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The mechanisms of platinum-catalyzed silicon nanowire growth

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Abstract
Platinum (Pt) has been known as a catalyst material for vapor-liquid-solid (VLS) synthesis since the mid 1960s with the potential to grow electronic grade silicon nanowires (SiNWs). In contrast to gold-based growth, Pt-catalyzed SiNW synthesis has rarely been studied, most likely due to higher synthesis temperatures and the formation of multiple Pt silicide phases. Here we present the growth of SiNWs from a Pt catalyst deposited by a focused ion or electron beam, which opens new strategies for the assembly of Pt-catalyzed SiNW-based devices, as well as SiNW growth from Pt nanoparticles and thin films. We show that single-crystalline SiNWs exhibit either the well-known catalyst tip or a polycrystalline silicon tip so far not reported. The local Pt concentration was found to be one key parameter triggering the growth mode. The proposed growth model for both types of SiNWs is based on a solid-state silicide-mediated crystallization rather than VLS. The discussion of the growth modes is supported by a variation of several growth parameters and SiNW synthesis using the substrate materials silicon nitride, single-crystalline silicon, fused silica, and sapphire.

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1. Introduction
Silicon nanowires (SiNWs) are one-dimensional semiconductors, which show great potential as building-blocks for the design of advanced nanoscale devices [1–5]. The bottom-up growth of SiNWs commonly uses metal catalysts in vapor-liquid-solid (VLS) [6] or vapor-solid-solid (VSS) [7] synthesis yielding SiNWs with a catalyst tip. From the variety of possible catalysts, [7, 8] platinum (Pt) represents a promising alternative to the typically used gold (Au). Platinum appears superior for electronic grade SiNW synthesis as it is expected to form fewer near-midgap traps in Si compared to Au [9–13]. Besides these considerations, it was recently demonstrated that SiNWs are readily grown from beam-deposited Pt [14]. Localized catalyst deposition onto complex 3D substrates by established focused ion beam-induced deposition (IBID) or electron beam-induced deposition (EBID) allows a precise control of the SiNW growth site enabling new and versatile concepts for advanced SiNW-based device assembly.

The catalytic function of Pt for SiNW synthesis has been known since the discovery of the VLS mechanism [6] but the number of studies, which have been published since then, is still rather limited. This may be related to the Pt-Si phase diagram comprising several Pt silicide phases and to the significantly higher eutectic temperatures compared to the Au-Si system [15, 16]. So far, solely VLS and VSS-SiNW growth using Pt as a catalyst were described despite differing...
growth conditions. Besides Pt deposited by IBID or EBID, Pt thin films [12, 17, 18], Pt colloids [13] or Pt particles [6, 19], and galvanically deposited Pt [20] were utilized for SiNW synthesis at temperatures between 500 and 1200 °C using either monosilane (SiH₄) or silicon tetrachloride (SiCl₄) as precursor. Several procedures stress a separate annealing step prior to growth aspiring catalyst dewetting or silicide formation. The growth of SiNWs without the typical catalyst tip was just recently reported with Pt deposits as thin as 2 nm [14]. However, neither the origin of this silicide growth mode nor the underlying mechanisms have been disclosed so far. Here we present a detailed discussion on growth characteristics of Pt-catalyzed silane-based SiNW synthesis proposing a consistent growth model for the Pt-Si system. Understanding the fundamental growth mechanisms should facilitate further research studies as well as the rational control of Pt-catalyzed SiNW synthesis.

2. Methods

As substrate material, (100)-Si with native oxide layer was used. The Pt catalyst was prepared in three different ways to study the effects emerging from the catalyst form: thin Pt films (thickness 5 nm) deposited by electron beam evaporation, ligand-free Pt nanoparticles (diameter 10 nm) suspended in water, as well as IBID and EBID Pt using gaseous (methylcyclopentadienyl)trimethyl platinum as precursor. Due to the organometallic nature of the precursor, a composite material of Pt and amorphous carbon rather than pure Pt is deposited. Furthermore, Ga ions are implanted in case of IBID. Nevertheless, SiNW synthesis appears unaffected as previously reported [14].

Cross-sectional lamellae for transmission electron microscopy (TEM) were prepared by microtome cutting using a sacrificial 500 nm thick amorphous Si₃N₄ interlayer between the (100)-Si substrate and the Pt catalyst. After SiNW growth, the whole sample was embedded in resin followed by the substrate removal in liquid nitrogen prior to lamellae cutting. The cut lamellae were transferred to TEM copper grids for imaging and energy-dispersive x-ray spectroscopy (EDX). Additional samples for single SiNW TEM imaging were prepared from suspensions obtained by ultrasonication of the growth substrate in ethanol and direct transfer to TEM copper grids.

