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Growth of GaAs Nanowire – Graphite Nanoplatelet Hybrid Structures

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We study the formation of GaAs nanowire - graphite nanoplatelet hybrid nanostructures. The quasi van-der-Waals epitaxy was used to grow the vapor-liquid-solid nanowires on a silicon substrate covered by graphite nanoplatelets. We have found that either horizontal or inclined nanowires can form depending on the relative positions of graphite nanoplatelets, as well as on the placement of catalyst nanoparticles. We present the model, which is capable of the description of the experimentally observed scenarios of planar and non-planar NW growth. Both theoretical and experimental studies show that the use of nanoplatelet substrate allows engineering the morphology of planar and inclined nanowires.

Introduction

In recent years, graphene and graphite substrates have been used as the base for a family of graphene-semiconductor hybrid materials^{1–4}. These materials have already found their use in several optoelectronic applications: photodetectors^{5–7}, LEDs, lasers, solar cells^{8,9}, wearable electronics, and novel conceptual devices¹⁰. Despite the successful realizations in particular systems, the epitaxial combination of graphitic materials with bulk and thin film semiconductors remains challenging due to the absence of dangling bonds and hard nucleation¹¹. Overcoming of these hurdles seems to be possible in the synthesis of semiconductor nanowires (NWs)^{12,13}.

It is well known that quasi van-der-Waals epitaxy (qvWE) provides the interaction mechanism for integration of 3D semiconductor materials with dangling bonds on graphene or graphite^{12,14,15}. In qvWE, the degree of strain with graphitic substrate depends on particular sites of absorption of the semiconductor atoms, which can help to accommodate the lattice mismatch^{12,15}. In addition, large lateral surface of NWs allows the elastic strain to relax on NW sidewalls¹⁶. Thus, qvWE is the promising approach for the formation of high-quality NWs-graphene hybrid structures for those semiconductor materials which cannot be integrated to graphitic substrates directly. Indeed, recent studies have demonstrated the epitaxial relation between graphitic surfaces

and III-V NWs grown either by molecular beam epitaxy (MBE)¹⁷ or metalorganic vapor phase epitaxy (MOVPE)^{18–20}. In these works, the vapor-liquid-solid (VLS) approach was used to assist the nucleation and growth of defect-free GaAs NWs on graphite and graphene. Various graphitic substrates have been used in the attempts of GaAs qvWE growth: epitaxial graphene¹⁹, graphite¹⁷, and carbon nanotubes²¹. Meanwhile, almost no attention was attracted to the NW growth on graphite nanoplatelets (GNPs).

GNPs are low defect graphitic surfaces with lateral sizes of few microns and thickness of tens of monolayers (MLs) which can be deposited on almost any substrate, including silicon, without complex processing with coverage up to centimeter range or more^{22–25}. Such nanomaterials are attractive due to their planar structure, lightweight, high aspect ratio, electrical conductivity, low cost, mechanical toughness. Moreover, GNPs can be transferred to another substrate after the NW growth^{26,27} or manipulation within the same substrate for 3D surface structuration. These various features enable the use of GNPs as building blocks for low-power, flexible and wearable electronics as well as for composite materials^{24,28,29}.

Despite the advantages of the nanoplatelets, NW growth on GNPs remains almost unexplored. Only recently, Meyer-Holdt et al. reported experimental results on Ag-catalyzed growth of InAs NWs on graphite flakes²⁷. In our work, the Au-catalyzed VLS growth of GaAs NWs on GNPs is studied for the first time. The millimeter-scale parts of SiO₂/Si (111) substrate were covered by micron-scale GNPs without any pre-defined ordering. As we show in this work, relative positions of GNPs, as well as placement of catalyst nanoparticles on the specific GNP, both strongly impact the NW growth. We present the model for the non-trivial process of NW formation, which brings together the impacts of supersaturation, catalyst composition, surface energies, and substrate features to describe the scenario of NW growth on GNPs.

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Results and discussion

In this work, we investigate the Au-catalyzed VLS MOVPE growth of GaAs NWs on the GNPs, which were sonicated to thermally oxidized Si (111) substrates. Prior the growth, colloidal Au nanoparticles were deposited on the sample surfaces. The detailed information on the GNP preparation, colloid processing and MOVPE growth parameters can be found in the Experimental section.

Figure 1a shows the typical top-view SEM image of GaAs NWs on GNPs obtained by scanning electron microscopy (SEM). The NWs have been found to grow either in or out of the plane of the substrate depending on the initial position of the droplet. NWs seeded by the droplets in the center of the nanoplatelet were observed to grow horizontally (in the plane of the substrate). Meantime, SEM images show that in the vicinity of GNP edge, Au particles initiate mostly inclined growth (out of the substrate plane). Furthermore, if horizontal NWs reach the edge of GNP, they are noticed to proceed with the inclined growth. Thus, the observed NWs belong to one of three types illustrated schematically in Figure 1c-e: (i) in-plane horizontal NWs (ii) non-planar inclined NWs (iii) NWs with the transition from planar to non-planar growth.

