High-resolution $(GaAs)_{1-x}(Ge_2)_x$ x-ray photoelectron valence-band spectra: Implications for proposed electronic and structural models

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Valence-band density of states from sputter-deposited epitaxial metastable $(GaAs)_{1-x}(Ge_2)_x$ alloys have been acquired by high-resolution x-ray photoelectron spectroscopy (XPS). Based upon a comparison of XPS results and previously published models of electronic and atomic structure, we conclude that (1) the virtual-crystal approximation is not valid for this system, (2) there are no significant numbers of Ga-Ga and As-As bonds, and (3) Ge is not incorporated randomly. The electronic and atomic structure of these metastable alloys is determined primarily by the large energy-level differences among Ga, As, and Ge atoms.

I. INTRODUCTION

Detailed studies of the growth and physical properties of metastable $(GaAs)_{1-x}(Ge_2)_x$ alloys[1,2] have aroused interest due to the possibility of tailoring the optical and electronic behavior of these materials between that of GaAs ad Ge, while retaining a good lattice match with GaAs substrates. The $(GaAs)_{1-x}(Ge_2)_x$ system is an example of a class of alloys composed of III-V and group-IV semiconductors which have been successfully grown using highly nonequilibrium techniques such as rf and ion-beam sputter deposition.[3] With increasing concentrations of group-IV species, $(A^{III}B^{V})_{1-x}(C_2^{IV})_x$ systems undergo a transition from a zinc-blende phase with distinct cation and anion sites to a disordered diamondlike state where cations and anions are found on both sublattices. X-ray-diffraction studies of the homologous $(GaSb)_{1-x}(Ge_2)_x$ system confirmed that a zinc-blende-to-diamond transition occurs near $x=0.3$,[4] while extended x-ray-absorption fine-structure (EXAFS) (Ref. 5) and Raman[6] data were interpreted as excluding Ga-Ga and Sb-Sb wrong-bond atom pairs. Optical-absorption measurements have also shown that the lowest direct band gap E_0 for the $(GaAs)_{1-x}(Ge_2)_x$ system has an unusually large (≈ 3 eV), and distinctly nonparabolic, bowing with a broad minimum near $x=0.3-3.5$.[1]

Considerable controversy still exists over the significance of the above results for structural and electronic models of $(A^{III}B^{V})_{1-x}(C_2^{IV})_x$ systems. Newman and Dow[7] (ND) modeled the zinc-blende-to-diamond transition in $(GaAs)_{1-x}(Ge_2)_x$ as a thermodynamic order-disorder transition with a critical composition of $x=0.3$ (the minimum in E_0 vs x). The alloy electronic properties were determined using an sp^3s^* tight-binding Hamiltonian whose matrix elements were constructed by averaging cation and anion energies [the virtual-crystal approximation (VCA)] according to the types and numbers of atoms calculated to be on each basis site. A direct consequence of the ND model is that sputter-deposited crystals have highly randomized structures and that Ga-Ga and As-As pairs form $\approx 9\%$ of the bonds in sputter-deposited GaAs. This latter prediction is, however, incompatible with Raman, EXAFS, and optical-absorption results.

Later, Koiller, Davidovich, and Osorio[8] and Gu, Newman, and Fedders[9] employed a modified VCA and attempted to include atomic correlations in their calculations. Both concluded that a reduced, but still sizable, number of wrong bonds should be present in $(A^{III}B^{V})_{1-x}(C_2^{IV})_x$ alloys. More recently, Davidovich *et al.*[10] found that the interaction parameters in all structural models (the thermodynamic as well as Monte Carlo simulations discussed below) were incompatible with calculated nearest-neighbor binding energies which increase from relatively weak Ga-Ga and As-As bonds to moderately strong Ge-Ga and Ge-As pairs to very strong Ga-As and Ge-Ge bonds. From this analysis, few wrong bonds but significant correlations among Ge atoms are expected.

