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Electronic and atomic structure of type-II semiconductor superlattices

J. C. Phillips
Bell Laboratories, Murray Hill, New Jersey 07974
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An explanation for the failure of the containment model to describe the composition dependence of E_1 optical edges in $(InAs)_{1-x}(GaAs)_x$-$(GaSb)_{1-x}(GaAs)_x$ superlattices is presented. It is proposed that the discrepancy between theory and experiment arises not from band-structure effects but rather from lateral chemical phase separation on a scale comparable to the vertical superlattice period (multiply periodic columnar growth). The data of Mendez, Chang, Landgren, Ludeke, Esaki, and Pollak can therefore be used to differentiate between phase separation on a 50-Å scale in molecular-beam-epitaxy samples and on a larger scale in bulk samples quenched from the melt.

The electronic energy structure of multiple-quantum-well semiconductor superlattices prepared by molecular-beam epitaxy (MBE) has been the subject of growing experimental interest. Many novel and striking effects can be observed in these films.[1-14] Most optical studies of these materials have been confined to the states near the E_0 fundamental gap Γ_{15V}-Γ_{1c} where the reduced optical mass μ given by $\mu^{-1} = m_e^{-1} + m_h^{-1}$ is of order $0.05 m_0$. The equivalent exciton Bohr radius is 100 Å, which is larger than the typical well of thickness of 50 Å in the samples of type-II $(InAs)_{1-x}(GaAs)_x$-$(GaSb)_{1-x}(GaAs)_x$ superlattices discussed recently.[15] Near the E_1 or L edge the m_e/m_0 and m_h/m_0 values in the [100] direction normal to the layers are estimated[16] to be 0.11 and 0.29, giving a reduced mass $\mu/m_0 = 0.08$ and an exciton Bohr radius of 60 Å. Nonparabolic saddle-point exciton[17] binding effects may further reduce this radius to as little as 30 Å, which is substantially smaller than the layer thickness.

Electroreflectance studies of the composition dependence of the E_1 and $E_1 + \Delta_1$ edges in type-II samples have shown drastically different results from those on type-I or GaAs-$(GaAs)_{1-x}(AlAs)_x$ superlattices. The data on type-I superlattices are well explained by confinement energies of order 0.15 eV for the E_0 edge and 0.09 eV for the E_1 edge. Similar confinement energy shifts are predicted for the type-II samples, but deviations from the predicted values are found for $0.2 < x < 0.8$. These deviations reach

a maximum value of order 0.2 eV for x near 0.5. It has been suggested[15] that these large deviations demonstrate the need for a more fundamental theory of superlattice band structures in the limit where the exciton localization length becomes comparable to the well width.

Quite generally one can describe quantum well states by Wannier wave functions of the form $\phi_c \psi_{\vec{k}}$ where ψ_k is the Bloch function at the critical point $\vec{k}$ and ϕ_c is an envelope function which confines the state to the quantum well. The corresponding energy is $E_c + E_{\vec{k}}$, where E_c is the confinement energy and $E_{\vec{k}}$ the critical-point energy. Regardless of the localization length, electronic corrections to this model are of order $\delta E_c = E_c^2/E_j$, where E_j is the interband energy of interest. In this case the energy δE_c is $\leq 10^{-2}$ eV, or 20 times too small to explain the observed discrepancies. Thus we must seek a different, nonelectronic explanation for the observed anomaly.

My explanation of the anomalies in the composition dependence of type-II E_2 band edges begins with the observation that for $0.4 \leq x \leq 1.0$ almost all the observed structure corresponds quite closely to the E_1 and the $E_1 + \Delta_1$ edges in GaAs. The layers have been grown on a (100)GaAs substrate. This suggests an explanation based not on electronic band theory but rather on the atomic morphology of multilayer film growth. I suggest that between $x_1 = 0.25$ and $x_1' = 0.75$ the GaAs-GaSb alloys lie under the spinodal instability phase-separation curve[18] shown in Fig. 1. Note that under the dashed curve homogeneous

$(Ga\ As)_X(Ga\ Sb)_{1-X}$
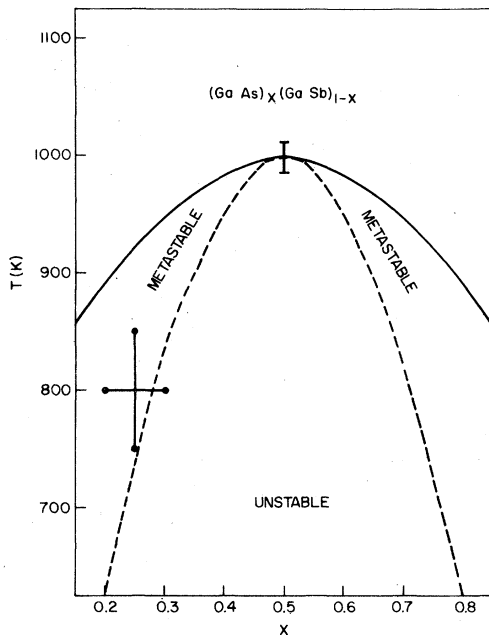
METASTABLE

METASTABLE

UNSTABLE

FIG. 1. Spinodal phase-separation diagram, showing the metastable and unstable regions appropriate to the GaAs-GaSb alloy system. The numerical values indicated roughly are derived from MBE and bulk melt-quenched samples, as described in the text. The MBE phase-separation point is indicated with a cross.