The majority of all three types of NWs show slight tapering with the similar mean diameter of 85 nm next to the base and of 60 nm next to the catalyst droplet. The mean length is also similar for different types of nanowires and is about 1.8 μm .

Statistics of NWs of different types is summarized in Figure 1b. 11% of NWs were obtained from the seeds in the vicinity of NW edge and all of them belong to the inclined type. 89% of NWs were observed to nucleate from the seeds in the central parts of GNPs. Among them, only 2% of the total number of NWs have grown inclined, which, as discussed below, can be related to substrate imperfections. 23% of NWs grew horizontally and did not encounter any substrate feature. 45% of NWs initiated the

horizontal growth and then switched to inclined by reaching the GNP edge. 9% of NWs were observed to change the direction of horizontal growth at the incidence with another GNP (GNP barrier) and 5% at the incidence with another NW (NW barrier). 3% of the obtained NWs show the transition from in-plane to inclined by contacting another horizontal NW. About 1% of NWs demonstrate the transition from horizontal to vertical direction by encountering a GNP defect.

Most of previous theoretical^{17,19,30,31} and experimental^{18,27,32,33} studies of VLS III-V and group IV NWs on graphitic substrates miss the detailed description of the planar to non-planar transitions and the impact of substrate features. In the study of Au-catalyzed GaAs NWs on Si(111) substrates the transition from horizontal to vertical growth was attributed to the coalescence of the horizontal NW trace with the parasitic non-VLS nanoislands³⁴. However, no measurable surface growth was indicated in our samples. Thus the explanation of the obtained shapes should rely on other principles.

In order to model the observed NW growth, we extend the recent nucleation-based approaches³⁵. Based on the experimental results, the model considers the NW growth on three types of GNP-structured surfaces: (i) flat central parts of the nanoplatelets, (ii) regions next to the nanoplatelet edge and (iii) areas next to the barrier, formed either by nanoplatelet or NW.

Growth in flat central regions of GNPs

The analysis of SEM images shows that the majority of NWs in flat central regions of GNPs growth horizontally (in the plane of the substrate). This observation generally agrees with the results of Au-seeded growth of GaAs NWs on pyrolytic graphite substrates¹⁹. Therefore, we follow and extend the previously suggested nucleation-based approaches^{19,35–37} to model the planar and non-planar NW growth in our experiments.

Figure 1. (a) Top-view SEM image of Au-catalyzed GaAs nanowires on GNP (dark area) and oxide surface (bright area). Scale bar corresponds to 500 nm. (b) NW statistics in different parts of the substrate (total number of NWs corresponds to 100%). Schematics for NW in-plane (c), inclined (d) modes and the combination of in-plane and inclined modes (e).

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The nucleation theory of VLS process assumes that the interface energies together with the supersaturation in the catalyst droplet are considered as the key quantities to determine whether NWs grow horizontally or inclined³⁸. In both modes, III-V NWs typically grow layer-by-layer within a VLS process^{39–43}. It presumes that the nucleation of a new ML occurs after the completion of the previous one.

Thus, theoretically, the stable growth regime corresponds to the highest nucleation probability or the lowest formation energy of the critical nucleus^{44–46}. The formation energy as the function of surface energy for a 2D nucleus of size i consist of two terms⁴⁵:

$$\Delta G = -(\Delta\mu - G_v)i + G_s i^{1/2}, \quad (1)$$

where $\Delta\mu$ is the difference in chemical potentials per III-V pair of atoms. The first term in the right-hand side of the equation (1) is proportional to i and, besides $\Delta\mu$, includes G_v , which denotes the energy per pair of atoms, required to form the top and the bottom interfaces. The second term is proportional to the square root of i and accounts the contribution of the side facets with total interface energy per pair G_s .

In the classical theory, the nucleation probability decreases exponentially with the maximum of formation energy⁴⁷, which we denote as ΔG_* . From the differentiation of Equation (1), ΔG_* can be found as

$$\Delta G_* = G_s^2/4(\Delta\mu - G_v). \quad (2)$$

It is well known that the thermodynamically preferred process corresponds to minimal possible ΔG_* . According to (2), the smallest value of ΔG_* is characterized by minimal G_s and G_v (which maximizes the difference $\Delta\mu - G_v$).

We use the above formalism of nucleation theory in our approach to the modeling of GaAs NWs on GNP surfaces. Obviously, the values of G_v and G_s depend on the position of the nucleus either on the bare substrate or top of the previous ML. If the nucleus forms on the bare substrate, G_v sums up the energies of top (Γ_{top}) and bottom (Γ_{bot}) interfaces with the contribution from the eliminated area of the surface (Γ_{surf}): $G_v = \Gamma_{top} + \Gamma_{bot} - \Gamma_{surf}$. Otherwise, if the new ML nucleates on top of the previous one, $\Gamma_{top} = \Gamma_{surf}$ and $\Gamma_{bot} = 0$ in the absence of twinning or defect formation. Hence $G_v = 0$ and according to (2), the mode of axial growth is defined by G_s . The energetics of side interfaces $G_s = \sum_k \alpha_k \gamma_k$ consists of the contributions from each side of the nucleus $\alpha_k \gamma_k$, proportional to interface energy γ_k and its fraction in the total area of all side facets α_i . In our notations, the index k corresponds to the type of interface: nucleus-graphite interface (α_{nG} and γ_{nG}), nucleus-vapor interface (α_{nV} and γ_{nV}), and nucleus-liquid interface (α_{nL} and γ_{nL} for arbitrary liquid and γ_{nGa} or γ_{nAuGa} for gallium and gold-gallium catalyst) as illustrated in Figure 2.

