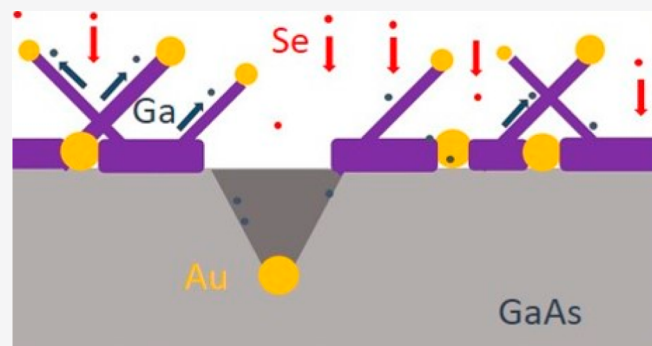


Ga₂Se₃ Nanowires via Au-Assisted Heterovalent Exchange Reaction on GaAs

Federico Berto, Niloofar Haghghian, Katja Ferfolja, Sandra Gardonio, Mattia Fanetti, Faustino Martelli, Valentina Mussi, Vladimir G. Dubrovskii, Igor V. Shtrom, Alfonso Franciosi, and Silvia Rubini*

ABSTRACT: Out-of-plane Ga₂Se₃ nanowires are grown by molecular beam epitaxy via Au-assisted heterovalent exchange reaction on GaAs substrates in the absence of Ga deposition. It is shown that at a suitable temperature around 560 °C the Au-decorated GaAs substrate releases Ga atoms, which react with the incoming Se and feed the nanowire growth. The nanowire composition, crystal structure, and morphology are characterized by Raman spectroscopy and electron microscopy. The growth mechanism is investigated by X-ray photoelectron spectroscopy. We explore the growth parameter window and find an interesting effect of shortening of the nanowires after a certain maximum length. The nanowire growth is described within a diffusion transport model, which explains the nonmonotonic behavior of the nanowire length versus the growth parameters. Nanowire shortening is explained by the blocking of Ga supply from the GaAs substrate by thick, in-plane worm-like Ga₂Se₃ structures, which grow concomitantly with the nanowires, followed by backward diffusion of Ga atoms from the nanowires down to the substrate surface.



■ INTRODUCTION

Ga₂Se₃ belongs to the III₂-VI₃ family of materials. These chalcogenides are characterized by intrinsically defective structures, with cation vacancies originating from the competition between the tetrahedral bonding typical of III-V and II-VI compounds and the presence of an extra electron per anion-cation pair.¹ Ga₂Se₃ crystallizes in a defective zincblende structure, where one-third of the Ga sites are vacant.^{2,3} The vacancies can be randomly distributed (α -phase) or ordered (β -phase), resulting in superstructures with different symmetries (orthorhombic or monoclinic)²⁻⁷ depending on the growth conditions.

Optical and electronic properties of Ga₂Se₃ have been widely investigated in the past, especially due to its role as interface material at III-V/II-VI junctions⁸⁻¹⁰ and to peculiar optical anisotropies related to the vacancy ordering.¹¹⁻¹³ The potential of Ga₂Se₃ as the negative electrode material for Li batteries has recently been evaluated.¹⁴ Ga₂Se₃ has also been proposed as a possible photocatalyst for water splitting under visible light.¹⁵ Furthermore, if doped with selected magnetic impurities, it becomes a promising diluted magnetic semiconductor. For example, room-temperature ferromagnetism has been observed in Cr-doped Ga₂Se₃.¹⁶

Epitaxial β -Ga₂Se₃ layers have been grown by molecular beam epitaxy (MBE) on III-V^{17,18,6} and Si^{7,1} substrates with different symmetries of the vacancy ordering depending on the

substrate (see, for example, ref 6 and references therein). It has been shown that GaAs strongly reacts with Se hydrides, leading to the formation of Ga₂Se₃ layers in the absence of any external Ga supply.^{10,19} A heterovalent exchange reaction between group V and VI elements, activated at high enough temperatures, was invoked to describe the growth mechanism. Formation of the α - or β -phase was found to depend on the substrate temperature. A similar process was more recently reported involving GaSb, where Ga₂Se₃ material was obtained by exposing GaSb to a Se flux at high temperature and then used as a buffer layer for epitaxial growth of Bi₂Se₃ by MBE.²⁰ Such a growth led to the formation of voids in the GaSb substrate, with the Ga₂Se₃ film being partially suspended and supported only by a few GaSb nanopillars.²⁰

No information can be found in the literature on Ga₂Se₃ in the form of freestanding nanowires (NWs), while a few examples of In-based III₂-VI₃ NWs are known. In₂Te₃ NWs were synthesized by a Au-assisted vapor-liquid-solid (VLS) mechanism.²¹⁻²³ The nanostructure properties were inves-

tigated, highlighting their performance as photodetectors in single NW devices.²² In₂S₃ nanocrystals with high aspect ratio were grown in the form columnar microcrystals by thermal evaporation without the use of a catalyst.²⁴ Finally, In₂Se₃ NWs were synthesized by the Au-assisted VLS mechanism by several groups.^{25–28} High quality nanostructures were obtained and investigated as possible Li-storage materials because of the intrinsic presence of structural vacancies²⁹ and as a potential material system for high-performance visible-light photodetectors²⁷ and field emitters.²⁸ Similar structural vacancies are also intrinsically present in Ga₂Se₃. On the other hand, silicon NWs³⁰ show excellent performance as Li battery anodes. We can thus envisage the use of Ga₂Se₃ NWs in high performance Li batteries.

Far less reports are available for Ga-based III₂–VI₃ nanostructures. Highly ordered horizontal Ga₂S₃ NWs were recently obtained by chemical vapor deposition on sapphire.³¹ One-dimensional horizontal growth was driven by Au particles in a VLS mechanism and was favored over vertical growth due to the high growth temperature and low precursor fluxes. The nanostructures showed excellent nonlinear optical properties. Finally, single crystalline Ga₂S₃ nanotubes were obtained by conversion of GaAs NWs exposed to sulfur vapor.³² The conversion process was investigated as a function of the exposure time. It was found to proceed via the formation of epitaxial core–shell GaAs–Ga₂S₃ NWs, followed by the development of hollow Ga₂S₃ tubes. The tubes formed by retraction of GaAs cores due to injection and coalescence of vacancies into the Kirkendall voids, with simultaneous evaporation of As.³²

In this paper, we demonstrate that freestanding Ga₂Se₃ NWs can be obtained by MBE on Au-decorated GaAs surfaces without any external Ga supply, via a heterovalent exchange reaction mediated by Au nanoparticles. We show that at a suitable temperature the presence of Au on the surface favors the decomposition of the GaAs substrate and the release of Ga atoms, which react with the incoming Se and feed the NW growth. We explore the growth parameter window and find that the NWs start to shorten after a certain maximum length. The NW composition, crystal structure, and morphology are characterized by Raman spectroscopy and electron microscopy. The growth mechanism is investigated by X-ray photoelectron spectroscopy (XPS). The NW growth is described within a kinetic model, which explains the peculiar nonmonotonic behavior of the NW length versus the growth parameters.

METHODS

Ga₂Se₃ NWs were grown on epi-ready n-type Si-doped GaAs (100) substrates in a multichamber ultrahigh vacuum system including an MBE growth chamber equipped with Se and Bi effusion cells, a metallization chamber for thermal evaporation of Au, and an analysis chamber for XPS. After thermal desorption of the surface oxide layer, the substrates were transferred into the metallization chamber where 1 nm of Au was deposited at room temperature. Following 15 min annealing at 600 °C for thermal dewetting of the Au layer, the substrate was exposed to Se flux. In only a few cases, Bi flux was used together with Se; however, no noticeable differences were found between the samples grown with or without Bi flux, and in the following we will not specify that (more information is given in the [Supporting Information \(SI\) 1](#)). Beam equivalent pressures (BEPs) of Se between 1×10^{-6} and 4

$\times 10^{-6}$ Torr were explored. The corresponding Se fluxes were measured by an ion gauge located at the substrate.

