Optical Absorption in Single-Crystal Metastable $(GaAs)_{1-x}(Ge_2)_x$ Alloys: Evidence for a Zinc-Blende–Diamond Order-Disorder Transition

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Single-crystal metastable $(GaAs)_{1-x}(Ge_2)_x$ alloys with $0<x<1$ have been grown on (100) GaAs substrates by use of ultrahigh-vacuum ion-beam sputter deposition. Optical-absorption measurements showed that the direct gap E_0 exhibited a large negative V-shaped bowing as a function of x with a minimum $E_0 \simeq 0.5$ eV near $x = 0.3$. A zinc-blende to diamond-lattice order-disorder transition model is proposed as a possible explanation for these results.

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The first detailed studies of the growth and physical properties of single-crystal metastable semiconductors have been reported recently.[1-4] In particular, two different $(III\text{-}V)_{1-x}(IV_2)_x$ (Ref. 5) substitutional alloy systems, $(GaSb)_{1-x}(Ge_2)_x$ (Refs. 2 and 3) and $(GaAs)_{1-x}(Ge_2)_x$,[4] have been grown epitaxially on (100) GaAs at compositions ranging across the pseudobinary phase diagram. A key factor in allowing the growth of these metastable materials was the use of low-energy ion bombardment of the growing film during deposition to alter elemental incorporation probabilities, enhance adatom diffusivities, and promote collisional mixing. $(GaSb)_{1-x}(Ge_2)_x$ films, typically 1 to 3 μm thick, were found to be stable for greater than 100 h at annealing temperatures of 475 °C and, from thermodynamic measurements,[3] were estimated to be stable against phase separation for 10^{29} yr at room temperature. The kinetic barrier to phase decomposition in $(GaAs)_{1-x}(Ge_2)_x$ alloys is expected to be of the same order as that found in $(GaSb)_{1-x}(Ge_2)_x$, 3 eV, because of the low self-diffusion coefficients in GaAs and Ge.

In this Letter we report experimental measurements and a model for the calculation of the direct Γ-point optical band gap E_0 of $(GaAs)_{1-x}(Ge_2)_x$ as a function of composition. The data show a large negative nonparabolic V-shaped bowing of E_0 as a function of x with a minimum near $x_c \simeq 0.3$. To explain this bowing, we propose that $(GaAs)_{1-x}(Ge_2)_x$ undergoes an order-disorder transformation from a zinc-blende structure to a diamond lattice at $x = x_c$.

$(GaAs)_{1-x}(Ge_2)_x$ alloys were grown in an ultrahigh-vacuum ion-beam sputtering system with a base pressure of 10^{-10} Torr. Two modified 2.5-cm-diam Kaufman-source ion guns with metal gaskets were used to simultaneously Ar^+-ion sputter 5-cm-diam high-purity, undoped, water-cooled, single-crystal GaAs and Ge targets. The ion-gun accelerating voltages were varied from 500 to 1500 V, depending on the desired film composition, to provide a constant deposition rate of 0.8 μm/h on Cr-doped semi-insulating (100)-oriented GaAs wafers. Surface oxides on the substrates were removed immediately prior to deposition by heating to 600 °C for 5 min. The film growth temperature T_s was varied between 550 °C for GaAs and 450 °C for Ge according to the equation $T_s = (550 - 100x)$ °C. A heated effusion cell charged with 99.9999% pure arsenic and aimed at the substrate provided an As_4 overpressure during film growth.

Film compositions were determined to within ±0.5 at.%, based upon elemental and compound reference standards, by dispersive analysis in a JEOL electron microprobe. Electron channeling, x-ray diffractometry, and x-ray topography indicated that the metastable-alloy films were highly perfect single crystals. Room-temperature thermoelectric measurements showed that Ge-rich alloys were p type while GaAs-rich alloys were n type.

Optical-absorption measurements in the range from 0.9 to 2.5 μm were carried out at room temperature with a Carey 14 spectrophotometer. The data were then fitted by the usual model[6] for

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a three-layer [air:$(GaAs)_{1-x}(Ge_2)_x$:GaAs] structure which requires the film thickness t and the refractive index n. The thickness t, typically ~1 μm, was obtained from the separation of the interference fringes and was in reasonable agreement with that inferred from calibrated deposition-rate curves. The refractive index of each film was determined in the low-absorption region and then fitted over the entire wavelength range with an inverse-square dependence on wavelength.