In the absence of the liquid phase $\Gamma_{top} - \Gamma_{sub}$ for the solid-vapor interface are typically larger than the energies of top interface with gold or gallium catalyst^{48–51}, while Γ_{bot} remains identical. Whereas, the value of $\Delta\mu$ inside the droplet is close to the value of $\Delta\mu$ for adatoms on the substrate without liquid⁵². Therefore, the nucleation of GaAs on graphite inside the droplet corresponds to a lower energy barrier ΔG_* than the nucleation on the bare substrate. Hence the GaAs is expected to crystallize preferably inside catalyst droplets. Indeed, all the observed NWs have droplets at one of the ends. We also relate the absence of parasitic growth in our experiments with hard nucleation without liquid catalyst, similar to previous works^{19,30}.

Figure 2. Schematic for facets of the critical nucleus and corresponding interface energies.

Next, we discuss the processes during the growth of individual NW. After the completion of the very first ML, each next one most probably nucleates on top of the previous one because it corresponds to minimal G_v (as we have shown previously, $G_v = 0$ in this case). Indeed, VLS NWs are known to grow layer-by-layer. From the thermodynamic point of view, the interface between the new ML and the substrate forms only if its energy is less than the total energy of liquid-nanowire and liquid-substrate interfaces. In this case, the NW is supposed to grow horizontally. Otherwise, if the formation of the interface with the substrate is unfavorable energetically, the inclined NW is expected to form. Thus, for arbitrary liquid (index “L”) and substrate (index “Sub”) materials, we can formulate the conditions for preferred horizontal and inclined growth as:

$$\begin{cases} \gamma_{nSub} - \gamma_{SubL} < \gamma_{nL}, & \text{planar growth,} \\ \gamma_{nSub} - \gamma_{SubL} > \gamma_{nL}, & \text{non-planar growth.} \end{cases} \quad (3)$$

Evidently, the values of interface energies γ_{SubL} and γ_{nL} depend on the composition of the liquid phase. The AuGa catalyst of 70% of gold and 30% of gallium was observed in the *in-situ* X-ray energy dispersive spectroscopic measurements during the Au-catalyzed growth of GaAs NWs at the temperatures similar to our growth temperature⁵³. For the aforesaid composition of liquid catalyst $\gamma_{nG} - \gamma_{GAuGa} = 0.13 \text{ J/m}^2$ and $\gamma_{nAuGa} = 0.15 \text{ J/m}^2$ ⁵¹. It means that $\gamma_{nG} - \gamma_{GAuGa} < \gamma_{nAuGa}$ and thus, the condition for planar growth in (3) is fulfilled. Other words, our model results are consistent with the observed in the experiments horizontal NW in the central parts of the GNPs.

We should note here that the encounter of defect or residual parts of poly-L-lysine (which were used for deposition of colloid particles) may affect the interface energies and thus cause the inclined growth in central parts of GNPs, which were observed in 2% of NWs.

Growth next to the edge of nanoplatelet

SEM studies (see Figure 1a) show that for the considered growth durations, many Au-seeded NWs are long enough to reach the edges of the nanoplatelets being nucleated in the central area. In the vicinity of GNP edge, the horizontal NWs are observed to switch to inclined growth.

At the GNP edge catalyst droplet moves on SiO_2 surface. Inside the droplet on oxide surface, the additional energy for the formation of the interface between the new ML and the substrate is estimated as $\gamma_{nO} - \gamma_{OAuGa} = 0.2 \text{ J/m}^2$ ⁵¹, where γ_{nO} and γ_{OAuGa} are energies of oxide-nucleus and oxide-gold catalyst interfaces respectively. One can note that the formation of the oxide-NW interface requires more energy than the formation of the inclined sidewall. Namely, $\gamma_{nO} - \gamma_{OAuGa} > \gamma_{nAuGa}$ which means that, according to (3), the condition for inclined growth is fulfilled. Hence, the inclined growth of Au-

catalyzed NWs is more probable than the horizontal growth on the oxide surface. Figure 3a illustrates the transformation of planar NW growing on GNP into inclined NW at the edge of oxide surface described by our model.

