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To cite this article before publication: Miroslav Kolibal *et al* 2018 *Nanotechnology* in press <https://doi.org/10.1088/1361-6528/aab474>

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Catalyst-substrate interaction and growth delay in vapor-liquid-solid nanowire growth

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Abstract

Understanding of the initial stage of nanowire growth on a bulk substrate is crucial for rational design of nanowire building blocks in future electronic and optoelectronic devices. Here, we provide in-situ scanning electron microscopy and Auger microscopy analysis of the initial stage of Au-catalyzed Ge nanowire growth on different substrates. Real time microscopy imaging and elementally-resolved spectroscopy clearly show that the catalyst dissolves the underlying substrate if held above certain temperature. If the substrate dissolution is blocked (or in the case of heteroepitaxy) the catalyst needs to be filled with nanowire material from the external supply, which significantly increases the initial growth delay. The experiments presented here reveal the important role of the substrate in the metal-catalyzed nanowire growth and pave the way for different growth delay mitigation strategies.

Keywords

nanowire, germanium, vapor-liquid-solid growth, MBE, nucleation, incubation time

Manuscript text

1. Introduction

Semiconductor nanowires (NWs) exhibit many promising properties for future applications in electronics and optoelectronics [1]. Their integration into functional devices is, however, a non-trivial task as it requires regular nanowire arrays with precisely defined nanowire length, diameter and growth direction. In this respect, vapor-liquid-solid (VLS) growth mechanism [2] is the most promising way for preparation of such one-dimensional building blocks. It utilizes a catalyst nanoparticle, which serves as a collector of the atoms supplied from the external source [3]. Soon after the beginning of the process the catalyst turns into an eutectic melt. If the atomic flux from the external supply to the nanoparticle is continued, the supersaturation becomes large enough to induce nucleation and a nanowire starts to grow by subsequent nucleation events [4]. It has been recognized before that the initial nucleation is crucial for further nanowire growth [5], and has been intensively studied mostly by real-time in situ transmission electron microscopy (TEM) [6-7], providing numerous valuable insights into the nanowire nucleation and growth mechanisms. However, due to the limiting requirements on the sample geometry in TEM, these studies usually do not involve a bulk substrate, which is normally used for nanowire growth.

It has been shown in many studies that the substrate significantly influences possible one-dimensional growth utilizing VLS mechanism [8]. The choice of a substrate is crucial; the out-of-plane nanowire growth can change to in-plane (along the substrate) growth on a different substrate [9-10], or the nanowire growth can be hindered on some substrates [11]. The nucleation theory, which has been successfully applied to explain these phenomena, underlines the importance of the substrate as its surface free energy plays a major role in determining the nuclei position in the supersaturated catalyst. However, the substrate can alter the nanowire growth even before reaching the supersaturated state. The catalyst nanoparticle may dissolve substrate atoms during heating up to the growth temperature and, hence, significantly change the conditions for nucleation and subsequent growth. The uptake of substrate atoms by nanoparticles deposited on the substrate at elevated temperatures has been observed for

different nanoparticle/substrate systems [12-17] and, in nanowire growth experiments, claimed responsible for changing growth directions [18] or optical properties of nanowires [19-20] (due to incorporation of substrate atoms into the nanowire). Another important consequence of the substrate dissolution into the catalyst is a delayed nanowire growth, which is suspected to cause broad nanowire length distributions [21], thus making such nanowire arrays unsuitable for device fabrication.

In this paper, we study the initial stage of Au-catalyzed Ge nanowire growth on different substrates utilizing real-time scanning electron microscopy (SEM) and Auger nano-spectroscopy (AEM). Real-time imaging allows decoupling all the stages during the initial growth period, which is complicated if attempted by ex-situ analysis [22-24]. Our experiments demonstrate that alloying of the catalyst nanoparticle with the substrate occurs already during annealing of the sample, i.e. before the external material supply is initiated. Filling of the droplet by the growth species in order to reach the eutectic composition represents a significant part of the growth delay. However, it could be mitigated in case of homoepitaxial growth above the eutectic temperature due to i) the droplet pre-filling by the substrate atoms and ii) a very small nucleation barrier for homoepitaxy.

