Topical Review

Assembling your nanowire: an overview of composition tuning in ternary III–V nanowires

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Abstract
The ability to grow defect-free nanowires in lattice-mismatched material systems and to design their properties has made them ideal candidates for applications in fields as diverse as nanophotonics, nanoelectronics and medicine. After studying nanostructures consisting of elemental and binary compound semiconductors, scientists turned their attention to more complex systems—ternary nanowires. Composition control is key in these nanostructures since it enables bandgap engineering. The use of different combinations of compounds and different growth methods has resulted in numerous investigations. The aim of this review is to present a survey of the material systems studied to date, and to give a brief overview of the issues tackled and the progress achieved in nanowire composition tuning. We focus on ternary III1–x,V nanowires (AlGaAs, AlGaP, AlInP, InGaAs, GaInP and InGaSb) and IIIV1–x nanowires (InAsP, InAsSb, InPSb, GaAsP, GaAsSb and GaSbP).

Keywords: III–V semiconductors, nanowires, ternary alloys

Introduction

Moore’s law, which is based on the observation that the number of transistors in an integrated circuit doubles about every two years, has been used to predict the development of computers since the 1970s [1]. However, we have now reached the physical limit of transistors, and smaller structures are needed if computing capacity is to continue to increase. Among nanostructures of different shapes and dimensions such as thin films [2], quantum dots [3], nanosheets [4, 5], nanoflags [6], and others [7, 8], nanowires are anisotropic structures with a radius of the order of a few tens of nanometres and a length of a few micrometres. They are considered ideal candidates for the further development of electronic and optoelectronic devices. Furthermore, the unique properties of semiconductor nanowires, such as their high degree of crystallinity [9], tuneable morphology [10] and composition [11], superior carrier mobility and flexibility of band alignment, have promoted research resulting in the development of device prototypes such as high-brightness light-emitting diodes (LEDs) [12], flexible displays [13], field effect transistors [14], logic gates [15]. Moreover, heterostructured nanowires are highly promising as energy efficient photovoltaic converters [16–18] and as infrared photodetectors [19–21].

The bandgap is a critical parameter in nanowire-based applications, especially in optoelectronics and photovoltaics,
as its width determines the emission wavelength of LEDs and lasers. In many cases, elemental and binary semiconductors have bandgaps with specific values, making them unsuitable for many applications. The ability to achieve the required bandgap and thus the desired operating wavelength in ternary nanowires, by tuning their composition, makes them promising candidates for optoelectronic devices. The combination of two binary semiconductors that have the same cation or anion with different bandgaps allows materials to be tailored to provide the appropriate bandgap. However, not all binary semiconductors can be combined into ternaries. A low solid solubility can lead to the formation of a so-called miscibility gap, characterized by the formation of domains of pure binary compounds, as this is more energetically favourable than the formation of a homogeneous solid solution. Such effects are observed in various structures including nanowires, thin films and bulk structures. A number of groups have, however, described the growth of nanowires or thin films with compositions in the miscibility gap. This is possible by the formation of a metastable phase as a result of highly non-equilibrium growth methods such as molecular beam epitaxy (MBE) or metal organic chemical vapour deposition (MOCVD). However, despite the publication of several theoretical studies in this area [22], the phenomenon is still not completely understood.

Among nanowire fabrication methods, growth catalysed by a foreign metal has become the most widespread due to its simplicity and universality, and the ability to control the size and density of the nanowire. Indeed, most III–V nanowires can be grown using this method [23–25]. Gold particles collect semiconductor material from the surrounding vapour and reduce the supersaturation to the level required for nanowire growth, while the solid–liquid interface provides favourable nucleation sites. When semiconductor materials undergo two phase changes the growth mechanism is called the vapour–liquid–solid (VLS) mechanism. In metal-catalysed growth, the group III and V precursor fluxes and their ratio, the V/III ratio are key parameters influencing the composition of the final structure. The composition of the nanowire also depends on its shape, the size of the catalyst particle, the growth temperature and the distance between the nanowires, since high nanowire density can lead to shadowing effects and competition for precursor material.

Despite the versatility of Au-catalysed growth, the introduction of a foreign metal may contaminate the nanowires, inducing deep-level traps. Self-catalysed nanowire growth, in which Au is replaced by one of the nanowire constituents, appears to be very promising [26–28]. In addition to removing unwanted contamination, self-catalysed nanowires exhibit a high degree of homogeneity in their radius and length [29]. The use of a patterned amorphous mask, which is deposited on the semiconductor substrate (selective-area epitaxy) allows the position and density of nanostructures to be controlled [30, 31]. Finally, a nanowire growth technique without a catalyst particle, so-called self-induced growth, can also be used [32].

In this review, we focus on composition control of ternary III–V semiconductor nanowires. This is, as we will see, an important research field with a considerable number of published investigations. Nanowire composition control in other materials systems (IV binary and II–VI ternary and quaternary solid-solutions) are presented in the reviews [33–35]. The III–V ternary nanowire materials systems and the compositions that have been realised are presented in table 1, where we have categorized the materials based on whether the composition control is with respect to group III or V. That is, III₃III₁₋ₓV and IIIIVₓV₁₋ₓ, respectively. It can be seen from this table that the composition of the majority of ternary alloys has been controlled over a wide range, while systems such as GaSb₀.₇P₀.₃ and InP₀.₇Sb₀.₃ have been less studied. In the following sections, which constitute the bulk of this review, we discuss the materials systems listed in table 1, in the order of appearance.

**Composition control in ternary III₃III₁₋ₓV nanowire materials**

**AlₓGa₁₋ₓAs**

The possibility of adjusting the wavelength of the emission from AlₓGa₁₋ₓAs to the infrared–red region would make it a suitable candidate for applications in nanowire LEDs, lasers, single-photon sources or wavelength shifters. In these applications, the AlₓGa₁₋ₓAs is often grown as thin heterostructures in GaAs nanowires, forming quantum wells [39, 116] or quantum dots [36, 39] (if the nanowire is thin enough). The emission wavelength can be tuned by changing the size of AlₓGa₁₋ₓAs quantum dots in the axial or radial direction. AlₓGa₁₋ₓAs is closely lattice-matched with GaAs, and therefore GaAs/AlₓGa₁₋ₓAs heterostructures have fewer non-radiative traps. Hence, the quantum efficiency is improved as a result of decreased threshold current. Moreover, AlₓGa₁₋ₓAs has a wider bandgap than GaAs or InₓGa₁₋ₓAs, which makes it promising for use in nanowire-based high-electron-mobility transistors [116–118].

Tateno et al [39] have grown axial and core–shell nanowire structures of GaAs/AlₓGa₁₋ₓAs using MOVPE. The core sections (GaAs, AlAs or segmented GaAs/AlAs) were VLS grown using gold as the catalyst, and the capping AlₓGa₁₋ₓAs layer was grown directly from the vapour phase. Capping layers of materials with x = 0.3, 0.4 and 0.5 were investigated. They found that a low Al content is preferable in the capping layer in order to obtain enhanced photoluminescence (PL). These nanowire structures are promising as single-photon sources for quantum cryptography and for vertical-cavity surface-emitting lasers. Chen et al [116] have also grown multiple-quantum-well-structured nanowires, as illustrated in figure 1(a), and investigated their luminescence properties. They also used gold catalysts, but growth by MBE. They found that alternating the Al contents of the wells and the barriers (between x = 0.22 and x = 0.52) led to higher light emission as compared to non-segmented nanowires with a fixed composition.