The NW morphology was investigated by scanning electron microscopy (SEM), using a field-emission SEM Zeiss SUPRA 40 operated at 10 keV, with a nominal point resolution of 1.5 nm. Lengths and diameters of more than 40 NWs were measured for each sample. Structural characterization was performed in a field-emission transmission electron microscope (TEM) Jeol JEM2100F-UHR operated at 200 keV. The material composition was investigated by energy-dispersive X-ray spectroscopy (EDX) in both SEM and TEM. For EDX in SEM, we used a JEOL JSM 7100 SEM equipped with an X-Max80 EDX (Oxford Instruments). For STEM/EDX analysis, the same TEM was used in scanning TEM (STEM) mode at 200 kV. STEM images were acquired with an annular dark-field detector. EDX analyses were performed with X-Max80T (Oxford Instruments).

Raman spectra were acquired in a DXR2xi Thermo Fisher Scientific Raman Imaging Microscope with laser excitation at 532 nm.

At selected stages of NW growth, XPS analysis was performed in an Al K α photoemission chamber (Surface Science Instrument) connected to the MBE system, with an overall energy resolution of 0.1 eV.

RESULTS

Ga₂Se₃ NWs were obtained by exposing the GaAs (100) surface decorated with Au nanoparticles (NPs) to a Se flux. [Figure 1](#) shows plan-view SEM images of the samples grown for 15 min with a Se BEP of 4×10^{-6} Torr at substrate temperatures between 480 and 600 °C. Within this temperature window, a percentage of thin and straight NWs is found with the projection aligned to the $\langle 001 \rangle$ directions of the substrate surface. Careful analysis of the SEM images shows

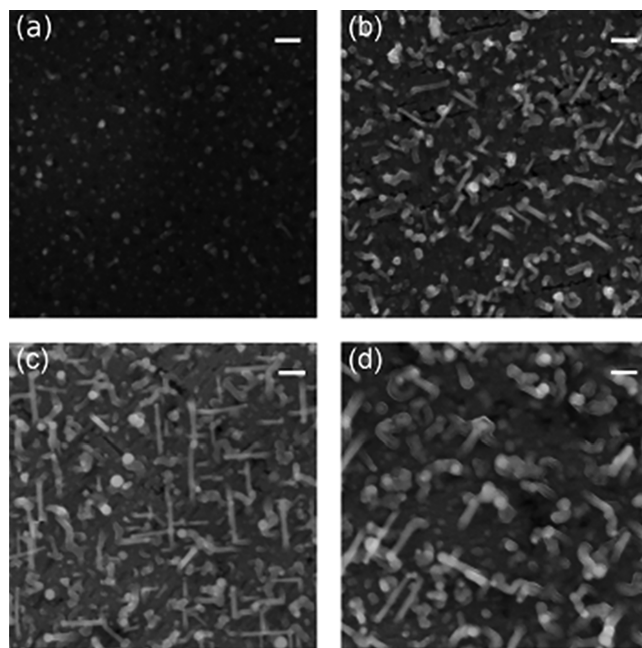


Figure 1. Plan-view SEM images of Ga₂Se₃ NW samples grown for 15 min under a Se BEP of 4×10^{-6} Torr at different substrate temperatures: (a) 480 °C, (b) 520 °C, (c) 560 °C, and (d) 580 °C. Scale bars correspond to 100 nm.

that the NW growth direction makes an angle of 45° with the substrate plane, indicating that they grow along the $\langle 110 \rangle$ directions of the GaAs substrate. The analysis of NW orientation with respect to the substrate is detailed in SI 2. In the following, the NW length quoted on the left of each graphic corresponds to the measured NW projection onto the (001) substrate surface. We report on the right scale the real NW length as calculated considering the angle they make with the substrate. Considering that in some samples we observe a wide majority of NWs with length concentrated in a relatively narrow range of values and a few nanowires with length quite far from the average value, and in order to maximize the information for the reader, we report the data in the form of a box plot: the extremes of each box correspond to the 25th and 75th percentile of the length distribution, respectively, the mark in the center to the median, while the whiskers span the entire range of the measured values.

The NWs can continue growing after the initial nucleation step only at high enough substrate temperatures. This is clearly seen from Figure 2(a), where the NW length after 15 and 60 min of growth is shown as a function of temperature. We will therefore focus on the samples grown at 560°C , with the longest Ga_2Se_3 NWs. A representative plan view of the sample after 30 min of growth is shown in Figure 2(b). Together with the NWs, some thicker, worm-like structures are also observed, most of which do not grow away from the substrate but rather develop along the substrate surface. Both NWs and worm-like structures exhibit Au NPs at the top, as can be observed in Figure 2(b) where the NPs are indicated by arrows. The NPs found at the top of the out-of-plane NWs are smaller and more uniform in size compared with those observed on the worm-like structures. This is illustrated in the histogram in Figure 2(c) where the statistics for a sample grown for 30 min with a Se BEP of 4×10^{-6} Torr are shown. The diameter of the Au NPs seems therefore to be a decisive factor in determining the formation of out-of-plane NWs or in-plane worm-like structures. More information about the size dependence of the nanostructure morphology can be found in SI 3.

The NW diameter was found to be in the range of 20–30 nm independently of growth time and Se BEP. SEM images of representative samples grown for different time and with different Se BEP are shown in SI 4. Kinks were occasionally observed along the NW axis, as indicated by the white arrow in Figure 2(b).

Figure 3 shows the dependence of the NW length on the growth time for different Se BEPs. In all cases, the NW length first increases almost linearly with time, then saturates at a maximum value and eventually decreases for longer times.

This is a quite uncommon behavior whose presence is independent of the Se flux. This feature is pointed out in particular in Figure 3(c) where one can see a white point placed at 480 min. The related NWs have been actually grown for 360 min and then exposed to a thermal annealing at the same growth temperature of 560°C for a further 120 min in the absence of a Se flux. It can be noticed that the NW length has decreased in those 120 min more than that of the wire continuously grown for 420 min. This feature is a clear indication that the shortening of the NWs after having reached a maximum length is a process completely independent of the Se flux: it occurs both in the presence of a Se flux, whatever its amount, and in the absence of it.

Several characterizations performed on the NWs confirmed that they are composed of Ga_2Se_3 .

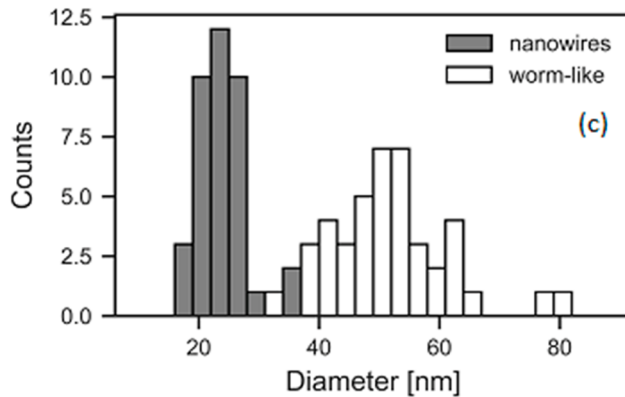
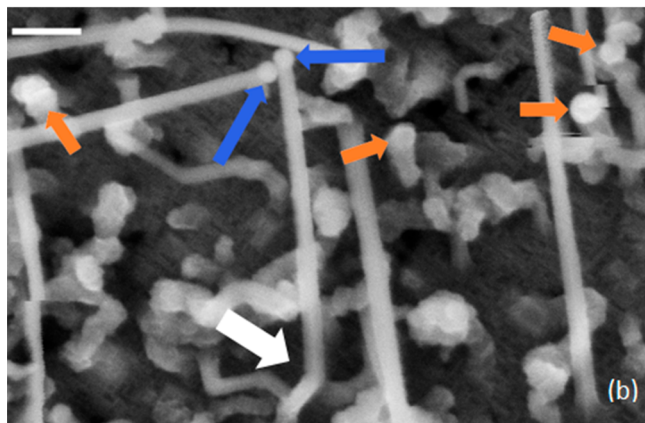
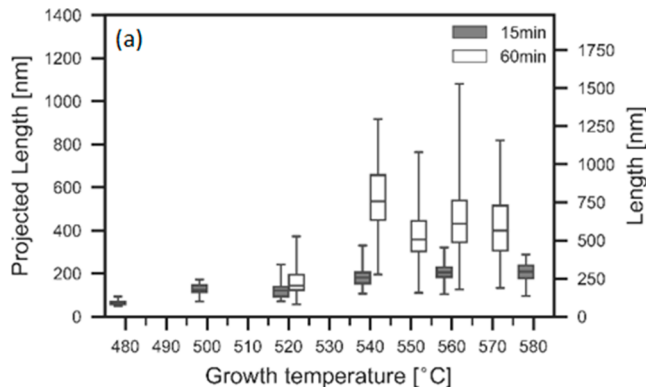


