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Effects of hydrogen on the electronic properties of Ga(AsBi) alloys

G. Pettinari,[1,a)] A. Patanè,[1] A. Polimeni,[2] M. Capizzi,[2] Xianfeng Lu,[3] and T. Tiedje[4]
[1]*School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, United Kingdom*
[2]*CNISM-Dipartimento di Fisica, Sapienza Università di Roma, P.le A. Moro 2, 00185 Roma, Italy*
[3]*Department of Physics and Astronomy, University of British Columbia, Vancouver, British Columbia V6T IZ4, Canada*
[4]*Department of Electrical and Computer Engineering, University of Victoria, Victoria, British Columbia V8W 3P6, Canada*

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The effects of hydrogen incorporation on the electronic properties of Ga(AsBi) alloys are investigated in a wide range of Bi-concentration ($0.6\% \leq x \leq 10.6\%$) by Hall effect measurements in magnetic fields up to 14 T and by photoluminescence spectroscopy. For all the investigated Bi-concentrations, we report the passivation of Bi-induced *shallow* acceptor levels—responsible for the native *p*-type conductivity in Ga(AsBi)—and a tenfold increase of the hole mobility upon hydrogen incorporation in the host lattice. The emission energy is, instead, negligibly affected by hydrogenation, indicating that the narrowing of the band-gap energy with Bi and the native *p*-type conductivity are two uncorrelated effects arising from different Bi-induced electronic levels. Passivation by hydrogen of the shallow Bi-acceptor levels makes also possible to identify *deep* Bi-acceptor states. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4768237]

In an effort to meet the growing demand of new technologies, a great deal of work has been devoted over the past years to explore and develop non-conventional III-V compounds. In this contest, highly mismatched III-Bi-V alloys have attracted an increasing interest because of the peculiar compositional dependence of their electronic properties and of their potential for a wide range of applications, which include spintronics,[1] high-efficiency solar cells,[2] heterojunction bipolar transitions,[3] Terahertz,[4] and infrared devices.[5–7] Indeed, the incorporation of large-size Bi-atoms in the GaAs crystal lattice leads to significant relativistic corrections[8,9] and strong perturbations of the host band structure parameters, such as the carrier effective mass.[10,11] Moreover, the hybridization of the Bi isoelectronic impurity wave-function with the GaAs extended valence-band states narrows the band-gap energy without affecting much the lattice parameter:[12,13] Room-temperature emission energies down to 0.86 eV ($\sim$1.44 μm) and a lattice constant mismatch of only $\sim$1% were reported for Bi-concentration of $\sim$10%. This corresponds to the largest band-gap reduction per lattice-constant variation observed so far among several GaAs-based ternary alloys. The recent achievement of crystalline Ga(AsBi) films with Bi-concentration up to 22%[14] is expected to extend even more the range of applications of this material system.

The implementation of Ga(AsBi) alloys in future applications requires, however, controlling carrier densities and achieving high electron and hole mobilities. On one hand, the electron mobility has been shown to be weakly affected by bismuth incorporation (at least for Bi-concentrations smaller than 1.4%).[15,16] On the other hand, different groups have reported a general degradation of the hole mobility[17–20] following the incorporation of Bi, which, in doped materials, can be avoided only under specific growth conditions.[21] Also, it was shown[20] that the incorporation of Bi in GaAs produces a relatively high density ($\sim 10^{17}$ cm^{-3} at $\sim$10% of Bi) of acceptor states, thus leading to a *p*-type conductivity in nominally undoped Ga(AsBi). The existence or absence of a correlation between the band-gap narrowing and the native conductivity in Ga(AsBi) has not yet been established and is critical to the future exploitation of Ga(AsBi).