MOVPE growth of gold-catalysed AlₓGa₁₋ₓAs nanowires can give rise to the spontaneous formation of core–shell
Table 1. A guide to the literature on composition control in III–V nanowire materials systems using various growth methods and mechanisms. The acronyms used in the table are MBE (molecular beam epitaxy), MOVPE (metalorganic vapour phase epitaxy), CBE (chemical beam epitaxy), and CVD (chemical vapour deposition).

| Category | Materials | Methods | Composition range | References |
|----------|-----------|---------|-------------------|------------|
| III, IIIₐ, V | AlₓGa₁₋ₓAs | MBE, MOVPE | 0.1 ≤ x ≤ 0.4 [36, 37] | [38] |
| | AlₓGa₁₋ₓP | MOVPE, selective-area growth | | |
| | AlₓIn₁₋ₓP | Selective-area growth | | |
| | InₓGa₁₋ₓAs | MOVPE, MBE, selective-area MBE, thermal evaporation | 0.14 ≤ x ≤ 0.89 [11, 44–46, 47, 48–50, 51–53] | x ≤ 0.05 [54, 55] |
| | GaₓIn₁₋ₓP | MOVPE, selective-area MOVPE | 0 ≤ x ≤ 1 [60–65] | |
| | InₓGaₓ₋ₓSb | MOVPE | 0.03 ≤ x ≤ 1 [67, 68] | |
| | AlₓGaₓ₋ₓSb | MBE | | |
| | AlₓInₓ₋ₓSb | Template-assisted vacuum hydraulic pressure injection | | |
| | GaSbxP₁₋ₓ | MOVPE, MBE, selective-area MBE | 0.03 ≤ x ≤ 0.6 [71–73, 74–76] | 0 ≤ x ≤ 0.93 [77–79, 80–85] |
| | InSbxSbn | MOVPE, MBE, CBE | 0.08 ≤ x ≤ 0.94 [86, 87–89] | 0 ≤ x ≤ 0.19 [90–94] |
| | InSbx₋ₓP₁₋ₓ | MOVPE, MBE, CBE | 0 ≤ x ≤ 1 [98, 99–102] | |
| | GaSbx₋ₓP₁₋ₓ | Vapor transfer method, MBE, MOVPE | 0 ≤ x ≤ 1 [107–109] | 0.1 ≤ x ≤ 0.75 [110, 111–113] |
| | GaSbx₋ₓP₁₋ₓ, Reac | Reactive transport with microwave plasma discharge | 0.06 ≤ x ≤ 0.12 [114] | |
| | InPₓ₋ₓSbₓ | CVD | 0.2 ≤ x ≤ 0.54 [115] | |
They grew Au-catalysed Al shell formation in the same material system, see [37, 119]. Reported that a change in the shell and core compositions could be achieved by varying the V/III ratio [119]. Dubrovskii et al [37] have also studied spontaneous core–shell formation in the same material system, see figure 1(b). They grew Au-catalysed AlGaAs nanowires with nominal Al contents of x = 0.2, 0.3, 0.4, 0.5 and 0.6 using MBE. In this case, the AI content in the core was lower than that in the shell. This is in contrast to the findings of Lim et al [119], who used MOVPE for nanowire growth. The lower AI content in the core was attributed to a shorter surface diffusion length of AI than Ga along the nanowires, resulting in a smaller collection area for AI in the case of MBE [37]. The composition of the shell was close to the nominal composition, i.e. the composition of the vapour [37], see figure 1(c).

In a recent study by Cirlin et al [36], axial AlGaAs/GaAs/AlGaAs heterostructure nanowires were grown with MBE. The optical properties of AlGaAs were optimized by investigating the effects of the AI content (x = 0.2, 0.3, 0.4, 0.5 and 0.6), substrate temperature and nanowire growth time. Their results were in agreement with those of Dubrovskii et al [37], in that the core–shell structure forms spontaneously and the AI content in the shell was higher than that in the core.

Ga-catalysed growth of GaAs/AlGaAs axial nanowire heterostructures using MBE has been carried out by Priante et al [38] using MBE. The composition control was studied experimentally in order to obtain sharp GaAs/AlGaAs interfaces and a theoretical model was proposed that matched the experimental observations. In the model, the composition of the pseudobinary solid nanowire was linked to the composition of the ternary liquid Ga–Al–As catalyst particle using a thermodynamic equilibrium model. According to the model, the solid is strongly enriched in Al compared to the liquid, in agreement with the experimental observations. The AlAs composition of the solid, x, is well described by

$$ x = \frac{\varepsilon y}{1 + (\varepsilon - 1)y}, $$

where y is the Al composition in the liquid, and \( \varepsilon \) is a ratio between reaction quotients, which is treated as a fitting parameter [38], see figure 1(d).

In summary, AlGa1−xAs is a well investigated materials system with many promising optical and optoelectronic applications. The composition of the nanowires can be varied over a wide range and composition control has been investigated in axial, core–shell, and heterostructure nanowires. Moreover, in this materials system there is a tendency for phase segregation leading to spontaneous core–shell formation, which could be a disadvantage for precise composition control.
Al<sub>x</sub>Ga<sub>1-x</sub>P

Al<sub>x</sub>Ga<sub>1-x</sub>P nanowires have a direct bandgap in the wurtzite structure, which is not possible in bulk or thin film structures. The bandgap is in the range suitable for optoelectronic devices that emit in the visible region; for example, strain-free Al<sub>x</sub>Ga<sub>1-x</sub>P heterostructures with a wurtzite structure emit green light. Such materials can thus be used in the development of colour-mixed red-green-blue LEDs and commercial green light. Such materials can thus be used in the development of colour-mixed red-green-blue LEDs and commercial green light.

\[ \text{E}_{\text{g}} = 0.39 \text{ eV} \]

\[ \text{GaAs} \quad (E_{g} = 1.46 \text{ eV}) \]

multishell nanowire structures. Single nanowires [44–46], axial heterostructures [54] and core–shell structures [47, 56] of InGaAs have been realized using MOVPE [44, 45, 48, 49], MBE [47, 54, 50, 55, 57], and CVD by a thermal evaporation technique [11]. InGaAs nanowires have a low electron effective mass, high electron mobility, and a small leakage current. These properties make InGaAs nanowires suitable building blocks for integration in transistor channels and long-wavelength optical transmission applications.

Several research groups have grown gold-catalysed InGaAs using MOVPE, with the aim of controlling the nanowire composition (see, for example, [44, 45, 48, 49], for growth on GaAs (111)B substrates and [46] for growth on InAs (111)B). Regolin et al and Kim et al have reported the growth of InGaAs nanowires nucleated from colloidal gold particles on a GaAs substrate in a MOVPE chamber. In the study by Regolin et al [44], indium concentrations of 14%, 16.4%, 27.6%, 54.3% and 88.6% were obtained, and the content was observed to change linearly with the trimethyl indium (TMIn) concentration in the vapour phase. It was found that the triethyl gallium flow had to be about three times higher than the TMIn flow to achieve 50% In in the InGaAs. Kim et al [45] investigated the effect of nanowire density on the height, shape and optical properties of the nanowires. Using energy dispersive x-ray spectroscopy (EDX) measurements, they found that the composition of the nanowires varied, showing In enrichment at the base. Similar observations were made by Wu et al [46], who outlined an experimental route for fabricating nanowires with uniform composition. Kim et al also found that when the surface density of nanowires was low, there was a red shift in the PL emission [45], corresponding to more In-rich nanowires. Both these effects were explained by a large difference in In and Ga surface diffusion lengths along the GaAs substrate and along the nanowire sides, which in turn determined the degree of In and Ga incorporation into the nanowires.