2. Methods

We have conducted nanowire growth in two growth chambers, which were already described in detail previously [25]. The first one is an ultra-high-vacuum chamber connected to an Auger Electron Microscope (AEM, Omicron). This setup allows to perform in-situ elemental analysis of the sample at very high lateral resolution (<6 nm) and surface sensitivity during annealing at the growth temperature before nanowire growth is initiated. A germanium evaporator connected to this chamber enables to grow Ge nanowires with a deposition rate of 1.35 nm/min. The same evaporator can easily be connected to a second chamber being part of a Scanning Electron Microscope (SEM, FEI) where the nanowire growth is performed under high vacuum at the same conditions (including the Ge atomic flux to the sample inclined by 30° with respect to the surface plane), allowing the observation of nanowire growth in real-time. We have used three types of substrates for the experiments presented here. For homoepitaxy, a

Ge(110) wafer was cleaned in acetone and isopropanol, water-rinsed and immersed for 10 minutes in a gold colloidal solution (40 nm in diameter) modified by HCl [26]. To study the catalyst interaction with the substrate, we have used Ge(110) with graphite flakes transferred by the scotch-tape technique, and GaP(111). Both types of substrates were prepared in the same way as pristine Ge(110). After the gold deposition the samples were immediately inserted into the growth chamber of choice.

