Giant Spin-Orbit Bowing in $GaAs_{1-x}Bi_x$

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We report a giant bowing of the spin-orbit splitting energy Δ_0 in the dilute $GaAs_{1-x}Bi_x$ alloy for Bi concentrations ranging from 0% to 1.8%. This is the first observation of a large relativistic correction to the host electronic band structure induced by just a few percent of isoelectronic doping in a semiconductor material. It opens up the possibility of tailoring the spin-orbit splitting in semiconductors for spintronic applications.

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Alloying of semiconductors provides an effectual method for tailoring electronic properties, and the band gaps and lattice constants of materials required for practical electronic and photonic devices are routinely obtained using this approach. Although the lattice parameters of alloys are well approximated by the concentration weighted average value of the alloy constituents, the measured band gap is generally lower than this value and the deviation is described by a bowing parameter b that for most semiconductor alloys has values ranging from a few meV to as high as 3 eV. During the past decade, a giant band gap bowing $b \approx 20$ eV was observed for the dilute alloy $GaAs_{1-x}N_x$ [1]. Extensive research has been devoted to understanding the origin of this phenomenon which results from a giant lowering of the conduction band with dilute nitrogen incorporation [2]. Recently a large lowering of the band gap has also been observed in $GaAs_{1-x}Bi_x$ [3]. The enormous band gap lowering observed in both these dilute isoelectronically doped alloys is appealing for the flexibility it adds to designing nearly lattice matched devices such as solar cells and lasers on GaAs substrates.

Aside from tuning the band gap, the ability to tailor the spin-orbit interaction would introduce exciting possibilities related to the field of spintronics. It has been shown that at zero magnetic field the spin-orbit interaction in bulk strained semiconductor materials can lead to a spin splitting of electrons that drift in response to an applied electric field [4], and that it plays a central role in the recently observed spin-Hall effect [5]. The spin-orbit (SO) splitting Δ_0 becomes more significant for compounds containing heavy elements such as Te and Bi because of the fact that since the potential near their nuclei is very strong and consequently the kinetic energy very large, the electron velocity becomes comparable to the speed of light, leading to large relativistic corrections [6,7]. Since Bi is the largest radioactively stable atom, one expects a strong perturbation on Δ_0 for the $GaAs_{1-x}Bi_x$ semiconductor alloy. For the virtual compound GaBi (this has never been synthesized) a very large value of $\Delta_0 = 2.2$ eV has recently been calculated [7] and results from the same pseudopotential calculation suggest a strong enhancement of Δ_0 in $GaAs_{1-x}Bi_x$. We now report a giant increase of the spin-orbit splitting in $GaAs_{1-x}Bi_x$ that is observed with the incorporation of dilute amounts of Bi, which for the first time introduces the possibility of using alloying to tailor the spin-orbit gap of semiconductors such as GaAs for spintronic applications.

GaAsBi layers of 0.2 to 0.3 μm were grown by molecular-beam epitaxy on GaAs substrates. Details of growth and concentration measurement are given in Ref. [8]. The as-grown samples were mounted on the cold finger of a continuous flow cryostat. Photoluminescence (PL) was excited by a dye laser at 647.1 nm and detected with a Raman edge filter, a single spectrometer, and a cooled CCD detector. A line focus of 20 W/cm^2 was used for spin-orbit PL measurements, whereas a point focus of 200 W/cm^2 was used for the band edge PL measurements. The laser was normally incident, and collection was in the backscattering geometry with detection polarized orthogonal to that of the incident laser excitation. The GaAsBi band gap was also measured in some samples by contactless modulated electroreflectance (ER) using methods previously discussed [3,9].

Figure 1 shows the band edge PL spectra of a sample containing 1.4% bismuth, for lattice temperatures ranging from 150 to 300 K. At 300 K, assigning the band gap energy to the peak of the PL curve is found to be in good agreement with the results of modulated electroreflectance measurements, for samples ranging up to 3.6% bismuth concentration [3]. We have verified that this agreement also holds for the present excitation conditions and more importantly at a temperature of 150 K. Figure 2 shows the PL and the electromodulated reflectance of a 1.36% bismuth sample. Despite the significant broadening of the PL, attributed to structural disorder [8], the PL peak energy remains within a few meV of the energy of the heavy-hole band gap transition found by ER. Below 150 K, it is not possible to identify the band gap from PL because at these lower temperatures the PL begins to be dominated by carriers localized at Bi pairs and clusters, leading to com-