As mentioned before, we consider the AuGa catalyst, which consists of 70% of gold and 30% of gallium⁵³. However, the composition of the catalyst is known to be sensitive to both growth temperature and precursor fluxes^{53,54}. Thus, our analysis should be extended to the cases of different Au content in the catalyst. Unfortunately, the exact dependences of interface energies on AuGa liquid composition are generally unknown. Nevertheless, the values of γ_{nL} and γ_{SubL} for pure gallium and aforesaid gold-gallium composition can be found in the literature^{48,51,55}. Hence, we approximate the dependences of the interface energies on Au concentration in the droplet by connecting the values for known liquid compositions (dots in Figure 3b) with the straight dashed lines. Figure 3b shows the approximations for $\gamma_{nO} - \gamma_{OL}$ (labeled "Oxide"), $\gamma_{nG} - \gamma_{GL}$ (labeled "GNP") and γ_{nL} as the functions of Au concentration in the catalyst. As one can see in Figure 3b, both $\gamma_{nO} - \gamma_{OL}$ and $\gamma_{nG} - \gamma_{GL}$ larger than γ_{nL} at low Au concentrations and smaller than γ_{nL} at high Au concentrations. Therefore, Au-rich particles should promote horizontal growth, whereas Ga-rich particles should induce inclined growth. Furthermore, the approximated points of intersection between γ_{nL} and $\gamma_{Sub} - \gamma_{SubL}$ can be considered as boundaries between inclined and horizontal growth for arbitrary substrate and variable liquid composition. Meantime, the catalyst with of 30% Ga and 70% Au in Figure 3b corresponds to horizontal NWs on GNP and inclined NWs on oxide surface, which correlates well with the experimental observations of horizontal to inclined transformation at the edges of GNPs.

Figure 3. (a) Schematic of Au-catalyzed GaAs NW growth at the GNP edge. (b) $\gamma_{nSub} - \gamma_{SubL}$ dependences on the atomic concentration of Au in catalyst approximated by straight lines for GNP and SiO_x surfaces on the substrate. The points of intersection with γ_{nL} line separate the concentrations of Au at which the inclined and in-plane NWs are expected (see the text).

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Growth next to the barrier

In central parts of GNPs, planar NWs were observed to change the character of their growth in the incidence with the barrier formed either by another GNP or by another NW. Based on SEM analysis (see Figure 1), we distinguish four different types of NWs depending on their behavior after contacting the barrier. NWs of the first and the second types are planar and either follow or avoid the barrier substrate boundary. Meanwhile, NWs of the third and the fourth types detaches from the substrate and either follow or avoid the surface of the barrier. All four types of NWs are summarized in Figure 4a-d. Thus the formation of each type of NWs depends on whether the interfaces with the barrier and with the substrate were formed during the growth or not. Further, we discuss the conditions required for each type of NWs to form after contacting the barrier.

The NWs of the first type were observed to form along the boundary between the barrier and the substrate, which we call "Alignment" growth mode illustrated in Figure 4a.

On the other hand, the realization of the "Alignment" mode is unexpected when NWs do not form the interface with the barrier. It is probable if the formation of the nanowire-barrier interface requires more energy than the formation liquid-nucleus interface. If the condition for formation of NW-substrate interface is still valid, after contacting the barrier, the NW will proceed to grow horizontally, but not along the barrier. Such NWs, we attribute to the second type shown in Figure 4b, which we label "Reflection". The latter behavior was also reported in Ref. ¹⁹ for GaP NWs, but it has not found any theoretical explanation up to now.

The NWs of the third type detach from the substrate and form on top of the barrier just after contacting it. Therefore, we label the corresponding growth mode as "On-barrier" (Figure 4c). It worth to mention that the conditions for detachment from the substrate should be valid only in the vicinity of the barrier. Otherwise the in-plane growth before the incidence with the barrier would be unfavorable.

	In contact with the barrier	Avoid the barrier
In contact with the substrate	(a) Type 1 – Alignment $\gamma_{nL} + \gamma_{SubL} > \gamma_{nSub}$$\gamma_{nB} - \gamma_{BL} < \gamma_{nL}$	(b) Type 2 – Reflection $\gamma_{nL} + \gamma_{SubL} > \gamma_{nSub}$$\gamma_{nB} - \gamma_{BL} > \gamma_{nL}$
Avoid the substrate	(c) Type 3 – On-barrier $\gamma_{nL} + \gamma_{SubL} < \gamma_{nSub}$$\gamma_{nB} - \gamma_{BL} < \gamma_{nL}$	(d) Type 4 – Vertical $\gamma_{nL} + \gamma_{SubL} < \gamma_{nSub}$$\gamma_{nB} - \gamma_{BL} > \gamma_{nL}$

Figure 4. The observed types of GaAs NWs on GNP: (a) "Alignment"; (b) "Reflection"; (c) "On-barrier"; (d) "Vertical". (e) Possible directions of NW growth in the incidence with the barrier. The scale bars correspond to 200 nm

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The SEM image in Figure 4d shows the example of the NWs of type 4, which grew vertically after contacting the barrier, and thus, they have formed the interfaces neither with substrate nor with the barrier. Thus we naturally call such NWs “Vertical”. The inclined growth of NW after contacting the barrier is also possible (but rarely observed) under similar conditions if the twin defects form in the NW structure⁵⁶.

