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Electronic density of states of $Al_xGa_{1-x}As$

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The recursion method, in conjunction with an empirical tight-binding model, is used to calculate the density of states of $Al_xGa_{1-x}As$ as a function of Al concentration x. Compositional disorder in the system is accounted for in terms of both the diagonal and off-diagonal elements of the tight-binding Hamiltonian. Our results are compared with results from other methods, as well as experimental data.

The main energy gap of $Al_xGa_{1-x}As$ is a sensitive function of the Al concentration x. Close to zero temperature, it ranges from 1.55 eV at $x=0$, to 2.26 eV at $x=1$.[1] Around $x=0.43$, the energy gap changes from direct to indirect. On the other hand, the lattice constant is almost independent of the Al concentration. This combination of properties has made $Al_xGa_{1-x}As$ a material which is rather desirable for the fabrication of quantum-well heterostructures and devices. Indeed, GaAs-$Al_xGa_{1-x}As$ heterostructures have served as a test bed for both material-growth techniques, device-fabrication techniques, and the verification of additional material properties due to quantum confinement effects.[2]

An accurate calculation of the band structure of this alloy is rather desirable, but has been made difficult because of the fact that the cation site is occupied by either a Ga or Al atom, prohibiting the use of (small) unit cells in band-structure calculations. To restore this possibility, the virtual-crystal approximation (VCA) has been used in most band-structure calculations of ternary alloys. For $Al_xGa_{1-x}As$, the VCA treats the cation as a fictitious atom which has properties that are obtained by linear interpolation between the Al and Ga properties. This simplification has been used in conjunction with a variety of band-structure models for both $Al_xGa_{1-x}As$ and quantum-well structures containing ternary alloys.[3] While ZnS-like unit cells may be used within this approximation, effects from compositional disorder are not accounted for. The coherent-potential approximation (CPA), which takes part of the disorder into account, has also been applied to ternary alloys.[4] However, if one accounts for both diagonal and off-diagonal disorder this method becomes rather inconvenient.

Here, we report on a calculation which does not rely on the use of the VCA or the CPA, yet is simple enough to allow calculation of the bulk density of states (DOS) at reasonable computational costs. The main incentive is a quantitative study of the effects of disorder on the DOS and the validity of the VCA.

Our model for $Al_xGa_{1-x}As$ is based on a semiempirical sp^3s^* tight-binding (TB) model which is treated within the recursion method to give the local density of states (LDOS).[5] The sp^3s^* model was originally designed to account for the band structure of indirect semiconductors and was later used to calculate the electronic structure of point defects, heterostructures, and more.[6] Every atom is characterized by five basis states: one s state, three p states, and one s^* state. In an attempt to keep calculations simple, only nearest-neighbor coupling is considered and one writes

$$H=\sum_{k\mu}\varepsilon_{k\mu}|k\mu\rangle\langle k\mu|+\sum_{k\mu,j\nu}V_{k\mu,j\nu}|k\mu\rangle\langle j\nu| , \qquad (1)$$

where $\varepsilon_{k\mu}$ is the on-site energy and $V_{k\mu,j\nu}$ is the overlap integral for two states $|k\mu\rangle$ and $|j\nu\rangle$ for neighboring lattice sites. The matrix elements are found empirically from experimental band-structure data and using the d^{-2} law, where necessary. Here, we directly use the parameters published in the original paper.[5]

As the TB parameters associated with an atom in general depend on the host material, we adopt the following procedure to determine them for atoms in the alloy. First, the diagonal elements $\varepsilon_{k\mu}$ of Al and As in AlAs are shifted by a common constant to reproduce the experimental value for the band offset at the GaAs/AlAs interface. Here, we take a valence-band offset of 0.45 eV, corresponding to a relative Γ-point conduction-band offset $Q_e \approx 0.70$ eV.[7] The valence-band edge of GaAs is taken as an energy-reference level. The on-site energy associated with an As atom in the alloy is determined according to

$$\varepsilon_{As}(AlGaAs)=\tfrac{1}{4}\,[N_{Al}\varepsilon_{As}(AlAs)+N_{Ga}\varepsilon_{As}(GaAs)] , \qquad (2)$$

where $\varepsilon_A(B)$ are on-site energies for atom type "A" in material "B" and N_i is the number of nearest neighbors of

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type "*i*." For on-site energies of Ga and Al, GaAs and AlAs values, respectively, are used. Off-diagonal elements are solely determined by the two atoms involved in the bond, i.e., for an Al—As bond, AlAs values; for a Ga—As bond, GaAs values are used.