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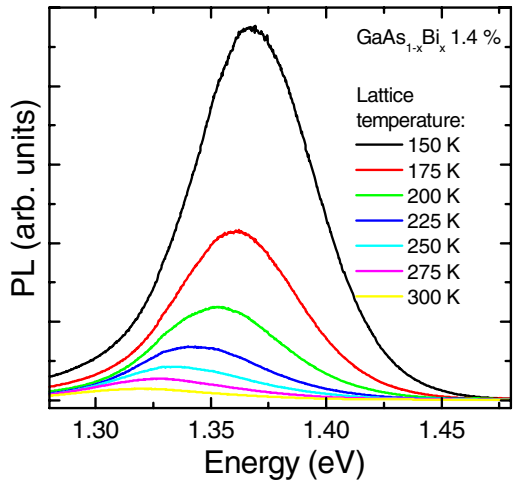

FIG. 1 (color online). PL spectra of the conduction band to heavy-hole transition, for varying lattice temperature.

plex emission spectra. However, for temperatures between 150 and 300 K, the carriers photogenerated at the band edges remain delocalized and, as seen in Fig. 1, the PL consists of a single peak, thus allowing the band gap E_0 to be tracked as a function of temperature or Bi concentration.

PL emission associated with the transition from the conduction band edge to the spin-orbit level that is split off from the valence band edge in GaAs, while much weaker than the E_0 emission, can still be observed under cw excitation, as is commonly encountered in resonant Raman scattering measurements, e.g., Ref. [10]. We have observed such PL in lightly n-type GaAs, both at low temperatures and at 150 K, verifying that under our experimental conditions the PL remains within a few meV of the SO transition energy previously measured for GaAs [11]. Figure 3 shows the results of our measurement on the 1.4% Bi doped GaAs sample. As the temperature is raised from 5 to 150 K, the PL peak evolves smoothly with a characteristic redshift and quenching, leaving no ambiguity in the assignment of the 1.818 eV peak measured at 150 K to the transition from the SO split-off band. To verify that this peak is in fact associated with the GaAsBi epilayer, we have measured room-temperature (RT) absorption of the 1.36% Bi sample with the GaAs substrate removed. This was done by mechanically lapping the substrate to an approximate thickness of 5 μm, followed by a secondary ion mass spectroscopy probe which sputtered off the GaAs in a 300 μm diameter window until Bi ions were detected. The lower curve in Fig. 4 shows transmission in the thickest region of this window where the presence of a few hundred nm of GaAs remaining beneath the epilayer is clearly revealed in the transmission by the abrupt step at 1.424 eV due to the GaAs band gap. In contrast, no such step occurs in the thinnest region of the window (upper curve), indicating that it consists entirely of the GaAsBi epilayer. Absorption in this epilayer occurs at lower energy (1.33 ev) from its broadened band edge, and subsequently from the distinct step near 1.77 eV attributed to the SO transition, a feature similar to that observed in the thickest window region. This verifies that the PL peak associated with the SO transition originates from the epilayer.

Above 150 K, PL emission is too weak to be distinguished from the background. We thus find that there is a narrow temperature range around 150 K where the SO transition can still be detected as in Fig. 3 and the band gap PL simultaneously measured as in Fig. 1. Measuring

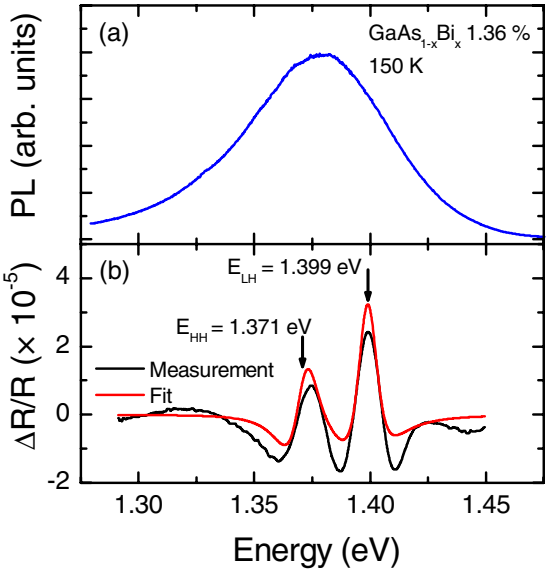

FIG. 2 (color online). Comparison of (a) the PL peak energy (1.379 eV) with (b) the heavy-hole to conduction band energy measured by contactless ER for a 1.36% $GaAs_{1-x}Bi_x$ sample at 150 K. The fit curve is composed of two third-derivative functions appropriate for an M_0 critical point in a three-dimensional system, under the low-field limit.