In another group of proposed models,[11–13] the alloy structure is determined by a Monte Carlo simulation of crystal growth, in which each element has a probability of incorporation that varies with the nearest-neighbor environment. Holloway and Davis[12] (HD) assumed that

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each Ga atom must always have a nearest-neighbor As atom and both Ga-Ga and As-As pairs are forbidden. HD calculated E_0 vs x with an sp^3s^* tight-binding Hamiltonian and the Haydock recursion method which goes beyond simple VCA averaging by including electron scattering from substitutional atoms (alloy disorder). In this view, the pronounced bowing in E_0 is due to alloy disorder and there can be no significant numbers of As-As wrong bonds since this would introduce states between the valence and conduction bands, thereby closing the band gap.

Recently, Hass and Baird[13] compared the VCA to the coherent-potential approximation (CPA), which is the best single-site theory of alloy disorder, by calculating E_0 vs x and densities of states (DOS) for both the ND model and a simplified structural model (SSM) in which Ge is randomly mixed into GaAs. While the SSM has no zinc-blende-to-diamond transition, Ga-Ga and As-As pairs are forbidden as in HD's model. The SSM plus CPA produced electronic properties (E_0 vs x) which differ greatly from the VCA calculations yet compare well with HD's results.

Figure 1 shows the VCA (dashed curves) and CPA (solid curves) DOS for (a) the ND model and (b) the SSM.[13] In agreement with previous work,[7] the VCA DOS for the ND model consist of a single set of averaged bands which change smoothly, and with little broadening, from GaAs to Ge as the long-range order changes

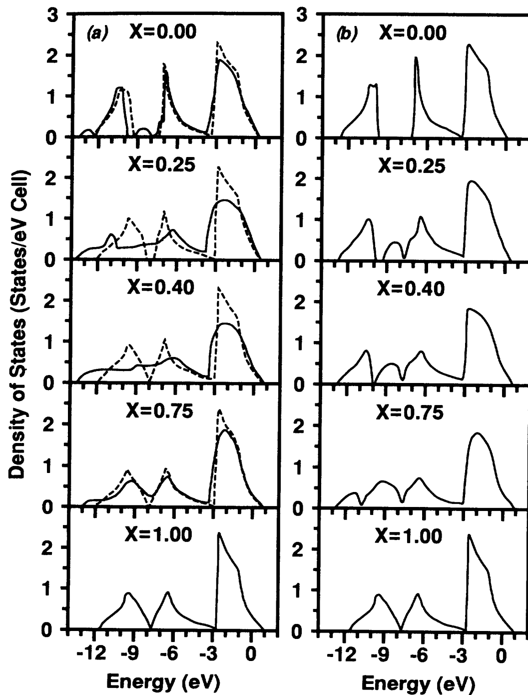

FIG. 1. Model $(GaAs)_{1-x}(Ge_2)_x$ DOS from Hass and Baird (Ref. 13). CPA DOS (solid curves) are for (a) the ND model and (b) the SSM, while VCA DOS for the ND model (dashed curves) are shown for comparison. [For $x>0$, CPA DOS in (b) have few or no states near -8.0 eV due to limitations in the Ge Hamiltonian.]

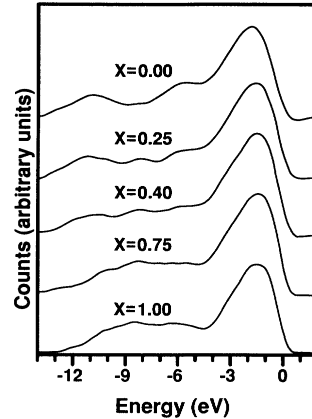

FIG. 2. $(GaAs)_{1-x}(Ge_2)_x$ VBDOS (resolution of 0.6 eV) from sputter-cleaned MBE-grown samples with different x values. The data are taken from Ref. 13.

from zinc-blende to diamond at $x=0.3$. The dependence of the VCA DOS solely upon long-range order is due to the average nature of the VCA and is not true for the CPA DOS. VCA and CPA DOS were also compared to the XPS valence-band density of states (VBDOS) (energy resolution of 0.6 eV) from $(GaAs)_{1-x}(Ge_2)_x$ alloys grown by molecular-beam epitaxy (MBE).[13] Before analysis, air-exposed MBE samples were sputter etched to remove surface (primarily O and C) contamination. While definitive conclusions on the extent of alloy disorder could not be made (all VBDOS were highly broadened), the XPS VBDOS, reproduced in Fig. 2, appeared somewhat closer to the CPA DOS.