As shown in previous sections, the formation of the interface with the substrate requires $\gamma_{nSub} - \gamma_{SubL} < \gamma_{nL}$. Similarly, the binding to the barrier implies that $\gamma_{nB} - \gamma_{BL} < \gamma_{nL}$, where γ_{nB} and γ_{BL} are energies of barrier interfaces with the nanowire sidewall and with catalyst liquid respectively. Thus, each of the aforementioned four growth modes corresponds to specific combination of two inequalities in terms of interface energies for the formation of NW-substrate and NW-barrier interfaces. Therefore, in theory, the discussed above comparison of $\gamma_{nSub} - \gamma_{SubL}$ and $\gamma_{nB} - \gamma_{BL}$ with γ_{nL} allows one to predict the growth mode in the incidence with the barrier. However, in practice, the considered interface energies depend on the barrier material and composition of the catalyst, which may fluctuate from wire to wire within one substrate. Meanwhile, γ_{nSub} is the only interface energy which remains constant for a given substrate and NW material. Hence, in order to characterize the impact of the barrier material and the catalyst composition, one should consider two variables $\gamma_{SubL} + \gamma_{nL}$ and $\gamma_{nB} - \gamma_{BL}$ instead of $\gamma_{nB} - \gamma_{BL}$, $\gamma_{nSub} - \gamma_{SubL}$, and γ_{nL} . The first

variable, $\gamma_{SubL} + \gamma_{nL}$, characterizes the liquid composition and, according to the criterion in (3), should be compared with the constant γ_{nSub} . The second variable, $\gamma_{nB} - \gamma_{BL}$, characterizes the dependence of interface energies on the material of the barrier and also depends on the liquid composition via γ_{BL} . Hence, one can consider $\gamma_{SubL} + \gamma_{nL}$ (liquid composition) as the independent variable and $\gamma_{nB} - \gamma_{BL}$ as the dependent variable. Thus, the $(\gamma_{nB} - \gamma_{BL}) - (\gamma_{SubL} + \gamma_{nL})$ diagram can be obtained if the dependences of interface energies on the concentration of gold in the catalyst are known.

Similar to Figure 3, Figure 5 was obtained by plotting and connecting with straight lines the values of $\gamma_{nB} - \gamma_{BL}$ calculated for pure Ga and AuGa catalyst in the cases of GNP and NW barrier with mismatched (γ_{nNW} , γ_{NWGa} and γ_{NWAuGa}) and matched ($\gamma_{nNW'}$, $\gamma_{NW'Ga}$ and $\gamma_{NW'AuGa}$) lattice. The positions of the left and the right axes correspond to pure Ga and AuGa catalyst, for which the values of surface energies were calculated (see the Electronic Supplementary Material for details). Solid lines for $\gamma_{SubL} + \gamma_{nL} = \gamma_{nSub}$ and $\gamma_{nB} - \gamma_{BL} = \gamma_{nL}$ in Figure 5 delineate four regions. Each region in Figure 5 corresponds to one preferred growth mode: “Alignment” – orange region, where $\gamma_{nSub} < \gamma_{SubL} + \gamma_{nL}$ and $\gamma_{nB} - \gamma_{BL} < \gamma_{nL}$; “Reflection” – green region, where $\gamma_{nSub} < \gamma_{SubL} + \gamma_{nL}$ and $\gamma_{nB} - \gamma_{BL} > \gamma_{nL}$; “Inclined or vertical” – red region, where $\gamma_{nSub} > \gamma_{SubL} + \gamma_{nL}$ and $\gamma_{nB} - \gamma_{BL} > \gamma_{nL}$; “On-barrier” – blue region, where $\gamma_{nSub} > \gamma_{SubL} + \gamma_{nL}$ and $\gamma_{nB} - \gamma_{BL} < \gamma_{nL}$.

Figure 5. $(\gamma_{nB} - \gamma_{BL}) - (\gamma_{SubL} + \gamma_{nL})$ diagram for NW growth on the graphitic surface. Solid lines correspond to $\gamma_{SubL} + \gamma_{nL} = \gamma_{nSub}$ (green) and $\gamma_{nB} - \gamma_{BL} = \gamma_{nL}$. Dotted lines show the linear approximations to $\gamma_{nB} - \gamma_{BL}$ estimated for different catalyst compositions in the cases of GNP and NW barrier with mismatched and matched lattice.

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Thus, according to Figure 5, NWs with Au-rich catalysts preferably proceed in "Reflection" growth mode after touching another NW. Meanwhile, the incidence with a graphene barrier promotes the "Alignment" mode. The in-plane growth of a NW with Ga-rich and purely Ga catalyst is generally unstable, as it was noted above. In the incidence with both types of barriers, the vertical or inclined growth is expected. The "On-barrier" mode is favorable only in the short interval of catalyst compositions in the case of GNP barrier.

The above four modes cover all possible combinations of surface energies in (3) for the substrate and the barrier. As well, they describe all the shapes of GaAs NWs observed in our growth experiments. Vice versa all the observed NW shapes match the thermodynamically preferred NW geometry. Therefore, the combination of catalyst composition and GNP relative positions define the most probable scenario of NW growth. Thus, the modeling results can be used for the controlled growth of NW on prepared substrates.

