Unidirectional lateral nanowire formation during the epitaxial growth of GaAsBi on vicinal substrates

Kristen N Collar1,3, Jincheng Li2, Wenyuan Jiao2, Wei Kong2,4 and April S Brown2

1 Department of Physics, Duke University, Durham, NC 27708, United States of America
2 Department of Electrical and Computer Engineering, Duke University, Durham, NC 27708, United States of America

E-mail: kristencollar@gmail.com

Received 11 October 2017, revised 14 November 2017
Accepted for publication 29 November 2017
Published 18 December 2017

Abstract
We report on enhanced control of the growth of lateral GaAs nanowires (NWs) embedded in epitaxial (100) GaAsBi thin films enabled by the use of vicinal substrates and the growth-condition dependent role of Bi as a surfactant. Enhanced step-flow growth is achieved through the use of vicinal substrates and yields unidirectional nanowire growth. The addition of Bi during GaAsBi growth enhances Ga adatom diffusion anisotropy and modifies incorporation rates at steps in comparison to GaAs growth yielding lower density but longer NWs. The NWs grown on vicinal substrates grew unidirectionally towards the misorientation direction when Bi was present. The III/V flux ratio significantly impacts the size, shape and density of the resulting NWs. These results suggest that utilizing growth conditions which enhance step-flow growth enable enhanced control of lateral nanostructures.

Keywords: planar nanowire, lateral nanowire, GaAsBi, molecular beam epitaxy, self-alignment, vicinal surfaces, self-catalyzing

(Some figures may appear in colour only in the online journal)
synthesis, the preferential steering of lateral NWs remains relatively unexplored.

In the current study, we demonstrate unidirectional lateral Ga-catalyzed NW growth which are self-forming during Ga-rich GaAsBi epitaxy on GaAs. The NWs are embedded in the epitaxial film due to the concurrent (100) growth of the GaAsBi film and the surface Ga nanoparticle forms lateral NWs. Embedded NWs have the potential to enhance performance due the inherent in situ surface passivation and epitaxial interfaces. As a result of the concurrent growth and preferential VLS growth of GaAs at the liquid nanoparticle–solid interface, the embedded NWs appear to be GaAs, i.e. Bi incorporation is excluded in the NW, see figure 1 [18]. Thus far, only Steele et al and Wood et al have published on embedded NWs [18, 19]. The realization of unidirectional NWs is important and we identify step-flow growth facilitated by the use of a miscut substrate and the behavior of Bi as a surfactant as key driving forces controlling NW growth directionality during epitaxy. Step density and direction can be controlled through the substrate miscut prior to growth. However, the step morphology can be modified during growth by growth conditions and by the addition of impurities and surfactants, which modify adatom migration and preferential incorporation sites and incorporation rates [20–25]. Limited steering of NWs has been achieved utilizing substrate orientation, pre-growth annealing conditions, polarity or chemical composition of the NW [6, 16, 26, 27], but the full parameter space that controls their movement is not well characterized. In this letter, we demonstrate control of the NW growth direction and density by utilizing vicinal surfaces to select the growth direction and the addition of Bi which segregates at the surface modifying growth dynamics to vary the shape, density, and unidirectionality of lateral NW growth.

The samples in this study were synthesized using a Riber 2300 molecular beam epitaxy (MBE) system with a stationary substrate, i.e. non-rotating, growth scheme. For the three GaAsBi samples, a 500 nm GaAs buffer is first grown on the substrate at 580 ºC, followed by 0.4 monolayers of Bi pre-deposition. After this step, 250 nm of GaAsBi is grown at 320 ºC. For the GaAs samples, the same buffer layer is grown, and then the temperature is reduced to 320 ºC for the growth of the subsequent 250 nm GaAs layer. The stationary growth condition enables the III/V flux ratio to smoothly vary across the sample. In our case, the spatial variation of growth conditions is from As-rich growth to Ga-rich growth [28]. During Ga-rich growth, Ga accumulates on the surface and we can discern the impact the III/V flux ratio on Ga nanoparticle, size, shape, density and III/V flux ratio droplet onset. The relationship between flux ratio and Bi incorporation in GaAsBi is well understood [29]. Our prior work investigated the use of vicinal substrates on Bi incorporation [28]. Wood et al studied GaAsBi growth under Ga-rich conditions on vicinal substrates oriented in the (111)A direction (GaAsBi A-step sample) with embedded lateral NWs that are primarily GaAs in a GaAsBi matrix [18]. The Bi incorporates into the Ga nanoparticles but appears to develop as inclusions and not participate directly in the GaAs VLS growth creating the NWs [18]. The tunneling electron microscopy (TEM) image of a NW in the GaAsBi A-step sample is imaged in figure 1, this image is reproduced from Wood, et al’s work [18]. In the wake of the GaAsBi and GaAs lateral NW growth we observe raised trails (greater thickness) using atomic force microscopy (AFM) and infer that the NW growth is faster than the concurrent epitaxial film growth.

