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Breakdown of the virtual-crystal approximation in $Ge_{2x}(GaAs)_{1-x}$

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New information on the electronic structure of $Ge_{2x}(GaAs)_{1-x}$ is obtained by use of the coherent potential approximation (CPA) and x-ray photoelectron spectroscopy (XPS). Two extreme structural models are considered. In each case, the CPA valence-band density of states differs significantly from that of the virtual-crystal approximation (VCA) but is consistent with measured XPS spectra. Large deviations from VCA behavior are also observed in the band-gap region where the present CPA results strongly support the conclusions of previous recursion calculations concerning the sensitivity of the gap to short-range order.

$Ge_{2x}(GaAs)_{1-x}$ is a potentially important optoelectronic material and the prototype of a new class of metastable semiconducting alloys containing both group-IV and -III-V constituents. Since the earliest reports of the successful growth of this material,[1,2] considerable controversy has existed over both its local and long-range structure and the origin of its deeply bowed optical gap versus composition curve.[1,2]

Newman and Dow[3] (ND) first attempted to explain this deep bowing in terms of a zinc-blende to diamond phase transition at a critical concentration x_c (chosen empirically to be 0.3). Their analysis was based on a thermodynamic, mean-field, structural model and an empirical tight-binding,[4] virtual-crystal-approximation (VCA) treatment of the electronic structure. The neglect of potential fluctuations in this approach was subsequently criticized by Holloway and Davis[5] (HD), who examined the same tight-binding model using the recursion method.[6,7] HD concluded that (1) the large bowing in this system is a consequence of alloy disorder, and (2) the presence of a finite gap is inconsistent with the large number of As-As nearest neighbors predicted by mean-field theory. Alternative structural models[8,9] which restrict the number of Ga—Ga and As—As bonds have since been found to provide a more consistent interpretation of existing experimental data.[1,2,10–12] Nevertheless, the fundamental inadequacy of the ND approach, and of the VCA itself, for this class of alloys has still not been universally accepted.[13,14]

In this paper, we present new evidence for the breakdown of the VCA in $Ge_{2x}(GaAs)_{1-x}$ based on new electronic structure information obtained from coherent potential approximation[15] (CPA) calculations and x-ray photoelectron spectroscopy (XPS) measurements. The CPA is well known to be the best single-site alloy theory[15] and, unlike the recursion method, does not introduce any spurious broadening due to truncation errors. The present CPA formalism is similar to that used previously[16] to account for deviations from VCA behavior in other semiconducting alloys, most notably $Hg_{1-x}Cd_xTe$. In $Ge_{2x}(GaAs)_{1-x}$, strong alloy scattering throughout the lower valence-band region gives rise to significant differences between calculated VCA and CPA densities of states. XPS measurements confirm the basic features of the CPA valence band densities but do not provide a sensitive test of the underlying structural model. A more pronounced dependence on structure is found in the band-gap region where the CPA yields nearly identical results to those of the recursion method.[5,9] The present work thus provides strong support for HD's conclusions concerning the origin of the deep bowing in this system and the sensitivity of the gap to short-range order[17] (SRO).

To implement the CPA, we assume that the Ge, Ga, and As atoms in $Ge_{2x}(GaAs)_{1-x}$ are randomly distributed over the nominal anion (a) and cation (c) sites of an undistorted zinc-blende lattice with single-site occupation probabilities $P_a^{Ge}=P_c^{Ge}=x$, $P_c^{Ga}=P_a^{As}=(1-x)(1-f)$, and $P_a^{Ga}=P_c^{As}=(1-x)f$. The "antisite fraction" (Ref. 5) f is 0.5 if the two sublattices are indistinguishable (diamond symmetry) and less than 0.5 if some degree of zinc-blende long-range order (LRO) is retained. We consider two extreme cases. The first corresponds to the original ND model[3] and assumes that f increases continuously from 0.085 at $x=0$ to 0.5 for all $x \geq 0.3$. The concentration $x=0.3$ at which the symmetry changes from zinc-blende to diamond is not constrained by this model but is consistent with recent diffraction measurements[10] on the closely related $Ge_{2x}(GaSb)_{1-x}$ system. [Note that the deviation from $f=0$ at $x=0$ is assumed to be a real prediction for metastable growth; other values of f for $x<0.3$ are easily derived from the zinc-blende order parameter $M=(1-x)(1-2f)$ plotted in Fig. 7 of Ref. 3.] The second case assumes that $f=0$ for all x. This does not properly describe the LRO of the alloy (since zinc-blende symmetry is preserved until $x=1$) but it does ensure the elimination of Ga—Ga and As—As bonds. More realistic structural models[8,9] which involve varying degrees of both LRO and SRO are difficult to treat within a CPA framework.