The optical-absorption coefficient exhibited a power-law dependence on the frequency ν of the exciting radiation: $\alpha \propto (h\nu - E_0)^\beta$, Fig. 1. The quantities E_0 and β are, strictly speaking, curve-fitting parameters, with E_0 defining the absorption threshold and β being a measure of the "softness." We define $E_0(x)$ to be the direct band gap of the alloy, because it is a continuous function of alloy composition x and has the values of the direct band gaps in equilibrium GaAs and Ge. Typical results for $E_0(x)$ and $\beta(x)$ are shown in Fig. 2. The absorption edge was relatively sharp in GaAs-rich samples but became softer somewhat before the transition. (The indirect band gaps were not determined, although a direct to indirect transition is expected with increasing x, because the absorption change at the indirect edge is small for these optically thin films.)

Figure 2 shows that there is a strong negative, but nonparabolic, bowing in the dependence of the direct gap E_0 on x. E_0 decreases rapidly with increasing x on the GaAs-rich side but varies much more slowly with x on the Ge-rich side. The results shown in Fig. 2 are not described by the conventional virtual-crystal model,[7] which would treat $(GaAs)_{1-x}(Ge_2)_x$ as a compound of average cations $Ga_{1-x}Ge_x$ and average anions $As_{1-x}Ge_x$ and would predict nearly parabolic bowing. In fact, the V shape of the data is well fitted by two straight line segments and is suggestive of a phase transition.

We propose that the V-shaped bowing is due to an order-disorder phase transition[8] in $(GaAs)_{1-x}$-$(Ge_2)_x$ between "ordered" (zinc-blende) and "disordered" (diamond) lattices at $x = x_c$. Both lattices are face-centered cubic with a two-atom basis[9]; however, the zinc-blende lattice is of lower symmetry as a result of the existence of distinct anion and cation sublattices. In $(GaAs)_{1-x}$-$(Ge_2)_x$, the lattice can, in our model, be occupied in either of two different ways (see Fig. 3). (1) In the GaAs-rich *ordered* zinc-blende phase, virtually all Ga atoms (dark circles) occupy nominal-Ga sites (labeled "Ga") and virtually all As atoms (empty circles) occupy nominal-As sites (labeled "As"), with Ge atoms (shaded circles) dispersed randomly on both sites. (2) In the *disordered* diamond phase, found for Ge-rich material, there are many "antisite" atoms: Ga atoms (dark circles) on nominal-As sites ("As" rows) and As atoms (empty circles) on nominal-

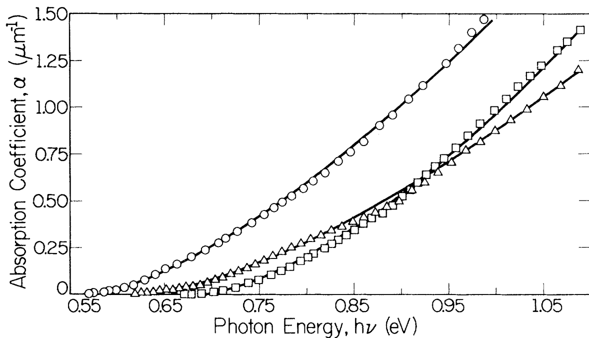

FIG. 1. Optical-absorption coefficient α (in μm^{-1}) vs photon energy $h\nu$ (in eV) for $(GaAs)_{1-x}(Ge_2)_x$ for three different compositions x; squares are for $x = 0.23$, circles are for $x = 0.3$, and triangles are for $x = 0.47$. The solid lines are fits by the equation $A(h\nu - E_0)^\beta$.