To characterize the direction, size, shape, and density of the NWs, we used a Digital Instruments Dimension 3100 AFM and Nanoscope Analysis software. All measurements in this paper are by AFM. We characterized the lateral NW using the characteristics of the raised trail of film in the wake of the moving Ga nanoparticle. The extruded section observed by AFM is a product of the increased growth rate due to the NW growth embedded within the (100) oriented
GaAsBi film. Both TEM and AFM measurements indicate that the trail length is $\sim 4 \mu m$ for nanoparticles nucleating spatially where the III/V flux ratio is $\sim 1.4$. This indicates that the AFM measurements, despite sensing only surface characteristics, is sensitive to the entire embedded NW.

At the low temperature required for GaAsBi growth, we expect GaAs growth to occur in a three-dimensional growth mode [30]. Two behaviors that modify this that are at play in our samples are: (1) the reentrant behavior of mound formation with increasing As$_2$ flux and (2) the impact of Bi which acts as a surfactant on the surface and incorporates into the film [31–33]. We introduce in these experiments an additional factor modifying the growth mode, which is the use of misoriented substrates to increase the linear step density in either the [110] or [1-10] direction. Herein, steps due to the miscut from (001) to the [110] direction (Ga terminated, (111)A face) will be called A-steps and steps due to the miscut from the (001) to the [1-10] direction (As terminated, (111)B face) will be called B-steps.

Vicinal surfaces enhance step-flow growth by reducing the distance a Ga adatom must diffuse before incorporating into a step edge, driving the balance between step incorporation versus island nucleation towards that of step incorporation [34, 35]. Incorporation and morphology evolution are significantly modified by the anisotropies introduced by the different reactivity of the A-steps and B-steps, particularly the anisotropic diffusion of Ga [35]. The B-step has a larger step velocity than the A-steps for MBE grown GaAs [20, 31, 36]. Surfactants, however, significantly impact growth dynamics including direction-dependent adatom diffusion. For example, Wixom et al found that Bi as a surfactant in the GaAs system enhances the lateral growth rate in the [110] by almost 300% and had negligible effects on the [1-10] lateral growth rate [37]. The low growth temperatures and step edge kinetics move the system away from equilibrium, while the misorientation increases the large number of reaction sites driving the system towards equilibrium. Hence, the interplay between temperature and step density provide a unique platform for controlling NW growth.

This study reveals the impact of the presence of Bi and substrate misorientation on lateral NW growth. Table 1 outlines the six distinct growth conditions for the six samples. GaAs and GaAsBi were each grown on GaAs substrates with three different surfaces: (001), (001) vicinal misoriented toward the (111)A by $3^\circ$, and (001) vicinal misoriented toward the (111)B by $3^\circ$. A $3^\circ$ miscut yields an approximate terrace length of 5.4 nm, assuming a surface atomic bilayer. The first column in table 1 outlines the names of the samples from which they will be referred to within this text. The NW direction column in table 1 describes along which plane the NWs are aligned. Also, further outlined is whether the NWs are unidirectional or bidirectional. Undulations created during growth in the Ga-rich regime are in the [111]B direction, except for the GaAsBi B-step sample wherein no discernable undulations were found, consistent with literature on low temperature GaAs growth [34]. The last column in the table is the amplitude of the surface undulations; the amplitude results from the limited diffusion of Ga on the surface resulting in step bunching and therefore surface mounds stretching long in the [1-10] direction. The GaAsBi (singular) sample has the largest undulation amplitude, suggesting strongly enhanced anisotropy in the Ga diffusion length in the [110] and [1-10] directions.

Typically, NW synthesis through a VLS mechanism exploits pre-deposited metal droplets (nanoparticles) on a substrate which are exposed to the NW constituent materials [1]. When supersaturation of the constituent material(s) is reached, nucleation of the NW occurs at the nanoparticle interface with the solid crystal. The NW formation continues so long as growth materials are provided [1]. The nanoparticles in this experiment are not pre-deposited, but rather form due to excess Ga on the surface during epitaxy. The nanoparticles herein are self-catalyzing, meaning that NW growth consumes the nanoparticle material. This experiment studies two simultaneous processes that have been previously studied independently: (1) the formation of Ga nanoparticles during epitaxy due to excess Ga on the surface determined by III/V flux ratio, the behavior of Bi as a surfactant, and the introduction of controlled step density and direction, and (2) Ga-catalyzed VLS NW growth. The formation of Ga nanoparticles is determined by excess Ga on the surface with respect to the Group V constituents, in this case, As and Bi, during epitaxy. The excess Ga spatially varies across the sample in relation to the flux distributions. In addition, two factors modify surface dynamics and, therefore, the incorporation rate of Ga and growth of GaAsBi. Under these

---

Table 1. Summary of the samples and the associated differently oriented nanowires.

