Effects of Bi incorporation on recombination processes in wurtzite GaBiAs nanowires

B Zhang 1, M Jansson 1, P-P Chen 2, X-J Wang 2, W M Chen 1 and I A Buyanova 1

1 Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden
2 State Key Laboratory of Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, Shanghai 200083, People’s Republic of China

E-mail: irina.bouianova@liu.se

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Abstract

The effects of Bi incorporation on the recombination process in wurtzite (WZ) GaBiAs nanowires are studied by employing micro-photoluminescence (μ-PL) and time-resolved PL spectroscopies. It is shown that at low temperatures (T < 75 K) Bi-induced localization effects cause trapping of excitons within band-tail states, which prolongs their lifetime and suppresses surface non-radiative recombination (SNR). With increasing temperature, the trapped excitons become delocalized and their lifetime rapidly shortens due to facilitated SNR. Furthermore, Bi incorporation in the GaBiAs NW is found to have a minor influence on the surface states responsible for SNR.

Keywords: GaBiAs, nanowires, wurtzite, exciton localization, surface recombination

(Some figures may appear in colour only in the online journal)

1. Introduction

One-dimensional semiconductor nanowires (NWs), such as GaAs-based NWs, have attracted intense research interests due to their enormous potential for applications in photonics and optoelectronics [1], including solar cells [2], near-infrared photosensitive detectors [3] and next-generation semiconductor lasers [4–6]. A promising material for realizing these applications is Ga(In)BiAs alloy. The giant bandgap bowing and strong Bi-induced perturbation of valence band states characteristic for this highly mismatched alloy offer high tunability in the band-gap energy that can be extended towards the telecommunication wavelength range of 1.3–1.55 μm by adjusting Bi compositions, beyond the reach of GaAs NWs. The large valence band splitting also quenches undesirable Auger recombination and reduced temperature sensitivity of the bandgap energy. [7–10] Moreover, the ability to fabricate this material in the NW geometry allows to utilize advantages of lattice structure engineering. It has been shown most recently that GaBiAs NWs can be fabricated with wurtzite (WZ) crystal structure [9], while this alloy in the bulk geometry typically crystallizes as zinc blende (ZB). Such changes of the lattice structure from ZB to WZ were shown to result in a substantial modification of the electronic band structure of GaBiAs NWs. This opens up new opportunities for band-engineering and photonic-engineering application based on dilute bismide alloys.

However, it is also known that in the case of ZB GaAs alloying with Bi affects the sample quality. For example, GaBiAs usually exhibits severe alloy disorder as a result of the fluctuations of the Bi content, which leads to the formation of localized band-tail states. [8, 11] The localization affects optical and transport properties, and thus the performance of practical devices. [12] In addition, due to a large miscibility gap caused by large disparity of atomic sizes between the As and Bi atoms, epitaxial growth of GaBiAs is usually performed at rather low temperatures. [11, 13, 14] This may facilitate the formation of point defects leading to enhanced non-radiative recombination [15, 16]. Presence of Bi during the growth is known to also affect surface conditions causing, e.g. surface reconstruction [17], formation of...
metallic droplets due to Bi segregation \cite{18, 19} and increased surface roughness. \cite{13, 18, 19} For example, it has been shown that ZB GaBi\textsubscript{0.02}As\textsubscript{0.98} NWs grown by self-catalyzed molecular beam epitaxy (MBE) exhibits corrugated surface morphology as a result of the Bi segregation and clustering. \cite{20} Surface-related effects become especially important in NW systems with an increased surface-to-volume ratio, as surface states often act as surface nonradiative recombination centers or charged traps affecting carrier recombination. \cite{21, 22} Up to date, however, impact of the Bi incorporation on recombination processes in one-dimensional WZ GaBiAs NWs remains unknown. Hence, in this work, we apply temperature-dependent micro-photoluminescence (\(\mu\)-PL) and time-resolved PL spectroscopies to clarify this essential issue.

2. Materials and methods

The investigated Ga(Bi)As NWs were grown on GaAs (111) B substrates by Au-assisted MBE via the vapor-liquid-solid mechanism. For comparison, reference GaAs NWs were also grown under the identical conditions but without a Bi beam flux. The substrate temperature was set to \(~\text{353 }^\circ\text{C}\), to ensure Bi incorporation. A detailed description of growth parameters can be found in \textsuperscript{9}. According to the performed transmission electron microscopy measurements \cite{9}, the NWs have WZ crystalline structure. They have a tapered shape with the NW diameter varying from about 33–43 nm at the NW top to 70–120 nm at the bottom. For all optical characterization, the nanowires were mechanically transferred onto gold-coated silica substrates, and then the samples were mounted in a He-flow cryostat. Continuous wave (cw-) and time-resolved PL measurements were performed by using as excitation light sources a solid-state 660 nm laser and a tunable mode-locked Ti:sapphire laser, respectively. The latter had a repetition frequency of \(~\text{76 MHz}\) and pulse width of \(~\text{150 fs}\). The induced PL signal was collected in a strict backscattering configuration by a long working distance objective \((50\times, \text{NA} = 0.5)\), and analyzed by a grating monochromator equipped with a cooled charge-coupled device detector or a streak camera system. The excitation spot during the \(\mu\)-PL measurements was about 0.8 \(\mu\)m.