Size and relative positions of GNPs can be controlled by means of synthesis, lithography, and micromanipulation. Together with our results, it opens the perspectives in NW shape engineering and design of hybrid graphite-semiconductor structures towards the alternatives to template-assisted⁵⁷ and template-free⁵⁸ approaches to guided growth.

In this work, we focus on GaAs growth whereas similar GNP-based approaches can be developed for other III-V materials, for example, InAs or GaP. In this way it is worth to mention that our modeling approach does not refer directly to the nature of the interactions in the epitaxial process and solely address the difference in energies of solid-NW and solid-liquid interfaces. Thus, on the one hand, it means that the generalization of our results to other substrates with van-der-Waals interaction requires the knowledge of corresponding surface energies. On the other hand, it also means that our theoretical approach may be used not only for qvdWE but also for conventional epitaxy with covalent bonding.

Experimental

GNPs were obtained by liquid phase chemically assisted sonication-induced exfoliation of natural graphite description. The exfoliation and the following thermal defect "healing" were similar to the methods reported in²³. The detailed analysis of individual GNPs (crystal structure, morphology, electrical properties) was reported in our previous works^{23,59} and revealed the presence of rare oxygen impurities. It was also demonstrated that during the exfoliation some ripplocations and dislocations could form in GNPs. However, the annealing process was shown to eliminate most of these defects²³.

GaAs NWs were grown on nanoplatelet substrates in a horizontal flow atmospheric pressure metalorganic vapor phase epitaxy (MOVPE). Trimethylgallium (TMGa) and tertiarybutylarsene (TBAs) were used as precursors. Hydrogen was used as a carrier gas and the total reactor gas flow rate was ~ 5 l/min (slm). Prior to the growth, the substrates were treated with poly-L-lysine (PLL) solution to enhance the NPs adhesion. Then, Au NPs were deposited onto the substrate, and kept 1 minute in air before drying the substrate with a nitrogen blow gun. A 60 nm diameter colloidal gold (Au) nanoparticles solution (BBI International, UK) was used as the catalyst. The substrates were annealed in situ at 650 °C for 10 minutes under hydrogen flow to desorb the surface contaminants. The growth temperature was fixed at 465 °C for 40 s and the TMGa and TBAs flows were 10.8 μmol/min and 270 μmol/min, respectively, yielding a nominal V/III ratio of ~25. After the growth TMGa source was switched off while keeping the TBAs flow on until the reactor cooled down to 250 °C to protect the NW surface from desorption. The growth temperatures reported in this work are thermocouple readings of the lamp-heated graphite susceptor, which are slightly higher than the real substrate surface temperature. Structural properties and morphology of the NWs were studied using scanning electron microscopy (SEM) (Zeiss Supra 40) operated at 10 keV.

Conclusions

In conclusion, the successful growth of Au-catalyzed GaAs NWs was demonstrated on GNPs. We have investigated, both theoretically and experimentally, the growth scenarios of planar and non-planar NW growth and describe how the edges and barriers on GNPs guide the horizontal NWs and switch the growth from horizontal to inclined regime. Namely, gold-rich seeds on flat central regions of GNPs promote the horizontal growth of GaAs NWs. Under the same conditions, the horizontal NW growth with gallium catalyst is unstable and tends to turn to the inclined or vertical direction. The use of nanoplatelet substrate allows engineering the morphology of planar NWs: (i) the GNP boundary induces the transition from planar to inclined growth; (ii) incidence with GNP barrier aligns the nanowire growth with the barrier interface; (iii) contact with nanowire changes the direction of planar growth in avoidance of the contacted nanowire.

Conflicts of interest

There are no conflicts of interest to declare.