| Sample name | Miscut direction and offcut angle | Bi | NW direction | Uni- or bi-directional | Undulation direction (Ga-rich) | Undulation amplitude (nm) |
|-------------|---------------------------------|----|--------------|------------------------|-------------------------------|---------------------------|
| GaAs        | None                            | N  | [1-10]       | Bi                     | B                             | 1                         |
| GaAs A-step | (111)A, 3°                      | N  | [1-10]       | Bi                     | B                             | 2.4                       |
| GaAs B-step | (111)B, 3°                      | N  | [1-10]       | Uni*                   | B                             | 2.0                       |
| GaAsBi      | None                            | Y  | [1-10]       | Bi                     | B                             | 8.1                       |
| GaAsBi      | (111)A, 3°                      | Y  | [110]        | Uni                    | B                             | 1.7                       |
| GaAsBi A-step | (111)B, 3°                  | Y  | [1-10]       | Uni                    | —                             | —                         |

Note. * indicates that the sample was mostly unidirectional, but $\sim 8\%$ of NW growth is in the opposite direction.
growth conditions Bi both incorporates and segregates at the surface: the III/V flux ratio modifies the ratio of incorporated to segregated Bi which, in turn, modifies the Ga incorporation rate. Furthermore, the use of vicinal substrates modifies the Ga incorporation rate due to the different chemistry and binding of Ga to A- and B-steps. The embedded lateral NW is particularly interesting and has only recently been observed as a consequence of studies exploring the incorporation of Bi into GaAs which necessitates Ga-rich growth conditions. Figures 2(a)–(d) is a schematic of the lateral embedded NW growth mechanism sketched with the blue trail attached to the nanoparticle above the epitaxial film, representing the trail which can be measured using AFM. The bottom row, figure 2(e), shows AFM images of the GaAsBi A-step sample as the III/V flux ratio. In the As-rich regime, undulations on the surface are observed associated with anisotropic Ga diffusion length and step-bunching, and in the Ga-rich regime nanoparticles form which increase in density with III/V flux ratio. What distinguishes these NWs from most other NW studies is that (100) film growth is occurring simultaneously with lateral NW growth.

During the VLS growth of NWs using self-catalyzing nanoparticles, a dynamic balance between the consumption and accumulation of the group III species must be achieved [11]. Self-catalyzed growth depends critically on growth temperature and III/V flux ratio. Generally, III–V NWs grow in the (111)B direction. In the case of lateral NWs on (100) substrates growth is along the surface projections of the (111)B direction [3]. Epitaxial growth of NWs on GaAs(100) substrates is out-of-plane in the (111)B direction, with equal probability of growth in either of the two (111)B directions [3, 13, 16]. This implies that for lateral growth on a (100) substrate, there is equal probability of growth in the [0 1 1] or [0 1 −1] direction, yielding bidirectional, but aligned NWs. The (111)B direction is preferred because it minimizes the surface energy at the liquid–solid interface where nucleation occurs [38, 39]. However, depending on the nanoparticle and substrate, lateral NWs moving in the (111)B and the (111)A direction have been observed [5, 6, 15, 18, 19, 40]. Reports with In, Au and Bi nanoparticles report lateral NW growth via VLS with growth in the (111)B direction regularly explained using the low surface energy of the plane guiding the growth direction [5, 15, 19, 40]. Alternatively, observed NW growth in the (111)A direction with Au nanoparticles is argued as a maximization of contact with the low surface energy plane [6, 27, 41]. This literature suggests that with careful architecture of the relative surface energies at the nanoparticle–solid interface, there is great potential in preferentially steering NWs along desired crystallographic directions.

The two GaAs samples have NWs that move along the same crystallographic direction, however achieving bidirectional versus unidirectional movement is dependent on the direction of the miscut. Figure 2 shows AFM images of nanoparticles and the extruded NW trails formed on the surface. Looking first at GaAs growth (figures 3(a) and (b)), we see that the nanoparticles terminate triangular-shaped trails aligned in the ± [1-10] direction. While the use of a vicinal substrate will generally enhance step-flow growth in the direction of the step motion, the low temperature used in these studies mitigate this effect, especially for GaAs growth which takes place without surfactant action, which we expect for GaAsBi. The nanoparticle motion we observe is in the same direction for both vicinal GaAs samples, independent of the miscut direction. Therefore, the modification of Ga dynamics and migration lengths, due to the different chemistry and incorporation rates of Ga at the A- and B-steps, are not