3. Results

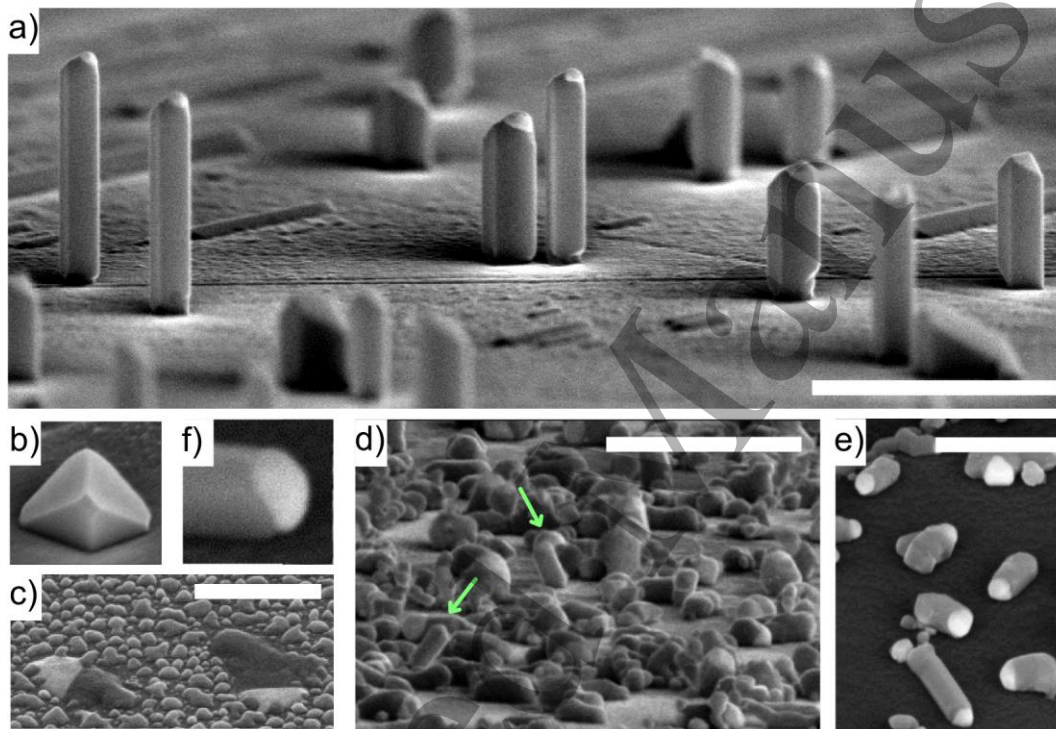


Fig. 1: Germanium nanowires grown for 90 minutes on the bare Ge(110) substrate (a), GaP(111) substrate (c) and for 360 minutes on graphite flake (d,e) using identical experimental conditions (substrates covered by Au nanoparticles, $T = 415^\circ\text{C}$, Ge evaporation rate 1.35 nm/min). Side views in (a,d) are tilted by 85° , in (c,e) by 52° . The scale bars are (a) $1\ \mu\text{m}$, (c,d) 400 nm, (e) 200 nm. The green arrows in (d) mark the sparse out-of-plane nanowires. In (b), a faceted nanowire stem (220 nm wide, after Au catalyst droplet removal) grown on the Ge(110) substrate is shown, with two inclined $\{111\}$ planes forming the growth interface clearly visible. Also the in-plane crawling nanowires on graphite exhibit the V-shaped interface, as shown in (f) (50 nm wire diameter).

First, we have performed several growth runs to see the differences in Ge nanowire growth on the Ge(110) substrate, graphite flakes and GaP(111) under identical conditions (Fig. 1). Homoepitaxial growth of Ge NWs (Fig. 1a) has been well documented before [25,27] and our growth results are in agreement with previous reports. Ge NWs grow in the $\langle 110 \rangle$ direction (perpendicular to the substrate surface plane), with a well-defined growth interface (two-inclined $\{111\}$ facets) and shape (rhombohedral cross-section, $\{111\}$ -oriented sidewall facets). The growth interface between the catalytic droplet and nanowire is clearly visible in Fig. 1b, where a nanowire stem is imaged after losing the droplet soon after nanowire elongation began. The growth on GaP(111) is strikingly different and the out-of-plane NW growth turns out to be unfeasible (Fig. 1c) even if the experimental conditions are changed. Instead, elongated in-plane (along the surface) Ge islands are formed by Au catalyzed growth. On graphite, the nanowires are very short and the majority of them grows in-plane despite four times longer growth time (Fig. 1d,e). Only a very small fraction grows out-of-plane. We have not observed any preferential growth direction, suggesting there is no epitaxial relationship with the underlying substrate. However, both in-plane and out-of-plane nanowires exhibit the same non-planar growth interface (Fig. 1f) as those grown on Ge(110). The difficulty of nanowire growth on graphite/graphene has been reported earlier [28-29], including the prevailing percentage of in-plane crawling nanowires over the out-of-plane growing ones [9,30].