Figure 2. (a) Ga_2Se_3 NW lengths measured after 15 min (gray boxes) and 60 min (white boxes) growth times at a fixed Se BEP of 4×10^{-6} and different substrate temperatures. (b) Plan view SEM image of sample grown for 30 min with a Se BEP of 4×10^{-6} Torr at 560°C : Au nanoparticles at the tip of NWs and worm-like structures are indicated with blue/long and orange/short arrows, respectively. A kinked NW is indicated by a white arrow. Scale bar corresponds to 100 nm. (c) Diameter distributions of NWs and worm-like structures, obtained from statistical analysis of the sample grown for 30 min with a Se BEP of 4×10^{-6} Torr at 560°C .

Unpolarized Raman spectra were acquired on the as-grown samples, therefore including both the standing NWS and the worm-like structures. A typical spectrum observed is shown in Figure 4, for a sample grown for 30 min with a Se BEP of 4×10^{-6} Torr. We observe a sharp peak at 155 cm^{-1} , which is a clear signature of the presence of Ga_2Se_3 .^{2,19} The typical GaAs TO and LO phonon scattering signals at 267 and 292 cm^{-1} , respectively, originate from the GaAs substrate. The broad

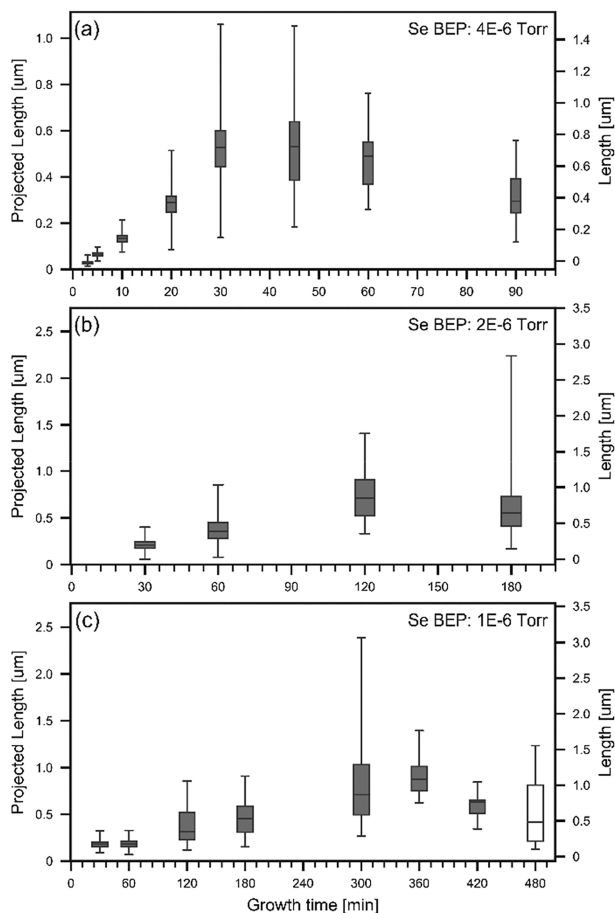


Figure 3. Ga_2Se_3 NW length versus the growth time at a substrate temperature of 560°C and three different Se BEP: (a) 4×10^{-6} Torr, (b) 2×10^{-6} Torr, and (c) 1×10^{-6} Torr. The point at 480 min in panel (c) displayed as white box, corresponds to a 360 min growth followed by 120 min annealing without Se flux, for a total time of 480 min at growth temperature.

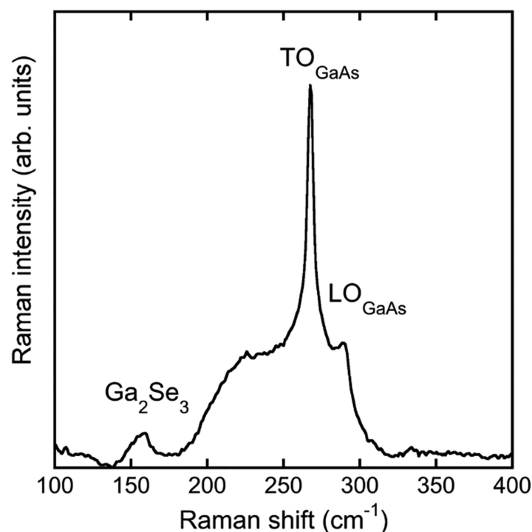


Figure 4. Raman spectrum of a NW sample under 532 nm excitation. The sharp signal at 155 cm^{-1} is characteristic of Ga_2Se_3 .

shoulder at the intermediate energies is due to unresolved contributions from several lines of Ga_2Se_3 . Broadening of the

Raman peaks is likely due to the presence of structural defects in Ga_2Se_3 .³³

In Figure 5 we report a SEM image and EDX compositional analysis of a bundle of NWs removed from the substrate and

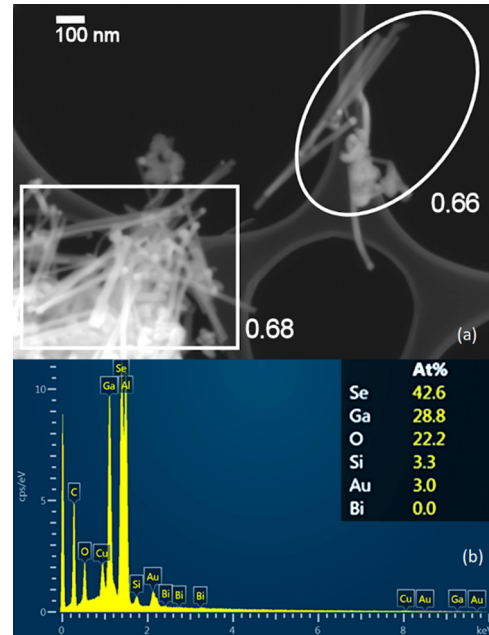


Figure 5. (a) SEM image of a bundle of NWs transferred from the substrate to a TEM copper grid. Scale bar corresponds to $1\ \mu\text{m}$. The evaluated Ga/Se ratio is indicated beside the boxes. (b) EDS spectrum acquired in the region boxed in (a).

supported by a TEM copper grid. In the low-resolution image we can still recognize the NW bodies and the spherical NPs at the tips. The EDS data indicate the presence of Ga, Se, and Au. Al and Cu come from the mounting stage and the TEM grid, respectively. The relative abundance of Ga and Se is 0.68, very close to the nominal 2:3 ratio.

STEM/EDX analysis of single NW samples confirmed that the NW body is composed only of Ga and Se, with Au (and Bi if used during growth) below the detection limit. A representative analysis is shown in Figure 6. STEM/EDX analysis on a single wire does not allow us to precisely address the Ga:Se NW stoichiometry. In fact, Ga and Se intensities are strongly affected by channeling effects that are particularly strong when NWs are imaged in a direction perpendicular to the growth axes.³⁴ EDX measurements of the NPs resting at the NW tip reveal that it is composed of Au and Ga, with Ga concentration around 5 atomic %. A weak Se signal from the NPs is also detected, around 1%. The worm-like structures are also composed of Ga and Se (see SI 3 for more details). TEM analysis of representative single NWs showed the NPs at the NW tip are 10–40% larger than the NW diameter.