Figure 2. Schematic of embedded NW growth of vicinal GaAsBi samples. (a)–(c) Excess Ga builds on the surface during film growth, coalescing into a droplet that adsorbs As and eventually supersaturates. When supersaturation is achieved, NW formation begins and propagates the droplet motion. The VLS NW growth is faster than the film, leaving a trail on the surface raised above the embedded NW. (d) A cross-sectional perspective from the dotted line in (c). (e) AFM images from GaAsBi A-step sample as the III/V flux ratio is varied spatially across the substrate surface.
significant enough to overcome the surface energy difference between VLS nucleation in the [111]A and [111]B directions. Consequently, the NWs both grow in the same, [111]B, direction. Lower temperature decreases the interface energy difference between the (111)A and (111)B facets [42]. However, this difference is clearly not large enough to impact VLS nucleation without surfactant action. When the surface energy is driving the NW growth, there is equal probability of traveling in the + or − [1-10] direction [3]. The GaAs A-step sample growth is bidirectional, however the GaAs B-step sample is largely unidirectional implying the step-flow growth velocity is enhanced by adding B-steps and drives the direction of the NW growth. The anisotropy in this behavior is consistent with the fact that Ga migration is known to be anisotropic and enhanced in the B direction due to the anisotropy in the incorporation rates at the two steps. In the [111]B direction, the step-flow propelled nanoparticles to move in a unidirectional manor aligned with the low surface energy direction (111)B. We should point out that approximately 8% of nanoparticles move in the opposite direction. This behavior is consistent with the presence of domains with different growth modes.

With the addition of Bi during growth, we observe significant differences in the behavior of the NW growth and nanoparticle characteristics. The GaAsBi vicinal samples found in figures 3(c) and (d). The addition of Bi during GaAs growth decreases the density and increases the size of Ga nanoparticles, consistent with an increased Ga diffusion length. Unlike GaAs nanoparticle/trail motion, both A and B misoriented substrates have unidirectional nanoparticle movement. We can determine that the addition of Bi enhances step-flow growth velocity in both [111]A and [111]B directions. Therefore, we conclude that the smaller difference in (111)A and (111)B interface energy at lower temperature, plus the enhancement of step-flow growth velocity with the addition of Bi is significant enough to drive NW growth in a controlled fashion in both (111)A and (111)B directions. We speculate that the addition of Bi may also modify the interfacial energies. Bi is not only on the surface as a segregant/surfactant, but also in the nanoparticle [18], resulting in variations to both the surface energies and the chemical potential of the nanoparticle. In summary, while the GaAs A-step sample demonstrated bidirectional NW growth, unidirectional growth was achieved through the use of vicinal substrates and the addition of Bi. The enhancement of step-flow growth velocity through the addition of Bi also enabled a 90° change in direction of the trails/nanoparticle motion for the GaAsBi A-step sample.
Bi in GaAs. The density of Ga nanoparticles as a function of how it is modified by the addition of steps and Bi is useful towards developing an understanding of the incorporation of Bi in GaAs. The density of Ga nanoparticles as a function of position and, therefore, III/V flux ratio, is shown in figure 4. GaAsBi growth introduces delayed onset of Ga nanoparticle formation in comparison to GaAs (delayed to a III/V flux ratio)\textsuperscript{1}, which is evidence of surfactant-like effects on Ga incorporation from Bi segregation. We speculate that Bi introduces enhanced step velocity and an increased Ga incorporation delaying excess Ga buildup on the surface. Numerous studies have shown that Bi incorporates into GaAs only under Ga-rich growth conditions (III/V flux ratio \textgtrsim 1), and the Bi incorporation profiles, determined by x-ray diffraction, for the GaAsBi samples studied herein are published elsewhere \cite{28}. Therefore, in the As-rich growth regime Bi segregates at the surface, GaAs growth on the miscut substrates exhibit nanoparticle formation at a III/V flux ratio of \textasciitilde 0.8, shown in figure 4. In comparison, GaAs growth on a singular (100) substrate manifests nanoparticle formation at a flux ratio of \textasciitilde 0.9. All the samples with Bi addition show a delayed nanoparticle onset to a III/V flux ratio of \textasciitilde 1.04.

In addition to the higher III/V flux ratio needed for excess Ga accumulation on the surface, figure 4 shows that the addition of Bi causes a decrease in nanoparticle density. GaAs surfaces have a Ga nanoparticle density roughly 13 times that of the GaAsBi surfaces. The average GaAs nanoparticle density is 2.2 nanoparticles/\textmu m\textsuperscript{2} and the maximum density of nanoparticles on the GaAsBi surface is 0.17 nanoparticles/\textmu m\textsuperscript{2}. The density of nanoparticles is indicative of the Ga diffusion length on the surface, and Bi is known to increase the Ga diffusion rate on GaAs when acting as a surfactant, decreasing the density \cite{37}. As expected, both GaAs and GaAsBi films show an increase in nanoparticle density with increasing GaAsBi flux ratio.

Both the GaAs and GaAsBi A-step show a steady increase in nanoparticle density with increasing III/V ratio. On the other hand, the Ga nanoparticle density on the GaAsBi B-step saturates at a 1.15 flux ratio which may be due to a saturation of Bi incorporation at a flux ratio of 1.05 \cite{28}. The GaAsBi B-step sample incorporates the least amount of Bi into the film (2.0\%, 2.2\% and 2.4\% for GaAsBi B-step, singular, and A-step, respectively), implying that this sample has the largest amount of excess Bi on the surface to act as a surfactant. The increase in the nanoparticle density, plotted in figure 4, is consistent with a decrease in Ga diffusion length and with the reduction of Bi on the surface due to increased incorporation into the film, ultimately reducing surfactant impact on growth dynamics. As such, the relative nanoparticle densities correlate with Bi incorporation into the GaAsBi film. For example, GaAsBi A-step incorporated the most Bi into the film, leaving the least amount of Bi on the surface (compared to the other two samples), yielding a decreased surface diffusion rate, which in turn increases the nanoparticle density. Overall, we infer that the introduction of Bi on the surface significantly and differentially (for A- and B-steps) changes the incorporation rate of Ga during GaAs/GaAsBi growth.