Ameruddin et al [48] studied the axial growth rate and In content of InGaAs nanowires as a function of V/III ratio and growth temperature. They synthesized Au-seeded InGaAs nanowires with MOVPE on GaAs(111)B substrates. In their experiments, the V/III ratio was varied, but the group III precursor ratio TMIn/(TMIn + TMGa) was kept constant. They observed that the In fraction in the solid decreased with increasing Au particle diameter and V/III ratio. The experimental results were explained using a kinetic model including mass transport and nucleation.

Andrade et al [50] detected Ga incorporation of 3%–19% during Au-seeded MBE growth of free-standing (nominally) InAs nanowires on a GaAs substrate. The Ga content increased with increasing growth temperature and decreased with the As<sub>4</sub> beam equivalent pressure. This effect was explained by the release of Ga adatoms from the substrate and their diffusion towards the nanowires. The ability of the substrate surface to supply Ga adatoms was found to be the limiting factor.

The growth of single In<sub>x</sub>Ga<sub>1-x</sub>As alloy nanowires over the whole composition range, via thermal evaporation of InAs and GaAs powders at 800 °C in the presence of Au particles, has been described by Jung et al [11]. The nanowires had a
superlattice structure composed of zincblende and wurtzite segments. Below \( x = 0.5 \), the zincblende structure was found to dominate, while at higher values of \( x \), longer stretches of wurtzite were observed. These nanowires emit in the THz region with the weakest emission at \( x = 0.5 \). The intensity of the THz emission peak increased above this point. This property makes these structures promising for THz radiation emission applications. Using a similar approach, Hou et al fabricated InGaAs nanowires over the whole composition range via chemical vapour deposition with varying ratios of InAs and GaAs powders [51]. They utilized a two-step growth method to synthesize composition- and bandgap-tuned InGaAs nanowires. For each ratio of InAs and GaAs source powders, a different source temperature was used. The nucleation and growth temperatures were also carefully adjusted to produce highly crystalline nanowires. The electrical properties of these nanowires were characterized, showing that as the In content was increased, the turn-off ratio and the \( I_{ON}/I_{OFF} \) ratios decreased, while the mobility was enhanced [52], see figure 2(a).

Jabeen et al [47] synthesized Au-catalysed In\(_{x}\)Ga\(_{1-x}\)As nanowires and core–shell InGaAs/GaAs nanowires using MBE with \( x = 0.09, 0.19, 0.45 \) and 0.55. Both structures showed compositional variation along the nanowires. Post-growth analysis of the seed particle showed that it was In-rich and ordered, and a superstructure containing Au, In and Ga was proposed. Passivation of the InGaAs nanowires by GaAs shells enhanced the luminescence intensity of the core by two orders of magnitude compared to bare InGaAs nanowires.

Shin et al performed one of the first systematic studies on the MOVPE growth of InGaAs nanowires on Si, over almost the whole composition range \((0.2 < x < 1)\) [58]. A schematic of a photovoltaic device with an n-doped In\(_{0.1}\)Ga\(_{0.9}\)As nanowire array based on these nanowires is shown in figure 2(b). The nanowires grew persistently in the \( (111) \) direction, regardless of the substrate orientation. No catalyst particles or substrate surface patterning were utilized. The diameter of the nanowires was found to be dependent on the In content: the higher the In content, the smaller the diameter. The optimum growth temperature (insignificant tapering and maximum vertical \( (111) \) growth) was found to change inversely with the In composition. However, an increase in In content led to sidewall growth. Regarding the crystal structure, the In-rich nanowires were predominantly zincblende, and the Ga-rich ones predominantly wurtzite, contrary to the findings of Jung et al [11]. A direct comparison is, however not possible, since very different growth methods were used. According to the model by Johansson and Leshchenko [121], In-rich nanowires exhibit the zincblende structure and Ga-rich ones the wurtzite structure when grown under otherwise similar conditions. If the conditions for In-rich and Ga-rich

Figure 2. (a) Turn-off ratio as a function of In concentration (the red dot represents the p-type GaAs nanowire-field effect transistor, FET). The inset shows a schematic of the back-gated nanowire-FET [52]. Reprinted (adapted) with permission from [52]. Copyright (2012) American Chemical Society. (b) Schematic of a complete solar cell device using n-type InGaAs nanowires grown on a p-type Si substrate [58]. Reprinted (adapted) with permission from [58]. Copyright (2011) American Chemical Society. (c)–(f) illustrate phase-separated InGaAs grown on graphene [59] as follows: (c) HAADF image of a region near the base of the nanowire and (d) the EDX line scan along the dashed line in (c). (e) HAADF image of the central portion of the same nanowire and (f) the EDX line scan along the dashed line in (e). The white arrows in (c) and (e) point towards the nanowire tip, and the scale bars represent 25 nm. Reprinted (adapted) with permission from [59]. Copyright (2013) American Chemical Society.
growth deviate significantly, which might be the case for Jung et al. [11] (for instance changed As concentration or catalyst particle contact angle), no general trend in crystal structure can be predicted. Finally, high resolution transmission electron microscopy (HRTEM) and x-ray diffraction (XRD) investigations have shown that these nanowires are phase segregated [58], resulting in In- and Ga-rich sides.

In a later study, Shin et al. [53] grew Au-seeded InGaAs nanowires on Si, also using MOVPE, and investigated the effects of growth temperature and the V/III ratio on the morphology and composition homogeneity of the nanowires. They observed that nanowire tapering and compositional variation from the base to tip could be prevented by lowering the growth temperature and V/III ratio. However, Ameruddin et al. [49] reported that higher temperatures allowed for uniform composition of InGaAs nanowires by preventing the spontaneous formation of shells. The major difference between these two studies lies in the different substrates: Si in the former and GaAs in the latter. Ameruddin et al. [49] also optimized the V/III ratio and observed that a pure zincblende phase was obtained at a low V/III ratio, while the wurtzite phase formed at a high V/III ratio.

Hertemberger et al. [57] have investigated homogeneity control and composition tuning in In$_x$Ga$_{1-x}$As (0.6 < x < 1) nanowire arrays. Growth was performed by MBE without catalyst particles on SiO$_2$/Si(111) substrates patterned by nanoimprint lithography. They compared the composition homogeneity of site-selective nanowires to that of particle-catalysed nanowires (grown under similar conditions), and found that site-selectively grown InGaAs nanowire arrays exhibited a lower degree of phase separation and composition inhomogeneity than particle-catalysed arrays. Later, Treu et al. [122] increased the Ga content in InGaAs nanowires to more than 80% Ga. They employed the same growth method as Hertemberger et al. [57], and found that a different growth temperature was required for each compositional range, similar to the findings of Shin et al. [58]. In-rich InGaAs nanowires (x$_{Ga}$ < 0.4) were obtained at a low growth temperature of 550°C, while nanowire arrays with intermediate compositions (0.4 < x$_{Ga}$ < 0.6) and Ga-rich nanowires (x$_{Ga}$ > 0.6) required higher growth temperatures, of 570°C and 590°C, respectively. They also observed that as the Ga composition increased, the growth rate decreased. Moreover, under these growth conditions, the In-rich InGaAs nanowires exhibited more wurtzite structure, while the Ga-rich nanowires exhibited predominantly a zincblende structure. At intermediate compositions, a mixture of zincblende and wurtzite was observed.