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References

- 1 W. Jie and J. Hao, *Nanoscale*, 2014, **6**, 6346–6362.
- 2 X. Li, L. Tao, Z. Chen, H. Fang, X. Li, X. Wang, J.-B. Xu and H. Zhu, *Appl. Phys. Rev.*, 2017, **4**, 021306.
- 3 A. Di Bartolomeo, *Phys. Rep.*, 2016, **606**, 1–58.
- 4 C. Xie, Y. Wang, Z.-X. Zhang, D. Wang and L.-B. Luo, *Nano Today*, 2018, **19**, 41–83.
- 5 A. V. Babichev, H. Zhang, P. Lavenus, F. H. Julien, A. Y. Egorov, Y. T. Lin, L. W. Tu and M. Tchernycheva, *Appl. Phys. Lett.*, 2013, **103**, 201103.
- 6 Y. Wu, X. Yan, X. Zhang and X. Ren, *Appl. Phys. Lett.*, 2016, **109**, 183101.
- 7 L. Shen, E. Y. B. Pun and J. C. Ho, *Mater. Chem. Front.*, 2017, **1**, 630–645.
- 8 C. Xie, P. Lv, B. Nie, J. Jie, X. Zhang, Z. Wang, P. Jiang, Z. Hu, L. Luo, Z. Zhu, L. Wang and C. Wu, *Appl. Phys. Lett.*, 2011, **99**, 133113.
- 9 P. K. Mohseni, G. Lawson, A. Adronov and R. R. LaPierre, *IEEE J. Sel. Top. Quantum Electron.*, 2011, **17**, 1070–1077.
- 10 S. Vaitiekėnas, A. M. Whitaric, M.-T. Deng, F. Krizek, J. E. Sestoft, C. J. Palmstrøm, S. Marti-Sanchez, J. Arbiol, P. Krogstrup, L. Casparis and C. M. Marcus, *Phys. Rev. Lett.*, 2018, **121**, 147701.
- 11 J. Hass, W. A. de Heer and E. H. Conrad, *J. Phys. Condens. Matter*, 2008, **20**, 323202.
- 12 Y. Alaskar, S. Arafat, I. Martinez-Velis and K. L. Wang, in *Two-dimensional Materials - Synthesis, Characterization and Potential Applications*, ed. P. K. Nayak, InTech, 2016.
- 13 Y. Alaskar, S. Arafat, D. Wickramaratne, M. A. Zurbuchen, L. He, J. McKay, Q. Lin, M. S. Goorsky, R. K. Lake and K. L. Wang, *Adv. Funct. Mater.*, 2014, **24**, 6629–6638.
- 14 A. Koma, *J. Cryst. Growth*, 1999, **201–202**, 236–241.
- 15 W. C. Lee, K. Kim, J. Park, J. Koo, H. Y. Jeong, H. Lee, D. A. Weitz, A. Zettl and S. Takeuchi, *Nat. Nanotechnol.*, 2015, **10**, 423–428.
- 16 F. Glas, *Phys. Rev. B*, 2006, **74**, 121302.
- 17 A. M. Munshi, D. L. Dheeraj, V. T. Fauske, D.-C. Kim, A. T. J. van Helvoort, B.-O. Fimland and H. Weman, *Nano Lett.*, 2012, **12**, 4570–4576.
- 18 P. K. Mohseni, A. Behnam, J. D. Wood, C. D. English, J. W. Lyding, E. Pop and X. Li, *Nano Lett.*, 2013, **13**, 1153–1161.
- 19 J. Wallentin, D. Kriegner, J. Stangl and M. T. Borgström, *Nano Lett.*, 2014, **14**, 1707–1713.
- 20 M. A. Baboli, M. A. Slocum, H. Kum, T. S. Wilhelm, S. J. Polly, S. M. Hubbard and P. K. Mohseni, *CrystEngComm*, 2019, **21**, 602–615.
- 21 P. K. Mohseni, G. Lawson, C. Couteau, G. Weihs, A. Adronov and R. R. LaPierre, *Nano Lett.*, 2008, **8**, 4075–4080.
- 22 A. V. Alaferdov, A. Gholamipour-Shirazi, M. A. Canesqui, Y. A. Danilov and S. A. Moshkalev, *Carbon N. Y.*, 2014, **69**, 525–535.
- 23 A. V. Alaferdov, R. Savu, M. A. Canesqui, Y. V. Kopelevich, R. R. da Silva, N. N. Rozhkova, D. A. Pavlov, Y. V. Usov, G. M. de Trindade and S. A. Moshkalev, *Carbon N. Y.*, 2018, **129**, 826–829.
- 24 A. V. Alaferdov, R. Savu, T. A. Rackauskas, S. Rackauskas, M. A. Canesqui, D. S. de Lara, G. O. Setti, E. Joanni, G. M. de Trindade, U. B. Lima, A. S. de Souza and S. A. Moshkalev, *Nanotechnology*, 2016, **27**, 375501.
- 25 K. Chen and D. Xue, *J. Colloid Interface Sci.*, 2014, **436**, 41–46.
- 26 J. Jeong, K.-A. Min, D. H. Shin, W. S. Yang, J. Yoo, S. W. Lee, S. Hong and Y. J. Hong, *Nanoscale*, 2018, **10**, 22970–22980.
- 27 J. Meyer-Holdt, T. Kanne, J. E. Sestoft, A. Gejl, L. Zeng, E. Johnson, E. Olsson, J. Nygård and P. Krogstrup, *Nanotechnology*, 2016, **27**, 365603.
- 28 D. D. L. Chung, *J. Mater. Sci.*, 2016, **51**, 554–568.
- 29 P. Cataldi, A. Athanassiou and I. Bayer, *Appl. Sci.*, 2018, **8**, 1438.
- 30 E. Mataev, S. K. Rastogi, A. Madhusudan, J. Bone, N. Lamprinakos, Y. Picard and T. Cohen-Karni, *Nano Lett.*, 2016, **16**, 5267–5272.
- 31 Y. Alaskar, S. Arafat, Q. Lin, D. Wickramaratne, J. McKay, A. G. Norman, Z. Zhang, L. Yao, F. Ding, J. Zou, M. S. Goorsky, R. K. Lake, M. A. Zurbuchen and K. L. Wang, *J. Cryst. Growth*, 2015, **425**, 268–273.
- 32 S. Fernández-Garrido, M. Ramsteiner, G. Gao, L. A. Galves, B. Sharma, P. Corfdir, G. Calabrese, Z. De Souza Schiaber, C. Pfüller, A. Trampert, J. M. J. Lopes, O. Brandt and L. Geelhaar, *Nano Lett.*, 2017, **17**, 5213–5221.
- 33 E. A. Anyebe, A. M. Sanchez, S. Hindmarsh, X. Chen, J. Shao, M. K. Rajpalke, T. D. Veal, B. J. Robinson, O. Kolosov, F. Anderson, R. Sundaram, Z. M. Wang, V. Falko and Q. Zhuang, *Nano Lett.*, 2015, **15**, 4348–4355.
- 34 S. Breuer, M. Hilse, A. Trampert, L. Geelhaar and H. Riechert, *Phys. Rev. B*, 2010, **82**, 075406.
- 35 M. Steidl, C. Koppka, L. Winterfeld, K. Peh, B. Galiana, O. Supplie, P. Kleinschmidt, E. Runge and T. Hannappel, *ACS Nano*, 2017, **11**, 8679–8689.
- 36 E. Mataev, S. K. Rastogi, A. Madhusudan, J. Bone, N. Lamprinakos, Y. Picard and T. Cohen-Karni, *Nano Lett.*, 2016, **16**, 5267–5272.
- 37 K. Sarkar, M. Palit, P. Banerji, S. Chattopadhyay, N. N. Halder, P. Biswas, B. Nagabhusan and S. Chowdhury, *CrystEngComm*, 2015, **17**, 8519–8528.
- 38 X. Yuan, J. Yang, J. He, H. H. Tan and C. Jagadish, *J. Phys. D. Appl. Phys.*, 2018, **51**, 283002.
- 39 A. D. Gamalski, C. Ducati and S. Hofmann, *J. Phys. Chem. C*, 2011, **115**, 4413–4417.
- 40 D. Jacobsson, F. Panciera, J. Tersoff, M. C. Reuter, S. Lehmann, S. Hofmann, K. A. Dick and F. M. Ross, *Nature*, 2016, **531**, 317–322.