In figure 4 the GaAs A-step sample does not act like the other samples in the As-rich regime. There is a much higher density of nanoparticles in the As-rich regime for the GaAs A-step sample, which decreases with increasing III/V flux ratio and settles to roughly the same density near stoichiometric conditions. To explain this, we must consider that over the flux ratio range investigated the B-step surface incorporates Ga more efficiently than the A-step surface \cite{25}. The nanoparticles in the As-rich regime for the GaAs A-step sample are aligned along well-defined mounds on the surface in the [1-10] direction. These mounds arise due to the Erlich-Schwoebel instability from the differences in down and up step crossing probabilities of Ga. In the Ga-rich regime the behavior of the GaAs A-step and B-step samples is similar, indicating that step crossing anisotropy becomes insignificant.

As a means of quantifying the excess Ga volume, we utilized the AFM bearing depth analysis tool in the NanoScope analysis software. Figure 5 shows the total excess Ga approximated by the total Ga nanoparticle volume in a 5 \times 5 \mu m AFM image plotted as a function of III/V flux ratio. The excess Ga is approximated by defining a plane that selects only the volume of the nanoparticle, this plane selection was above the NW trails, so some of the Ga volume (that etched into the film and the disc-shaped cross-section of height consistent with the NW trail) is not included in this analysis. The three GaAs samples show a steady increase in excess Ga with increasing Ga flux up until a flux ratio of 1.10, where the excess may plateau. Consistent with the earlier discussion of nanoparticle III/V flux ratio onset, the addition of Bi shows that Bi significantly decreases the excess Ga (compared to the GaAs samples), due to an increase in incorporation rate. It should be noted that the nanoparticle volume that we are defining as excess Ga, will also include any excess Bi that the nanoparticle absorbs, but we expect most of the droplet to be Ga (observed by TEM for the GaAsBi A-step sample \cite{18}). The GaAsBi singular and A-step samples exhibit a steady increase in excess Ga with increasing Ga-flux. The GaAsBi B-step sample at first tracks

**Figure 4.** Droplet density as a function of III/V flux ratio. Note that the y-axis is broken such that the GaAs and GaAsBi samples can be shown on the same plot. AFM images of the singular GaAs and GaAsBi are also shown for two chosen points on the plot. Density measurements for the GaAs samples are from 5 \times 5 \mu m images. Density measurements for the GaAsBi samples are from 15 \times 15 \mu m images.
with the other GaAsBi samples, but then there is a reversal at a III/V flux ratio of \(\sim 1.1\), where the excess Ga decreases. These observations are consistent with Bi acting as a surfactant and tracking with the nanoparticle density variations observed in the GaAsBi B-step sample in figure 4.

The length of the NWs, as inferred from the trail length, is increased through the addition of Bi. NW length as a function of III/V ratio is plotted versus V flux ratio. Error bars represent the standard deviations of more than ten droplets. The first point for the GaAsBi B-step sample does not have error bars because only one NW in the selected image for measurement.

Figure 5. The total droplet volume (defined as the volume of droplet measured above the plane of the film surface per a 5 × 5 μm image) versus III/V flux ratio. Data extracted using a bearing depth analysis tool in Nanoscope Analysis software.

Figure 6. (a) NW length and (b) droplet diameter variations with III/V ratio. GaAsBi vicinal films have longer NW trails and larger droplets than GaAs samples. Error bars represent the standard deviations of more than ten droplets. The first point for the GaAsBi B-step sample does not have error bars because only one droplet/NW was in the selected image for measurement.

Figure 7. Nanowire cross-section characteristics: (a) heights of the NW trail, (b) length of the base of the NW trail, and (c) length of the top facet of the NW trail plotted versus the III/V flux ratio. Error bars represent the standard deviations of more than ten droplets. The first point for the GaAsBi B-step sample does not have error bars because only one NW in the selected image for measurement.
This is consistent with Miwa and Nishinga’s studies of the dependence of Ga incorporation at A- and B-steps on flux ratio [43]. They found that the Ga incorporation at A-steps is independent of III/V ratio while that at B-steps decreases with increasing III/V flux ratio [43]. Knowing the growth times for the GaAs/GaAsBi epitaxial films, we can calculate the approximate growth rates of the NWs. The growth rates calculated from the length of the trails are 0.33 nm s$^{-1}$ for GaAs, 1.7–2.5 nm s$^{-1}$ and 1.3–2.2 nm s$^{-1}$ for GaAsBi A-step and B-step samples respectively. The Ga nanoparticle diameter reflects similar trends to the NW length as shown in figure 6(b). This validates that the Ga diffusion rate determines the size and density of nanoparticles and plays an integral role in determining the velocity of the NW growth. This is consistent with literature on step-flow growth for vicinal GaAs with Bi enhancing this anisotropy [37, 43].