The local density of states for a certain orbital $|l\mu\rangle$, where l is the site index and μ denotes the type $(s,p,\ldots)$ of orbital, is given by

$$n(E,l\mu) = -\frac{1}{\pi} \lim_{\varepsilon \to 0+} \mathrm{Im}\langle l\mu|G(Z)|l\mu\rangle . \quad (3)$$

Here, $Z = E + i\varepsilon$ and G is the resolvent operator for the system characterized by the Hamiltonian H. For the calculation of the LDOS, we first select an orbital $|l\mu\rangle$ and define a nearly cubic cluster around the corresponding site. A cluster of typically $50 \times 50 \times 50$ atomic monolayers is sufficient to suppress boundary effects, i.e., the type of boundary conditions invoked to treat the cluster surface does not affect our numerical results. The elements of the TB Hamiltonian are determined from the type and location of atoms. We assume that the atoms sit on a perfect ZnS lattice and that the occupation probability of the cation site is solely determined by the Al concentration x. Next-nearest-neighbor correlations are not accounted for in the construction of the alloy.

The recursion method is used to obtain the LDOS for a selected orbital. This method has been applied to a variety of systems, but has been most valuable in connection with nonperiodic structures.[8] It has been thoroughly discussed in the literature and will not be outlined here in any detail. Suffice it to say that one transforms the initial TB Hamiltonian of the cluster into tridiagonal form via a unitary basis transformation, using the selected orbital to provide the first normalized basis state. The resulting matrix formally represents a semi-infinite linear chain with nearest-neighbor coupling in terms of which the desired matrix element of the resolvent operator can be expressed in form of a continued fraction,

$$\langle l\mu|G(Z)|l\mu\rangle = \cfrac{1}{Z - a_0 - \cfrac{b_1^2}{Z - a_1 - \cfrac{b_2^2}{Z - a_2 - \cfrac{b_3^2}{\ddots}}}} . \quad (4)$$

Here, $\{a_n\}$ and $\{b_n\}$, respectively, are the diagonal and off-diagonal matrix elements of the linear-chain Hamiltonian. Because of the large cluster which we construct for the calculation, the continued fraction is simply truncated without any terminator attached to it. The truncated continued fraction is calculated in backward fashion. The parameter ε is typically on the order of 10^{-2}, but, depending on application, may be as small as 10^{-6}. Using a highly vectorized code, calculation of the LDOS per orbital requires about 1.3 min of CPU time on a Cray Y-MP supercomputer.

The LDOS calculated here is obtained as an average over the LDOS of all orbitals corresponding to an anion site and one of its nearest-neighbor cation sites. The bulk DOS is obtained by averaging the LDOS for typically 20 different pairs of atoms, where the weight is given according to the composition x, i.e., the fraction of Al-As bonds considered is x, the fraction of Ga-As bonds is $(1-x)$.

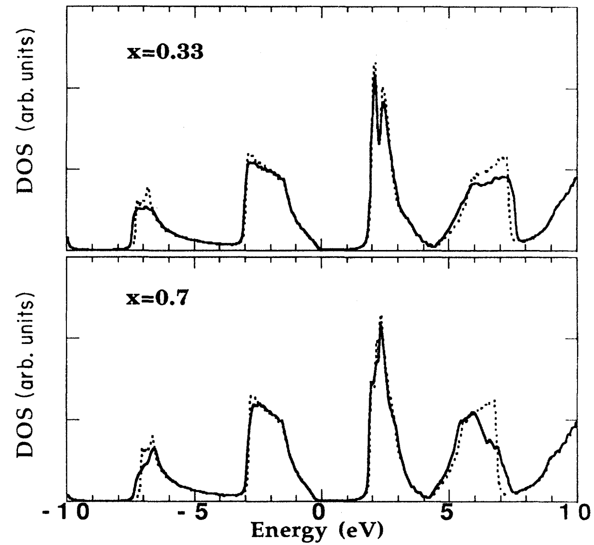

FIG. 1. Overall density of states for $Al_xGa_{1-x}As$. Solid line, present model; dotted line, virtual-crystal approximation.

We calculated the DOS of $Al_xGa_{1-x}As$ for an energy range from -10 to 10 eV and, for a higher resolution, around the main energy gap for x between zero and one. For $x = 0.33$ and $x = 0.7$, the DOS is given in Figs. 1 and 2 and displayed by solid lines. For comparison, the DOS within the VCA is given by dotted lines. Our version of the VCA is identical to the approach outlined above, except that now we define virtual cations by linear interpolation between Al and Ga TB parameters. It can be seen that our results confirm the qualitative picture that disor-

