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Bi-induced *p*-type conductivity in nominally undoped Ga(AsBi)

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We report *p*-type conductivity in *nominally undoped* $GaAs_{1-x}Bi_x$ epilayers for a wide range of Bi-concentrations ($0.6\% \leq x \leq 10.6\%$). The counterintuitive increase of the conductivity with increasing x is paralleled by an increase in the density of free holes by more than three orders of magnitude in the investigated Bi-concentration range. The *p*-type conductivity results from holes thermally excited from Bi-induced acceptor levels lying at 26.8 meV above the valence band edge of $GaAs_{1-x}Bi_x$ with concentration up to $2.4 \times 10^{17}\ cm^{-3}$ at $x = 10.6\%$. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3690901]

The unique electronic properties and uncommon dependence on composition of the band structure in dilute bismide alloys are attracting increasing interest and are boosting several exciting lines of research in Materials Science.[1] Indeed, the large size of Bi-atoms leads to significant relativistic corrections[2,3] and a strong perturbation of the GaAs host band structure parameters, such as the band-gap energy[4,5] and carrier effective mass.[6,7] These properties make dilute bismides of technological interest for several applications that span from spintronics to high-efficiency solar cells,[8] heterojunction bipolar transistors,[9] terahertz,[10] and infrared devices.[11–13]

Despite numerous studies on dilute bismides, the transport properties of this material system are still largely unknown and debated. Previous studies of $GaAs_{1-x}Bi_x$ ($x \leq 2.5\%$) have shown that the Bi incorporation does not degrade significantly the electron transport properties of GaAs (at least for $x \leq 1.4\%$).[14,15] This finding is in line with the introduction by Bi-atoms of energy levels resonant in, or close to, the GaAs valence band,[16] thus affecting mainly the hole transport. The first experimental studies of the effects of Bi on the hole mobility (μ_h) have been reported only recently by Hall measurements on *p*-type (C- or Be-doped) $GaAs_{1-x}Bi_x$ samples ($x \leq 1.2\%$, see Ref. 17; and $x \leq 5.5\%$, see Ref. 18) and by picosecond transient-grating technique experiments on undoped $GaAs_{1-x}Bi_x$ ($2.5\% \leq x \leq 6.3\%$, see Ref. 19). These works have revealed a general decrease of the hole mobility following Bi incorporation. On the other hand, the behavior of μ_h at high x ($\sim$10%) as well as the influence of Bi on the free-hole concentration (p) is still not clear. Kini *et al.*[17] reported a large decrease of p with increasing x (about one order of magnitude for $x \sim 1\%$) in C- and Be-doped $GaAs_{1-x}Bi_x$ and ascribed this decrease to the effect of Bi_{Ga} heteroantisite defects, which act as double donors and compensate partially the extrinsic *p*-type doping of the alloy. In contrast, Nargelas *et al.*[19] reported *p*-type conductivity in *undoped* $GaAs_{1-x}Bi_x$ samples ($2.5\% \leq x \leq 6.3\%$), thus suggesting an acceptor behavior for Bi in GaAs, but without reporting any compositional dependence of p or μ_h.

In this letter, we report *p*-type conductivity in *nominally undoped* $GaAs_{1-x}Bi_x$ epilayers for a wide range of Bi-concentrations ($0.6\% \leq x \leq 10.6\%$). Hall effect measurements reveal a monotonic increase of p with increasing x, which is accompanied by an increase of the conductivity. These results support the existence of Bi-induced acceptor levels,[3,19] whose density increases with x. In the same concentration range, the free-hole mobility exhibits an overall decrease, with values in good quantitative agreement with those in the literature.

We investigate a series of $GaAs_{1-x}Bi_x$ epilayers ($x = 0.6\%$, 3.8%, 5.6%, 8.5%, and 10.6%; thickness $t = 30$–56 nm) grown by solid source molecular beam epitaxy on a semi-insulating (100) GaAs substrate. Further details of the growth conditions and sample parameters can be found elsewhere.[5,7] The Bi-concentration was determined by combining x-ray diffraction and optical data. All samples were processed into 1-3-3-1 Hall bars of width $W = 45\ \mu m$ and length $L = 1200\ \mu m$ with Ti/Au metal depositions providing ohmic contacts [see inset in Fig. 2(b)]. Hall effect measurements were performed using a high impedance system with high current stability ($\sim$50 pA) in a superconductive-magnet cryostat with magnetic field (B) up to 14 T and temperatures (T) ranging from 65 K to 290 K.