The SiNW growth was carried out in a quartz tube furnace at temperatures between 700 and 800 °C and total pressures between 38 and 225 mbar, respectively. The SiH₄ (2% in helium) flux was either 4 or 30 sccm, respectively. The flow of hydrogen was kept constant at 270 sccm. To explore SiNW p-type doping, 3 to 20 sccm of B₂H₆ (100 ppm in helium) were additionally admixed in some experiments. The growth process was initiated by ramping the system from room temperature to 800 °C under vacuum (pressure around 0.1 mbar) within approximately 80 min, followed by a cooling down to the respective growth temperature. After the growth temperature was set, all gases were opened at once and kept constant at their particular flow rates throughout the growth process. Finally, the gases were turned off and the chamber was purged with argon but kept evacuated while cooling down to room temperature.

3. Experimental results and discussion

3.1. Catalyst formation at the initial growth stages

During initial heating, here to 800 °C in vacuum, Pt diffuses on the substrate surface and forms silicide layers or Pt droplets as shown in figures 1(a) and (b), respectively. Silicide layers are formed only if oxide-free silicon substrates are used allowing a silicide phase formation with the substrate [21, 22]. However, SiNWs could not be grown from these silicides embedded in the substrate (figure 1(a)). If substrates such as silicon oxide (figure 1(b)), silicon-nitride, or silicon-free sapphire are used, silicide formation is inhibited and pure Pt droplets were observed for all used Pt catalyst forms. The resulting droplet size and spacing as well as the diameter distribution (see supplementary information figure S1) is governed by the initial local Pt concentration, Pt surface diffusion, the thermo-migration of Pt nanoparticles, and Ostwald ripening [21, 23–25]. The onset of the SiNW growth
process, initiated by the inlet of gaseous SiH₄, induces the Pt droplets to form a Pt silicide phase at temperatures between 250 and 400 °C [26]. It is expected that first the Pt₂Si phase is formed, followed by a PtSi phase as soon as all available Pt is consumed [15, 27–29]. As some oxygen is present, which can be commonly assumed for systems operating above ultra-high vacuum, several Pt silicide phases may coexist [27]. Nevertheless, the catalyst phase is denominated as PtSi in the following according to [12] and [15]. The Pt droplets, originating from the dewetted 5 nm Pt thin film, are significantly changed due to incipient Pt silicide formation within the first 30 s of the growth process (figure 1(c)). Although first nuclei of SiNWs may be assumed, the initially separated Pt droplets coalesce forming a rough PtSi network at the surface (figure 1(c) inset).

### 3.2. Pt-catalyzed SiNW growth modes

Distinct SiNW growth was observed after 60 s of growth yielding SiNWs with already up to 4 μm in length (figure 2(a)). However, only a few SiNWs grow in a straight manner away from the surface and not all of them seem to have a catalyst tip. A significant number of SiNWs grow laterally across the surface in an undulated manner, suggesting unstable growth conditions or the growth of polycrystalline SiNWs. Also, the shape of the Pt silicide catalyst seems to vary (figure 2(a) inset) indicating different crystallographic orientations [30] between Pt silicide phase and SiNW as observed before for Pt [12], Pd [31], and Ni [32] silicides. The predominant silicide morphology and orientation is most likely affected by the initial Pt droplet formation conditions [30] such as annealing in hydrogen [12] or under vacuum. The substrate as an effective silicon source was ruled out by growth experiments without SiH₄ maintaining all other parameters. Regardless of the growth time, no SiNW growth was observed. Moreover, in the presence of SiH₄, using silicon-free sapphire as a substrate, SiNWs growth was observed as equivalent to silicon-based substrates. The importance of Pt for the SiNW growth becomes evident if localized Pt spots, here deposited by EBID, are used. Here, SiNW growth occurs solely confined to formerly Pt covered locations as shown in figure 2(b).

After extending the growth time to 1 h, two distinct types of single-crystalline SiNWs were observed as indicated exemplary in figure 2(b). The first type of single-crystalline SiNWs has top diameters of 80 to 100 nm and exhibits a Pt silicide catalyst at the tip (figure 3(a)). Due to post-growth analysis, it still remains unclear whether the catalyst droplet is liquid or solid during growth. According to the phase diagram, the lowest melting point derived from the bulk phase diagram exists for a Pt-rich eutectic phase with 23 at. % Si in Pt melting at 830 °C [15]. However, this phase is not expected to precipitate Si. To precipitate a pure Si phase, a PtSi phase appears to be mandatory. The melting points of PtSi and its eutectic phase with Si are 1229 and 979 °C, respectively [15] and will not differ significantly taking the nanoscale dimension of the droplets into account [33]. Therefore, a VSS-mode appears reasonable for this type of SiNW growth at 700 °C denoted as VSS-SiNW in the following.