In this letter, we use post-growth hydrogenation to control the transport properties of $GaAs_{1-x}Bi_x$ alloys for a wide range of Bi-concentrations ($0.6\% \leq x \leq 10.6\%$, as estimated from high resolution x-ray diffraction and photoluminescence measurements). Upon hydrogen incorporation, *the native p-type conductivity is strongly suppressed and the hole mobility increases*. On the other hand, the photoluminescence emission energy of the alloy remains unchanged. These results indicate that hydrogen passivates the Bi-induced acceptor levels responsible for the prevailing *p*-type conductivity of Ga(AsBi), without affecting the electronic activity of the isolated Bi atoms responsible for the band-gap narrowing. This provides a means for obtaining a high-mobility "intrinsic" alloy of strategic technological interest for far-infrared and mid-infrared photonics.

Atomic hydrogen has been post-growth incorporated by low-energy (100 eV) proton irradiation on a series of Hall bars (1200 μm-long, 45 μm-wide) processed on Ga(AsBi) epilayers (thickness $t = 30$–56 nm; bismuth concentration $x = 0.6\%$, 3.8%, 5.6%, 8.5%, and 10.6%) grown by molecular beam epitaxy on an intrinsic GaAs buffer layer on top of a semi-insulating (100) GaAs substrate. Further details of the growth conditions, samples, and Hall bar parameters can be found elsewhere.[11,13,20] The transport properties and the typical *p*-type conductivity induced by Bi-acceptor levels in the Ga(AsBi) samples have been extensively investigated before hydrogenation in Ref. 20. Following the hydrogenation, Hall effect measurements in magnetic fields (B) up to 14 T have been performed in a superconductive-magnet cryostat with temperatures (T) ranging from 230 K to 300 K using a high-impedance system with high current stability ($\sim$50 pA).

[a)]Electronic mail: giorgio.pettinari@nottingham.ac.uk.

Optical properties were investigated by photoluminescence (PL) spectroscopy on unprocessed layers of the same samples. The PL was excited by a 532 nm solid-state laser and detected by a 0.75 m focal-length monochromator coupled with a liquid nitrogen-cooled InGaAs array detector.

Figure 1 shows the magnetic field dependence of the Hall resistance (R_{xy}) and its temperature dependence ($225\,\mathrm{K} \le T \le 300\,\mathrm{K}$) for the Ga(AsBi) sample with the highest concentration of bismuth ($x = 10.6\%$) and of native Bi-induced acceptors ($2.4 \times 10^{17}\,\mathrm{cm}^{-3}$, see Ref. 20). After hydrogen incorporation (dose $d_H = 2 \times 10^{18}$ ions/cm^2), the room-temperature Hall resistance exhibits a sign reversal, from positive to negative; see panels (a) and (b). This indicates that the *p-type conductivity* of the virgin sample turns into a dominating *n-type conductivity* upon hydrogenation. Also, whilst the virgin sample exhibits a linear B-dependence of R_{xy} typical of single-carrier conduction, the hydrogenated sample shows a *strong non-linear* dependence of R_{xy} on magnetic field, with a minimum whose position in B and strength depend on temperature. This behavior suggests that after hydrogenation *both electrons and holes* contribute to the conduction, which requires a detailed analysis of the dependence of R_{xy} on B to extract information about transport properties.

An ambipolar conduction model[22] with electrons and holes flowing in the Ga(AsBi) layer (and subjected to the mass action law) does not reproduce the measured magnetic field dependence of R_{xy}. Therefore, we consider a *two-layer model of conduction*[23] with electrons and holes flowing in two adjacent layers of thicknesses d_n and d_p, respectively, i.e., electrons in the GaAs buffer layer and holes in the Ga(AsBi) layer. Within this model, the Hall coefficient R_H, which is related to the Hall resistance through $R_{xy} = R_H B/d$, depends on the magnetic field according to[24]

$$R_H = \frac{d_p p \mu_h^2 - d_n n \mu_e^2 + (\mu_h \mu_e B)^2 (d_p p - d_n n)}{(d_p p \mu_h + d_n n \mu_e)^2 + (\mu_h \mu_e B)^2 (d_p p - d_n n)^2} \cdot \frac{d}{e}, \quad (1)$$

where n (p) and μ_e (μ_h) are the electron (hole) density and mobility, respectively, e is the electron charge, and $d = d_p + d_n$. We use Eq. (1) to fit the Hall resistance data under three constraints: (i) the zero-field longitudinal resistivity $\rho_{xx} = d/(e d_p p \mu_h + e d_n n \mu_e)$ is equal to that measured by four-terminal electrical measurements; (ii) d_p is equal to the Ga(AsBi) layer thickness; (iii) d_n is the same at all temperatures.[25]