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ARTICLE

- 41 J.-C. Harmand, G. Patriarche, F. Glas, F. Panciera, I. Florea, J.-L. Maurice, L. Travers and Y. Ollivier, *Phys. Rev. Lett.*, 2018, **121**, 166101.
- 42 C.-Y. Wen, J. Tersoff, M. C. Reuter, E. A. Stach and F. M. Ross, *Phys. Rev. Lett.*, 2010, **105**, 195502.
- 43 J. Johansson and K. A. Dick, *CrystEngComm*, 2011, **13**, 7175.
- 44 N. V. Sibirev, M. A. Timofeeva, A. D. Bol'shakov, M. V. Nazarenko and V. G. Dubrovskii, *Phys. Solid State*, 2010, **52**, 1531–1538.
- 45 F. Glas, J.-C. Harmand and G. Patriarche, *Phys. Rev. Lett.*, 2007, **99**, 146101.
- 46 X. Yuan, J. Yang, J. He, H. H. Tan and C. Jagadish, *J. Phys. D. Appl. Phys.*, 2018, **51**, 283002.
- 47 I. V Markov, *Crystal Growth for Beginners*, WORLD SCIENTIFIC, 2013.
- 48 N. V. Sibirev, M. A. Timofeeva, A. D. Bol'shakov, M. V. Nazarenko and V. G. Dubrovskii, *Phys. Solid State*, 2010, **52**, 1531–1538.
- 49 C. Messmer and J. C. Bilello, *J. Appl. Phys.*, 1981, **52**, 4623–4629.
- 50 S. B. Zhang and S.-H. Wei, *Phys. Rev. Lett.*, 2004, **92**, 086102.
- 51 S. Sakong, Y. A. Du and P. Kratzer, *Phys. Rev. B*, 2013, **88**, 155309.
- 52 V. G. Dubrovskii, N. V Sibirev, J. C. Harmand and F. Glas, *Phys. Rev. B*, 2008, **78**, 235301.
- 53 C. B. Maliakkal, D. Jacobsson, M. Tornberg, A. R. Persson, J. Johansson, R. Wallenberg and K. A. Dick, .
- 54 E. D. Leshchenko, M. Ghasemi, V. G. Dubrovskii and J. Johansson, *CrystEngComm*, 2018, **20**, 1649–1655.
- 55 F. Glas, M. R. Ramdani, G. Patriarche and J.-C. Harmand, *Phys. Rev. B*, 2013, **88**, 195304.
- 56 K. Tomioka, J. Motohisa, S. Hara and T. Fukui, *Nano Lett.*, 2008, **8**, 3475–3480.
- 57 M. Knoedler, N. Bologna, H. Schmid, M. Borg, K. E. Moselund, S. Wirths, M. D. Rossell and H. Riel, *Cryst. Growth Des.*, 2017, **17**, 6297–6302.
- 58 L. Neeman, R. Ben-Zvi, K. Rechav, R. Popovitz-Biro, D. Oron and E. Joselevich, *Nano Lett.*, 2017, **17**, 842–850.
- 59 A. V Alaferdov, R. Savu, M. A. Canesqui, E. Bortolucci, E. Joanni, J. Peressinoto and S. A. Moshkalev, *Int. J. Metrol. Qual. Eng.*, 2017, **8**, 5.

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