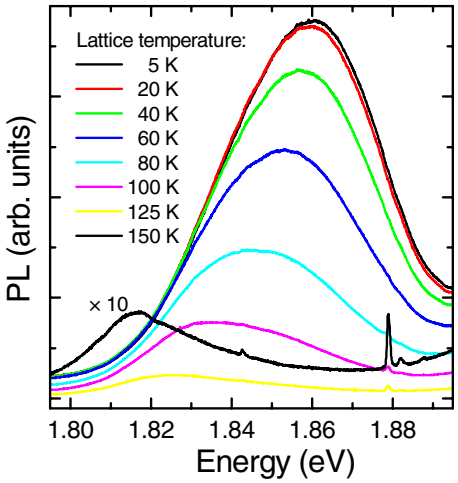

FIG. 3 (color online). PL spectra at the SO transition energy for 1.4% $GaAs_{1-x}Bi_x$ and varying lattice temperature. Magnified curve for 150 K shows the 1.818 eV PL used to track the SO transition as a function of Bi concentration. The peaks near 1.88 and 1.843 eV are leakage of forbidden Raman scattering.

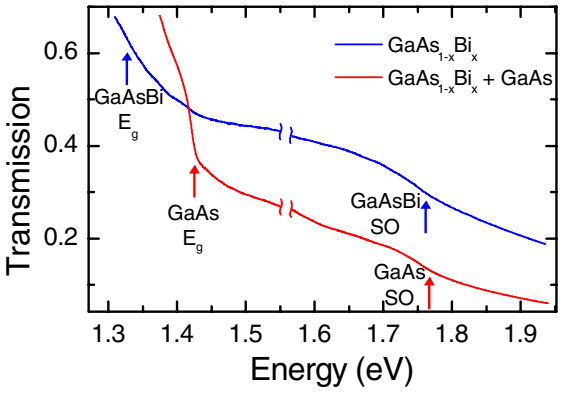

FIG. 4 (color online). Transmission spectra for the 1.36% $GaAs_{1-x}Bi_x$ sample. The substrate is partially removed in the lower curve (red or light gray), and completely removed in the upper curve (blue or dark gray). Vertical arrows show critical point energies of GaAs taken from Ref. [11], and of $GaAs_{1-x}Bi_x$. The SO transition at RT for $GaAs_{1-x}Bi_x$ was estimated from Fig. 5 using the known temperature dependence of the GaAs band edge from Ref. [11].

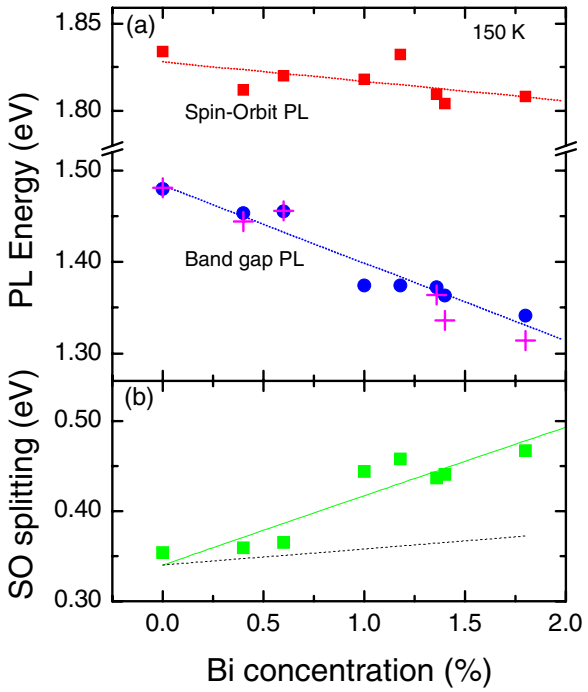

FIG. 5 (color online). (a) Energies of the 150 K SO PL (squares) and band gap PL (circles) similar to Figs. 1 and 3 for a set of 8 samples of varying bismuth concentration, after correction for strain-induced energy shifts. Solid lines are linear fits to the PL points and crosses are ER band gap energies, also strain corrected. (b) The spin-orbit splitting obtained by subtracting the band gap energies from the spin-orbit energies of (a). The dashed line is the linearly interpolated spin-orbit splitting using $\Delta_0 = 0.340$ eV for GaAs, and 2.15 eV for GaBi. The solid line is a quadratic fit to the data, $\Delta_0 = \Delta_{\text{interpolated}} - x(1-x)b$, with the bowing parameter $b = -6.0$ eV.