As shown in Fig. 1, the dependence of R_{xy} on B—namely, the position of the R_{xy}-minimum and the gradual recovery of the linear dependence of R_{xy} on B for decreasing temperature in the hydrogenated sample—is well reproduced by the fitting curve (dashed lines). Also, the fitting parameters, which are shown in panels (c) and (d), reveal that the sign reversal of R_{xy} after hydrogenation results from the strong reduction of the free-hole density in the Ga(AsBi) layer (from $p \sim 10^{17}\,\mathrm{cm}^{-3}$ to $< 10^{15}\,\mathrm{cm}^{-3}$) and from the presence in the GaAs buffer layer of a small density of free-electrons ($n < 10^{12}\,\mathrm{cm}^{-3}$) with a high electron mobility, as expected for intrinsic GaAs.[26] This electron density likely originates from H-related donor states introduced in the GaAs buffer layer by hydrogenation.[27] The linear dependence of the Hall resistance on magnetic field (and its positive sign) in the virgin sample excludes that this small density of free-electrons was already present before hydrogenation.

The strong temperature-dependence of the Hall effect in the hydrogenated sample, as well as its change from a non-linear to a linear behavior for decreasing temperature, can be explained in terms of a free-electron density more sensitive to temperature than the free-hole density. With decreasing T, the electron contribution to the total conductivity decreases and the conduction by free-holes dominates at low temperature ($T \le 230\,\mathrm{K}$), thus leading to a linear B-dependence of R_{xy} at low T.

We attribute the residual free-hole density still present in the Ga(AsBi) layer after hydrogenation to a *deep acceptor state* different from that responsible for the native p-type conductivity: Indeed, its activation energy [$E_A = 278 \pm 24$ meV, as