3. Results and discussion

Figures 1(a) and (b) show scanning electron microscopy (SEM) images of representative GaBiAs and GaAs NWs arrays, respectively. In both cases, the nanowires form rather dense arrays, with a smooth surface but tapered morphology with diameters in the range of 70–120 nm at the NW bottom and between 33 and 43 nm at the top. Most of GaAs NWs have a syringe-like shape with an abrupt diameter reduction near the top. This could be attributed to lateral growth at the NW bottom as a result of a short diffusion length of adatoms at low growth temperature, as was discussed in detail previously \cite{23}. However, in the case of GaBiAs NWs, a gradual change of the NW diameter is observed, and the NW length slightly increases as compared to the GaAs NWs (see figure 1(a)). Such changes in the NW morphology can be explained considering that Bi can function as a surfactant during epitaxial growth. Therefore, its presence increases a mean surface diffusion length of adatoms \cite{19, 24, 25}. This facilitates the diffusion of the adatoms on the NW sidewalls allowing them to reach the top growth front, thereby promotes the axial growth.

Typical \(\mu\)-PL spectra measured at 5 K from an individual GaBiAs NW and a reference GaAs NW are shown in figure 1(c). The PL emission from the GaAs NW (shown by the black dotted curve) peaks at 1.517 eV and is dominated by free exciton (FE) recombination in WZ GaAs. In contrast, the PL emission in the GaBiAs NW (shown by the red solid curve) exhibits a considerable redshift of \(~\text{34 meV}\) and a significant broadening with a full width at half maximum of \(~\text{36.5 meV}\). Measurements performed on several individual NWs show that Bi composition does not vary significantly between the NWs, judging from similarity of their low-temperature PL spectra. The reasons for the observed transformation of the PL spectra could be twofold. Firstly, the strong anticrossing interaction between the localized Bi state and extended valence band (VB) states of the host GaAs pushes upward the VB maximum, therefore leading to a corresponding reduction of band gap energy, as has been discussed in detail in \cite{9}. Secondly, non-uniformity in the alloy composition causes large fluctuation in the VB edge and, therefore, localization of excitons within these band-tail states. This should cause a further red shift of the PL spectra accompanied by the line broadening. Such localized excitons (LE) recombination has been observed in highly-mismatched
excitation-dependent PL measurements. As the time elapses, the PL maximum position experiences a significant red shift of \(\sim22\) meV, which reflects the energy relaxation of the localized excitons from shallow to deeper localized exciton states. This exciton transfer process shortens lifetime of the FE and also weakly localized excitons emitting within the high-energy side of the spectrum, as can be clearly seen from the PL decays monitored at different detection energies—see figure 3(b). All PL decay curves exhibit two components and, therefore, could be described by a bi-exponential function in the following form

\[
I_{PL} = A_f \exp \left(-\frac{t}{\tau_f}\right) + A_s \exp \left(-\frac{t}{\tau_s}\right).
\]

Here \(A_f(A_s)\) is the amplitude of fast (slow) decay component with a time constant \(\tau_f(\tau_s)\). These decay times can be determined by fitting the measured PL decays at different detection energies \(E_{det}\). The corresponding results for the fast (slow) component are shown in figure 3(a) by the open red stars (the open red circles). It is found that \(\tau_f\) essentially does not change with the detection energy and is around 32 ps. In contrast, \(\tau_s\) increases from \(\sim133\) ps to \(\sim335\) ps with decreasing \(E_{det}\). The bi-exponential decay in nanowires usually indicates that it involves exciton recombination within two spatial regions. [22] The fast component can be attributed to exciton recombination in the surface region and is governed by surface non-radiative recombination (SNR), as will be further confirmed below. The slow component reflects exciton recombination within the bulk region of the NW, where photogenerated excitons are trapped by the localized states and the exciton diffusion to the NW surface is suppressed. The lifetime of localized excitons (LEs) is usually spectral-dependent [12, 22, 31] and is shorter at high exciton energies due to exciton transfer from shallow to deep localized states, as indeed observed experimentally. In contrast, no red shift of the PL emission is observed in the reference GaAs NWs, where the exciton lifetime is found to be \(\sim23\) ps and remains practically constant within the PL contour—see the black filled squares in figure 3(a). This is not surprising since alloy disorder leading to the exciton localization is not expected to occur in GaAs. The corresponding PL decays at the specific emission energies are shown in figure 3(b).