II. EXPERIMENTAL PROCEDURE

In this paper, we report high-resolution XPS VBDOS from $(GaAs)_{1-x}(Ge_2)_x$ alloys grown by ultrahigh-vacuum ion-beam sputter deposition.[14] Electron channeling, x-ray diffractometry, x-ray topography, and TEM studies have previously shown that $(GaAs)_{1-x}(Ge_2)_x$ alloys deposited by rf and ion-beam sputtering are homogeneous single crystals.[1,2] XPS VBDOS were acquired with monochromatic Al $K\alpha$ (1486.6 eV) radiation in both a PHI 5000 ESCA (with the energy analyzer set for a resolution of ≈ 0.5 eV) and an HP5950A (resolution of ≈ 0.6 eV). To avoid possible sputter cleaning artifacts, GaAs and alloy samples were passivated *in situ* with an As cap layer immediately after growth. The As-capped samples were then degassed at 150 °C in load-lock processing chambers attached to the analytical instruments, and the As layer desorbed by heating to 300 °C for 30 min. All spectra were smoothed and the inelastic contribution was removed following the procedure of Shirley.[15]

III. RESULTS AND DISCUSSION

Figure 3 shows XPS VBDOS with an analyzer pass energy of 17.90 eV for the alloys and 8.95 eV (higher resolution) for GaAs and Ge. GaAs and Ge VBDOS consist of a single three-peak structure: *P*I, *P*II, and *P*III, which

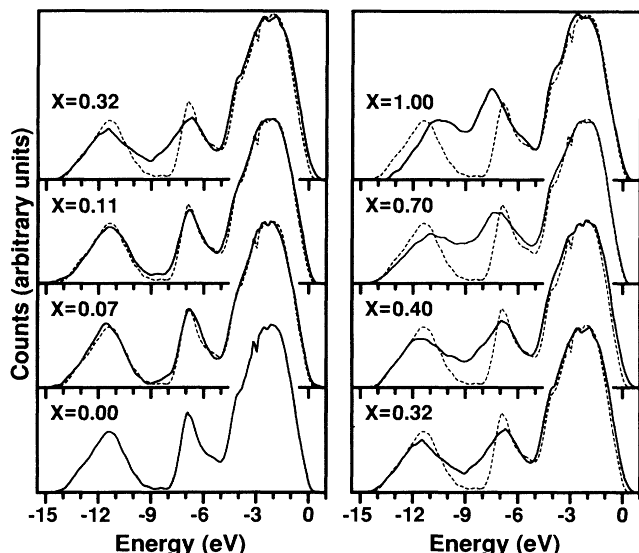

FIG. 3. High-resolution ($\approx$0.5 eV) $(GaAs)_{1-x}(Ge_2)_x$ XPS VBDOS from samples with different x values (solid curves) compared to GaAs VBDOS (dashed curves).

correspond to the upper, middle, and lower bands, respectively. In GaAs, *P*I is primarily from anion *p*-like states, while *P*II is a mixture of cation *s*-like and anion *p*-like states, and *P*III is mostly anion *s*-like states. *P*I is virtually identical in GaAs and Ge, and overlaps with *P*II. However, in GaAs (as opposed to covalently bonded Ge), *P*II and *P*III are separated at the X_3-X_1 symmetry points (-7.5 and -10 eV, respectively) due to the ionicity of the GaAs bond.