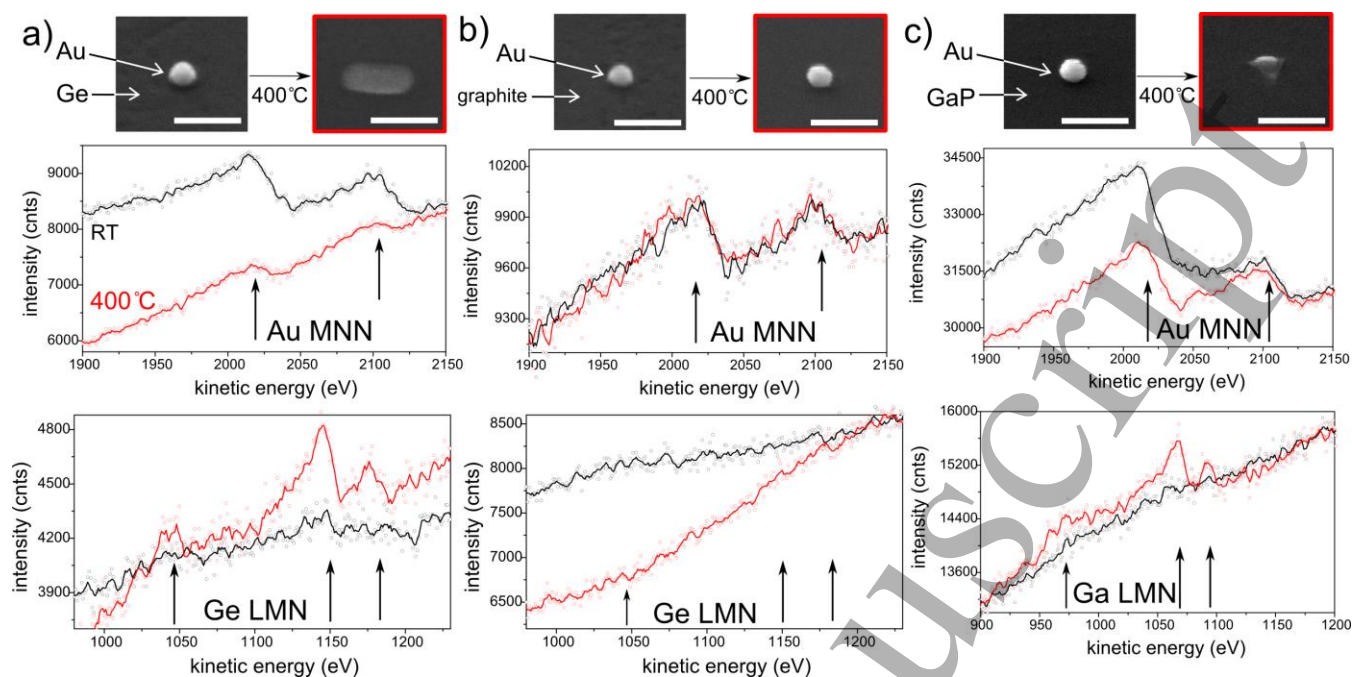


Fig. 2: Catalyst particle shape and composition changes after the growth temperature is reached. SEM images taken at room temperature and nanowire growth temperature (415 °C, red border) show that the catalyst droplet changes the shape on germanium (a) and GaP (c) substrates, while it remains intact on graphite (b). Scale bars are 100 nm. The Auger spectra below, measured using spot exposure of the droplet to the electron beam, demonstrate that the substrate atoms are dissolved in the nanoparticles. The arrows in the spectra mark the relevant Auger lines of interest.

3.1 Catalyst morphology and composition during annealing

Next, we aimed to study the uptake of the substrate atoms by the catalyst nanoparticle. We have monitored the shape and composition of gold nanoparticles deposited on surfaces of Ge(110), graphite flakes and GaP(111) during ramping to the common growth temperature (415 °C). The SEM images of the nanoparticles and the corresponding Auger spectra are shown in Fig. 2. The collected data clearly demonstrate that while on the Ge(110) and GaP(111) substrates the nanoparticles change the composition by incorporating substrate atoms, it is not the case on graphite, as C is not soluble in Au at this temperature [31] and acts as a barrier for diffusion from the underlying Ge substrate [32]. The consumption of substrate atoms on Ge and GaP substrates results in sinking of the nanoparticles

partially below the surface plane and changing their shape. Our experiments have revealed that depending on the substrate crystallographic orientation, the nanoparticles acquire irregular hexagonal (with two opposite sides significantly longer than the others), square and triangular cross-section (as viewed from top) on (110), (100) and (111) oriented substrates, respectively (not shown here). Such shapes are reminiscent of etch pits in crystalline germanium, bound by {111} planes which etch as the slowest ones [33]. Studies of the interface between eutectic AuSi melt and solid Si show that it is formed by {111}-oriented planes as well [34,35]. Hence, it is plausible to conclude that during annealing the catalytic nanoparticles dissolve the substrate beneath (if possible), thus reaching the corresponding eutectic composition at given temperature. The resulting droplet is positioned within an etch pit bound by {111} planes. The catalyst composition and shape differ on distinct substrates, giving rise to nanowires with different growth direction, morphology etc. (see Fig. 1) even under the same growth conditions. Here, we aim to study one particular consequence of this effect, the growth delay.