We note that the exciton lifetimes in both GaBiAs and reference GaAs NW are much shorter than that reported in WZ GaAs NW with an AlGaAs passivation shell, where the FE lifetime was found to be as long as \(\sim11.2\) ns [34]. This suggests that in the studied structures it is governed by non-radiative recombination processes. Indeed, the measured exciton lifetime \(\tau\) is determined by contributions of all recombination channels, including radiative \(\tau_{rr}\), bulk non-radiative \(\tau_{nr}\) and SNR in the following manner:[35]

\[
\frac{1}{\tau} = \frac{1}{\tau_{rr}} + \frac{1}{\tau_{nr}} + \frac{4S}{d}.
\]

Here \(d\) denotes the NW diameter and \(S\) is the surface recombination velocity. Under 738 nm excitation, the penetration depth of the excitation light is around 540 nm, which

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**Figure 2.** Excitation power dependence of PL spectra from a single WZ GaBiAs NW measured at \(T = 5\) K, with the excitation power varying from \(P_0 = 0.11\) mW \(\mu\text{m}^{-2}\) to 53\(P_0\). The solid and dashed arrows trace the shift of the FE and LE components, respectively. The inset depicts the PL maximum energy as a function of the excitation power density.

ZB alloys, including GaBiAs [11, 26–28], GaAsSb [12, 29, 30], GaAsN [31–33], in planar and NW geometry.

To examine and demonstrate the localized exciton characteristics in WZ GaBiAs NWs, we conducted excitation power-dependent \(\mu\)-PL measurements on single GaBiAs NWs. A careful analysis of the PL spectra shows that they in fact contain two PL components—see figure 2. The low-energy component dominates under the lowest excitation power \(P_0 = 0.11\) mW \(\mu\text{m}^{-2}\) and exhibits a gradual blue shift with increasing excitation power \(P\). This is also seen from the inset in figure 2, where the excitation power dependence of PL peak position is shown. On the other hand, the high-energy PL component becomes more pronounced at the highest \(P\) and is fixed in energy. Based on this behavior we attribute the low-energy and high-energy components to recombination of LE and FE, respectively. With increasing excitation power, the photogenerated excitons gradually fill the localized states, which correspondingly leads to a significant blue shift of the PL spectra related to the LE recombination. Under the highest \(P\), the photogenerated excitons almost saturate the localized states. Therefore, the FE recombination dominates the PL spectra.

To further understand effects of alloying with Bi on recombination processes we have performed time-resolved PL measurements. The corresponding results are summarized in figure 3. Evolution of the PL spectra measured at \(T = 5\) K from GaBiAs NWs as a function of the time delay \((\Delta t_d)\) after a 738 nm excitation pulse is shown in figure 3(a). Just after the excitation pulse \((\Delta t_d < 50\) ps\), the PL spectra peaking at 1.50 eV mainly stems from FE recombination. This is because the high excitation density during each laser pulse \((\sim9 \times 10^5\) mW \(\mu\text{m}^{-2}\)) can generate sufficiently high exciton density to saturate the localized states of a density on the order of \(10^{19}\) cm\(^{-3}\) as estimated from cw- and transient

**Figure 2.** Excitation power dependence of PL spectra from a single WZ GaBiAs NW measured at \(T = 5\) K, with the excitation power varying from \(P_0 = 0.11\) mW \(\mu\text{m}^{-2}\) to 53\(P_0\). The solid and dashed arrows trace the shift of the FE and LE components, respectively. The inset depicts the PL maximum energy as a function of the excitation power density.
means that the non-equilibrium carriers are generated within the whole volume of the thin NW. (We will refer to this excitation condition as bulk excitation). In the case of GaAs, even under such bulk excitation, the decay of highly mobile FEs is most likely determined by SNR, considering a large surface-to-volume ratio in NW systems. On the other hand, both bulk and surface-related non-radiative recombination processes are likely of importance in GaBiAs, where severe exciton localization may impede the exciton diffusion to the surface. We note that the determined LE lifetime is shorter than the radiative lifetime of free excitons, which suggests that it is still affected by non-radiative recombination. The possible reasons could be the formation of Bi-induced point defects that act as efficient non-radiative centers, thereby shortening exciton/carryer lifetime, [15, 36] and also possible exciton tunneling to surface states.