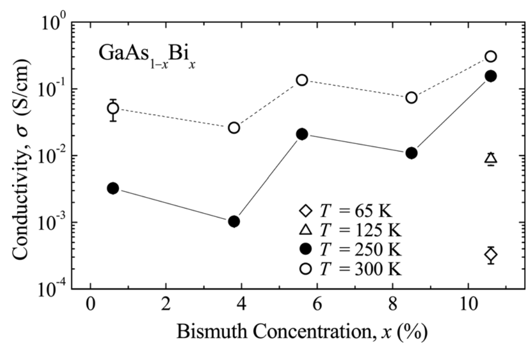

FIG. 1. Compositional dependence of the longitudinal conductivity σ measured in nominally undoped $GaAs_{1-x}Bi_x$ epilayers at different temperatures.

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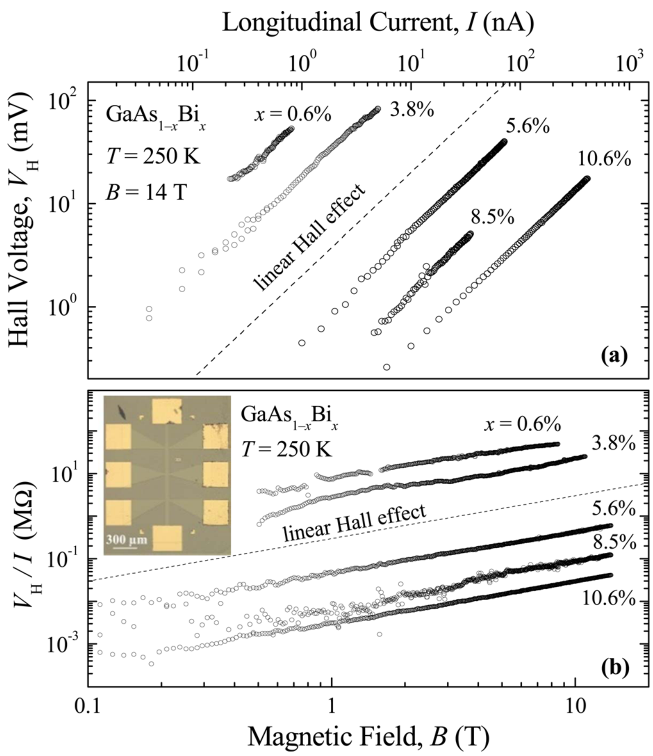

FIG. 2. (Color online) (a) Hall voltage V_H acquired at fixed magnetic field ($B = 14$ T) as a function of the longitudinal current I for different values of the Bi-concentration. (b) V_H/I as a function of B for different x ($I = 0.3$ nA, 2.5 nA, 60 nA, 35 nA, and 400 nA for $x = 0.6\%$, 3.8%, 5.6%, 8.5%, and 10.6%, respectively). Inset: optical-microscope image of a 1-3-3-1 Hall bar employed for transport measurements. The dashed lines indicate, in both panels, the slope for the linear Hall effect from free holes.

Figure 1 shows the longitudinal conductivity (σ) at $B = 0$ T for $GaAs_{1-x}Bi_x$ epilayers with different x. The data reveal a significant increase of σ with increasing x, which becomes steeper with decreasing T. The inhomogeneity in the conductivity along the Hall bar was measured to be less than 20% in all samples. The Bi-induced increase of σ differs from the systematic reduction of conductivity for increasing alloying reported for other highly mismatched alloys, such as Ga(AsN) and In(AsN).[20,21] We investigate further this counterintuitive behavior by Hall effect measurements.

For each sample, the Hall voltage (V_H) was acquired in two different experimental conditions: either as a function of the longitudinal current (I) at fixed B (14 T) or as a function of B at fixed I. In both configurations and in all samples, V_H exhibits a linear dependence on I and B, see Fig. 2. The sign of V_H is consistent with a dominant *p-type conductivity*. The values of the free-hole concentration $p = (IB)/(eV_H t)$ (where e is the electron charge and t is the thickness of the $GaAs_{1-x}Bi_x$ epilayers) are shown in Fig. 3(a) as a function of x at $T = 250$ K. Within the experimental uncertainty,[22] the same values of p are obtained by measuring the Hall voltage at fixed or variable magnetic field. The measured free-hole concentration increases monotonically with increasing x, reaching values of $\sim 10^{17}$ cm^{-3} at $x = 10.6\%$. This indicates the existence of Bi-induced acceptors and supports previous findings by different techniques; see Refs. 3 and 19. However, such an acceptor behavior of Bi-atoms is incompatible with the presence of a large density of donor levels due to Bi_{Ga} heteroantisites suggested for p-type doped $GaAs_{1-x}Bi_x$