Self-catalysed MBE growth of InGaAs nanowires has been reported in two studies by Heiss et al. who investigated the amount of In incorporated by varying the In and Ga beam fluxes [54] and the growth temperature [55]. In neither of these studies did the In content of the nanowires exceed 5%. In their first investigation, axial heterostructures of GaAs/InGaAs were grown which had different lengths of GaAs and InGaAs segments. PL measurements showed that the transition energy increased as the In exposure time decreased (i.e. shorter InGaAs segments). In their second study, they systematically investigated the influence of the growth temperature on the In content of the nanowires. Varying the temperature did not lead to any enhancement of the In incorporation, but the red shift of the PL peak confirmed the presence of In in the nanowires. An inhomogeneous distribution of In was observed along the wires, and attributed to the growth of shells with a higher indium content. The reason that no more In could be incorporated in these nanowires could be that a further increase in indium concentration in the catalyst would lead to a negative chemical potential difference between the liquid catalyst and the solid nanowire. That is, the driving force for nanowire growth is lost [123].

Mohseni et al. [59] studied the growth of InGaAs nanowires on graphene using a catalyst-free self-assembly approach in MOVPE. The nanowires interact with the substrate through the van der Waals interaction, which allows for the formation of dislocation-free, incommensurate structures. XRD and TEM investigations showed that a self-organized InAs-InGaAs core–shell structure was formed. This phase separation was spontaneous and was attributed to the lattice mismatch between the graphene and the InAs. The core–shell formation terminated at a certain nanowire length, which was found to be independent of the In composition. Thereafter, a pure InGaAs segment with the same diameter as that of the core–shell segment continued to grow. The formation of this kind of core–shell structure appears to be unique to growth on graphene, as similar growth on 2D MoS$_2$ films [59] and Si [58] has been reported to result in only single-phase InGaAs nanowires. Au-seeded growth did not result in phase segregation, even when the same kind of graphene substrate was used [59]. For this case of Au-seeded growth, radial and axial heterostructures and their composition profiles are presented in figures 2(e)–(f). In another study, by Tchoe et al. [56], catalyst-free InAs/InGaAs core–shell nanowires were grown on graphene layers using a two-step MBE method. The InAs cores were synthesized at a higher temperature, and then compositionally uniform InGaAs shell layers were grown at a lower temperature.

To sum up, In$_x$Ga$_{1-x}$As is probably the most investigated of the III/III, III/V systems. Nanowire field effect transistors and long wavelength optical transmission are promising application areas. Several techniques have been utilized to grow composition controlled axial and core–shell nanowires as well as heterostructures over a wide range of compositions. Composition control over the entire range have actually been achieved using high temperature evaporation CVD techniques.

Ga$_x$In$_{1-x}$P

Ga$_x$In$_{1-x}$P has a tuneable bandgap of 1.35–2.26 eV (between those of InP and GaP) [120, 124]. As InP has a direct bandgap and GaP an indirect bandgap, Ga$_x$In$_{1-x}$P has a direct bandgap at low values of x and an indirect bandgap at high values of x; the crossover Ga content being x = 0.68 [125]. Ga$_x$In$_{1-x}$P nanowires emit in the red region of the visible spectrum, and therefore have applications in the fabrication of LEDs and multi-junction solar cells. It has been demonstrated that Ga$_x$In$_{1-x}$P nanowires can be used as biosensors due to their inherent fluorescence [126].
Fakhr et al [60] studied the growth of Au-seeded GaInP nanowires on GaAs(111)B using MBE. They used Au particles with a wide range of diameters, from as small as 3–4 nm, to greater than 100 nm, and fixed growth temperature of 430°C. Spontaneous formation of core–shell structures with an In-rich core and a Ga-rich shell was observed. As well as the effect of particle size, they also investigated the effect of the total group III flux and the V/III ratio. Decreasing the group III flux resulted in an increase in growth in the radial direction. Inhomogeneity in composition was observed along the length of the nanowires; the In composition increasing towards the top. The In composition of the core was found to decrease as the size of the Au particles was decreased. No In was detected in the cores when using the smallest particles. Structurally, the nanowires showed a primarily wurtzite crystal structure with a small amount of zincblende, which decreased with increasing group III flux. The same authors later presented a growth model for these nanowires with which they could explain the observed features [61]. The model is based on mass transport where the constituting materials, GaP and InP, are handled separately and Ga and In are considered the limiting species. Both axial and side wall growth were considered.

Jacobsson et al [62] have reported the growth of Au-catalysed GaIn1−xP nanowires on InP(111)B over the whole composition range, using MOVPE. Tapering was prevented by in situ etching with HCl. The Ga content was varied by changing the TMIn molar fraction while the TMGa molar fraction was fixed at a constant value. The effect of growth temperature was studied from 420°C to 480°C. The contents of Ga and In were found to be almost uniform along the nanowires at all temperatures.

Another MOVPE approach for the growth of Au-seeded GaInP nanowires has been reported by Gagliano et al [63]. They deliberately grew GaP/GaInP core–shell nanowires, with VLS-formed GaP cores at 615°C. After growing the cores, the Au particles were removed and shells were grown over the whole composition range via a vapour–solid mechanism at a lower temperature of 585°C. The GaInP shell layer exhibited a wurtzite structure, which was defect-free at high Ga concentrations, but contained misfit dislocations at low Ga concentrations. The optical emission was tuned from 590 nm (2.1 eV) to 760 nm (1.6 eV) at high and low Ga contents, respectively. In another study, Gagliano et al [64] investigated the bending of the GaP/GaInP nanowires grown in their previous work, and found that it was due to the lattice mismatch between the core and the shell layer and asymmetry in the shell thickness.

Ishizaka et al [65] studied the growth of In-rich GaIn1−xP (0 < x < 0.15) nanowires on InP(111)A substrates by selective-area MOVPE, at 650°C. Growth was optimized with respect to group III supply and the V/III ratio. The nanowire length was found to decrease with increasing Ga content, while higher V/III ratios resulted in longer nanowires. In a study by Cerqueira et al [66], GaInP nanowires were synthesized from InP powder and triethylgallium with no catalysts in an MOCVD reactor. The In content was varied by changing the reactor pressure. Three types of structures were realized: straight nanowires, wool-like or bent nanowires, and branched nanowires with non-uniform composition along their length. An intense red-orange visible light was emitted, which was explained by the formation of Ga1−xInxP/Ga1−xInxP interface structures along the wires with x = y.

In summary, GaIn1−xP nanowires are promising for LED and solar cell applications. Both MBE and MOVPE have been used to grow these nanowires with MOVPE as the most common method. Compositions over the entire range, 0 < x < 1, have been achieved. As an effect of unwanted vapour–solid growth on the nanowire side walls, it can be difficult to realize a uniform composition along the nanowires. Such side wall growth can be avoided using in situ etching during growth, leading to nanowires with uniform composition.

Ga2In1−xSb
Ga2In1−xSb has a zincblende structure and its small bandgap is tuneable between 0.18 eV (InSb) and 0.725 eV (GaSb) [120] over the whole composition range. The emission is in the infrared region. The high electron and hole mobility and tuneable bandgap make these nanowires promising for use in IR detectors, optical and thermophotovoltaic devices, and high-speed THz electronics [67].

Two studies on composition tuning of ternary GaIn1−xP nanowires have been performed by Gorji et al using Au-seeded MOVPE. In the first study [68], a short segment of InAs was grown on InAs(111)B substrates in order to initiate growth. This was followed by the growth of an InSb segment and on top of that, a GaIn1−xSb segment. The composition of the ternary section was changed by varying the TMIn, TMSb and TMGa molar fractions. A constant growth temperature of 450°C was used. The nanowires showed a uniform composition and a defect-free, zincblende structure. An increase in diameter was seen upon switching from InAs to InSb, and another increase upon switching to the ternary segment. The Ga incorporation increased with decreasing TMSb fraction.