alloys are absolutely unstable, whereas under the solid curve homogeneous alloys are metastable and phase separation requires nucleation. The limits x_2 and $x_2' = 1 - x_2$ of the dashed curve are related in regular solution theory to the maximum spinodal temperature T_c by $4x_2x_2' = T/T_c$, where T is the quenching temperature. Studies of bulk GaAs-GaSb phase separation[19] have given $T_c = 1000 \pm 10$ K, whereas the value predicted[18] by global dielectric theory (which does not involve adjustable parameters specific to this pseudobinary system) is 905 K. The corresponding absolute instability values are $x_2 = 0.28$ and 0.34, respectively, at $T_s = 800$ K, the substrate temperature at which the type-II films were grown.[20] The value $x_1 = 0.25 \pm 0.05$ is so close to the thermodynamic instability curve that one can conclude that on a scale of 50 Å local thermodynamic equilibrium is nearly attained.

It has previously been stated,[20] on the basis of diffraction data, that phase separation does not occur in GaAs-GaSb molecular-beam-epitaxy (MBE) alloys at $T = T_s = 800$ K. However, on a scale of 50 Å or less it would be extremely difficult to detect phase separation by diffraction. The measurement of Raman scattering frequencies[21] and infrared oscillator strengths[22] as a function of composition is much more informative on this distance scale.

There are two reasons why the GaAs edges dom-

inate the spectra over most of the composition range. Assuming columnar growth on a GaAs substrate, the GaAs regions may be nearly strainfree. Because electroreflectance is a derivative technique, the GaAs regions will contribute a larger signal than the InAs-GaSb regions which are not lattice-matched to the substrate or perfectly to each other, as shown in Fig. 2. The second reason is that the internal electric fields penetrate only weakly the GaSb regions because of internal interfacial space-charge depolarization fields.[23] Phase separation also explains the small dips at $x = 0.8$ which correspond to GaAs-based homogeneous alloys containing small amounts of InAs and GaSb before phase separation has begun at $x_2' = 0.75$. Finally, there is much less tendency[18] for GaAs-InAs phase separation ($T_c = 226$ K) and some signals associated with $(InAs)_{1-x}(GaAs)_x$ are seen at intermediate compositions where no $(GaSb)_{1-x}(GaAs)_x$ signals are resolved. The situation here is complicated by the competition between the demands of lattice matching and the tendency towards phase separation, but the qualitative features are correctly predicted by global dielectric theory.[18]
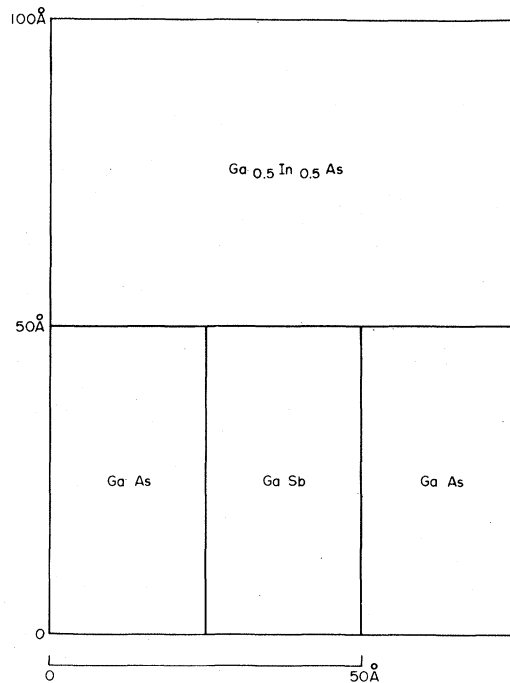
A comment on GaAs-AlAs superlattice layers may

$Ga_{0.5}In_{0.5}As$

Ga As   Ga Sb   Ga As

FIG. 2. One possible columnar structure for $x = 0.5$ in $(InAs)_{1-x}(GaAs)_x$-$(GaSb)_{1-x}(GaAs)_x$ superlattice layers. The phase separation of GaAs-GaSb is definite, but some of the GaAs-InAs layers may be homogeneous, while others are partially phase separated by epitaxial interactions between GaAs-GaAs and InAs-GaSb columns (not shown). This latter question requires further experimental investigation, preferably by supplementing the electroreflectance experiments with Raman scattering.

not be amiss here. Recently it has been suggested that "clustering" (or phase separation) may explain some luminescence anomalies in multiple quantum well films grown by organo-metallic vapor deposition.[12] However, this is exactly the alloy system where phase separation does not take place in alloys grown by liquid phase epitaxy.[24] Thus some experimentalists have proposed phase separation in GaAs-AlAs (where it may not occur), while some others have ignored it in GaAs-GaSb (where it does occur). More study of this problem appears to be in order.[18,21,22]

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