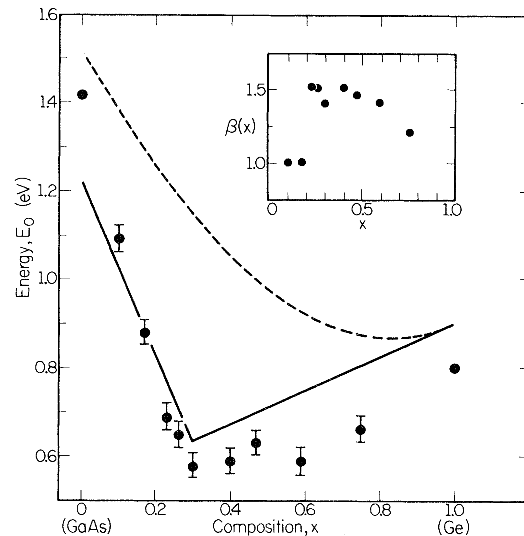

FIG. 2. Experimental data (closed circles) for the direct gap $E_0(x)$ in $(GaAs)_{1-x}(Ge_2)_x$ alloy compared with mean-field theory (solid curve) and the conventional virtual-crystal approximation (dashed curve). The mean-field theory exhibits a zinc-blende–diamond order-disorder transition at $x_c = 0.3$. Note that both theories use 4-K empirical tight-binding parameters, while experimental data are taken at room temperature, where the band gaps are smaller. Also shown (inset) is the curve-fitting parameter $\beta(x)$ (closed circles) for the alloys (typically uncertain by $\pm$ 0.15).

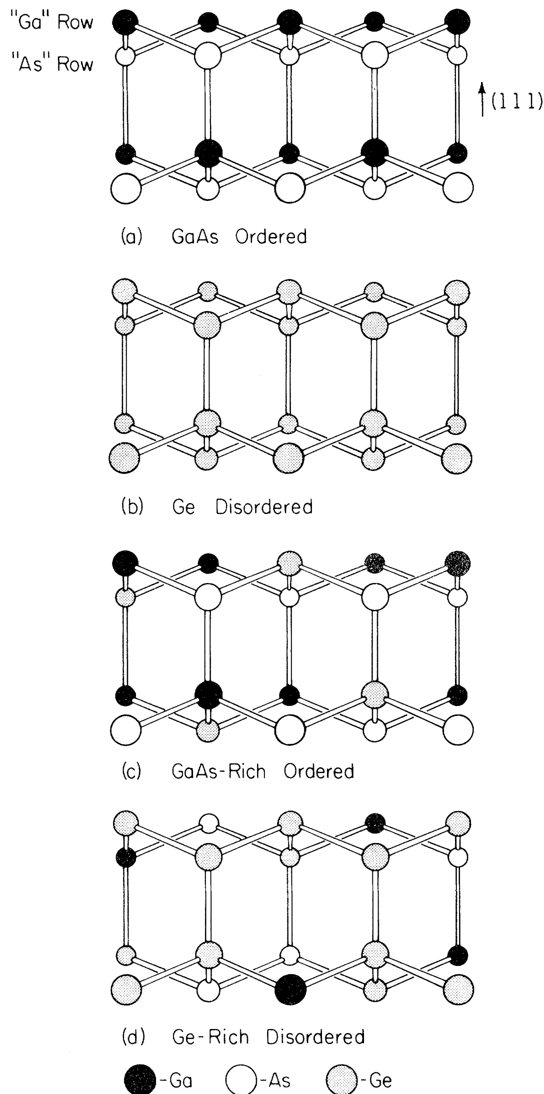

FIG. 3. Schematic model of the structure of $(GaAs)_{1-x}(Ge_2)_x$ alloys: (a) GaAs ordered zinc-blende structure, (b) Ge disordered diamond structure, (c) GaAs-rich ordered phase, and (d) Ge-rich disordered phase.

Ga sites ("Ga" rows).

The zinc-blende structures of Figs. 3(a) and 3(c) will be referred to as *ordered* since the great majority of Ga atoms are found on a single nominal sublattice (e.g., "Ga"). The diamond structure of Fig. 3(d), on the other hand, is *disordered* since comparable numbers of Ga atoms are found on nominal-As and nominal-Ga sites. The disordered phase contains a high concentration of antisite defects.

To treat the order-disorder transition between these two types of phases, we first define the order parameter of the transition in terms of the average sublattice occupancies of each type of atom. For example, we define $\langle P_{\text{Ga}}\rangle_{\text{"Ga"}}$ to be the average occupancy of cation atoms on the nominal-Ga sublattice. The order parameter M is then

$$M \equiv \langle P_{\text{Ga}}\rangle_{\text{"Ga"}} - \langle P_{\text{Ga}}\rangle_{\text{"As"}}. \quad (1)$$

M can assume any value from $x-1$ to $1-x$, and is $1-x$ if all the Ga atoms occupy nominal-Ga sites. If the Ga atoms are distributed evenly over nominal-Ga and nominal-As sites, then we have $M=0$; if all Ga atoms are on the nominal As sites, then we have $M=x-1$ and the phase is ordered. Thus M is an average of "pseudospins" that are either up (+) or down (−) at each site; if all the Ga atoms are on site (ordered), M has amplitude $1-x$, but M is zero if Ga is randomly distributed.