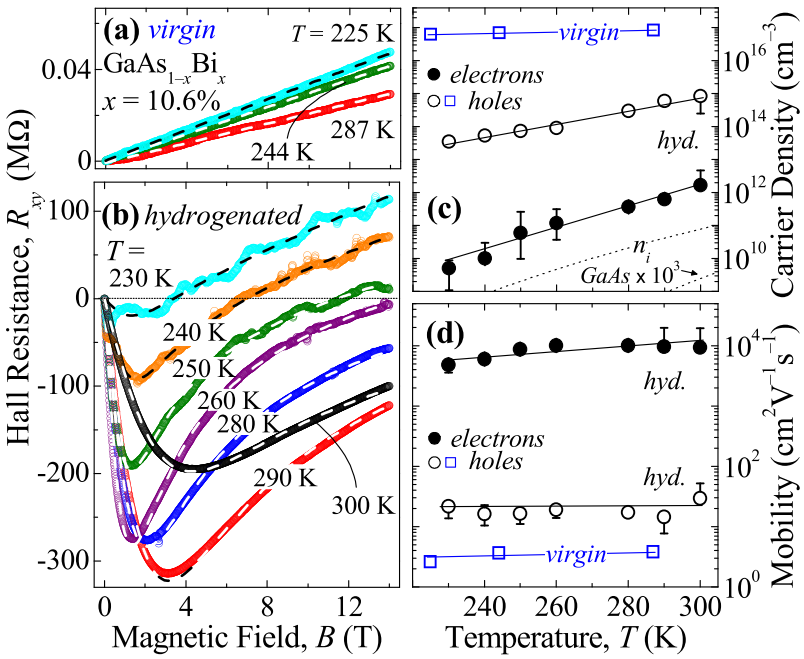

FIG. 1. Hall resistance (R_{xy}) as a function of applied magnetic field (B) in $GaAs_{1-x}Bi_x$ ($x = 10.6\%$) at different temperatures ($225\,\mathrm{K} \le T \le 300\,\mathrm{K}$) before (a) and after (b) hydrogen incorporation (dose $d_H = 2 \times 10^{18}$ ions/cm^2). Data for the virgin sample are reproduced from Ref. 20. Dashed lines are fits to the data according to a two-layer model of conduction [see Eq. (1) and Ref. 25]. Carrier density and mobility derived from the fit are shown in panels (c) and (d), respectively, where error bars indicate the interval in which all the three constraints (see text) are satisfied. When not shown, the error bar is smaller than the symbol size. The intrinsic carrier density (n_i) in the Ga(AsBi) and GaAs layer are also shown (dotted lines). Solid lines are guides to the eye.

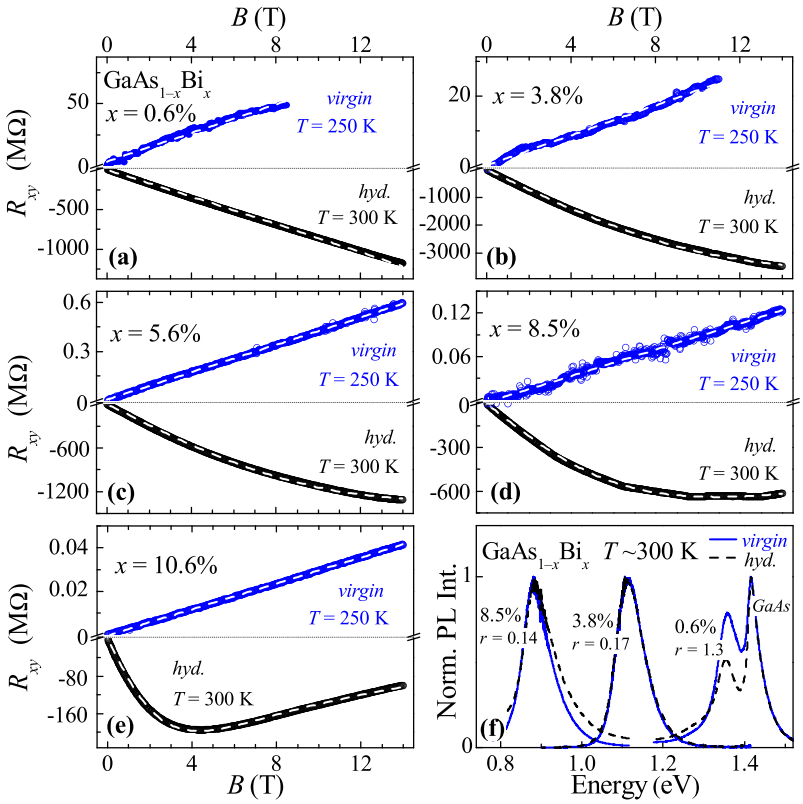

FIG. 2. (a)-(e) Hall resistance (R_{xy}) as a function of applied magnetic field (B) in Ga(AsBi) samples with increasing bismuth concentration (indicated in each panel) before (*virgin*, $T = 250$ K) and after (*hyd.*, $T = 300$ K) hydrogen incorporation (dose $d_H = 2 \times 10^{18}$ ions/cm^2). Data for the virgin sample are reproduced from Ref. 20. Dashed lines are fits to the data according to a two-layer model of conduction [see Eq. (1) and Refs. 25 and 28]. (f) Room-temperature photoluminescence spectra of representative Ga(AsBi) samples before (solid lines) and after (dashed lines) hydrogen incorporation (dose $d_H = 1 \times 10^{18}$ ions/cm^2). The ratio of PL intensity before (I_{before}) and after (I_{after}) hydrogenation ($r = I_{after}/I_{before}$) is also shown.

estimated by the relation $p \propto \exp(-E_A/k_BT)$] is much higher than the activation energy of the shallow Bi-induced acceptor level ($E_A = 26.8 \pm 0.5$ meV, see Ref. 20) observed in virgin samples. The origin of this new acceptor state will be discussed later.