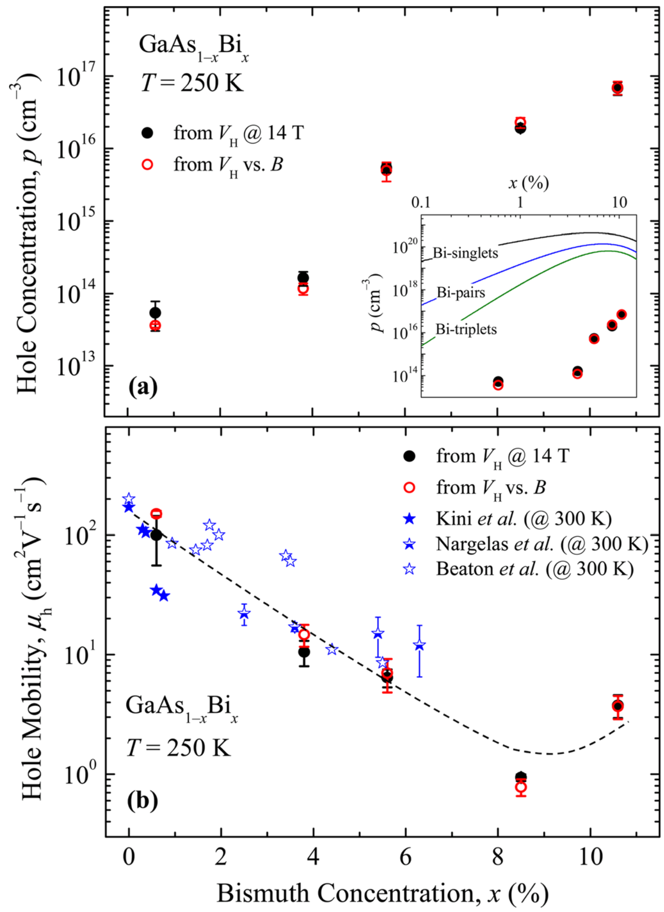

FIG. 3. (Color online) (a) Compositional dependence of the free-hole concentration p in $GaAs_{1-x}Bi_x$ at $T = 250$ K, as obtained from the analysis of V_H acquired for fixed (dots) and variable (circles) B. Inset: comparison between experimental data of p and concentration of Bi-clusters of 1, 2, and 3 Bi-atoms as estimated for a random alloy by including next-nearest-neighbor interactions (solid lines), after Ref. 24. (b) As panel (a) for the free-hole mobility, μ_h. Data of μ_h available in the literature are reported by stars (Refs. 17–19, at $T = 300$ K). The dashed line is a guide to the eye.

with $x \leq 1.2\%$.[17] Therefore, Bi-related donor states, if present, should become rapidly negligible with increasing x.

The Hall mobility of free holes, $\mu_h = \sigma/(ep)$, is shown in Fig. 3(b) as a function of x at $T = 250$ K. Our results (dots and circles) agree well with those reported in the literature (stars), thus providing a general overview of the compositional dependence of μ_h over a wide range of x.[23] Although the different sets of data show some scatter, a clear-cut decrease of μ_h is observed for x up to $\sim$8.5%; whilst μ_h increases from 0.9 ± 0.1 $cm^2/(Vs)$ to 3.7 ± 0.8 $cm^2/(Vs)$ for x going from 8.5% to 10.6%. This compositional dependence of μ_h agrees with recent magneto-optical studies on the same series of samples.[7] These measurements highlight a strong hybridization between the Bi-related levels and the host band-states for $x < 6\%$. In turns, this results into an increase of the carriers effective mass, paralleled here by a decrease of the free-hole mobility. On the contrary, the softening of this hybridization for $x > 8\%$ leads to a decrease of the carriers effective mass, paralleled here by an increase of the free-hole mobility.

A deeper insight into the mechanism responsible for the p-type conductivity in $GaAs_{1-x}Bi_x$ was obtained from a detailed temperature-dependent study of μ_h and p at $x = 10.6\%$, as

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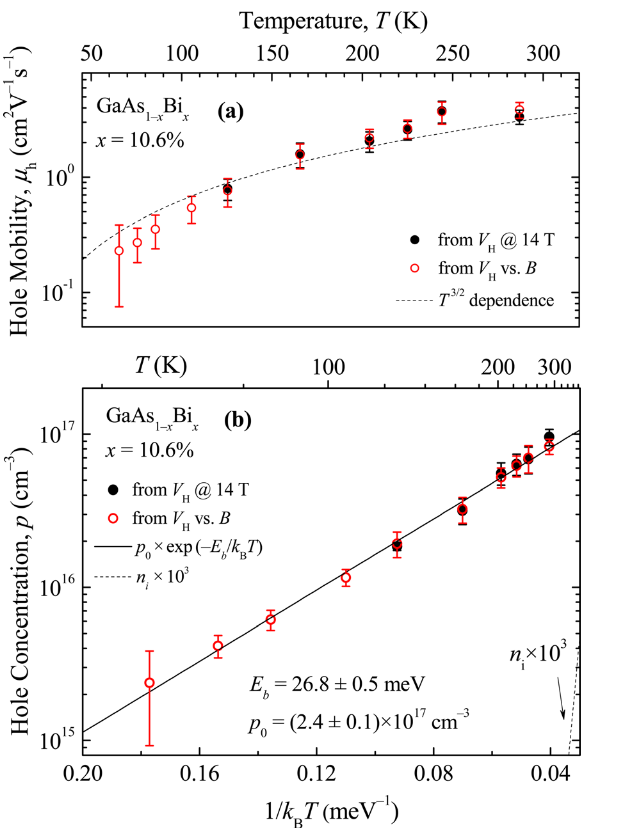