3.2 Initial stage of nanowire growth on germanium substrate (homoepitaxy)

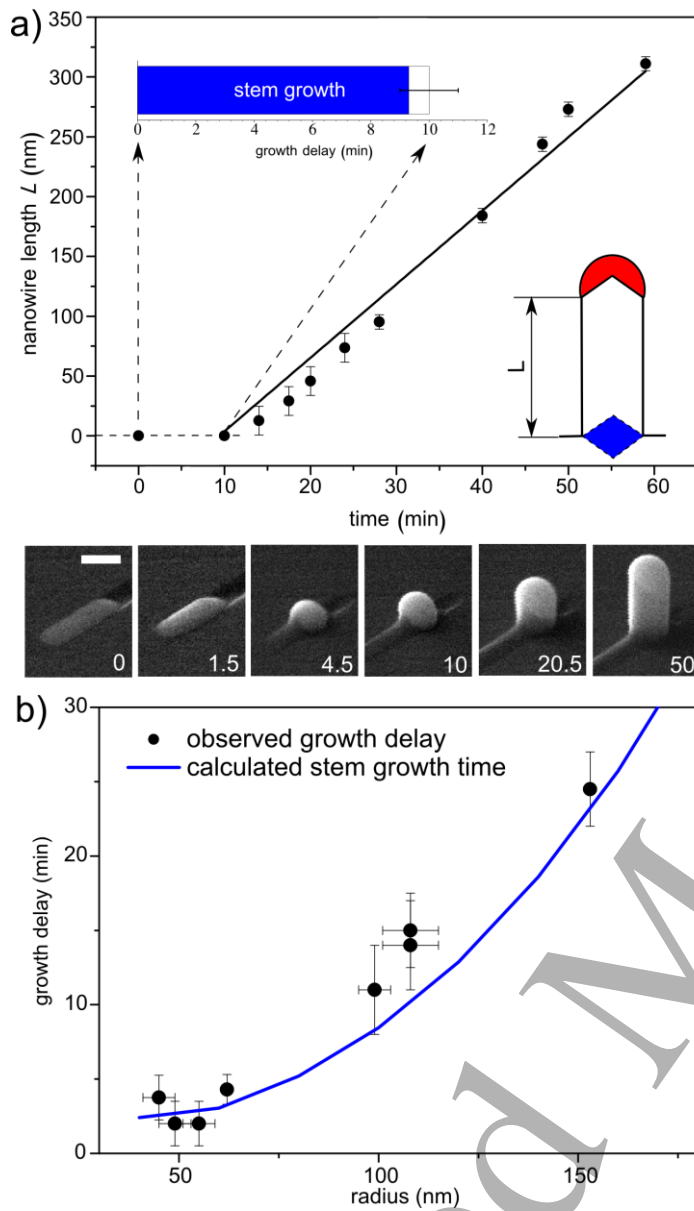


Fig. 3: Initial stage of Ge nanowire growth on the Ge(110) substrate (homoepitaxy). a) The SEM image sequence shows the catalyst and nanowire evolution in time since the start of Ge evaporation ($t=0$, time is shown in minutes). Scale bar 200 nm. The nanowire length L (measured as depicted in the schematic) versus time is shown, with apparent growth delay at the beginning. The observed growth delay is depicted in the inset, including the calculated stem growth time, demonstrating negligible growth delay (see text). More data is shown in b), where the experimentally measured growth delay of nanowires with different dimensions (scatter data) is shown together with the calculated stem growth time (solid line).