High-resolution (HR) TEM study reveals that both NWs and worm-like structures are crystalline. Unfortunately, more accurate analysis of the structure by electron diffraction along the NW zone axes was hindered by fast degradation of the NWs under the electron beam. Still, in several cases, a structure equivalent to the one reported in ref 6 was observed. In Figure 7 we show two representative NWs, one of them kinked, as occasionally observed (see for instance Figure 2(b)). In the absence of selected area diffraction images, we analyzed the fast Fourier transformation (FFT) of the high-resolution images.

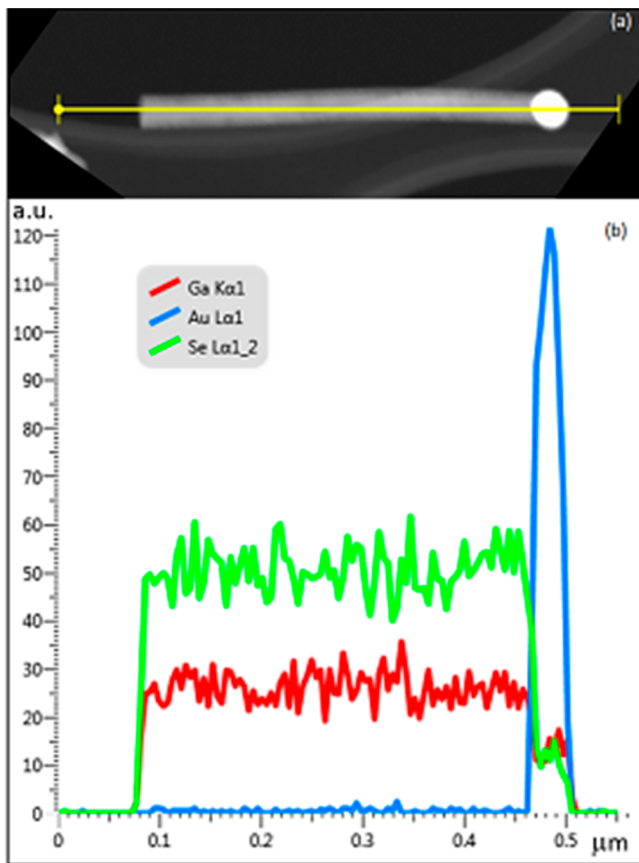


Figure 6. (a) Dark-field STEM image and (b) EDX line scan of a representative Ga_2Se_3 NW.

As illustrated in Figure 7, the most frequently observed periodicities are 1.9, 2.7, and 3.1 Å, which correspond to the $\langle 220 \rangle$, $\langle 200 \rangle$, and $\langle 111 \rangle$ directions of α - Ga_2Se_3 , respectively.³ The wires appear to be characterized by a high density of stacking faults on the two sets of $\{111\}$ planes. Most of the stacking faults stop at the intersection of both $\{111\}$ planes. These features were observed in Ga_2Se_3 epitaxially grown on GaAs⁶ and associated with the ordering of the Ga vacancies on the $\{111\}$ planes of the α - Ga_2Se_3 , leading to the monoclinic β - Ga_2Se_3 structure described in ref 2.

Many of the observed NWs grow in the $\langle 110 \rangle$ direction, as the one in Figure 7(a–c). In this case, the NWs are in epitaxial relation with the GaAs substrate, with the $\langle 100 \rangle$ directions of the defective zinc-blende α -phase Ga_2Se_3 and of the GaAs substrate aligned with each other. No direct information could be drawn from the FFT about the presence or absence of any ordered superstructures. However, the high density of stacking faults along the $\{111\}$ planes suggests that ordering of the vacancies characterizing the β -phase is present.⁶

The NP at the NW top has a nearly spherical shape, and the interface with the NW is neither flat nor perpendicular to the growth axis, which may suggest a vapor–solid–solid (VSS) growth mechanism³⁵ or be due to a NP reconfiguration during the cooling process. Some NWs are kinked due to a change of their growth direction, as shown in Figure 7(d).

XPS spectra were acquired at selected stages of growth under a Se BEP of 4×10^{-6} Torr. Figure 8 shows that, after annealing at 600 °C, the Au $4f_{7/2}$ emission shifts from 84.00 eV typical of pure Au to 85.54 eV. This reflects the well-known alloying process with Ga, with a Ga content of 67% or higher.³⁶

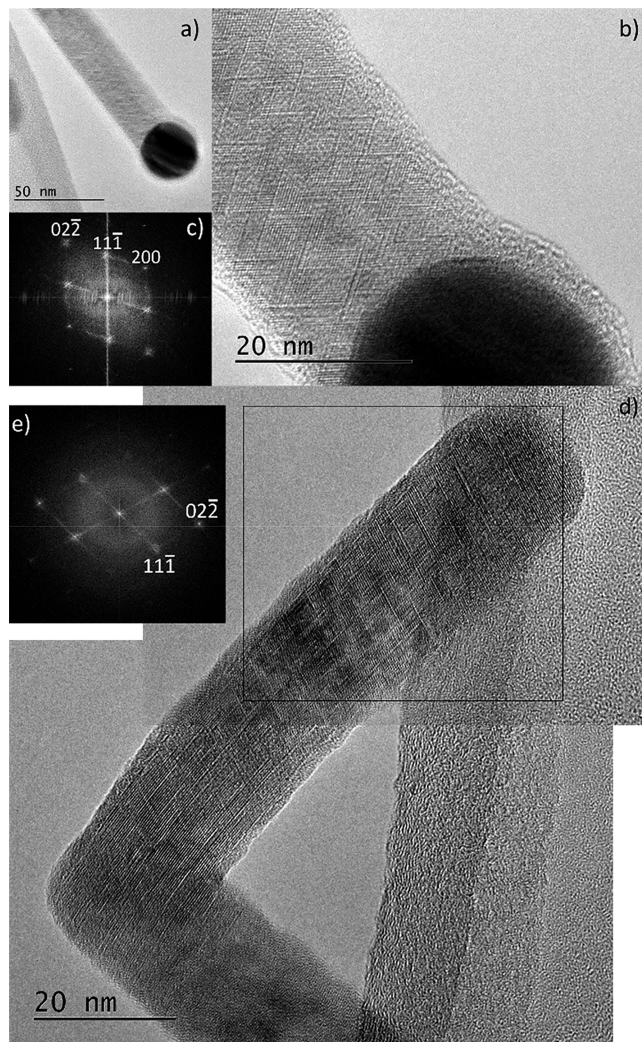


Figure 7. (a) TEM image of a straight NW. (b) HR-TEM image of the same NW. (c) Fast Fourier transform (FFT) of the image from the NW body. (d) HR-TEM of a kinked NW. (e) FFT of the image from the boxed region in (d).

When the NW growth starts, the shift is reduced, and the Au $4f_{7/2}$ line is detected at 84.7 eV. This shift corresponds to a Au–Ga alloy with 33% Ga and does not change much with the growth time until the Au line becomes invisible. Due to the surface sensitivity of the XPS measurements, the measured concentration corresponds to Ga content in an ~ 2 nm thick surface layer of the NPs, while the EDX data presented above reveal only 5% Ga content in the whole NP. After 45 min of Se deposition, the Au line is barely visible (Figure 8(d)) and becomes undetectable after 60 min.

The As 3d and Ga 3d emissions at different stages of the growth process are shown in Figure 9. The As 3d line is fitted by a spin–orbit doublet,³⁸ shown by the dashed blue lines, and the position of the As $3d_{5/2}$ component is marked by a vertical line. The As 3d core level emission does not display any line shape change throughout the entire growth process but becomes weaker for longer exposures to Se flux. After 45 min of exposure, it is no longer visible [Figure 9(d)].