The second study by Gorji et al [67] deals with the growth of GaAs–GaSb–GaIn1−xSb nanowires. In this case, a short segment of GaAs was first grown on GaAs(111)B substrates, on top of which a GaSb segment was grown, and later a ternary GaIn1−xSb (0.03 < x < 1) segment. The TMSb fraction was fixed and the Ga content was tuned by varying both TMGa and TMIn. They also investigated the effect of varying the temperature from 450°C to 550°C. No change in the diameter was observed upon switching from binary to ternary sections, except at high TMIn molar fractions. At the lowest temperature, the Ga content did not exceed 65%. As the temperature was increased, the In content decreased to below 10%, and the Ga content subsequently increased. This was explained by temperature-dependent TMIn and TMGa pyrolysis. The composition of the Au alloy particles was also studied. At lower temperatures, the particles were In-rich, but a shift in composition occurred at 490°C towards Ga-rich compositions.


The bandgap of Al$_x$Ga$_{1-x}$Sb lies between that of GaSb (0.725 eV direct) and that of AlSb (1.6 eV indirect). It is a direct material for $x < 0.27$ [120]. The lattice mismatch between GaSb and InSb is quite small, <1.2%.

This material system has been little investigated, but it has been studied by Rieger et al [69], who grew Al$_x$Ga$_{1-x}$Sb shells with Al contents of $x = 0$–1 around InAs core nanowires. They employed self-seeded growth in MBE at 360 °C. These core–shell nanowires are promising candidates for tunnel field-effect transistors. A shell thickness of 20–25 nm was obtained after 60 min growth. At Al contents below 40 at% the upper surface of the nanowire was flat, and the diameter was somewhat increased compared to the rest of the nanowire. At higher Al contents the top of the nanowire became faceted, similar to that of pure InAs nanowires. Higher amounts of Al in the shell also increased the carrier mobility due to reduced surface scattering. EDX measurements showed homogeneous incorporation of Al into the shell in both the radial and axial directions. Moreover, no misfit dislocations were observed, due to the small lattice mismatches between InAs, GaSb and AlSb. Oxidation of the Al$_x$Ga$_{1-x}$Sb shell was prevented by growing a thin GaSb cap on the nanowire.

Al$_x$In$_{1-x}$Sb

Al$_x$In$_{1-x}$Sb is a combination of InSb, with the narrowest direct bandgap of 0.18 eV [120] and the highest electron mobility, and AlSb, with an indirect bandgap of 1.6 eV [120]. This is a poorly investigated materials system for nanowire growth. According to the review on InSb nanowires by Shafa et al [127] from 2016, no research had been published on AlInSb nanowires. It was pointed out that such nanowires would be promising to explore for optoelectronic device applications [127].

Two years later, Wang and Wang [70] demonstrated growth of AlInSb nanowires. In order to tune the bandgap of InSb-based nanowires, they replaced In with varying quantities of Al. They used a template-assisted vacuum hydraulic pressure injection process, and reported the successful fabrication of Al$_x$In$_{1-x}$Sb nanowires with the desired composition [70].

**Composition control in ternary III$_V$V$_{1-x}$ nanowire materials**

GaAs$_{1-x}$Sb$_x$

Among nanowires containing different III$_V$V$_{1-x}$$_x$ materials, GaAs$_{1-x}$Sb$_x$ nanowires have probably been the subject of the most intensive research. This is because of their pure zincblende crystal structure and the wavelength range of their emissions. Adding Sb to GaAs allows the wavelength range to be extended from 870 to 1700 nm [77], making this system interesting for the optoelectronics and the telecommunications industries. However, existing growth techniques suffer from poor composition control. Thus, the current–voltage characteristics of GaAsSb nanowire-based photodetectors vary between the top and the base of the nanowire due to the reservoir effect [78]. Sb diffusion may result in the formation of point defects and the spatial dependence of the conductance, leading to a decrease in device power efficiency, as demonstrated in the case of GaAs/GaAsSb quantum wells [128]. Understanding the growth processes will allow the potential of these nanowires to be fully realized, and their functionality expanded. One example is to utilize the surfactant nature of Sb, favouring [112]A-polar facets, in order to achieve a nanowire with triangular cross-section and smooth sidewalls during Au-catalysed MOVPE growth of GaAsSb/InP core–shell nanowires [71]. Such shapes can be used for the fabrication of plasmonic cavities [129, 130]. Another example is the periodic triangular quantum wells arising from the ‘sawtooth’ compositional profile [131]. Single-mode and room-temperature laser devices based on GaAsSb nanowires with multiple axial superlattices have been reported to exhibit effective carrier collection and radiative recombination [131]. Finally, GaAsSb nanowires provide a good foundation for flicker noise measurements at low frequencies, and thus the development of verification methods for materials quality, interface property and photosensitivity of nanowire-based devices [132].

The morphology, composition and crystal structure of Au-seeded GaAs$_{1-x}$Sb$_x$ nanowires, first synthesized by Dheraj et al in 2008 using MBE [72], have been studied systematically by Yuan et al [73]. Their results showed that the solid composition could be controlled over a wide range of compositions $(x = 0.09–0.6)$ by tuning the AsH$_3$ flow, while the morphology depended primarily on the TMSb flow. The addition of Sb resulted in a higher radial growth rate and the suppression of axial growth due to surfactant effects. The synthesis of GaAs$_{1-x}$Sb$_x$ nanowires with high Sb contents is hampered by the combination of high TMSb and AsH$_3$ flows, which may lead to kinking of the nanowires. This phenomenon has been explained by lower Sb incorporation efficiency under such conditions, and unstable wetting of the catalyst particle as a result of its high Sb concentration. Optimization of the growth parameters allows the axial concentration gradient to be reduced [79].

Todorovic et al reported on Au-catalysed axial zincblende GaAs$_{1-x}$Sb$_x$ inserts in wurtzite GaAs nanowires, and on wurtzite GaAs/AlGaAs core–shell nanowires grown with MBE [74]. A clear trend towards higher Sb concentrations with longer inserts was observed. This observation was suggested to be related to different growth rates as a result of the wide size distribution of the initial gold particles. Comparison of the Sb content in nanowires characterized by EDX, quantitative high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) and a combined micro-PL-(S)TEM-EDX approach has shown that EDX underestimates the Sb content at relatively low concentrations $(x < 0.1)$ and for core–shell nanowires [74]. A reduction in the Sb content near the surface has been observed during Au-catalysed growth of GaAsSb nanowires and GaAs nanowires with GaAsSb inserts, and was investigated using STEM and
diffusion modelling by Kauko et al [75]. The observed radial concentration gradient, with a plateau at the centre of the nanowire, was assumed to be caused by As–Sb exchange together with simultaneous Sb diffusion towards the nanowire surface. A schematic illustration of the notation and geometry is shown in figure 3(A). The Sb concentration profiles were calculated by solving a diffusion equation for the corresponding geometry (note that in this particular case, \( x \) indicates position and not composition):

\[
\tilde{C}(x, t) = \frac{C_0}{\sqrt{\pi D t}} \int_{0}^{\infty} \frac{\sqrt{\sin 30^\circ}}{2} \text{erf} \left( \frac{z \sin 30^\circ}{2 \sqrt{Dt}} \right) dz,
\]

where \( \tilde{C}(x, t) \) is the average Sb concentration at position \( x \) and at time \( t \), \( D \) is a diffusion coefficient, \( z \) is the distance from the origin, \( C_0 \) is the Sb concentration for very large \( z \), and \( L \) is half of the width of the hexagonal nanowire. The model was also adapted to describe the Sb concentration distribution in core–shell nanostructures. Figure 4 shows the HAADF STEM image of a GaAsSb nanowire, and experimental and modelled intensity profiles at the tip, middle and bottom of the nanowire, showing good agreement.