The growth delay, which is a time interval between starting the external material flux and the beginning of nanowire growth, was studied in detail by TEM [6,7]. However, the substrate significantly affects the growth delay, as will be shown in the following. We have studied the growth delay by real-time SEM for both interacting (germanium) and non-interacting (graphite) substrates. In Fig.3a), a germanium NW homoepitaxial growth is shown, as captured by SEM. The images allow tracking the nanowire growth in time. The experiment begins by opening the germanium cell shutter at $t=0$. The secondary electron imaging does not allow to track the growth from the very first monolayer like in TEM, however, the image contrast between the eutectic droplet and the growing nanowire allows to determine the moment when the droplet unpins from the substrate. At this moment, nanowire stem is already grown below the droplet (Fig. 1b), and apparent out-of-plane growth starts (here at $t=10$ min, Fig. 3a). The observed growth delay, which includes the period of nanowire stem formation, is plotted in the Fig. 3b) for several nanowires of different diameters. The time uncertainty is related to the interval between the consequent frames in the image sequence, the measurement of nanowire diameter is limited by the SEM resolution (twice the pixel size in the image).

To decouple different mechanisms contributing to the observed growth delay, we have examined the growth in detail. The real-time growth experiment allows to determine the growth rate of nanowires precisely from the slope of the length dependence as apparent from Fig. 3a). Since the nanowire stem geometry is well-defined (it is bound by $\{111\}$ and $\{100\}$ planes) [36], knowledge of the growth rate, dL/dt , allows to calculate the stem growth time t_{stem} as

$$t_{\text{stem}} = \frac{V_{\text{etch}} + V_{\text{stem}}}{A \frac{dL}{dt}},$$

where A is the nanowire cross sectional area and V_{etch} and V_{stem} is the volume of the etch pit below the droplet and nanowire stem, respectively. Although the dimensions of the etch pit cannot be directly obtained, V_{etch} can simply be calculated from the amount of dissolved germanium substrate atoms, which corresponds to the equilibrium Ge concentration in the eutectic AuGe droplet according to the

phase diagram (33% at the growth temperature used here) [37], and etch pit geometry [33]. Comparison of the calculated stem growth time with experimentally observed growth delay time gives a good match (inset in Fig. 3a) and Fig. 3b)), which leaves us to conclude that i) the growth delay observed in SEM is in this case caused only by the growth of nanowire stem below the droplet, while ii) other mechanisms contributing to the delayed growth are negligible (see discussion below). In other words, the growth begins immediately after the external material flux is started (see Fig. 3b), with growth delay within the time uncertainty of our measurement.