We analyze the evolution of the Ga 3d line versus growth time relative to the GaAs-related component (corresponding to the solid blue lines in Figures 9). The latter is fixed (rightmost vertical line) at the position expected from the

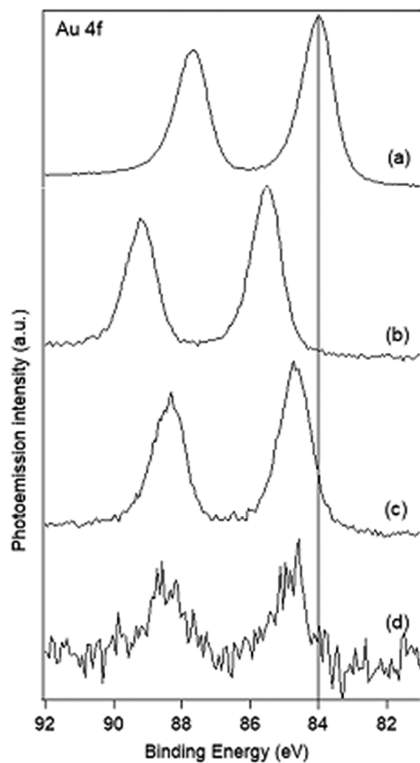


Figure 8. Au 4f core level emission at selected stages of a NW growth experiment: (a) after 1 nm Au deposition on GaAs at room temperature, (b) after annealing at 600 °C, (c) after 2 min of Se deposition, and (d) after 45 min of Se deposition. The vertical line indicates the 4f_{7/2} binding energy in pure Au (84.0 eV according to ref 37).

observed As 3d position (leftmost vertical line) in each case and the measured energy separation between the As 3d_{5/2} feature and the Ga 3d peak for clean GaAs (21.67 eV in Figure 9(a)). After the Au deposition and annealing at 600 °C [Figure 9(b)], we detect the appearance of a component at higher binding energy, shown by the yellow line. This emission should correspond to metallic Ga alloyed with Au. Upon exposure to Se flux, a third component appears at a lower binding energy, shown by the red line in Figure 9 (c). This component becomes dominant for longer deposition times and is related to the Ga–Se reaction. After 45 min of exposure to the Se flux, the GaAs-related component is no longer visible, as shown in Figure 9 (d). A low energy peak is still visible, at an energy close to that of metallic Ga.³⁹

Figures 10(a) and (b) show the Se 3d core level emission observed from the Au-decorated GaAs surface after exposure to a Se flux for 2 and 45 min, respectively. As soon as detected, the Se 3d spectrum appears to be composed of two spin–orbit doublets. The observed line shape is compellingly similar to that reported for β -Ga₂Se₃, where the two doublets correspond to the two inequivalent Se sites in the lattice.^{1,5,8} The separation between the two doublets is close to 1 eV. The separation between the Se 3d main peak and the high binding energy peak of Ga 3d is 34.55 eV. This value is in good agreement with reported data for Ga₂Se₃, for example, 34.65 and 34.73 eV for Ga₂Se₃ grown by MBE on Si¹ and GaAs,⁸ respectively, and 34.66 eV for selenized GaAs (100).⁸ The observed intensity ratio of the two peaks in Figure 10 is 0.43,

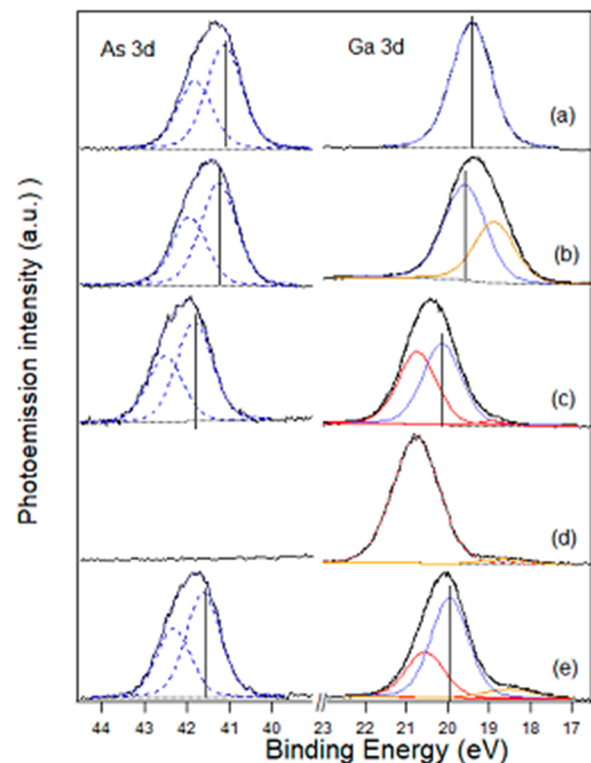


Figure 9. As 3d (left panels) and Ga 3d (right panels) XPS spectra at different stages of the growth process. (a) Clean GaAs surface; (b) after deposition of 1 nm Au and 15 min annealing at 600 °C; (c) after 3 min exposure to Se flux; (d) after 45 min exposure to Se flux. For comparison, we also show the spectra obtained after exposing the GaAs surface to Se flux for 45 min in the absence of Au in (e). The dashed blue lines show the deconvolution of the As 3d peak into the spin–orbit doublet. The rightmost vertical lines mark the expected position of the GaAs-related Ga 3d emission as obtained from the observed As 3d position (leftmost vertical line) and the measured energy separation between As 3d and Ga 3d peaks for clean GaAs. The blue line denotes such a GaAs-related component of the Ga 3d line shape. The yellow and red lines denote Ga 3d contributions shifted to higher and lower binding energies, respectively.

which is close to the expected ratio 1:2 for Se atoms bound to two and three Ga atoms, respectively.

The bottom panels of Figures 9 and 10 show the Ga 3d, As 3d [Figure 9(e)], and Se 3d [Figure 10(c)] core level emissions from the samples grown for 45 min under the same conditions but on clean GaAs without any Au. It is seen that GaAs-related As 3d and Ga 3d emissions are still dominant, while a higher binding energy component appears in the Ga 3d spectrum. The Se 3d emission is also observed, confirming the selenization of the surface, with the two spin–orbit doublets separated by 0.9 eV. The separation between this peak and the high energy peak of Ga 3d emission equals 34.61 eV, which is in agreement with the literature data for the Se-reacted GaAs (100) surface (34.66 eV according to ref 8). The situation remains identical after 60 min of Se deposition (not shown), indicating that a Se-containing layer is present on the surface, but its thickness (on the order of 1 nm) does not increase with exposure time to the Se flux.

Figure 11 shows the cross-sectional morphology and chemical profile of a sample grown for 60 min with a Se BEP of 4×10^{-6} Torr on Au-decorated GaAs (100), compared with a sample exposed for the same time and under the same

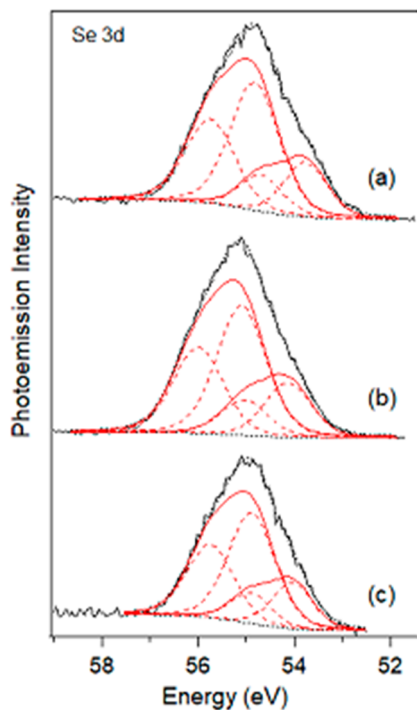


Figure 10. Se 3d core level emission after exposing the GaAs surface with 1 nm of Au annealed at 600 °C to Se flux for 2 min (a) and 45 min (b). For comparison we also show the Se 3d emission from GaAs upon exposure to Se flux for 45 min in the absence of Au. The spectra are fitted with the two spin-orbit doublets (red dashed lines), corresponding to the two inequivalent sites of Se. The envelope of each doublet is shown by the red solid lines.

conditions to the Se flux in the absence of any Au on the substrate. In the sample with Au, we can see some voids penetrating into the substrate, with Au nanoparticles possibly accumulating in the voids. Ga- and Se-rich nanostructures are detected on the substrate surface, with thin Ga₂Se₃ NWs growing away from the substrate. No thick Se-rich layer is found on the surface. Therefore, the decrease in the measured NW length at longer growth times is not caused by burying the bottom part of the NWs in a Se-rich layer. This conclusion is confirmed by the data shown in Figure 3(c), where the NW shortening also takes place during annealing in the absence of a Se flux. No cavities are visible in the cross-sectional SEM image of the sample grown without Au. The substrate surface is flat and contains no detectable Se-rich layer.