From these studies, we conclude that hydrogen *passivates* the native Bi-induced acceptor levels in the Ga(AsBi) layer and, as a side effect, introduces donor states in the GaAs buffer layer thus leading to a small density of free-electrons ($n \sim 10^{12}$ cm^{-3} at room temperature).

The effects described for the Ga(AsBi) layer with $x = 10.6\%$ are common to all the other epilayers, as shown in Fig. 2. Indeed, after the incorporation of a same dose of hydrogen ($d_H = 2 \times 10^{18}$ ions/cm^2), all samples show a sign reversal of the Hall resistance, from positive to negative.[28] Moreover, in the hydrogenated samples the *non-linearity* in $R_{xy}(B)$ gradually decreases for decreasing bismuth concentration, and the sample with the lowest Bi-concentration [$x = 0.6\%$, see panel (a)] shows a linear dependence on B (now with negative sign). This compositional behavior results from the introduction of a similar concentration of donor levels in the GaAs buffer layer of each sample and from the Bi-dependence of the residual free-hole concentration and mobility shown in Fig. 3 (as obtained from the results of the analysis of the Hall resistance data according to the two-layer model of conduction).[25,28] Note that the electron parameters were fixed to the values obtained from the temperature studies of the 10.6% sample [$\mu_e = 9400$ cm^2/(Vs) and $d_n \sim 100$ nm] for the analysis of the hydrogenated samples.[29] The values of the free-electron density ($\sim 1.6 \times 10^{12}$ cm^{-3}) for samples largely differing for growth conditions but subject to an identical hydrogen treatment are all very similar. This confirms that the electron component in the two-layer model of conduction is due to H-induced donor states in the GaAs buffer layer.

As regards the hole mobility in Ga(AsBi), the decrease of μ_h for x up to $\sim 8.5\%$ followed by an increase for x going from 8.5% to 10.6% reported in the virgin samples (see also Ref. 20) is maintained upon hydrogenation, with an overall *increase* of μ_h by about *one order of magnitude* [see dashed lines in panel (b) of Fig. 3]. This is attributed to an increase of the carrier scattering time, thus supporting hydrogen *passivation*—rather than compensation—of shallow Bi-acceptor states by formation of neutral Bi–H complexes.

Finally, the compositional dependence of the free-hole density upon hydrogenation mimics that in the virgin system [see dashed lines in panel (a) of Fig. 3], thus suggesting a Bi-related origin also for the *deep acceptor state* ($E_A \sim 278$ meV), which is not fully passivated by hydrogen. Most likely, such deep state is present also in the virgin samples, but its observation is hampered by the presence of the shallow acceptor level ($E_A \sim 27$ meV). Recent theoretical calculations[30] have predicted that Bi-clusters of 2 and 3 atoms introduce electronic levels at 10 meV and 8–17 meV above the valence band maximum, respectively. The same calculations have also predicted that Bi-cluster levels rapidly move deeper into the GaAs energy gap with increasing the cluster size. Thus, large Bi-clusters of increasing size could account for our observations.

These experimental findings indicate that hydrogen in Ga(AsBi) passivates shallow and deep Bi-levels to a different extent, similarly to what observed for the different N-cluster states in Ga(AsN).[31] However, at variance with the Ga(AsN) case, the electronic activity of the isolated Bi atoms—responsible for the Ga(AsBi) band-gap narrowing (Ref. 32)—is *not* affected by hydrogen incorporation. Indeed, the room-temperature PL *emission energy of Ga(AsBi) does not change upon hydrogen incorporation*; see panel (f) in Fig. 2.