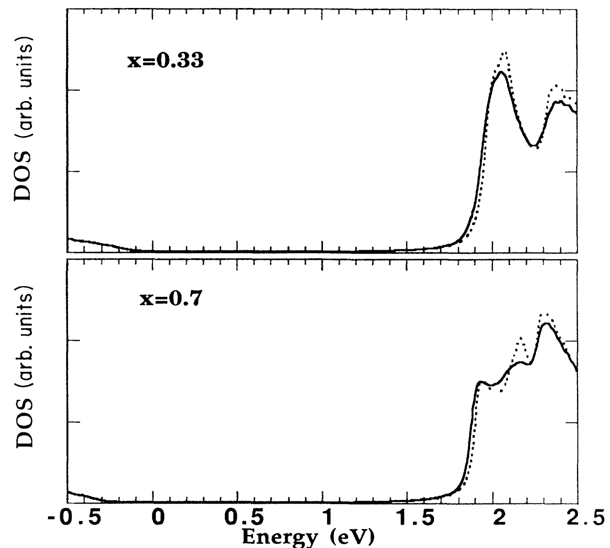

FIG. 2. Density of states for $Al_xGa_{1-x}As$ near the main energy gap. Solid line, present model; dotted line, virtual-crystal approximation.

der tends to widen the bands at the expense of the width of the energy gaps and the peak DOS in the bands. This has also been concluded from studies of the system within the CPA.[4] In particular, we find that the main energy gap within the VCA is wider by 90 and 48 meV for $x=0.33$ and 0.7, respectively. A more-detailed analysis of the band edges shows that the transition from the gap to the band regions occurs more gently in the alloy than predicted by the VCA. Furthermore, alloy effects are more evident at the conduction-band edge than at the valence-band edge. This is due to the fact that here we are dealing with disorder on the cation site.

We also investigated the dependence of the energy gap as a function of composition x. The VCA applied to the TB model used here has been shown to incorrectly predict a transition from a direct Γ-Γ gap to an indirect Γ-L gap at $x\approx 0.3$, followed by a transition to an indirect Γ-X gap at $x\approx 0.47$.[9] This is confirmed by our results within the VCA which are displayed by open circles in Fig. 3. For comparison, the solid line in Fig. 3 gives the energy gap obtained experimentally from exciton energies as a function of x.[10] These data were taken at a sample temperature of $T=2$ K. Finally, the results from the present model are given by asterisks, whereby their size reflects the error bars. Although we did not try to fit the GaAs and AlAs band structure to this particular set of data, we see that the present calculation which is based on a random distribution of cations gives a significant improvement over the VCA, concerning both the x dependence of the gap, as well as the direct-band-gap–indirect-band-gap transition. Quantitative agreement with experiment is obtained. It should be noted that no extra fitting parameters are needed in the model for the alloy.

In conclusion, we find that the VCA gives a good overall picture of the DOS, but overestimates the energy gap of the alloy for medium values of x. Details, such as correct identification of direct-band-gap–indirect-band-gap transitions may be lost. Our results which account for substitutional disorder, on the other hand, are in excellent agreement with experimental data, indicating that alloy disorder can fully account for earlier discrepancies between theory and experiment.

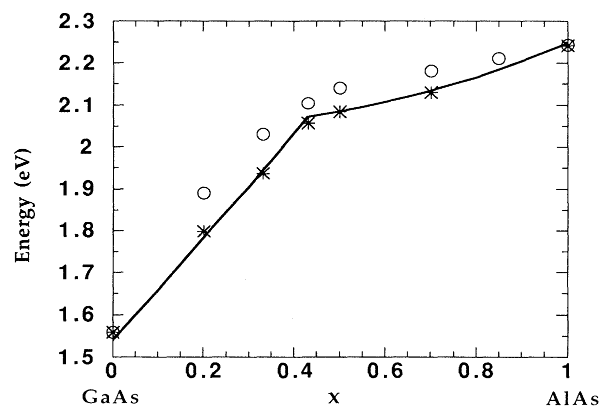

FIG. 3. Main energy gap vs Al concentration x. Asterisks, present model; open circles, virtual-crystal approximation; solid line, extrapolation from experimental data on free excitons (Ref. 10).

Our calculations do not account for the possibility of any long-range order in $Al_xGa_{1-x}As$. While some experimental evidence for such an effect has been reported,[11] its existence in $Al_xGa_{1-x}As$ is still under dispute. In any case, it is not needed to reproduce experimental data on the x dependence of the energy gap. A specific form of long-range order, however, could be easily incorporated into the present approach. Finally, we would like to mention that we also studied disorder effects in $Al_xGa_{1-x}As$ on the LDOS in GaAs-$Al_xGa_{1-x}As$ single quantum wells using the same method. We found that the differences in the local density of states near the center of the GaAs well due to the alloy disorder in $Al_xGa_{1-x}As$ are minimal, but are noticeable near the interfaces.[12]

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