The possibility of growing wurtzite and zincblende GaAs–GaAsSb core–shell and axial heterostructures by tuning the crystal structure of the nanowire cores has been demonstrated by Zhou et al [76]. They established that Sb acts as a phase-switching factor, allowing the wurtzite structure to be changed into the zincblende structure.

A systematic study of MBE growth of GaAs\(_{1-x}\)Sb\(_x\) nanowires, over almost the complete composition range (0 < \( x \) < 0.93), has been performed by Li et al [77].

Figure 3. (A) Schematic illustration of the cross-section of a nanowire. Reprinted from [75], with the permission of AIP Publishing. (B) Bandgaps of GaAs\(_x\)Sb\(_{1-x}\) nanowires versus the Sb concentration. Reprinted (adapted) with permission from [77]. Copyright (2017) American Chemical Society. (C) EDX elemental composition map of a GaAs\(_x\)Sb\(_{1-x}\) nanowire showing signals from As, Ga and Sb. Reprinted (adapted) with permission from [83]. Copyright (2014) American Chemical Society. (D), (E) SEM images of GaAs\(_x\)Sb\(_{1-x}\) nanowire arrays grown directly on Si(111) substrates (D), and on GaAs stems (E). The upper and lower rows in (D) and (E) correspond to nanowire arrays obtained by increasing the Sb flux and decreasing the As flux, respectively. Reprinted (adapted) with permission from [77]. Copyright (2017) American Chemical Society.
Composition tuning of the nanowire was confirmed by PL analysis, and bandgaps are presented in figure 3(B). It can be seen that GaAsSb nanowires with Sb contents lower than \( x = 0.6 \) can be fabricated directly on Si substrates or GaAs nanowire stems, whereas GaAsSb growth with high Sb content is only possible on GaAs nanowire stems by tuning the As pressure. A transition to two-dimensional growth was observed with increasing Sb flux. Therefore, the diameter of the nanowire increased with increasing Sb flux, while its length decreased (figure 3(D)). This can be explained by the surfactant role of Sb, which reduces Ga diffusion, leading to radial growth. This surfactant effect also explains why the growth of GaAsSb nanowires is impossible with Sb contents higher than 0.6 on Si substrates. GaAs stems were used to grow GaAs\(_{1-x}\)Sb\(_x\) nanowires with high Sb contents (figure 3(E)). It was found that the axial growth of GaAs\(_{1-x}\)Sb\(_x\) nanowires could be suppressed by both Sb addition, due to the exhaustion of Ga particles, and decreasing the As flux, which resulted in the reduction of the group V supersaturation.

To avoid undesirable effects that reduce the quality of nanowires at high Sb contents (such as a high density of planar defects, tapered morphology, multiple facets and compositional gradients), Ahmad et al grew GaAs\(_{1-x}\)Sb\(_x\) nanowires using a two-step growth process [80]. This method involved initial growth at a high substrate temperature of 620 °C for two minutes, followed by a reduction in temperature. The GaAsSb nanowires obtained combined homogeneous Sb composition up to 34% and emission in the optical communication band of 1.3 μm with a narrow FWHM of the PL peak. Growth was optimized with respect to temperature and the V/III flux ratio in order to achieve the best structural quality and maximum nanowire density. A drastic reduction was observed in the nanowire density with increasing V/III ratio, and an increase in the Sb content with decreasing substrate temperature. The Sb content \( x \) in the nanowires, as a function of flux ratio \( \phi \), was found to be given by:

\[
\frac{1}{x} = \chi \left( \frac{1}{\phi} - 1 \right) + 1,
\]

where \( \chi = (1 + \Psi_{Sb}/K_{Sb})/(1 + \Psi_{As}/K_{As}) \), \( \Psi \) is the liquid-to-solid incorporation coefficient and \( K \) the desorption coefficient from the catalyst particle.

Ahmad et al continued to study the incorporation of Sb and the composition modulation of GaAsSb nanowires [81]. In this investigation, GaAsSb nanowires with Sb contents of 2.8, 7.5, 11, and 16 atomic % were grown on Si substrates using MBE. It was found that small amounts of Sb caused inhomogeneities in the Sb distribution, an increase in nanowire density, and a decrease in nanowire diameter. Higher Sb contents, \( x > 0.16 \), resulted in a more uniform composition. The increase in Sb incorporation was confirmed by Raman investigations. Finally, an Al\(_{0.2}\)Ga\(_{0.8}\)As passivating shell was used to improve the optical emission characteristics.

GaAs/GaAsSb axial heterostructure nanowires grown on Si(111) substrates using MBE have also been studied [79, 82]. It was assumed that the inserted segments of GaAsSb changed the catalyst particle contact angle, leading to the formation of a GaAs nanowire with a wurtzite structure. It was therefore suggested that such GaAs\(_{1-x}\)Sb\(_x\) inserts could be used for crystal phase engineering.

Conesa et al [83] were the first to demonstrate the growth of Au-free GaAsSb nanowires on silicon using patterned arrays in a SiO\(_2\) mask. This method provides the opportunity to change the pitch, allowing further investigation of the underlying growth processes and the impact of growth.

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**Figure 4.** (a) HAADF STEM image of a GaAsSb nanowire and corresponding intensity profiles taken from the tip (b), middle (c) and bottom (d) of the nanowire. Reprinted from [75], with the permission of AIP Publishing.
parameters on the final structure and optical properties of the nanowires. According to TEM data, these GaAsSb nanowires had a pure twin-free zincblende crystal structure. EDX analysis showed that the Sb concentration increased slowly from 17% at the base to 27% at the tip of the nanowires (figure 3(C)). It was also shown in the same study that low Sb concentrations may lead to planar defects. Two other studies have been performed on the composition of GaAsSb nanowires grown on patterned substrates by Ren et al [84, 85]. In the first, the impact of pitch on the morphology and luminescence properties of self-catalysed GaAsSb nanowires was investigated. A PL peak shift from 1.231 to 1.213 eV was observed with decreasing pitch length. This shows that the pitch influences the incorporation of As via the catalyst particle contact angle and Ga diffusion. In their second study, Ren et al demonstrated, for the first time, the possibility of wavelength tunability of the optical emission from self-catalysed nanowire arrays using GaAsSb/AlGaAs core–shell nanowires [85].

In summary, GaAs_{1−x}Sbx nanowires are the most extensively studied of all the IIIV_{1−x}Vx ternary materials systems (0.1 eV at room temperature [133]), which covers the atmospheric infrared window. Thus, InAs_{1−x}Sbx nanowires are promising building blocks for infrared photodetectors, gas detectors and industrial and pollution monitoring devices [86]. Hybrid nanowires combining Al and InAs_{1−x}Sbx are also promising topological materials [134].