The nonequilibrium nature of these alloys can be accounted for by recognizing that metastable $(GaAs)_{1-x}(Ge_2)_x$ differs in one important aspect from equilibrium $(GaAs)_{1-x}(Ge_2)_x$ alloys. That is, the equilibrium phase diagram[10] exhibits a miscibility gap whereas phase separation in the metastable alloys is prevented by rapid quenching from the collisionally mixed state. We argue that the distinction between metastable and equilibrium $(GaAs)_{1-x}(Ge_2)_x$ alloys must be one of equilibration time scales and that the time before quenching is sufficient for the alloy to reach the metastable state but not equilibrium. Phase separation involves movement of atoms over distances[11] which, for typical self-diffusion constants in GaAs,[12] takes on the order of a day at the growth temperatures used in these experiments. It can be inhibited if the crystal is quenched in a highly mixed (due to secondary ion bombardment during growth) state. However, the zinc-blende–diamond order-disorder transition (which is masked by phase separation in alloys grown at equilibrium) is not inhibited since the question of an ordered versus disordered state can be settled by simple interchanges of nearest-neighbor atomic pairs of a spatial scale of 30 nm, and occurs on a time scale of order minutes. Thus a calculation of the equilibrium phase diagram can be applied to the metastable alloy if phase separation, which takes place on a time scale of order hours, is not allowed.

We have calculated the order parameter M using equilibrium statistical mechanics, mean-field theory, and a three-component "spin" Hamiltonian similar to that of the Blume-Energy-Grif-

fiths[13] model of ^{3}He-^{4}He solutions. Here, spins up, zero, and down associated with a given site correspond to occupancy by Ga, Ge, and As, respectively, and the spin coupling is antiferromagnetic. Consequently, M is the solution of the equation

$$JzM/k_B T_{eff} = \tanh^{-1}[M/(1-x)], \quad (2)$$

where J is a spin coupling, z is the crystal coordination number ($z=4$), k_B is Boltzmann's constant, and T_{eff} is the effective growth temperature. These four quantities may be related to the experimentally determined transition composition, $x_c \simeq 0.3$, by assuming that T_{eff} is a constant and using $k_B T_{eff} = Jz(1-x_c)$,[13] thus allowing determination of $M(x)$.

The resulting order parameter is inserted into an empirical sp^3s^* tight-binding[14,15] modified virtual-crystal approximation to the band structure. For example, the s-diagonal on-site tight-binding matrix element for the nominal-Ga sublattice is expressed in terms of the Ga, As, and Ge matrix elements:

$$2E(s, \text{"Ga"}) = E(s, \text{Ga})(1-x+M) + E(s, \text{As})(1-x-M) + xE(s, \text{Ge}). \quad (3)$$

The direct band gap $E_0(x)$ predicted by the tight-binding theory is shown in Fig. 2 and describes the observed V-shaped bowing. Note that the theory distinguishes a hypothesized *metastable* form of GaAs ($x=0$, solid line) from an equilibrium form ($x=0$, dashed line). The metastable form of GaAs would have a lower band gap than equilibrium GaAs because of the large number of antisite defects characteristic of the growth temperature T_{eff}. To date, the optical transmission and Hall data for the $x=0$ ion-bombarded films are indistinguishable from those of equivalently doped bulk GaAs. The theory predicts that there are two metastable phases of the alloy, ordered zinc-blende ($x<x_c$) and disordered diamond ($x>x_c$), which have qualitatively different electronic behavior as functions of x, resulting in a "kink" in the direct gap at the transition composition x_c.

In summary, metastable $(GaAs)_{1-x}(Ge_2)_x$ alloys exhibit a nonparabolic V-shaped bowing of the direct band gap E_0 that has not been observed previously in either III-V or group-IV semiconductor materials. This bowing appears to be a consequence of a new kind of order-disorder transition, and is well explained by a combination of a three-component "spin" Hamiltonian treated in a mean-field approximation and a modified virtual-crystal sp^3s^* model of the band structure.

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