DISCUSSION

According to the data presented above, our Ga₂Se₃ NWs grow on GaAs (100) without any external Ga flux and only in the presence of Au nanoparticles. Such growth can only occur due to an Au-assisted release of Ga atoms from the GaAs substrate, which subsequently reacts with the available Se to form Ga₂Se₃. The NW growth should proceed at the tip and be assisted by the nanoparticle consisting of an alloy of Au with the NW material (Ga and Se). We can most probably rule out the root growth of NWs because all our experimental data show the presence of a nanoparticle at the NW top as well as at the tip of worm-like parasitic structures. No NW growth occurs without Au. We believe that when a metallic nanoparticle seats at the NW top the Au-catalyzed growth at the root is unlikely, as discussed, for example, in refs 40 for GaAs and in ref 41 for

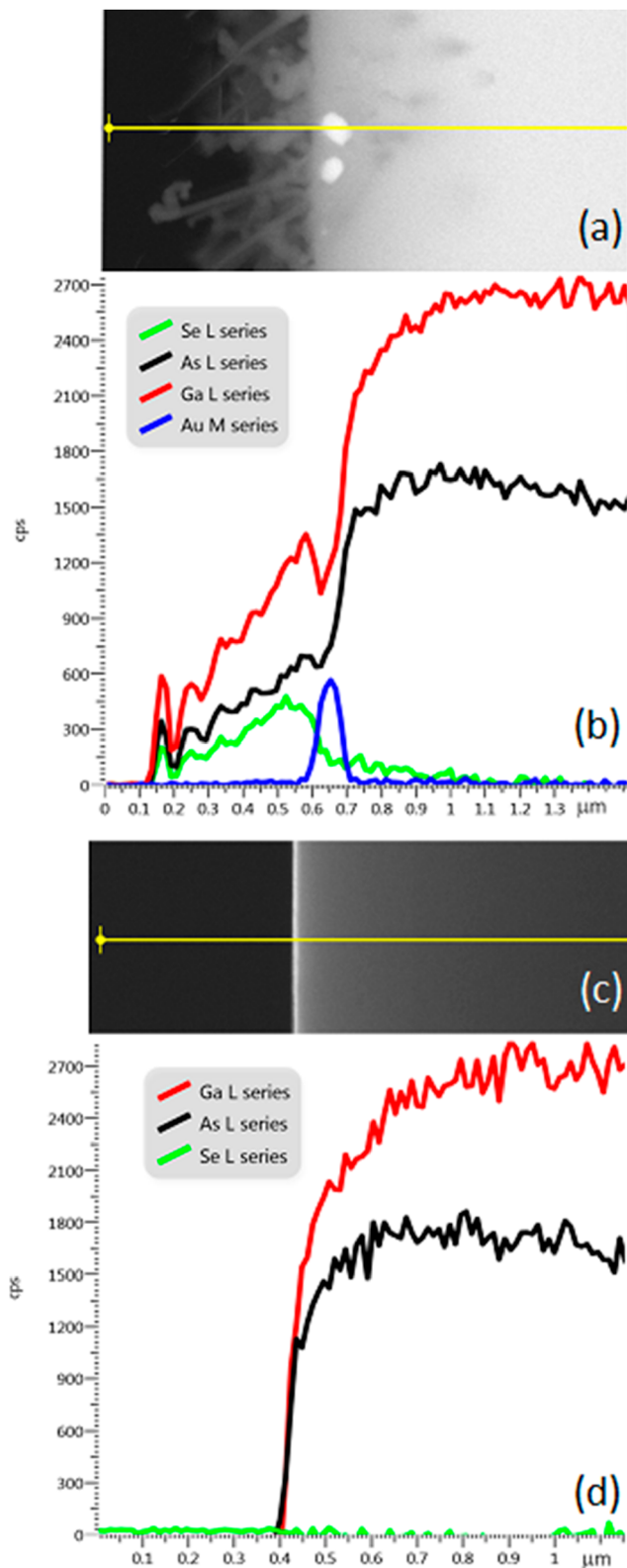


Figure 11. (a) Cross-sectional SEM image (top panel) and (b) EDX profile (along the line shown in the image) of a NW sample grown for 60 min with a Se BEP of 4×10^{-6} Torr on Au-decorated GaAs (100) surfaces. (c) Cross-sectional SEM image (top panel) and (d) EDX profile (along the line shown in the image) of a GaAs (100) surface exposed for 60 min to the same Se flux at the same temperature in the absence of any Au nanoparticles.

CdTe NWs obtained by different techniques. Therefore, the very first NW layer emerges under the nanoparticle and nucleates from the nanoparticle (liquid or solid). This process has a much higher probability compared to catalyst-free nucleation due to a higher degree of supersaturation of Ga₂Se₃ inside the nanoparticle with respect to the rest of the surface. Root growth may occur without the presence of such nanoparticles, but this mechanism may be relevant only for catalyst-free selective area epitaxy, which is not the case of this study. Surface diffusion of Ga from the substrate surface to the droplet is required for NW growth from the nanoparticle in the absence of Ga supply from vapor.

Growth of Ga₂O₃ NWs with no external supply of Ga or O₂ was previously achieved via low vacuum thermal treatment of the GaAs (100) substrate covered with a thin Au film.⁴² Similarly to our case, some voids were found in the substrate,⁴³ and the Ga₂O₃ NW formation was explained by the reaction of GaAs with the Au layer, allowing a supply of Ga atoms which bind with the residual oxygen in the growth chamber.

The stability of GaAs in contact with Au was extensively studied in the past in connection with the electrical properties of metal/semiconductor junctions. It is well documented that Ga migrates into Au at temperatures above 400 °C (see, for example, ref 44 and references therein). Decomposition of the reacted volume of GaAs releases As, which diffuses through a polycrystalline Au–Ga layer and re-evaporates.⁴⁵ The rate of this process can be controlled, for example, by tuning the As₂ pressure in the chamber or using encapsulating layers.⁴⁴

On the basis of the experimental evidence depicted above, we can outline a phenomenological description of the NW growth process in our system as follows: Au-assisted decomposition of GaAs in the annealing step leads to the formation of binary Au–Ga NPs (with a negligible As content), which are usually liquid at temperatures higher than 400 °C depending on the actual Ga content.⁴⁴ The formation of the Au–Ga alloy is demonstrated by the XPS data in Figures 8(a,b) and 9(a,b). Subsequent deposition of Se onto Au–Ga NPs promotes the formation of a supersaturated ternary Au–Ga–Se alloy NP from which the NWs grow. Ga supply comes from the decomposition of the GaAs substrate. Figure 11 clearly demonstrates the presence of voids deep in the GaAs substrate decorated with Au, while in the absence of Au and under otherwise identical conditions the surface remains flat upon exposure to the Se flux. Based on the EDX and XPS data, we suggest that Ga alloys with Au and that this leads to re-evaporation of excess As atoms and explains the formation of voids.