Schematic diagrams of the trail shapes are shown in the last column of figure 3, demonstrating clear faceting above the film surface from the lenticular NW growing beneath the surface [18] (schematic also in figure 2(d) for GaAsBi A-step sample). Cross-sectional data on the GaAsBi A-step and B-step samples are taken approximately $\sim$3 $\mu$m from the trail end ($\sim$2/3 of the way up the NW). This location was chosen because it is far enough away from the nanoparticle to isolate the measurement from any post growth effects from the nanoparticle, but far enough into the trail that the trail was well developed and relatively large. For the GaAs samples, the measurement was taken at the approximate center of the trails, due to the limited length of the trails. The cross-section measurements highlight the differences in the different step character and its role in defining the NW shape. These differences arise from the anisotropic lateral growth rates in GaAs and are attributed to a combination of different sticking coefficients at the $[-110]$ and $[110]$ steps along with the asymmetry for the different surface reconstructions varying the diffusions coefficients [37].

Three characteristic measurements of the cross sections of the NW trails are shown in figure 7: (a) height, (b) length of the base (which reflects the NW diameter) and (c) length of the top facet (runs parallel to the base). Examination of the cross sections of the NW shows that Bi increases the diameter of the NW, consistent with the change in nanoparticle size. The GaAsBi A-step sample is more triangular and never fully develops a top flat facet, and therefore it was not characterized as having a top facet in figure 7(c). The GaAsBi B-step sample experiences the most drastic increase in size and this increase is observed in all three characteristic measurements. Three main conclusions can be drawn: (1) the samples with Bi experience an increase in width, (2) the flat plateau top of the NW is wider with Bi and (3) only the GaAsBi B-step sample experiences an enhanced out-of-plane growth rate creating NW trails that were almost twice as high as the other samples. It is interesting to note that despite the GaAsBi B-step sample having on average larger values in all three measures, the aspect ratio of these parameters for the GaAsBi A-step and GaAsBi B-step (data not shown) remain very similar indicating that similar surface energies control the shape of the NW when Bi is in the film, despite the different miscut substrates.

The trails are triangular when viewed from above, which implies that the nanoparticle diameter is increasing as the NW forms throughout the epitaxial film growth. Correlations between the nanoparticle diameter, NW length and NW diameter (base) can be found in figure 8. The nanoparticle diameter linearly scales with the trail length and the base of the NW for the GaAsBi B-step sample. All other samples have minimal variation or no correlation. It is possible that the GaAsBi A-step sample reaches a maximum nanoparticle diameter and then seeds more nanoparticles with excess Ga content, yielding little
variation in NW length and width. It was expected that the trail length is proportional to the step velocity, and only the GaAsBi B-step shows an increase in length and lateral growth rate with a linear relationship. In figure 8(b), the length of the base is plotted against the NW length; effectively this is the lateral growth rate versus the velocity of the nanoparticle. Only the GaAsBi B-step sample showed a dependence between the two, where the longer NW yielding a wider NW. The dependence on III/V flux ratio of the trail length and nanoparticle diameter (figure 6), along with the characteristics in figure 8, demonstrate that the linear relationship is likely due to the differences in the nature of the different step character between the two samples. The GaAsBi B-step sample has both A-steps and B-steps present on the surface where the B-steps are generating the dependence on III/V ratio [43, 44]. Whereas, the GaAsBi A-step sample can be characterized as having only A-steps, so the NW growth is III/V flux ratio independent [43, 44]. There was little variation found between the GaAs vicinal samples, but this anisotropy (but to a lesser degree) is expected to be present. This observation of anisotropy may be damped due to the oxide growth, the NWs being buried, and the smaller sizes of the NWs in the GaAs samples. The presence Bi amplifies the differences in the step character, making trends are more pronounced in the GaAsBi vicinal samples.

In conclusion, we use a surfactant (Bi) and vicinal surfaces to enhance the control of lateral growth of GaAs NWs embedded in epitaxial GaAsBi films. The presence of Bi increases the Ga diffusion and incorporation rates yielding larger unidirectional NWs than in GaAs films, but also delays NW onset to higher III/V ratios than were required for GaAs films. The unidirectional growth was guided by the misorientation of the substrate for the GaAsBi films: [111]A or [111]B. Without Bi, the NWs follow the lowest surface energy facet, [111]B. We also use the III/V flux ratio to vary the size, shape, and density of the nanoparticles.

Acknowledgments

This research was primarily supported by the University of Wisconsin Materials Research Science and Engineering Center (DMR-1121288).

