND thermodynamic model is inconsistent with the observed energy gap of $(\text{GaAs})_{1-x}\text{Ge}_{2x}$.

All of the preceding information has been given in previous publications³⁻⁵ with a level of detail that we

thought was quite adequate. However, a recent paper by Gu, Newman, and Fedders⁷ (GNF) misrepresented our work so egregiously that a correction is needed. Specifically, an incorrect description of our calculation of the energy gap was used to discredit our results by imputing to us the shortcomings of a method that we never used.

In reference to our papers GNF state "They find that if one calculates the densities of states by combining the recursion method with MFT, the existence of As—As bonds in the structure closes the band gap. Thus results from the recursion method for the electronic densities of states are in apparent disagreement with optical-absorption data for the direct gap. . . . We suspect, however, that it is the recursion method that is at fault. That is, we have found that the *method* fills gaps in the density of states. For example, . . ." with MFT denoting mean-field theory.

To define somewhat more precisely than GNF what we actually did, we applied the recursion method to the structure that is defined by the ND thermodynamic model. In so doing we took account of the filling of gaps in the density of states (DOS) that is reported by GNF. In fact, this consequence of nonphysical rounding of the band edges is already well documented.⁸ Thus, we did not (as asserted by GNF) fall into the trap of determining the gap from the DOS. Examination of our papers (Ref. 3 or 4) will reveal that our gap was derived instead from the separation of peaks in the spectral weight functions for the conduction- and valence-band states at $\mathbf{k}=0$. That is,

$$E_g = E(\Gamma_1) - E(\Gamma_{15}) ,$$

with $E(\Psi)$ the energy of the peak in the spectral weight function

$$A(\mathbf{k}=0, E) = \sum (\Psi | \Psi_i)^2 \delta(E - E_i) ,$$

where $\Psi = \Gamma_1$ or Γ_{15} , corresponding to the bottom of the conduction band or the top of the valence band, respectively. This definition of the gap is common in alloy physics and its use is not confined to the recursion method. (For example, it is also used with the coherent-potential approximation.⁹)

Spectral weight functions for $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ are shown in Fig. 1 of Ref. 3 and Fig. 11 of Ref. 4. It is noteworthy that the first of these figures shows quite clearly that the gap vanishes [i.e., that $E(\Gamma_{15}) \geq E(\Gamma_1)$] when one uses structures that are consistent with the ND model of $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ and its large concentrations of wrong bonds. We note also that our recursion calculations for the gap of this material are in excellent agreement with the optical-absorption data, provided only that we use a physically realistic structure without significant concentrations of wrong bonds (particularly without As-As nearest neighbors). Testing of the recursion method and comparison with other methods have been published elsewhere.^{10,11}

In summary, we did not make the methodological mistake that has been attributed to us. As was described earlier,^{3,4} our recursion calculations avoided the influence of spurious filling of gaps in the DOS by deriving the gap from the separation of peaks in the spectral weight functions. The conclusion³ that the VCA is invalid for the alloy $(\text{GaAs})_{1-x}\text{Ge}_{2x}$ cannot be dismissed on the basis that we used a faulty method.

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