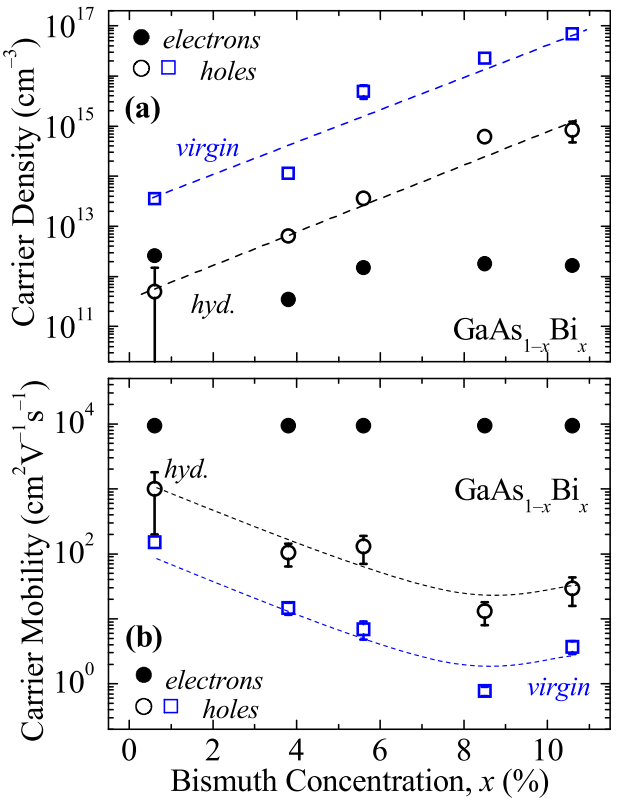

FIG. 3. Compositional dependence of carrier densities (a) and mobilities (b) before (*virgin*, open squares, $T = 250$ K) and after (*hyd.*, circles and dots, $T = 300$ K) hydrogen incorporation (dose $d_H = 2 \times 10^{18}$ ions/cm^2), as derived from the analysis of the Hall resistance data shown in Fig. 2. Data for the virgin samples are reproduced from Ref. 20. When not shown, the error bar is smaller than the symbol size. Dashed lines are guides to the eye (see Ref. 28).

The observation of the different effects that hydrogen has on the transport and optical properties of the Ga(AsBi) system is an important finding from both a technological and a physics point of view. On one hand, it makes possible to obtain a high-mobility "intrinsic" material with wavelength emission up to ~1.5 μm (and beyond, owing to recent developments in growth techniques). On the other hand, it fosters further theoretical investigations of the effects of Bi in GaAs. It shows, indeed, that the narrowing of the band-gap energy and the *p*-type conductivity in Ga(AsBi) originate from different bismuth-related electronic levels. This behavior differs from the most investigated case of highly mismatched Ga(AsN) alloys, where modifications in the transport properties upon hydrogen incorporation are accompanied by a restoration of the energy gap of N-free GaAs.[33]

In conclusion, an accurate analysis of the Hall effect as a function of magnetic field has shown that hydrogen *passivates* Bi-induced shallow acceptor levels and produces an increase of the hole mobility by about one order of magnitude, at all the bismuth concentrations investigated (x up to ~11%). This passivation effect has made possible the observation of a deep Bi-acceptor level ($E_A \sim 278$ meV). However, hydrogen does not influence the electronic activity of the isolated Bi atoms responsible for the band-gap narrowing. Therefore, the *p*-type conductivity and the band-gap narrowing are two uncorrelated effects induced by the introduction of Bi in GaAs. The hydrogenation of III-Bi-V alloys may provide, therefore, a versatile tool for obtaining high mobility "intrinsic" materials suitable for far-infrared and mid-infrared photonic applications. Finally, it may open the way to a spatial control of the transport properties of these alloys by a controlled removal/incorporation of H.[34]

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