The electronic structure is calculated using the same sp^3s^* empirical tight-binding[4] parameters considered by ND (Ref. 3) and HD.[5,9] For reasons discussed in Ref. 9, we assume a somewhat larger intrinsic band offset between Ge and GaAs than is observed experimentally[18] (1.0 eV vs 0.3–0.5 eV) but this has little bearing on the final results. The resulting diagonal s, p, and s^* tight-binding parameters for Ge, Ga, and As are given in Table I. The diagonal parameters associated with a given "anion" or "cation" site in the disordered alloy are assumed to take on either the Ge, Ga, or As values with the

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TABLE I. Diagonal s, p, and s^* tight-binding parameters (in eV) for Ge, Ga, and As.

	Ge	Ga	As
ε_s	−4.880	−2.671	−8.359
ε_p	2.610	3.669	1.041
ε_s^*	7.390	6.739	8.591

probabilities P_τ^i ($\tau = a$, c; $i =$Ge, Ga, As). The off-diagonal parameters are assigned average values as calculated in Ref. 3. By averaging the diagonal parameters in a similar manner, one obtains the full VCA Hamiltonian considered by ND.[3] In the CPA, by contrast, the random diagonal levels are replaced by periodic, complex, and energy-dependent effective potentials $\Sigma_{\tau\alpha}$ ($\tau = a$, c; $\alpha = s$, p, s^*) whose real and imaginary parts reflect the disorder-induced shifting and damping of VCA eigenstates. These and other CPA quantities are calculated here using a slight generalization of the iterative procedure described in Ref. 16.

Figure 1(a) shows a comparison of VCA and CPA densities of states for the ND structural model at various x values. The corresponding CPA results for $f=0$ are shown in Fig. 1(b). The VCA behavior is easily understood by comparing the density of states of pure GaAs [top panel of Fig. 1(b)] to that of pure Ge (bottom panel of either figure). In each case the valence-band density of states contains three peaks. The gap between the lowest two in GaAs, which is absent in the case of Ge, is a direct consequence of the lower symmetry of the zinc-blende structure compared to diamond. As x increases in the ND model, the VCA predicts a gradual shift in the location of the three peaks plus a vanishing of the gap near −8 eV at $x=0.3$, where the symmetry changes from zinc-blende to diamond. The VCA also predicts only three valence peaks for $f=0$ (not shown) with a finite gap between the lowest two persisting all the way to $x=1$.

Much different behavior is observed in the CPA results for the lowest valence states. In Fig. 1(b) a new peak appears at −8.5 eV for $x=0.25$ and increases in intensity with increasing x while the lower peak at −11 eV decreases in intensity. This characteristic split-band behavior[15] results from the fact that the differences between the atomic s levels in Table I are much larger than the widths of the individual spectral features. The fluctuations in potential are felt more strongly by the lowest valence-band states because of their predominantly s-like character. The peak near −11 eV in Fig. 1(b) is composed primarily of Ga-As and Ge-As bonding states while the peak near −8.5 eV is composed primarily of Ga-Ge and Ge-Ge bonding states. Similar features are observed in the CPA results in Fig. 1(a) although an additional broadening is exhibited which we attribute to the appreciable antisite fraction in the ND model. The effects of antisites are seen most clearly in the top panel of Fig. 1(a) where new valence-band structure is observed at −13 and −7 eV due to As−As bonds and at −9 eV due to Ga−Ga bonds. The CPA predictions for the two structural models become increasingly similar at larger x due to the decreasing number of As-As and Ga-Ga nearest neighbors in the ND model for $x > 0.3$.