both PL energies at this temperature enables us to track the SO splitting as a function of Bi concentration. The band gap and spin-orbit transition energies measured from PL at 150 K for a set of samples with Bi concentration ranging from 0% to 1.8% are shown in Fig. 5(a) along with linear fits to the data. Band gap energies obtained from ER are also plotted for several of the samples where the ER signal could be detected unambiguously. Because the layers studied are pseudomorphic with the GaAs substrate [8], the influence of strain on the band energies has to be taken into account. Using the results of a Luttinger strain-Hamiltonian approach [12] to analyze the effects of biaxial compressive strain on the energy band structure, and using the $GaAs_{1-x}Bi_x$ lattice constant measured by x-ray diffraction [8], we find that a correction of -5 meV/% is necessary to obtain the dependence of the spin-orbit splitting in free standing (unstrained) films of GaAsBi. This strain is also evident in the 28 meV valence band splitting seen in the ER spectrum of Fig. 2(b), and this value is very close to that reported in Ref. [8].

Note that at 0% Bi concentration the linear fits yield PL energy values very near the transition energies reported for GaAs at 150 K, i.e., 1.82 eV for the SO and 1.484 eV for the band gap transition [11]. Second, the slope of the band gap reduction measured by PL, -85 ± 10 meV/% Bi, agrees with the more precise slope of -88 meV/% Bi previously measured at RT [3], and the band gap shift from 300 to 150 K is in good agreement with the temperature dependence found in that work. It is interesting to note in Fig. 5(a) the weak bismuth composition dependence of the SO PL transition energy (the SO PL energy scale is magnified by a factor 2) in contrast to the strong dependence of the band edge PL transition energy on Bi composition. By subtracting the band edge energy from the SO energy, the SO splitting Δ_0 was extracted and plotted in Fig. 5(b). It clearly rises much more sharply with Bi concentration than expected from the linearly interpolated Δ_0 (dashed line). The fit to a quadratic curve yields a giant spin-orbit bowing parameter of -6.0 eV.

Like $GaAs_{1-x}N_x$, $GaAs_{1-x}Bi_x$ is an abnormal alloy. The substitution of N (Bi) on anion sites in GaAs generates bound states near the host conduction (valence) bands as opposed to the expected simple alloying-induced shifts of these bands observed in normal substitutional alloys, and the N (Bi) dopants generate trap states for electrons (holes). It is the strong localization of conduction (valence) band Bloch states at these N (Bi) traps that generates the giant band gap bowings observed in these abnormal alloys [7]. Since in III-V compounds the valence band (VB) maximum consists mostly of the anion p state, Δ_0 increases monotonically when anion atomic number increases. This is because the atomic p-state SO splitting increases with increasing atomic number [13]. Because of the strong localization of host VB states at the Bi sites, the huge GaBi Δ_0 becomes even more pronounced for the $GaAs_{1-x}Bi_x$ alloy than would be expected from a linear average weighting of the As and Bi anion p states in the

alloy. In contrast, for $GaAs_{1-x}N_x$ Δ_0 remains nearly constant due to the antilocalization of VB states at N sites [7].

Most significantly, the calculations indicated a giant increase in the spin-orbit splitting equal to approximately 70% of the band gap reduction [7]. Our data indicate that for $GaAs_{1-x}Bi_x$ the increase in Δ_0 with bismuth doping is in reasonable agreement with the values computed in Ref. [7]. The strong localization of host VB states at Bi sites is in stark contrast to the delocalized behavior of Bloch-like host VB states observed for conventional semiconductor alloys. Thus $GaAs_{1-x}Bi_x$ is clearly an abnormal alloy, exhibiting a giant bowing not only for E_0, but also for Δ_0, making it unique amongst the known isoelectronically doped alloys. In cubic semiconductors, the spin-orbit splitting Δ_0 pushes the heavy-hole valence band upward by $\Delta_0/3$ (Ref. [12]), and this is also expected to approximately hold true for the dilute alloys [7]. The observed giant increase in Δ_0 therefore contributes significantly to the large band gap reduction in the $GaAs_{1-x}Bi_x$ alloy.