Borg et al demonstrated Au-assisted MOVPE growth of InAs/InAsSb heterostructured nanowires (InAsSb nanowires grown on InAs stems) over a wide range of composition, with a InSb fraction from 0.08 to 0.77 [86]. Sb incorporation rates in planar and nanowire growth was compared. It was shown that, contrary to the case of planar epitaxy, the incorporation of Sb into the nanowires was much higher under the same conditions. This was attributed to a decrease in the effective V/III flux ratio, and was confirmed by thermodynamic calculations [86]. The Sb contents in the nanowire and in the epitaxial layer, as a function of the vapour phase composition, is illustrated in figure 5(a). It is clear that the Sb incorporation is much higher in nanowire growth. Figure 5(b) shows the influence of the vapour phase composition on the Sb content in the nanowires at different V/III flux ratios, where it can be seen that the vapour–solid curve becomes linear at low V/III flux ratios. In addition to the different Sb incorporation rates in planar and nanowire growth, Sb incorporation may also depend on crystal structure. The analysis of InAsSb branches grown on wurzite and zincblende InAs stems using MOVPE, by Dahl et al [87], showed that Sb incorporation was higher in zincblende than in wurzite and explained this by antimonides being particularly unfavourable in the wurzite phase. Such branched nanowires are promising candidates for the investigation of Majorana fermions.

InAs/InAsSb single- and double-heterostructured nanowires have been grown by Ercolani et al [88] over a wide range of Sb contents (0.1−0.94) using Au-assisted chemical beam epitaxy. As in the study by Borg et al [86], Sb incorporation into nanowires is not a linear function of the V/III flux ratio. A growth model, involving nucleation of a new layer on the [110] facets and rapid growth completion by a step-flow mechanism was used to explain the nanowire composition dependence on the V/III ratio.

Namazi et al [89] studied the growth of InAs_{1−x}Sbx nanowires in the broad range of x = 0.08−0.75 directly on InAs(111) substrates. These InAsSb nanowires were grown with MOVPE using Au seed particles of different diameters and surface densities. The shape (figures 6(a)−(f)) and InSb content (figure 6(g)) of the InAsSb nanowires are presented as a function of the gas phase composition. As can be seen from figure 6(f), no vertical growth was observed at the highest gas phase Sb fraction (0.96). EDX measurements showed the presence of an axial Sb composition gradient, with a minimum at the nanowire base and a constant value after a certain
height. Furthermore, spontaneous formation of core–shell structured nanowires, with lower contents of Sb in the shell, was observed in Au-seeded growth. The results of this investigation show that the Sb content is sensitive to the initial particle density (a low initial Au particle density corresponds to a higher Sb content in the nanowires), and depends more weakly on Au particle diameter. However, significantly increasing the group III content may shift the growth regime from Au-assisted growth to semi In-assisted growth, which would enable the growth of InAs$_{1-x}$Sb$_x$ nanowires with compositions unattainable for Au-catalysed growth. Du et al [95] have demonstrated the self-catalysed growth of InAsSb nanowires on Si(111) substrates by MOVPE. In these experiments, the Sb content was varied in the range $x = 0–0.43$. The Sb composition was found to have a considerable impact on the axial and radial growth rates of the nanowire. Furthermore, the crystal quality of these nanowires could be improved by the addition of Sb.

Self-catalysed InAsSb nanowires have been studied in a number of investigations by Anyebe et al [90–92]. In the first study, InAsSb nanowires with an Sb content of up to 12% were grown on graphite substrates by MBE for the first time. Based on low-temperature PL measurements, they showed a distinct redshift that was a function of Sb content, demonstrating successful Sb incorporation in nanowires. Ultrahigh-aspect-ratio nanowires could also be achieved using highly As-enriched growth conditions. In another study, they demonstrated the growth of self-catalysed InAsSb nanowires directly on Si substrates by MBE without using stems [91]. Sb concentrations of 0%, 4.3% and 4.5%, as determined by high resolution XRD, were obtained. Such low values are due to the large differences in lattice parameters and thermal expansion coefficients of the InAsSb/Si system. The Sb incorporation rate was significant at relatively low Sb gas phase contents, while Sb incorporation increased slightly with increasing Sb flux, which was attributed to severe Sb segregation. Finally, the dependence of the morphology on composition in self-catalysed InAsSb nanowires was investigated [92]. InAs$_{1-x}$Sb$_x$ nanowires with $x = 4.3\%$, 4.5\%, 10.2\% and 14.5\% were grown by MBE on Si substrates, where the Sb content of 14.5\% corresponded to almost 2D structures. The axial and radial growth rates were explained in terms of Sb segregation, which led to an increase in the contact angle of the catalyst particle. Sb segregation can be caused by a number of factors, for example, the difference in surface energy between Sb and the solvent, the difference in atomic size, and the tendency towards phase segregation.

Zhuang et al [93] demonstrated, for the first time, the realization of high-quality InAsSb nanowires for Si-based optoelectronics operating entirely in the mid-wavelength infrared region with emission of up to 5.1 $\mu$m [93]. InAsSb nanowires with an Sb content of up to 19% were grown after successful suppression of the Sb surfactant effect by optimizing the growth parameters.

Ji et al [94] were the first to perform selective-area growth of InAsSb/GaSb core–shell nanowire heterostructures on Si substrates without using foreign catalysts. A small amount of Sb was added to the InAs core to reduce planar density. Nanowires with 0%, 4.6%, 6.8%, 7.9% and 9.4% of Sb were grown using MOCVD, and exhibited a crystal structure switching from a mixed wurtzite/zincblende structure to a pure zincblende phase.

Catalyst-free MOCVD growth of high-quality InAsSb nanowires has been performed by Farrell et al [96]. InAs$_{1-x}$Sb$_x$ nanowires with $x = 0.15, 0.30, 0.45$ and 0.6 were synthesized on InAs (111)B substrates with patterned SiO$_2$ masks with different hole sizes and pitches. It was shown that the low Sb flux could cause condensation of Sb on the substrate if the thermodynamics were not carefully controlled. Sb condensed on the growth mask at a V/III ratio of 2, negatively affecting nanowire growth. Another study on catalyst-free InAsSb nanowires has been performed by Potts et al [97]. Sb addition allowed the defect density to be reduced by up to a few tens per micrometre.

In conclusion, InAs$_{1-x}$Sb$_x$ is the second most investigated III$_x$V$_{1-x}$ material for nanowires. Its narrow tunable bandgap in the infrared atmospheric window makes InAs$_{1-x}$Sb$_x$ nanowires relevant for infrared photodetectors, gas detectors and pollution monitoring devices. While Au-catalysed InAs$_{1-x}$Sb$_x$ nanowires can span almost the entire composition range, it is difficult to reach high Sb content in self-catalysed nanowires of the same material.

InAs$_{1-x}$P$_x$

The InAsP system has attracted considerable interest as a direct, narrow-bandgap semiconductor that can be tuned in

Figure 6. (a)–(f) SEM images of InAs$_{1-x}$Sb$_x$ nanowires grown at 450 °C under various gas phase compositions. (g) The solid Sb content at different gas phase compositions. Reprinted from [89]. © (2017) IOP Publishing. Reproduced with permission. All rights reserved.
the infrared region (0.35–1.42 eV [120]) and, as such, has potential in applications such as near-IR and mid-IR light-emitting and -detecting devices [98].

Ren et al reported the successful growth of InAs$_{1-x}$P$_x$ nanowires over the whole composition range (0 ≤ x ≤ 1) using a new two-step technique [98]. This method involves the initial growth of InAs nanowires via the VLS mechanism, and a subsequent ion exchange process, constituting annealing in a P containing vapour. By varying the ion exchange time, nanowires with x = 1, 0.75, 0.48, 0.2 and 0 were synthesized and investigated for infrared photodetector applications.