The VSS-SiNWs are tapered with a diameter decrease over length of approximately 15 nm/μm. The tapering can be primarily linked to Si deposition by thermal SiH₄ decomposition at the SiNW sidewalls. Dissolution of the catalyst in the SiNW should be ruled out as Pt could not be detected within the SiNW using TEM/EDX. However, some SiNWs exhibit an additional polycrystalline segment at their top with crooked and tapered morphology as exemplary shown in figure 3(b). The tapering of these polycrystalline regions is more distinct compared to the single-crystalline part due to the incorporation of Pt into the Si. Therefore, the final tip diameter is significantly smaller than the top diameter of the single-crystalline segment. The growth of these polycrystalline regions might be triggered by the drop of both...
temperature and SiH₄ partial pressure inside the chamber at the end of the growth sequence. Consistent with [29] and [34], an approximately 3.5 nm thick amorphous SiO₂ layer at the catalyst surface indicates the silicide nature of the catalyst (figure 3(a), marked by an arrow).

Besides PtSi catalyzed VSS-SiNWs, a second and so far undescribed type of single-crystalline SiNWs exists. This type exhibits larger diameters between 100 nm and 1 μm, is significantly shorter, and lacks a silicide catalyst tip. The SiNW tip is instead decorated with a blunt polycrystalline segment exhibiting a polycrystalline, highly tapered tip extension with catalyst tip, and EDX could not detect any Pt in this kind of SiNW, neither at the tip of the nanowire nor at the interface between the poly- and single-crystalline part (EDX data available in supplementary information figure S2). Similar SiNW growth characteristics were reported for TiSi₂ islands but lacked a growth model [35]. Although no silicide or Pt seems to be present in the SiNW, significant amounts of Pt silicides remain beneath the SiNWs at the substrate surface buried by a polycrystalline Si layer or embedded in it as shown in figure 3(d). The growth of single-crystalline SiNWs from a silicon deposit in the presence of a Pt silicide phase shows similarities with Pd [36] and Ni [32] silicide-mediated crystallization (SMC) utilized to transform amorphous silicon films into polycrystalline films. In the following, this second type of SiNW is therefore denoted as SMC-SiNWs to distinguish them from the VSS-SiNWs, although the VSS-SiNW mode can also be explained by SMC [31].

The proposed growth model for VSS and SMC-SiNWs is based on the assumption that the initial PtSi crystals have a specific orientation. The growth process comprises (i) gaseous SiH₄ transport and adsorption onto the catalyst or in its vicinity, (ii) decomposition of SiH₄ releasing free Si, (iii) diffusion of Si towards or across the PtSi catalyst and finally, (iv) precipitation of a SiNW. The differences in surface free energy between the PtSi/substrate, PtSi/amorphous-Si, and PtSi/crystalline-Si interfaces can be considered as the overall driving forces for directed and opposing solid-state diffusion of Si and Pt [32].

In analogy to NiSi₂-SMC, the lowest surface free energy is assumed to exist for the PtSi/crystalline-Si interface. Therefore, free or amorphous Si will be consumed by the PtSi catalyst, an orthorhombic crystal [37], while simultaneously crystalline diamond cubic Si is precipitated. Based on the available lattice sites, different growth velocities and directions, as well as Si crystal orientations have to be assumed as observed for the crystallization of amorphous Si films assisted by NiSi₂ [32]. To nucleate a single-crystalline SiNW exhibiting the PtSi catalyst at the tip, stable PtSi droplets must exist on the surface, which precipitate crystalline Si towards the substrate while the catalyst moves continuously away from the surface fed by the SiH₄. Other Pt silicide crystal orientations would result in lateral silicon crystallization or growth of heavily kinked SiNWs (cf figure 2(a)). Terminated VSS-SiNW growth due to unstable growth conditions is most likely the reason for the observed PtSi inclusions in the polycrystalline Si overgrowth (cf figure 3(d)). The growth of VSS-SiNW using an SMC model is supported by the needle-shaped crystal formation exhibiting a NiSi₂ tip, which was observed for SMC of amorphous silicon films [32]. However, the growth of SMC-SiNWs having polycrystalline tips is not described yet in connection with SMC to the best of our knowledge. The formation of silicide networks during the initial growth stages requires that Pt diffuses from the droplets into thermally deposited silicon on the substrate surface. Si crystals are precipitated but the catalyst stays at the substrate surface, which could be simply due to its crystallographic orientation or inhomogeneities of the silicide network. The role of oxygen must be further investigated in this context. Repeated precipitation of Si crystals at the silicide top surface can trigger needle-shaped crystals [32], forming the polycrystalline tip of SMC-SiNWs. As described for Pd silicide catalyzed SiNWs [31] and PtSi droplets on a silicon surface [37, 38], the silicide/silicon interface is highly dynamic and can readily reshape to lower the surface free energy or to reach a favored silicide/silicon interface state. Once a preferred orientation is precipitated, the SiNW will elongate as single-crystal. Notably, in addition, some SMC-SiNWs
nucleation of SCM-SiNWs can be assumed and stable PtSi droplet formation should become favorable, as required for VSS-SiNW synthesis. Using IBID PtC, a distinct thickness gradient was generated in the form of a chessboard-like pattern as previously reported \cite{14}. The deposited patterns have a Pt content of about 35–45 at.\% \cite{39}. If the height increased from about 2 to 3 nm, exclusively SMC-SiNWs with homogeneous but short length was observed (figure 5(a)). At increased heights of about 4 to 6 nm, a co-appearance of both SMC- and VSS-SiNWs was observed as expected (figure 5(b)). Notably, the thickness difference of only about 2 nm is affecting the length of the SiNW drastically. A further increased height (gradient from 6 to 13 nm) reflecting an overall higher amount of Pt further promotes the VSS-SiNW growth but is still accompanied by SMC-SiNW growth as shown in figure 5(c).