The spin degeneracy of electron and hole states results from the combined effect of the crystal Hamiltonian's spatial and temporal inversion symmetry. If the crystal Hamiltonian lacks spatial inversion symmetry, then despite Kramers degeneracy, zero-field spin-splittings can occur for nonzero wave vectors $\mathbf{k}$. Spatial inversion asymmetry can arise from a zinc-blende crystal's bulk inversion asymmetry (BIA), or from structure inversion asymmetry (SIA) induced by heterostructure potentials or electric fields. The Γ_{6c} conduction band Rashba Hamiltonian $H_{\mathrm{SIA}} = \alpha_R(\sigma_x k_y - \sigma_y k_x)$, where σ_x and σ_y are the Pauli spin matrices and α_R is the Rashba coefficient, leads to a spin splitting $E_{\pm}^{\mathrm{SIA}}(\mathbf{k}_\parallel) = \pm\alpha_R k_\parallel$, where $\mathbf{k}_\parallel = (k_x, k_y, 0)$, $\alpha_R \approx \frac{1}{3}P^2[E_g^{-2} - (E_g + \Delta_0)^{-2}]\mathcal{E}e$, E_g and Δ_0 are the band gap and valence band spin-orbit splitting, P the $\Gamma_{1c} \rightarrow \Gamma_{15v}$ interband matrix element, e the electron charge, and $\mathcal{E}$ an effective field [14,15]. Since $E_{\pm}^{\mathrm{SIA}}(\mathbf{k}_\parallel) \propto \Delta_0, (E_g)^{-1}$, and since Bi doping drastically increases (decreases) Δ_0 (E_g) for GaAs, the SIA spin splittings for electrons will be significantly enhanced in $GaAs_{1-x}Bi_x$ [14,15]. For the Datta-Das spin field-effect transistor, the differential phase shift $\Delta\theta \propto \alpha_R$; thus a larger α_R implies shorter channel lengths or lower gate voltage requirements [16].

Although the above linear-k spin splitting vanishes in bulk GaAs, there is a BIA related lifting of the spin degeneracy in the conduction band, proportional to the third power of the wave vector, given by $E_{\pm}^{\mathrm{BIA}} = \pm\gamma_D[k_x^2(k_y^2 - k_z^2)^2 + cp]^{1/2}$, where the Dresselhaus coefficient $\gamma_D = \gamma_0 + \gamma_1$, with $\gamma_0 = -\frac{4}{3}\frac{PQP'}{E_g'(E_g+\Delta_0)}[\frac{\Delta_0}{E_g} + \frac{\Delta_0'}{E_g'+\Delta_0'}]$ and $\gamma_1 = -\frac{4}{9}\Delta_0^- Q\frac{P^2(3E_g'+2\Delta_0')-P'^2(2E_g'+3E_g+\Delta_0)}{E_g'(E_g+\Delta_0)}$ using the 5-band Luttinger formalism [17]. E_g' is the $\Gamma_{6c} \rightarrow \Gamma_{7c}$ antibonding band gap, and Δ_0' is the $\Gamma_{7c} \rightarrow \Gamma_{8c}$ spin-orbit splitting [17]. Q and P' are the $\Gamma_{15v} \rightarrow \Gamma_{15c}$ and the $\Gamma_{1c} \rightarrow \Gamma_{15c}$ interband matrix elements and Δ_0^- is the off-diagonal spin-orbit coupling between the $(\Gamma_{7v}, \Gamma_{8v})$ and $(\Gamma_{7c}, \Gamma_{8c})$ subspaces [17]. Clearly γ_0 is proportional to Δ_0 and $(E_g)^{-1}$ since $(E_g + \Delta_0)$ remains almost constant in $GaAs_{1-x}Bi_x$. γ_1 is proportional to Δ_0^- which in turn is proportional to the difference between the anion and cation atomic spin-orbit splittings [17]. Thus in $GaAs_{1-x}Bi_x$ the strong localization of host valence band states at Bi sites [7] coupled with the giant atomic spin-orbit splitting [13] of Bi favors a giant enhancement of γ_D. This is important in quasi-2D systems where a k-linear conduction band spin splitting $E_{\pm}^{\mathrm{BIA}}(\mathbf{k}_\parallel) \approx \pm\alpha_D\langle k_z^2\rangle k_\parallel$ due to the Dresselhaus interaction arises in [001] heterostructures leading to an interplay between the BIA and SIA terms [14]. Finally, spin-orbit coupling is key to both the extrinsic spin-Hall effect, which necessarily requires spin-dependent impurity scattering, or the intrinsic spin-Hall effect, which occurs even in the absence of any scattering process [18].

In summary, we have observed a giant increase in the spin-orbit splitting energy Δ_0 with the incorporation of only a few percent of Bi in GaAs. It is the first experimental observation of the manifestation of an unusually large relativistic correction to the host electronic band structure of a very dilute semiconductor alloy system. Comparison of the experimental results for the SO splitting with theoretical estimates indicates that $GaAs_{1-x}Bi_x$ belongs to a class of abnormal alloys whose properties deviate substantially from those of conventional semiconductors alloys and can be exploited for the spin-orbit engineering required in the field of spintronics.

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