This work was performed in part at the Duke University Shared Materials Instrumentation Facility (SMIF), a member of the North Carolina Research Triangle Nanotechnology Network (RTNN), which is supported by the National Science Foundation (Grant ECCS-1542015) as part of the National Nanotechnology Coordinated Infrastructure (NNCI).

ORCID iDs

Kristen N Collar https://orcid.org/0000-0003-3111-6930

References

[1] Dick K A 2008 A review of nanowire growth promoted by alloys and non-alloying elements with emphasis on Au-assisted III–V nanowires Prog. Cryst. Growth Charact. Mater. 54 138–73
[2] Hobbs R G, Petkov N and Holmes J D 2012 Semiconductor nanowire fabrication by bottom-up and top-down paradigms Semiconductor nanowire fabrication by bottom-up and top-down paradigms Chem. Mater. 24 1975–91
[3] Dowdy R S, Walko D A and Li X 2013 Relationship between planar GaAs nanowire growth direction and substrate orientation Nanotechnology 24 35504
[4] Zhang Y, Wu J, Aagesen M and Liu H 2015 III–V nanowires and nanowire optoelectronic devices J. Phys. D: Appl. Phys. 48 463001
[5] Fortuna S A, Wen J, Chun I S and Li X 2008 Planar GaAs nanowires on GaAs (100) substrates: self-aligned, nearly twin-defect free, and transfer-printable Nano Lett. 8 4421–7
[6] Sun W, Gao Y, Xu H, Gao Q, Hoe Tan H, Jagadish C and Zou J 2013 Polarity driven simultaneous growth of free-standing and lateral GaAsP epitaxial nanowires on GaAs (001) substrate Appl. Phys. Lett. 103 1–5
[7] Wang J, Plissard S R, Verheijen M A, Feiner L-F, Cavalli A and Bakkers E P A M 2013 Reversible switching of InP nanowire growth direction by catalyst engineering Nano Lett. 13 3802–6
[8] Christiansen S, Schneider R, Scholz R, Gösele U, Stelzner T, André G, Wendler E and Wesch W 2006 Vapor–liquid–solid growth of silicon nanowires by chemical vapor deposition on implanted templates J. Appl. Phys. 100 84323
[9] Perea D E, Allen J E, May S J, Wessels B W, Seidman D N and Lauhon L J 2006 Three-dimensional nanoscale composition mapping of semiconductor nanowires Nano Lett. 6 181–5
[10] Bar-Sadan M, Barthel J, Shtrikman H and Houben L 2012 Direct imaging of single Au atoms within GaAs nanowires Nano Lett. 12 2352–6
[11] Dick K A and Caroff P 2014 Metal-seeded growth of III–V semiconductor nanowires: towards gold-free synthesis Nanoscale 6 3006
[12] Tersoff J 2015 Stable self-catalyzed growth of III–V nanowires Nano Lett. 15 6609–13
[13] Hiruma K, Yazawa M, Katsuyama T, Ogawa K, Haraguchi K, Koguchi M and Kakibayashi H 1995 Growth and optical properties of nanoscale GaAs and InAs whiskers J. Appl. Phys. 77 447–62
[14] Lindberg C, Whiticar A, Dick K A, Skold N, Nygard J and Bolinsson J 2016 Silver as seed-particle material for GaAs nanowires—dictating crystal phase and growth direction by substrate orientation Nano Lett. 16 2181–8
[15] Rathi S J, Smith D J and Drucker J D 2013 Guided VLS growth of epitaxial lateral Si nanowires Nano Lett. 13 3878–83
[16] Dowdy R, Walko D A, Fortuna S A and Li X 2012 Realization of unidirectional planar GaAs nanowires on GaAs (110) substrates IEEE Electron Device Lett. 33 522–4
[17] Hilner E, Zakharov A A, Schulte K, Kratzer P, Andersen J N, Lundgren E and Mikkelsen A 2009 Ordering of the nanoscale step morphology as a mechanism for droplet self-propulsion Nano Lett. 9 2710–4
[18] Wood A W, Collar K, Li J, Brown A S and Babcock S E 2016 Droplet-mediated formation of embedded GaAs nanowires in MBE GaAsx–yBiy films Nanotechnology 27 115704
[19] Steele J A et al 2016 Surface effects of vapour–liquid–solid driven Bi surface droplets formed during molecular-beam-epitaxy of GaAsBi Sci. Rep. 6 28860
[20] Johnson M D, Orme C, Hunt A W, Graff D, Sudijono J, Sander L M and Orr B G 1994 Stable and unstable growth in molecular beam epitaxy Phys. Rev. Lett. 72 116–9
[21] Tarsa E J, Heying B, Wu X H, Fini P, DenBaars S P and Speck J S 1997 Homoepitaxial growth of GaN under Ga- stable and N-stable conditions by plasma-assisted molecular beam epitaxy J. Appl. Phys. 82 5472