In serious disagreement with the VCA DOS, GaAs-like features persist in the lower valence band of all alloys. As seen from alloy VBDOS, overlaid with GaAs (dashed curves in Fig. 3), the outer edges of *P*III (near -14.5 eV) and *P*II (≈ -5 eV) have virtually the same separation as in GaAs (while the VCA DOS predicts a smaller Ge-like separation for $x \geq 0.3$). For $x=0.07$, GaAs-like *P*II and *P*III have additional states near -6.5, -8.5, and -12 eV. At $x=0.11$, *P*II and *P*III appear smoother and decrease in intensity as new states fill the valley. By $x=0.32$, and particularly for $x \geq 0.40$, GaAs-like *P*II and *P*III diminish rapidly, as the states in the valley become increasingly Ge-like, i.e., the intensity grows more rapidly near the X_3-X_1 symmetry points alongside *P*II and *P*III than in the center of the valley. Unlike *P*II and *P*III, *P*I shows only subtle changes: it broadens symmetrically with increasing x up to 0.4, while at larger x the broadening decreases.

Discrepancies among the XPS VBDOS and the VCA DOS are greater at lower energies where *s*-like states predominate and alloy disorder increases. Alloy disorder is enhanced for *s*-like states, due both to the larger energy differences between, and the smaller bandwidth of, *s*-like as compared to *p*-like GaAs and Ge features. From model CPA DOS, Onodera and Toyozowa[16] and others[17] classify alloy DOS into two regimes depending upon Δ/T, where Δ is the difference in diagonal Hamiltonian matrix elements for the pure constituents, and T is the bandwidth. For large Δ/T (≥ 0.5), the DOS consists of distinct peaks, with each peak arising from a different alloy constituent (persistence or split-band behavior). When $0.25 < \Delta/T < 0.5$, the DOS are persistent at low concentrations, while at higher compositions peaks from alloy constituents overlap (amalgamation) but may not completely merge. For small Δ/T ($\lesssim 0.25$), there is only one set of merged-alloy peaks and the VCA is a good approximation for DOS.

The magnitude of Δ/T for a random, but equal, substitution of Ge on Ga and As sites (the simplest approach is to omit the zinc-blende-to-diamond transition and calculate the alloy disorder from each sublattice separately) can be estimated as follows. In the sp^3s^* tight-binding model used in all previous band-structure calculations, the difference in diagonal Hamiltonian matrix elements is approximately a factor β times the differences in the atomic energy levels ΔE_a. E_a values for Ga, Ge, As are (in eV) -11.55, -15.05, -18.66 for *s* states and -5.76, -7.81, -10.05 for *p* states; while β is 0.8 for *s* levels and 0.6 for *p* levels. The anion *p*-like states of *P*I have a spectral bandwidth of $\approx$5.5 eV, while the predominantly *s*-like *P*II states (ignoring the smaller *p*-state component) and *P*III states are $\approx$3.0 and 5.0 eV, respectively. For Ge on anion sites, Δ/T is $\simeq$0.24 for *p*-like *P*I and 0.56 for *s*-like *P*III, while on cation *s*-like *P*II, $\Delta/T \simeq 0.93$. The VCA thus applies only to *p*-like *P*I, and not *s*-like *P*II or *P*III, in agreement with the present XPS VBDOS and the Hass and Baird CPA DOS.

With the failure of VCA averaging, all atom-pair combinations—Ga-As, Ga-Ga, Ga-Ge, Ge-Ge, Ge-As, and As-As—have distinct *s*-state distributions. From VCA and CPA DOS for the ND model of GaAs, Hass and Baird assign small peaks immediately below *P*II and *P*III to Ga-Ga and As-As bonds, respectively.[13] Karcher, Wang, and Ley,[18] studying amorphous GaAs, found somewhat different energies for wrong bonds: Ga-Ga at -9 eV and As-As by -15 eV (separated from *P*III). Using either assignment, our XPS VBDOS in Fig. 3 show no trace of Ga-Ga (best seen at small Ge concentrations) and As-As features.