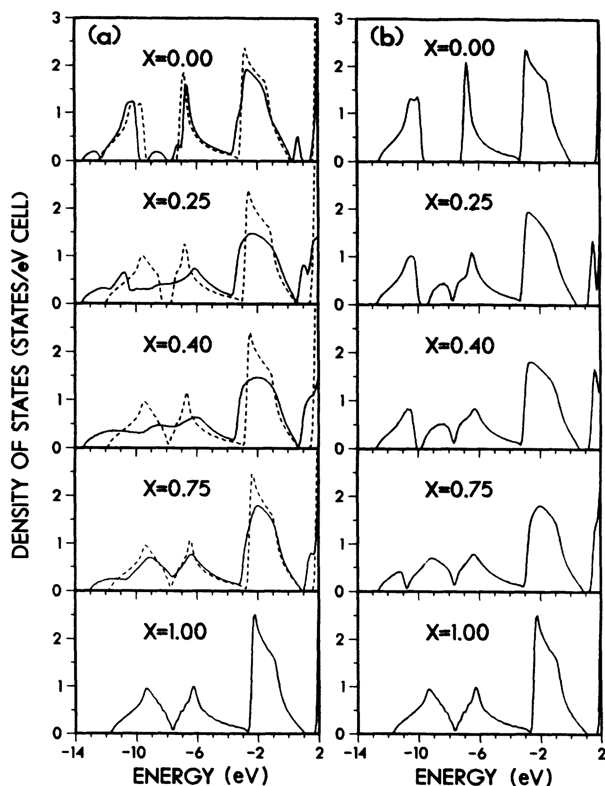

FIG. 1. CPA densities of states (solid curves) in $Ge_{2x}(GaAs)_{1-x}$ for (a) the ND model and (b) $f=0$ (no antisites). Corresponding VCA results (dashed curves) shown in (a) for comparison. The zero of energy is the GaAs valence-band maximum.

Figure 2 shows the XPS valence-band spectra of several $Ge_{2x}(GaAs)_{1-x}$ alloys grown by molecular beam epitaxy.[19] X-ray diffraction measurements and transmission electron microscopy indicated that the alloy layers were single phase, homogeneous, and single crystalline. The spectra were excited with monochromatized Al $K\alpha$ radiation and recorded at an instrumental resolution of 0.6 eV. The samples were lightly sputtered to remove carbon and oxygen contaminants prior to recording the valence-band spectra. The data have been smoothed, and the contribution from inelastic scattering has been approximated by an integral function and subtracted from the data. The XPS results are qualitatively consistent with either set of CPA results but show somewhat better agreement with the calculations for $f=0$ [Fig. 1(b)]. With increasing x, the peak at −11 eV decreases in intensity but remains fixed in energy while a new peak appears in the valley at −8.5 eV and increases in intensity. This behavior is unlike that of the VCA where the peak at −11 eV moves to higher energy with increasing x and closes the gap at −8.5 eV without the appearance of a new feature. The present XPS data also contradict the VCA prediction of a decrease in overall valence-band width for $x \le 0.4$. The conclusions drawn from Fig. 2 seem to be in essential agreement with those of Kramer, Tomasch, Ray,

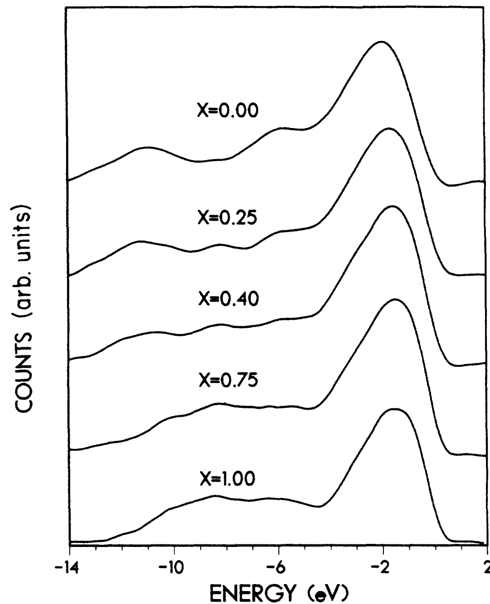

FIG. 2. XPS spectra of several $Ge_{2x}(GaAs)_{1-x}$ samples with different x values. Energies are measured relative to the valence-band maxima.