InAs$_{1-x}$P$_x$ alloys have mainly been synthesized in the form of quantum wells [103], segments [99, 100] and quantum dots [101] in InAs nanowires using Au-catalysed growth. InAs$_{1-x}$P$_x$ nanowires and InAs/InAs$_{1-x}$P$_x$ heterostructured nanowires, in which x ranged from 22% to 100%, have been achieved by Persson et al via Au-catalysed VLS using chemical beam epitaxy [99]. They investigated the effect of flux ratio, growth temperature and nanowire diameter on the solid composition. It was found that P incorporation was lower than As incorporation due to their different sticking coefficients. As can be seen from figure 7(a), the incorporation of P increases with growth temperature. The crystal structure of the nanowires grown was confirmed by HRTEM to be wurtzite. In a study by Tchernycheva et al [100], InP nanowires with InAsP insertions with P fractions between 0.5 and 0.65 were grown using Au-catalysed growth in MBE. The As/P flux ratio was varied in order to tune the bandgap, however, an InP shell was required to achieve a strong PL signal.

A comprehensive study has been performed by Harmand et al with the aim of identifying the most important growth parameters and their influence on the growth of individual InAsP nanowires [102]. The nanowires were grown by Au-catalysed MBE on [111]B oriented InP substrates. An indirect modulation technique was used to control the nanowire composition in which substrate rotation was used to cause small variations in the fluxes, leading to periodic fluctuations of the As fraction of ±0.03 around its average value of 0.66. The catalyst particle contact angle was found to be a critical parameter affecting the growth chronology.

Au-free InAsP nanowires with a P content in the range of 0%–10% were grown on Si(111) substrates by Isakov et al [105] using a two-step MBE route: InAs nanorods 150 nm long were grown first, and P was then introduced. This method allowed the growth of vertical nanowires with a regular hexagonal cross-section, and the composition could be tuned by varying the P flux. However, the nanowires obtained suffered from stacking faults at the tip, intermixing of wurtzite and hexagonal structures, parasitic growth of clusters with complicated shapes. It should be noted that no particle was observed. As was found to be incorporated 10 ± 5 times more efficiently than P.

The growth of InAs$_{1-x}$P$_x$ nanowires with compositions of x = 0.21 and x = 0.33 have been demonstrated by Ren et al [106], using catalyst-free selective-area MOCVD. The experimental and theoretical curves for the vapour–solid composition dependence are presented in figure 7(b). It was shown that the bidirectional property of InP nanowires could hamper the growth of InAsP nanowires. However, this problem could be overcome by growing a thin layer of InAs on InP(111)B substrates, allowing very high vertical yields. Finally, self-seeded axio-radial InAs/InAsP nanowire heterostructures have been reported by Mandl et al [104]. Figure 7(c) shows the aspect ratio and the solid composition of the InAsP nanowire cores and the final heterostructures as a function of the PH$_3$/AsH$_3$ flux ratio.

GaAs$_{1-x}$P$_x$

The GaAs$_{1-x}$P$_x$ system provides bandgap tunability from the near-infrared to the visible region (1.42 ≤ $E_g$ ≤ 2.3 eV), with a direct bandgap for x < 0.45 [120], which is promising for advanced photovoltaic devices including LEDs, photodetectors and photon sources.

Im et al grew Au-catalysed GaAs$_{1-x}$P$_x$ nanowires on Si substrates over the complete composition range (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, and 1) using a vapour transport method [107]. This method involves thermal evaporation of GaAs and GaP powders, and the nanowire composition is controlled by varying the GaAs/GaP powder ratio. Nanowires with a high density of planar defects, such as twinned zincblende phases and wurtzite with stacking faults, were observed. It was found that a higher P content in the nanowires led to a lower density of twin planes.

MOCVD growth of Au-catalysed GaAs$_{1-x}$P$_x$ nanowires can result in the spontaneous formation of core–shell heterostructured nanowires, in which the P content in the core is higher than in the shell [108]. Such spontaneous formation has also been observed in the self-catalysed growth of GaAs$_{1-x}$P$_x$ nanowires [110].

Metaferia et al synthesized compositionally tuned GaAs$_{1-x}$P$_x$ nanowires by aerotaxy, which is a continuous gas-phase mass production process [109]. GaAs$_{1-x}$P$_x$ nanowires with a P content uniformly distributed in the wires were obtained by varying the temperature and the gas phase ratio. P contents from 0 to 0.43 were achieved (see figure 7(d)). The growth temperature was found to have a small influence on the incorporation of P with low and high values of P content, but a strong influence for x = 0.5. P incorporation into the nanowire was, however, not a linear function of the flux ratio. The following equation was found to be valid:

\[ x = \frac{\gamma X_g}{\gamma X_g - \beta (1 - X_g)} \]  

where γ and β are the incorporation rate constants of P and As and $X_g$ is the gas phase composition, determined by the ratio of gas fluxes, $X_g = [PH_3]/([PH_3] + [AsH_3])$.

Self-catalysed growth of GaAs$_{1-x}$P$_x$ nanowires has been studied by several groups [110, 111–113]. Zhang et al studied the effect of particle size on GaAs$_{1-x}$P$_x$ nanowire growth [111], and found that fluctuations in particle size attributed to self-catalysed growth resulted in large variations in the length and diameter of the nanowires. Furthermore, nanowires with small radii exhibited higher P contents, which was attributed
to the Gibbs–Thomson effect. A report on the growth of core–shell GaAsP nanowires has been given by Yang et al [112].

GaSb$_{1-x}$P$_x$

Composition control in GaSb$_x$P$_{1-x}$ nanowires has been little studied, especially the growth of GaSb$_x$P$_{1-x}$ nanowires with different solid composition. To the best of our knowledge, the only study has been carried out by Russell et al [114]. They grew nanowires with Sb contents ranging from $x = 0.06$ to $x = 0.12$ by reactive transport utilizing a microwave plasma discharge.

InP$_{1-x}$Sb$_x$

The impact of precursor flux on the Sb composition in self-catalysed InP$_{1-x}$Sb$_x$ nanowires has been investigated by Ngo et al [115]. Zincblende nanowires were grown on InP(111)B substrates by chemical vapour deposition. The nanowires obtained were tapered, with wider tips and narrower bases. It was found that the Sb content increased nonlinearly with Sb flux. Furthermore, a high Sb flux could lead to a wurtzite InSb segment at the tip of the nanowire due to rapid crystallization.

Conclusions

In this review, we have summarized the state of the art in controlling the composition of ternary III$_{1-x}$V and III$_x$V$_{1-x}$ nanowires. As reflected in this report, the GaAsSb, InAsSb, InGaAs and GaInP material systems have been well studied, while there is a lack of knowledge on composition control in the GaSbP, InSbP, AlInP and AlGaP systems. The composition of
the majority of ternary material systems can be varied over almost the complete range (0 \leq x \leq 1). The exceptions to this are InP:Sb and GaSbP, in which the composition has only been tuned within a narrow range, of less than 30%. The problems encountered in synthesis are often related to non-uniform morphology and strong tapering, due, for example, to the Sb surfactant effect. More sophisticated growth methods will have to be developed to overcome these problems.

On a more general note, even if nanowires of the two subsystems can be grown, there is no guarantee that ternary nanowires combining these materials can be grown with an arbitrary composition. One reason is that the two materials can have very different growth parameter windows, meaning that they require different temperatures and precursor pressures in order to grow. If these windows do not overlap, growth of ternary nanowires will be very challenging, if at all possible. Even if the ternary material can be grown it can still be difficult to reach all compositions. The reason is that the species in the catalyst particle influence each other’s solubilities. When one varies the concentration of these species, which is necessary for VLS growth of ternaries, the chemical potentials might change in a way that the driving force for nanowire growth ceases. Such thermodynamic aspects of VLS growth are further discussed in [135, 136].

In conclusion, composition control is a key factor in nanowire-based device design as it will allow us to fabricate materials not found naturally, with the properties required for specific technical and industrial applications.

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