The nanostructure nucleation strictly depends on the presence of the Au nanoparticles that are found at the free end of the NWs and at one extremity of the worm-like structures. Growth is indeed observed only if the GaAs substrate is Au-decorated, either by dewetting of a continuous Au film as in the experiments described above or through size-selected colloidal nanoparticles as in SI 3. In the absence of Au, neither NWs nor worm-like nanostructures are obtained (see Figure 11). This strongly supports the fact that further growth of Ga₂Se₃ NWs and worm-like structures fed by the Ga supply is catalyzed by the ternary Au–Ga–Se nanoparticles. The process is thermally activated: if the substrate temperature is too low, after nucleation as soon as the nanoparticle is depleted from Ga the growth stops, as demonstrated by the data in Figures 1 and 2. The growth process can occur via the VLS or VSS mechanism depending on the Ga and Se content and its

spatial distribution in the NPs (including the shell layer). Solidification of the NP may also be due to a low Ga concentration under insufficient Ga supply from the substrate. The presence of nearly spherical NPs instead of a spherical cap, together with the kinks seldom observed in the NWs, as in Figure 2(b) and Figure 7(d), and the morphology of the worm-like nanostructures that grow when the nanoparticles are large is suggestive of the morphology observed in ZnSe NWs grown by Au-assisted VSS reported by Zannier et al.^{35,46} However, our data do not presently allow for any definite conclusion on the VLS or VSS growth mode. This important question will be addressed elsewhere. It is clear, however, that Ga₂Se₃ forms by binding Ga and Se atoms in the NPs. The known formation enthalpies of the compounds of interest are –87.7 kJ/mol for GaAs,⁴⁷ –159.0 kJ/mol for GaSe,⁴⁸ –405.9 kJ/mol for Ga₂Se₃⁴⁸ (at room temperature), 5.58 kJ/mol for metallic Ga,⁴⁹ –23.9 kJ/mol for AuGa (at 433 °C),⁴⁹ and 24.8 kJ/mol for AuGa₂ (at 427 °C).⁴⁹ Therefore, Ga₂Se₃ is by far the most stable compound and crystallizes from the ternary Au–Ga–Se NPs regardless of their state (solid, liquid, or partially molten). With Ga₂Se₃ being more stable than the Au–Ga compounds, the growth of the Ga₂Se₃ nanostructure continuously depletes from Ga the Au agglomerates lying on the substrate, that therefore continue to trigger the GaAs decomposition, with the formation of voids and penetration of Au agglomerates deep in the substrate (see Figure 11a).

Figure 3 shows that the NW length exhibits a strikingly nonmonotonic dependence on exposure time to the Se flux, with initially linear correlation and saturation at a maximum value, followed by shortening for longer exposure times. Out-of-plane NWs, catalyzed by the smallest Au nanoparticles, always grow simultaneously with thicker in-plane worm-like structures, similarly to what was observed for the VSS-grown ZnSe NWs in ref 46. We speculate that these in-plane structures effectively encapsulate the GaAs substrate⁴⁴ and/or stop the Ga diffusion flux to the NWs at a certain coverage, thus stopping the growth.

According to the data in Figure 2, higher Se fluxes yield smaller maximum NW lengths and shorter critical times after which the NWs start to shorten. The time necessary to cover the GaAs free surface with worm-like structures is shorter in the case of higher Se flux, resulting in the stop of Ga feeding of NW growth at a shorter length.

As the Ga flux is stopped, we can imagine that the Se flux may induce the crystallization of a thin Ga₂Se₃ shell at the surface of the metal nanoparticle. A few nm thick shell is indeed observed in the TEM images as shown in Figure 7(a). Due to the surface sensitivity of XPS, the presence of this shell, the penetration of the larger Au agglomerates deep in the substrate, and the coverage of the GaAs surface with Ga₂Se₃ worm-like structures well justify the complete attenuation of the XPS signal of both the Au 4f and As 3d observed in Figures 8 and 9.

The maximum NW length observed in the explored growth condition was 3 μm and was obtained in the case of growth with low Se BEP. This could not be an intrinsic limit but the results of the competition between in-plane coverage of the surface and out-of-plane NW growth as described above. Backward diffusion of Ga from the NWs to the substrate surface may lead to the NW shortening in the late stage of growth.

We now try to understand more deeply the NW growth process within a diffusion transport model. In the absence of

Ga deposition, growth should be limited by surface diffusion of Ga adatoms released from the GaAs substrate. The standard diffusion equation for Ga adatoms on the NW sidewalls⁵⁰ is then given by

$$D \frac{d^2 n}{dz^2} = \frac{n}{\tau}, \quad n(z=0) = n_s(t), \quad n(z=L) = n_l \quad (1)$$

Here, z is the coordinate along the NW axis; L is the actual NW length (not to be confused with the projected length used elsewhere in this paper); D is the diffusion coefficient; and τ is the effective lifetime of Ga adatoms.⁵¹ The concentration n_s at the substrate surface may be time-dependent because the morphology and even material of the substrate surface (initially GaAs and then Ga₂Se₃) change with the growth time t . In contrast, the concentration n_l at the liquid–solid interface is assumed independent of time under the stationary conditions. The axial NW growth rate is given by⁵⁰

$$\frac{dL}{dt} = -\frac{\Omega}{R} D \frac{\partial n}{\partial z} \Big|_{z=L} \quad (2)$$

Here, Ω is the elementary volume of Ga₂Se₃ in the solid state and R is the NW radius. This growth rate is transport-limited and hence independent of whether the NP is liquid or solid.

From eqs 1 and 2, it is easy to obtain

$$\frac{dL}{dt} = \frac{\Omega \lambda}{\tau R} \frac{[n_s(t) - n_l]}{\tanh(L/\lambda)} \quad (3)$$

with $\lambda = \sqrt{D\tau}$ as the effective diffusion length of the Ga adatoms. This expression is similar to that previously obtained in ref 41, where the growth of CdTe NWs was controlled by a diffusion flux of Te from the substrate in the absence of Te deposition. The NW length saturates at $L/\lambda \gg 1$ when $n_s > n_l$, meaning that no further growth is possible when all adatoms are trapped on the sidewalls or re-evaporated from the surface, as observed in ref 41. Clearly, the growth rate given by eq 3 is positive only if $n_s > n_l$, that is, when Ga adatoms on the substrate surface have a higher concentration than in the liquid droplet and negative otherwise. The case of $n_s < n_l$ corresponds to the so-called negative growth,⁵⁰ in which NWs shorten by evaporating excess Se atoms and transferring Ga atoms from the NP to the substrate along the sidewalls by surface diffusion.

According to ref 52, the diffusion length of Ga adatoms at the growth temperatures is larger than 2 μm (for GaAs NWs), while our Ga₂Se₃ NWs are typically shorter than 1 μm . Therefore, we can use the approximation of $L/\lambda \ll 1$, in which case integration of eq 3 gives

$$L = \sqrt{\frac{2\Omega D}{R}} \left\{ \int_0^t dt' [n_s(t') - n_l] \right\}^{1/2} \quad (4)$$

which does not contain λ . At a time-independent $n_s - n_l > 0$, this results in the diffusion-like growth law $L \propto (Dt/R)^{1/2}$,⁵³ showing that thinner NWs grow faster. The NW length scales as the square root of time and increases toward higher temperatures due to enhanced thermally activated diffusion ($L \propto D^{1/2}$). This qualitatively explains why our NWs grow only at elevated temperatures, as observed in Figure 2. However, according to Figure 3, the NW length first increases linearly with time and then decreases after a critical length has been reached.

This behavior is likely to be associated with a time-dependent concentration of Ga adatoms n_s in eq 4, which is

initially higher than n_l to enable nucleation and growth of NWs and then becomes lower than n_l to start the NW shortening by negative diffusion from the NP to the substrate. We assume that Ga adatoms are produced at the rate J_+ per unit time per unit area of the GaAs substrate exposed to the Se flux and consumed by growing parasitic worm-like structures, which block surface diffusion of Ga to the NW tip. Progressive coverage of the surface by these parasitic structures is described by the simplest Kolmogorov model⁵⁴ in the form $1 - \exp(-\omega t)$, with ω as the corresponding growth rate (1/min). These considerations yield

$$\frac{dn_s}{dt} = J_+ e^{-\omega t} - J_- (1 - e^{-\omega t}), \quad n_s(t=0) = n_l \quad (5)$$

The initial condition corresponds to equilibrium between the droplet and the substrate at $t = 0$, where no growth occurs. Solving this, we obtain the adatom concentration in the form

$$n_s(t) - n_l = \frac{(J_+ + J_-)}{\omega} (1 - e^{-\omega t}) - J_- t \quad (6)$$

showing that $n_s - n_l = J_+ t$ at $\omega t \ll 1$ and $n_s - n_l = (J_+ + J_-)/\omega - J_- t$ at $\omega t \gg 1$. Hence, the force driving the surface diffusion increases linearly with time at the beginning of the growth, the GaAs substrate being still clean. Toward the end of the growth, it decreases due to nucleation and growth of the parasitic worm-like structures and finally becomes negative, which is why the NW lengths finally shorten.