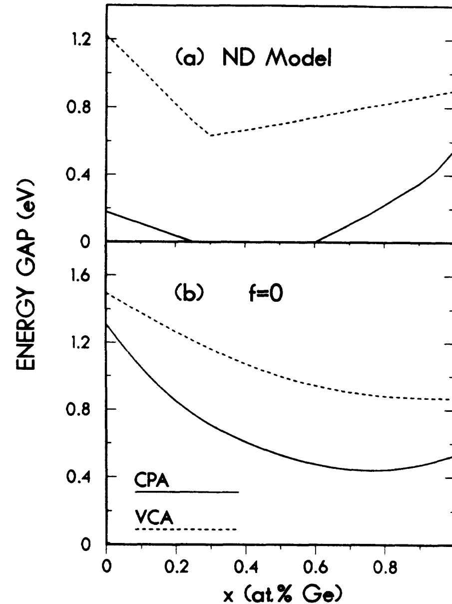

FIG. 3. Comparison of VCA (dashed curves) and CPA (solid curves) direct band gaps (at Γ) for (a) the ND model and (b) $f=0$ (no antisites).

and Greene who performed XPS measurements on $Ge_{2x}(GaAs)_{1-x}$ alloys grown by sputtering.[20]

The VCA also fails to provide an adequate description of the band-gap region of $Ge_{2x}(GaAs)_{1-x}$. Here the CPA results differ dramatically for the two structural models but are in excellent agreement with previous recursion-method calculations.[5,9] Figure 3 shows a comparison of VCA and CPA predictions for the direct gap at Γ in the two models. In analogy with Refs. 5 and 9, we define the CPA gap here as the separation between peaks in the $k=0$ spectral density function, which should really be viewed as an upper bound. In both models, the CPA gaps lie well below those of the VCA. The vanishing of the CPA gap in the ND model for $0.25 < x < 0.6$ is contrary to experiment and confirms HD's previous conclusions[5,9] concerning the effects of As—As bonds (see next paragraph). The CPA results for $f=0$, on the other hand, are in satisfactory agreement with measured optical data.[1,2] The similarity of these results to previous recursion calculations[17] for structural models with different LRO also supports HD's conclusions concerning the dominant role of SRO in determining the band gap.

The gap behavior in $Ge_{2x}(GaAs)_{1-x}$ is in sharp contrast to that of isovalent semiconducting alloys, where the VCA usually provides a reasonable description of the band-edge region even it if is inadequate for describing states deep in the valence band.[16,21] The present CPA results are best understood in terms of the bound-impurity states which result from nonisoelectronic substitutions. An As antisite impurity in GaAs, for example, produces a deep level at 0.6 eV above the valence-band maximum.[5,9,22] The large number of such antisites in the ND model results in a broadening of this level [cf. the mid-gap states for $x=0$ in Fig. 1(a)] and a closing of the gap in sufficiently concentrated alloys. The dilute limits of the CPA for $f=0$ can also be understood in terms of the shallow donor levels associated with a Ge impurity on a Ga site in GaAs and an As impurity in Ge (which produce levels at 1.35 and 0.55 eV above the valence-band maximum, respectively, in the sp^3s^* tight-binding model). The reduction of the CPA gap for $f=0$ compared to the VCA again results from a broadening of these states in more concentrated alloys, as can be seen directly in Fig. 1(b).

In summary, we have presented new theoretical and experimental evidence for the failure of the VCA to provide an adequate description of both the deep valence states and the band-gap region in metastable $Ge_{2x}(GaAs)_{1-x}$ alloys. The present CPA results are in complete agreement with previous recursion calculations[5,9] and provide additional support for structural models which do not contain significant numbers of Ga—Ga and As—As bonds.[8,9]

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