FIG. 4. (Color online) (a) Temperature-dependence ($65\,K \leq T \leq 290\,K$) of the free-hole mobility μ_h in $GaAs_{1-x}Bi_x$ with $x = 10.6\%$, as obtained from the analysis of V_H acquired for fixed (dots) and variable (circles) B. The dashed line represents the $T^{3/2}$-dependence for impurity scattering. (b) As panel (a) for the free-hole concentration, p. An analysis in terms of free holes thermally activated from a single acceptor level reproduces well the experimental data for $E_b = 26.8$ meV and $p_0 = 2.4 \times 10^{17}\,cm^{-3}$ (see solid line). The contribution of the intrinsic carrier concentration n_i is largely negligible (see dotted line).

reported in Fig. 4. The free-hole mobility increases monotonically with increasing T, as shown in Fig. 4(a), thus indicating that the contribution of elastic collisions by alloy disorder and/or defects is significantly larger than that due to inelastic collisions with phonons, at least for $x = 10.6\%$. The dependence of p on temperature is shown in Fig. 4(b). It is well described by the exponential law $p = p_0 \times \exp(-E_b/k_BT)$, where $E_b = 26.8 \pm 0.5$ meV is a single activation energy and $p_0 = (2.4 \pm 0.1) \times 10^{17}\,cm^{-3}$ is the density of acceptor levels. The value of E_b agrees with the binding energy of Bi-induced acceptor levels ($\sim$25 meV) determined by far-infrared absorption spectroscopy,[3] whereas the value of p_0 points towards a significant concentration of acceptors. This gives strong evidence that the p-type conductivity in $GaAs_{1-x}Bi_x$ results from holes thermally excited into the valence band from Bi-induced acceptor levels. The intrinsic carrier contribution to the conductivity is more than 5 orders of magnitude smaller than the measured values and can be neglected even at room temperature, see dotted line in Fig. 4(b).

In the inset of Fig. 3(a), the compositional dependence of p is compared with that of the density of clusters composed by 1, 2, or 3 Bi-atoms, as calculated for a random distribution of impurities.[24] This comparison indicates that low-order Bi-clusters cannot account for the compositional evolution of the acceptor density. The fast, exponential-like increase of p with x suggests the existence of a driving force ruling the formation of the acceptor centers during the growth process that cannot be explained in a pure random framework. Theoretical investigations are now required to address the geometry and number of Bi-atoms forming these clusters or defect levels.

In conclusion, we have shown that the p-type conductivity of *nominally undoped* $GaAs_{1-x}Bi_x$ epilayers is enhanced by Bi atoms. This behavior differs fundamentally from that found in other highly mismatched alloys and suggests that the Bi-incorporation in GaAs leads to the formation of acceptor levels lying at $\sim$27 meV above the valence band edge with concentration of up to $\sim 2 \times 10^{17}\,cm^{-3}$ at $x = 10.6\%$. The systematic increase of the free-hole concentration with increasing Bi-concentration is paralleled by a non-monotonic decrease of the free-hole mobility, the latter being explained in terms of the hybridization of the Bi-induced localized states with the extended band-states of GaAs. These findings provide evidence for an unique compositional dependence of the hole transport properties of $GaAs_{1-x}Bi_x$ that will stimulate further theoretical works on the electronic properties of dilute bismides. The Bi-induced increase of conductivity is also of technological interest in the context of current research on the device applications of dilute bismides.

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[22]The uncertainties on the values of μ_h and p are calculated taking into account the conductivity inhomogeneity along the Hall bar and measurements in three different points on the bar, as well as measurements on two Hall bars. V_H is determined by averaging between positive and negative values of I and B.
[23]We estimate the difference in temperatures at which μ_h has been measured in our work ($T = 250$ K) and in Refs. 17–19 ($T = 300$ K) to produce variation on μ_h within the experimental uncertainty, therefore not affecting the comparison between different sets of data.
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