To further evaluate the role of surface states in exciton recombination dynamics, time-resolved PL measurements were repeated under 405 nm light excitation. Under these conditions the penetration depth is reduced to ~15 nm so that carrier generation predominantly occurs in the vicinity to the NW surface. Now the PL spectra of the GaBiAs NWs peak at 1.491 eV and no longer show a red shift with increasing $\Delta t_d$ (see figure 3(c)), in sharp contrast to the case of bulk excitation shown in figure 3(a). Simultaneously, a significant acceleration of the PL transients is observed so that the decay time, which is now governed by SNR, shortens to about 15 ps. We explain these findings by rapid depletion of photo-generated carriers within the near-surface region via the SNR centers, so that the localized states can no longer be filled during the excitation pulse. This is consistent with a much lower PL intensity under such excitation conditions. We note that changes from the bulk to surface excitation do not substantially affect dynamics of the FE recombination in GaAs NWs, consistent with our suggestion that it is largely governed by SNR. Judging from similar decay times in GaAs and GaBiAs NWs, it is also possible to conclude that Bi incorporation does not significantly affect the SNR process at 5 K.

The observed differences in the exciton dynamics under 738 and 405 nm excitations imply that Bi incorporation...
significantly decrease the diffusion length of excitons at low temperatures, such that it becomes shorter or comparable with the NW radius, i.e. of the order of 50 nm. Considering that the localized exciton lifetime in the studied NWs is $\sim 335$ ps, the corresponding diffusion coefficient should be around $0.07$ cm$^2$ s$^{-1}$, which is very close to the hole diffusion coefficient reported for GaAs$_{1-x}$Bi$_x$ ($x = 0.025$) epilayers at low temperatures. This slow-down of the exciton diffusion, however, is not surprising as a minor change in the Bi composition leads to a large variation in the VB edge that is amplified by the giant bowing effect.

From figure 3, trapping of excitons to localized states at low temperatures has significant impacts on the PL dynamics in GaBiAs that is especially pronounced under the 738 nm excitation. With increasing temperature, the trapped excitons gradually become thermally delocalized, which is obvious from the so-called ‘S shape’ evolution of the PL maximum position—see figure 4(a). At $T > 75$ K, when the localized excitons acquire enough thermal energy to be fully activated into the extended states, the PL decay time is no longer spectral-dependent confirming that the PL emission is now due to free exciton/carrier recombination. Along with exciton delocalization, capture of excitons/free carriers by the SNR channel accelerates leading to faster decays of the integrated PL intensity as shown in figure 4(b). At $T > 75$ K, when the photo-created carriers/excitons move freely across the NW, the PL intensity decays very fast with a decay time of $\sim 9$ ps at 90 K. This is accompanied by the fast decline of the PL intensity in time-resolved and cw-PL measurements—see figure 4(c). Applying the Arrhenius equation [33] to fit the temperature-dependent cw-PL data yields an activation energy of $85 \pm 5$ meV. This activation energy is attributed to surface related non-radiative component, based on the experimental fact that similar activation energies are deduced within this temperature range for the bulk (660 nm) and surface (405 nm) excitation. Moreover, it is found that the same PL thermal quenching is also observed in the reference GaAs NWs (see figure 4(c)), which suggests that the SNR-active centers have the same origin and also comparable densities in the studied GaAs and GaBiAs NWs.

4. Conclusions

In summary, we have investigated recombination processes in WZ GaBiAs NWs grown by Au-catalyzed MBE. The fabricated NWs form dense arrays with good structural quality and smooth NW surface, as confirmed from the performed SEM measurements. By employing the $\mu$-PL and time-resolved PL spectroscopies, it is demonstrated that Bi incorporation causes formation of band-tail states due to alloy disorder. At temperatures below 75 K, this leads to trapping of excitons within band-tail states, which suppresses effects of SNR and prolongs exciton lifetime. Based on the time-resolved PL
measurements performed under surface excitation and also temperature-dependent cw- and transient PL measurements, it is concluded that the formation of the SNR-active centers in the studied NWs is not affected by alloying with Bi. Our results, therefore, demonstrate that WZ GaBiAs NWs have good structural and optical properties comparable to those of their WZ GaAs counterpart. Combined with the advantages provided by bandgap engineering, this makes GaBiAs NWs promising for future applications of this novel structures in nano-optoelectronics and nano-photonic.

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ORCID iDs

B Zhang https://orcid.org/0000-0001-7862-2377
M Jansson https://orcid.org/0000-0001-5751-6225
X-J Wang https://orcid.org/0000-0002-4833-4339
W M Chen https://orcid.org/0000-0002-6405-9509
I A Buyanova https://orcid.org/0000-0001-7155-7103

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