While Fig. 3 is similar to the CPA DOS in Fig. 1(b), there are two significant differences. Unlike the CPA DOS, which for intermediate x have a rapidly growing peak at $\simeq -8.5$ eV and few, or no, states near -10–11 eV (depending upon x), the XPS VBDOS have states in the valley between *P*II and *P*III that grow slowly and continuously with no depression near -10–11 eV. It might be argued that broadening the CPA DOS would better replicate the XPS VBDOS. However, Fig. 4 shows higher-resolution VBDOS (under 0.5 eV, a pass energy of 8.95 eV on the PHI ESCA) for $x=0.11$ and 0.32, and an $x=0.21$ VBDOS (with a lower resolution of 0.6 eV) revealing that *P*II and *P*III are double-peaked structures (the extra states near -6.5 and -12 eV are also in the $x=0.07$ VBDOS of Fig. 3).

Double-peaked *P*II and *P*III suggest that two types of bonds with highly different energies occur on the same sublattice. We assign the second peak in *P*II (*P*III) to Ga-Ge (As-Ge) bonds, which have a higher (lower) aver-

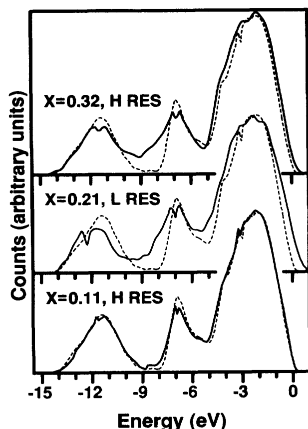

FIG. 4. High-resolution $(GaAs)_{1-x}(Ge_2)_x$ XPS VBDOS exhibiting a double-peaked *P*II and *P*III. *H* Res, the highest resolution, was under 0.5 eV and was obtained at a pass energy of 8.95 eV on a Phi 5000 ESCA, while *L* Res, a lower resolution of 0.6 eV, was acquired on an HP5950A. As in Fig. 3, the dashed curves represent GaAs VBDOS.

age energy than a Ga-As bond, i.e., a Ge atom has a higher (lower) energy than the As (Ga) atom it replaces. From the relative sharpness of the two second peaks at small Ge concentrations, they are likely due to isolated Ge atoms surrounded primarily by either Ga and/or As atoms. Assuming that Ge mixes randomly in the alloy, the probability of obtaining isolated Ge atoms is $x(1-x)^4$, which has a maximum at $x_m=0.2$. Correlation among Ge atoms, or greater binding to Ga or As, would shift x_m. That the second set of peaks is clearly resolvable in the lower-resolution VBDOS at $x=0.21$ (and less intense in the higher-resolution VBDOS of $x=0.11$ or 0.32) suggests $x_m \approx 0.20$ (consistent with randomly mixed Ge).

However, features with a larger spectral weight in the -7.5–11 eV region of the VBDOS are interpreted as indicative of greater Ge correlation. In the CPA DOS, the peak near -8.5 eV arises from random mixtures of Ga-Ge and Ge-Ge bonds, while the peak at $\simeq -11$ eV is due to Ga-As and Ge-As pairs. The gap or depression between these two peaks (near -10–11 eV) is analogous to the gap between *P*II and *P*III in partially ionic GaAs. Agreement with our XPS VBDOS requires a decrease in the number of CPA Ga-Ge (As-Ge) pairs and an increase in the number of Ge-Ge bonds for a more Ge-like DOS in the valley, i.e., a set of states growing more rapidly alongside *P*II and *P*III than at $\simeq -8.5$ eV, with no depression near -10–11 eV.