Integrating eq 6 and using the result in eq 4, our final expression for the NW length is given

$$L = vt \left[-\alpha + \frac{4(1+\alpha)}{x} - \frac{2(1+\alpha)}{x^2} (1 - e^{-\omega t}) \right]^{1/2} \quad (7)$$

with $v = \sqrt{(\Omega D J_+)/R}$, $\alpha = J_-/J_+$, and $x = \omega t$. As expected, the linear growth law $L = vt$ always occurs at $\omega t \ll 1$. Figure 12 shows the fits to the mean NW lengths versus time under different Se fluxes, obtained from eq 7 with the parameters summarized in Table 1.

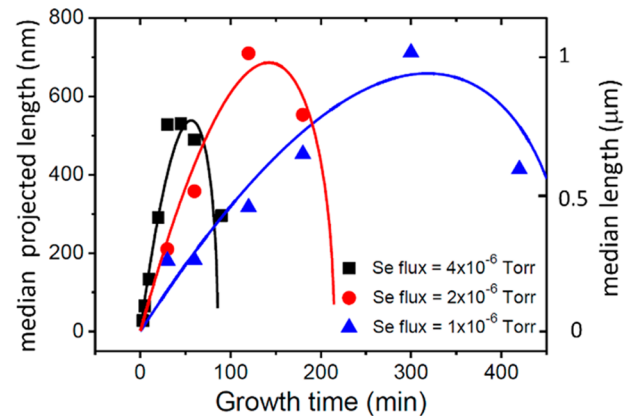


Figure 12. Evolution of the median length of Ga₂Se₃ NWs with time at the fixed temperature of 560 °C and for different Se fluxes (symbols from Figure 3), fitted by eq 7 (lines) with the parameters summarized in Table 1. The elongation rate in the initial linear growth stage is increased for higher Se fluxes. On the other hand, parasitic structures also emerge faster on the rest of the surface, which is why the NW length starts to decrease earlier at higher Se fluxes.

Table 1. Fitting Parameters of Ga₂Se₃ NWs Obtained from the Fits in Figure 12

Se BEP (Torr)	linear elongation rate ν (nm/min)	growth rate of surface coverage ω (L/min)	critical coverage	ratio J_+/J_-
4×10^{-6}	17	0.0058	0.25	5.8
2×10^{-6}	8.6	0.0017	0.24	7.8
1×10^{-6}	3.6	0.00037	0.15	16.7

According to the model, the NW growth in the initial stage is controlled by the production rate of Ga adatoms released from the GaAs surface. This depends on the Se flux: the higher is the latter, and the faster is the GaAs decomposition providing Ga for nucleation and growth of Ga₂Se₃ NWs in the absence of Ga supply from vapor. The NW growth process is therefore limited by Ga transport, but its production rate is enhanced for higher Se input. The axial NW growth rate is therefore faster for higher Se fluxes. On the other hand, parasitic structures also emerge faster under higher Se fluxes, which explains why the NW lengths starts to decrease earlier.

This explains the very different slope angles of the linear parts of elongation rates in Table 1, decreasing from ~ 24 nm/min to ~ 5.3 nm/min as Se BEP decreases from 4×10^{-6} Torr to 1×10^{-6} Torr (these values are given for the actual NW lengths). On the other hand, the maximum NW length is limited by the growth of the parasitic worm-like structures, whose rate should also increase for higher Se fluxes. According to Table 1, the growth rate of the surface coverage decreases from ~ 0.0058 L/min at 4×10^{-6} Se BEP to ~ 0.00037 L/min at 1×10^{-6} Se BEP. It is interesting to note that the maximum NW length is reached at a critical fractional coverage of ~ 0.2 in all cases. Finally, the best fits to the data are obtained for the J_-/J_+ ratio much larger than unity and increasing toward lower Se fluxes. Overall, both the NW growth process and the coverage of the GaAs surface by the parasitic structures occur faster at higher Se fluxes. According to our data, the maximum NW lengths are reached at lower Se fluxes, but this requires much longer growth times (~ 300 min at a Se BEP of 1×10^{-6} Torr).

CONCLUSIONS

In conclusion, we have presented a set of experimental data showing how thin epitaxial Ga₂Se₃ NWs can be obtained on GaAs substrates in the absence of any external Ga supply by a heterovalent exchange reaction assisted by Au NPs. Thicker worm-like Ga₂Se₃ nanostructures are also found lying on the substrate surface. Both kinds of nanostructures display Au-rich NPs at the tip. Chemical and structural analysis of the NPs and NWs at different stages of growth demonstrated that the presence of Au NPs is essential for obtaining Ga₂Se₃ NWs by this method. It has been found that the NW elongation stops at a growth time that depends on the incoming Se flux. Further increase in time at the growth temperature leads to NW shortening at a rate which is independent of the Se supply. This growth mechanism has been described within a diffusion transport model, which explains the nonmonotonic behavior of the NW length as due to the blocking of the Ga supply from the substrate when covered with parasitic worm-like structures and the ensuing negative diffusion of the Ga atoms from the NPs to the NW sidewalls. The growth of Ga₂Se₃ NWs has been demonstrated here for the first time to our knowledge and can work equally well in a wide range of epitaxy techniques.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.0c03216>.

Growth with and without bismuth flux. Determination of the growth direction of the NWs. Influence of the Au NP diameter on the morphology of Ga₂Se₃ nanostructures. Diameter of the NWs versus growth time and Se BEP. Chemical composition of worm-like nanostructures (PDF)

AUTHOR INFORMATION

Corresponding Author

Silvia Rubini – Istituto Officina dei Materiali, Consiglio Nazionale delle Ricerche, Trieste, Italy; orcid.org/0000-0001-5215-2223; Phone: +39 040 3756437; Email: rubini@iom.cnr.it

Authors

Federico Berto – Istituto Officina dei Materiali, Consiglio Nazionale delle Ricerche, Trieste, Italy; Dipartimento di Fisica, Università di Trieste, Trieste, Italy; orcid.org/0000-0001-7602-2749

Niloofar Haghghian – Istituto Officina dei Materiali, Consiglio Nazionale delle Ricerche, Trieste, Italy

Katja Ferfolja – University of Nova Gorica, Nova Gorica, Slovenia; orcid.org/0000-0001-8228-3232

Sandra Gardonio – University of Nova Gorica, Nova Gorica, Slovenia; orcid.org/0000-0002-5560-718X

Mattia Fanetti – University of Nova Gorica, Nova Gorica, Slovenia; orcid.org/0000-0002-2437-5179

Faustino Martelli – Istituto per la Microelettronica e Microsistemi, Consiglio Nazionale delle Ricerche, Roma, Italy; orcid.org/0000-0002-4496-4165

Valentina Mussi – Istituto per la Microelettronica e Microsistemi, Consiglio Nazionale delle Ricerche, Roma, Italy

Vladimir G. Dubrovskii – ITMO University, 197101 St. Petersburg, Russia; orcid.org/0000-0003-2088-7158

Igor V. Shtrom – St. Petersburg State University, 199034 St. Petersburg, Russia

Alfonso Franciosi – Istituto Officina dei Materiali, Consiglio Nazionale delle Ricerche, Trieste, Italy; Dipartimento di Fisica, Università di Trieste, Trieste, Italy

Complete contact information is available at:

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Author Contributions

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Notes

The authors declare no competing financial interest.

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