[22] Tejedor P, Crespiillo M L and Joyce B A 2006 Growth mode transitions induced by hydrogen-assisted MBE on vicinal GaAs(110) Mater. Sci. Eng. C 26 852–6
[23] Young E C, Tixier S and Tiedje T 2005 Bismuth surfactant growth of the dilute nitride GaNAs1−x J. Cryst. Growth 279 316–20
[24] Asai H 1987 Anisotropic lateral growth in GaAs MOCVD layers on (001) substrates J. Cryst. Growth 80 425–33
[25] Daweritz L and Ploog K 1994 Contribution of reflection high-energy electron diffraction to nanometre tailoring of surfaces and interfaces by molecular beam epitaxy Semicond. Sci. Technol. 9 123–36
[26] Paladugu M, Zou J, Guo Y N, Zhang X, Joyce H J, Gao Q, Tan H H, Jagadish C and Kim Y 2009 Crystallographically driven Au catalyst movement during growth of InAs/GaAs axial nanowire heterostructures J. Appl. Phys. 105 073503
[27] Fonseka H A, Caroff P, Wong-leung J, Ameruddin A S and Tan H H 2014 Nanowires growth on InP (100): growth directions, facets, crystal structures, and relative yield control ACS Nano 8 6945–54
[28] Li J, Collar K, Jiao W, Kong W, Kuech T F, Babcock S E and Brown A 2016 Impact of vicinal GaAs(001) substrates on Bi incorporation and photoluminescence in molecular beam epitaxy-grown GaAs1−xBi Appl. Phys. Lett. 108 43524
[29] Rodriguez G V and Millunchick J M 2016 Predictive modeling of low solubility semiconductor alloys J. Phys. Appl. Phys. 120 125310
[30] Clarke S and Vvedensky D D 1988 Growth kinetics and step density in reflection high-energy electron diffraction during molecular-beam epitaxy J. Appl. Phys. 63 2272–83
[31] Apostolopoulos G, Herfort J, Daweritz L, Ploog K H and Lysberg M 2000 Reentrant mound formation in GaAs(001) homoepitaxy observed by ex situ atomic force microscopy Phys. Rev. Lett. 84 3358–61
[32] Vardar G, Paleg S W, Warren M V, Kang M, Jeon S and Goldman R S 2013 Mechanisms of molecular beam and Bi incorporation during molecular beam epitaxy of GaAsBi Appl. Phys. Lett. 102 42106
[33] Jun S W, Stringfellow G B, Shurtleff J K and Lee R T 2002 Isoelectronic surfactant-induced surface step structure and correlation with ordering in GaInP J. Cryst. Growth 235 15–24
[34] Apostolopoulos G, Boukos N, Herfort J, Travlos A and Ploog K H 2002 Surface morphology of low temperature grown GaAs on singular and vicinal substrates Mater. Sci. Eng. B 88 205–8
[35] Shitara T, Vvedensky D D, Wilby M R, Zhang J, Neave J H and Joyce B A 1992 Misorientation dependence of epitaxial growth on vicinal GaAs(001) Phys. Rev. B 46 6825–33
[36] Kawabe M and Sugaya T 1989 Anisotropic lateral growth of GaAs by molecular beam epitaxy Japan. J. Appl. Phys. 28 L1077
[37] Wixom R R, Rieth L W and Stringfellow G B 2004 Sb and Bi surfactant effects on homo-epitaxy of GaAs on (0 0 1) patterned substrates J. Cryst. Growth 265 367–74
[38] Braun W, Kaganer V M, Trampert A, Schönherr H P, Gong Q, Nötzel R, Daweritz L and Ploog K H 2001 Diffusion and incorporation: shape evolution during overgrowth on structured substrates J. Cryst. Growth 227–228 51–5
[39] Cheppy N and Martin R M 1992 GaAs (111) and (111) surfaces and the GaAs/AlAs (111) heterojunction studied using a local energy density Phys. Rev. B 45 6089–100
[40] Mattila M, Hakkarainen T, Jiang H, Kauppinen E I and Lipsanen H 2007 Effect of substrate orientation on the catalyst-free growth of InP nanowires Nanotechnology 18 155301
[41] Zhang G, Tateno K, Gotoh H and Nakano H 2010 Parallel-aligned GaAs nanowires with 110 orientation laterally grown on [311]B substrates via the gold-catalyzed vapor–liquid–solid mode Nanotechnology 21 95607
[42] Yuan X, Caroff P, Wong-Leung J, Fu L, Tan H H and Jagadish C 2015 Tunable polarity in a III–V nanowire by droplet wetting and surface energy engineering Adv. Mater. 27 6006–103
[43] Miwa K and Nishinaga T 1995 Theoretical-studies of step-edge supersaturation and its As/Ga flux dependence in molecular-beam epitaxy of GaAs on vicinal surfaces J. Cryst. Growth 146 177–82
[44] Tanaka I, Ohkouchi S and Hashimoto A 1992 Step structures and terrace width ordering of molecular beam epitaxially grown GaAs surfaces observed by scanning tunneling microscopy Japan. J. Appl. Phys. 31 2216–20