Besides the Pt content, the temperature and the SiH\(_4\) partial pressure could potentially influence the effectiveness of the growth mechanisms and alter the SiH\(_4\) decomposition, the silicide phase formation, and the SiNW precipitation. Changing the growth temperature from 700 to 800 °C in steps of 20 K revealed that the overall density of SiNWs is highest around 720 °C resulting in the longest VSS-SiNWs with an average length of 15 \(\mu\)m after 1 h (figure 6(a)). With increasing temperature, VSS-SiNW growth appears to be continuously hampered so that at 780 °C almost exclusively SCM-SiNWs are present (figure 6(b)). This indicates that thermal SiH\(_4\) decomposition rate is another important parameter. Therefore, at 800 °C no SiNW nucleation is observed (figure 6(c)).

Reducing the SiH\(_4\) partial pressure at 720 °C from 0.14 mbar down to about 0.01 mbar by about one order of magnitude reduces the absolute number of SiNWs as well as their length by about one order of magnitude (figure 6(d)). An increase of the SiH\(_4\) partial pressure from 1.1 · 10\(^{-2}\) mbar by a factor of two (figure 6(e)) or six (figure 6(f)) leads to increased SiNW growth rates but hardly affects the ratio of VSS- and SMC-SiNWs.

The control over both the SiNW morphology and their electronic properties is a prerequisite for the application of SiNWs in electronic devices. The admixture of phosphine for

### 3.3. Influence of local Pt concentration, temperature, SiH\(_4\) partial pressure, and doping on the growth modes

The local Pt concentration prior to silicide formation or silicon crystallization appears fundamental for both SMC-SiNW and VSS-SiNW growth. At higher Pt concentrations, faster
n-type doping of Si completely inhibited the SiNW growth. This may be related to an accumulation of phosphorus at the PtSi/Si interface [40] suppressing the nucleation of SiNWs. A similar effect is not reported for boron [41]. Boron-doped SiNW synthesis, using a silicon/boron gas phase ratio of 400:3, was realized without any observable impact onto the growth mechanisms or the morphologies in comparison to intrinsic SiNWs. The detailed investigation of the electronic transport properties of boron-doped VSS- and SMC-SiNWs will be addressed in future studies.

4. Conclusion

The Pt-catalyzed growth of single-crystalline SiNWs was investigated. Consistent with previous studies, single-crystalline SiNWs were grown exhibiting the well-known catalyst tip. The growth mode for these SiNWs appears to be VSS rather than VLS. Besides the VSS-SiNWs, a so far unreported type of single-crystalline SiNWs was studied having a polycrystalline tip instead of a Pt silicide. In analogy to the crystallization of amorphous Si thin films by silicides such as Ni3Si, a silicide-mediated crystallization growth mode, driven by directed solid-state diffusion, was proposed also comprising the VSS-SiNW growth. The influence of substrate material as well as the type of the Pt catalyst deposition including thin films, nanoparticles, and beam-deposited Pt was studied. Except for pure Si substrates, no significant influence on the overall SiNW growth characteristics was observed. It was demonstrated that higher local Pt concentrations promote the nucleation of VSS-SiNWs, which was attributed to the formation of stable PtSi droplets rather than silicide networks spreading across the substrate surface. The derived growth characteristics should inspire more frequent functional implementation of Pt-catalyzed SiNWs in future.

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