3.3 Initial stage of nanowire growth on graphite flakes (heteroepitaxy)

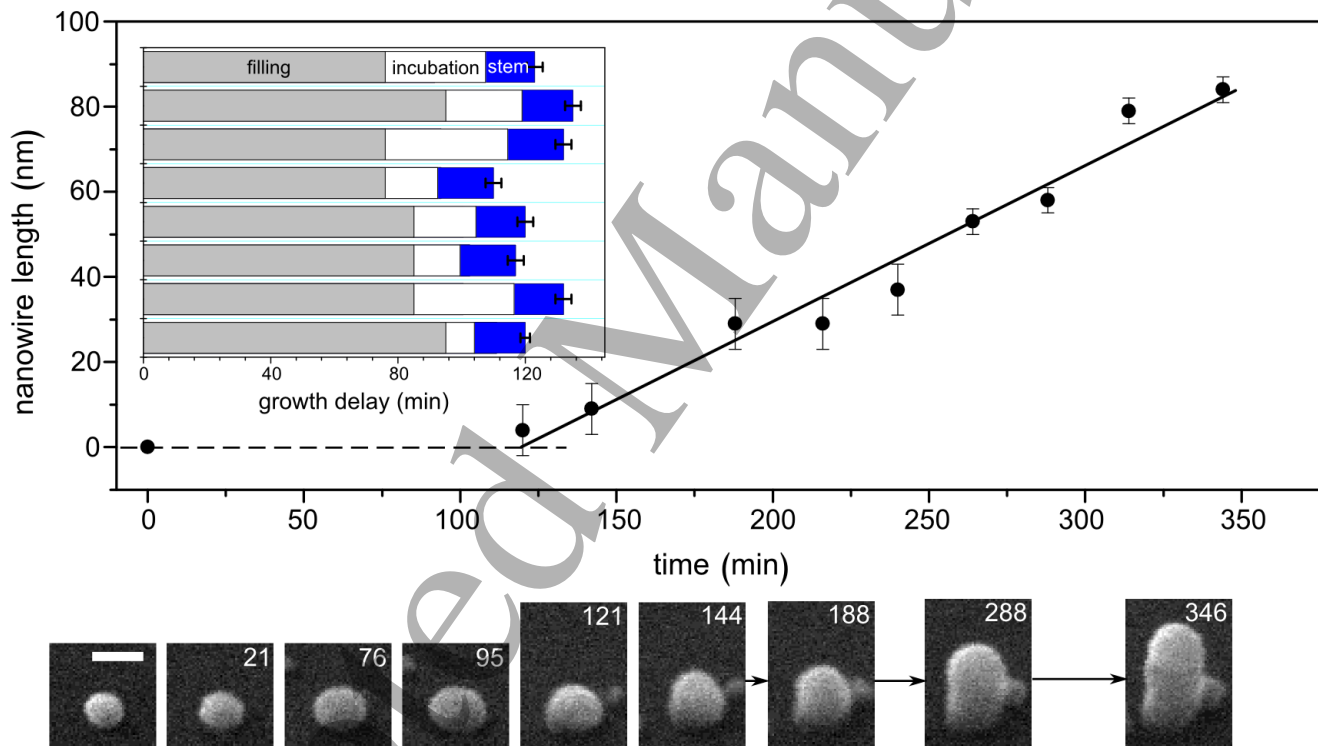


Fig. 4: Initial stage of Ge nanowire growth on graphite flakes (heteroepitaxy on non-interacting substrate). The SEM image sequence shows the catalyst and nanowire evolution in time since the Ge evaporation started ($t=0$, time is shown in minutes). Scale bar is 50 nm. The nanowire length versus time dependence exhibits a growth delay again. Compared to homoepitaxy (Fig.3), the growth delay involves filling the droplet with Ge atoms, incubation time and stem growth. The duration of these processes, as derived from real-time SEM data for eight different nanowires, is shown in the inset (each

bar represents measured growth delay including uncertainty at the end; grey part – experimentally observed droplet filling time, blue part – calculated stem growth time, white part – remaining time, identified as the incubation time).

The growth delay is observed also for out-of-plane Ge NW growth on graphite flakes, as shown in Fig. 4. However, the initial stage of growth is strikingly different. After opening the germanium cell shutter ($t=0$) the nanoparticle is continuously changing its shape. A decreasing contrast in the secondary electron image suggests that the contact angle decreases as the droplet melts while being filled with germanium from the evaporator [7]. After the droplet reaches the eutectic composition, the contrast increases again ($t=95$ min; $t=121$ min) as the nanowire growth is initiated, which is accompanied by another change in the contact angle [38]. We have quantified the observed growth delay for several nanowires having a similar nominal diameter (50-54 nm) and, additionally, we have also measured the droplet filling time (we assume that the eutectic composition is reached once the droplet stops increasing its volume). Plotting the observed growth delay and filling time together (see the inset in Fig. 4) clearly shows that there exists an undefined time interval left, even if we account for the calculated stem formation time. We assume this is the incubation time, necessary to promote the initial nucleation event during heteroepitaxy.