The lack of Ga-Ga and As-As wrong bonds, and increased correlation among Ge atoms, agrees with the trends in nearest-neighbor binding energies calculated by Davidovich *et al.* Sputter-deposited $(GaAs)_{1-x}(Ge_2)_x$ alloys are thus in a well-mixed metastable state at a local free-energy minimum. That XPS VBDOS from MBE alloys appear to follow the CPA DOS (randomly mixed Ge), implies that MBE alloys are in a higher-energy metastable state. A key factor in sputter deposition that is lacking in MBE is low-energy ion bombardment, which has previously been shown to affect all stages of crystal growth ranging from enhanced adatom mobilities[19] to changes in elemental incorporation probabilities and nucleation kinetics.[20] Molecular-dynamics simulations have shown that excess kinetic energy, coupled to the crystal surface, allows adatoms to sample one or two additional sites and, hence, relax into lower-energy configurations.[19,21–23]

In summary, a comparison of high-resolution XPS VBDOS and model VBDOS shows that electronic and structural models for sputter-deposited $(GaAs)_{1-x}(Ge_2)_x$ alloys should incorporate (1) the effects of alloy disorder on the band structure, (2) very few wrong bonds (doping concentrations), and (3) greater correlation among Ge atoms.

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[1]S. A. Barnett, M. A. Ray, A. Lastras, B. Kramer, J. E. Greene, P. M. Raccah, and L. L. Abels, Electron. Lett. **81**, 891 (1982).
[2]L. T. Romano, I. M. Robertson, J. E. Greene, and J. E. Sundgren, Phys. Rev. B **36**, 5723 (1987).
[3]J. E. Greene, CRC Crit. Rev. Solid State Mater. Sci. **11**, 47 (1983).
[4]S. I. Shah, B. Kramer, S. A. Barnett, and J. E. Greene, J. Appl. Phys. **59**, 1482 (1986).
[5]E. A. Stern, F. Ellis, K. Kim, L. Romano, S. I. Shah, and J. E. Greene, Phys. Rev. Lett. **54**, 905 (1985).
[6]T. C. McGlinn, M. V. Klein, L. T. Romano, and J. E. Greene, Phys. Rev. B **38**, 3362 (1988).
[7]See, for example, K. E. Newman and J. D. Dow, Phys. Rev. B **27**, 7495 (1983).
[8]B. Koiller, M. A. Davidovich, and R. Osorio, Solid State Commun. **55**, 861 (1985).
[9]B.-L. Gu, K. E. Newman, and P. A. Fedders, Phys. Rev. B **35**, 9135 (1987).
[10]M. Davidovich, B. Koiller, R. Osario, and M. Robbins, Phys. Rev. B **38**, 10 524 (1988).
[11]K. Kim and E. A. Stern, Phys. Rev. B **32**, 1019 (1985).
[12]See H. Holloway and L. C. Davis, Phys. Rev. B **35**, 3823 (1987), and references therein.
[13]K. C. Hass and R. J. Baird, Phys. Rev. B **38**, 3591 (1988).
[14]B. Kramer, G. Tomasch, M. Ray, J. E. Greene, L. Salvati, and T. L. Barr, J. Vac. Sci Technol. A **3**, 1572 (1978).
[15]D. A. Shirley, Phys. Rev. B **5**, 4709 (1972).
[16]Y. Onodera and Y. Toyozawa, J. Phys. Soc. Jpn. **24**, 341 (1968).
[17]R. J. Elliott, J. A. Krumhansl, and P. L. Leath, Rev. Mod.

Phys. **46**, 465 (1974).

[18]R. Karcher, Z. P. Wang, and L. Ley, J. Non-Cryst. Sol. **59/60**, 629 (1983).

[19]See J. E. Greene, in *Deposition Technologies for Films and Coatings,* edited by R. F. Bunshak (Noyes, Park Ridge, NJ, in press).

[20]W.-X. Ni, J. Knall, M.-A. Hassan, G. V. Hassan, J.-E. Sundgren, S. A. Barnett, L. C. Markert, and J. E. Greene, Phys. Rev. B **40**, 10 449 (1989).

[21]K. H. Müller, Phys. Rev. B **35**, 7906 (1987).

[22]M. Kitabatake, P. Fons, and J. E. Greene, J. Vac. Sci. Technol. A **8**, 3726 (1990).

[23]M. Kitabatake, P. Fons, and J. E. Greene, J. Vac. Sci. Technol. A **9**, 91 (1991).