4. Discussion

We will start the discussion by commenting the differences in the observed growth rates of Ge NWs on Ge(110) and graphite. Note that both experiments were conducted under the same experimental conditions, including the deposition rate of the evaporator (1.35 nm/min). Yet the NW growth rate on graphite is in an order of magnitude smaller than on germanium (0.4 nm/min on graphite, 14 nm/min on Ge(110) for nanowires with $r = 50$ nm). A post-growth analysis revealed almost absent non-catalytic

growth of Ge on graphite (see Fig. 1e) and, additionally, no clustering at the edges of graphite flakes. This is indicative of very low sticking coefficient of Ge on graphite and fast desorption of Ge. As a result, the diffusion length of Ge on graphite is very small. Given the surface diffusion is the main mechanism supplying the atoms for nanowire growth in this type of experiment [39], it is clear that under identical growth conditions the nanowire growth rate on graphite is significantly smaller compared to the Ge substrate, where the diffusion length is large [25,36]. Also, we have not observed any significant ripening of the Au catalyst nanoparticles, suggesting the diffusion of Au on graphite is also very small. Thus, the Au ripening cannot be used to explain the shape changes of nanoparticle in the initial stage of growth (Fig. 4) and the only size-change mechanism remains the filling of the droplet by deposited germanium.

Excluding the stem formation time, we have identified that the growth delay can be divided into two parts [23,40] - diffusion of atoms into the nanoparticle to form an eutectic alloy (filling time) [7,41,42] and the time required to reach the supersaturation for the first nucleation event (incubation time) [22,24]. While the catalyst filling stage is commonly assumed to begin when the external material flux is started, our experimental evidence directly shows that in many cases the droplet is already pre-filled with the dissolved substrate atoms after reaching the growth temperature. Such a pathway is plausible when the solubility of the substrate atoms in the catalyst particle material is non-negligible at the growth temperature. This mechanism thus renders a situation similar to the reservoir effect in the growth of segmented heteroepitaxial nanowires [43], causing diluted interfaces. Consequently, unintentional nanowire doping by the substrate atoms may be introduced [19,20] or nanowire growth direction is different than expected [18].

A growth delay is strongly dependent on the substrate-induced reservoir effect (see Fig. 4, inset). If the solubility of the substrate in the catalyst is non-negligible, the droplet is initially filled with substrate atoms and in case of heteroepitaxy it is necessary to re-fill it with the nanowire material from the external supply. The need to re-fill the catalyst may even increase the delay and result in its possible

consequences, e.g. broad nanowire length distributions. This is indeed mitigated in homoepitaxial growth (see Fig. 3), as the droplet reaches the eutectic composition while heating up. Then, once the external material flux is started the nanowire growth begins almost immediately. The only contribution to the growth delay in this particular case is the incubation time, which is small because the nucleation barrier for homoepitaxy is very low. It is worth noting that the similar situation appears for Au-catalyzed III-V nanowire growth, where heteroepitaxy with significantly reduced delay is possible if the substrate with the same group III element as the desired nanowire is used [44]. Although our experiments involve only Au catalyst nanoparticles, the conclusions are not specific to Au only. E.g. gallium, which is often used for self-catalyzed growth of Ga-based compound nanowires, is well known to induce a melt-back etching effect on Si. It has been already proposed that the Ga-induced substrate etching is possibly important in determining the growth direction of GaAs nanowires on Si [45].

5. Conclusion

In conclusion, we have presented the results of several experiments designed to decouple different contributions to the nanowire growth delay. Monitoring of the catalyst nanoparticle composition and dimensions in real-time by SEM and Auger nano-spectroscopy reveals that the substrate is in many cases etched by the catalyst nanoparticle during ramping to the nanowire growth temperature, resulting in formation of an alloyed catalyst droplet. Filling of the droplet by the nanowire material is the largest contribution to the nanowire growth delay. Our results emphasize the importance of substrate-induced effects on nanowire growth, which has to be taken into consideration when designing the growth conditions for nanowires that are to be used in electronic and optoelectronic devices.

Acknowledgement

This research has been financially supported by the Grant Agency of the Czech Republic (16-16423Y), Ministry of Education, Youth and Sports of the Czech Republic under the project CEITEC 2020

(LQ1601). MK acknowledges the support from FEI Company. Part of the work was carried out with the support of CEITEC Nano Research Infrastructure (ID LM2015041, MEYS CR, 2016–2019).

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