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Growth of axial SiGe heterostructures in nanowires using pulsed laser deposition

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Abstract

Axial heterojunctions between pure silicon and pure germanium in nanowires have been realized combining pulsed laser deposition, chemical vapor deposition and electron beam evaporation in a vapor–liquid–solid nanowire growth experiment using gold nanoparticles as catalyst for the 1D wire growth. Energy dispersive x-ray mappings and line scans show a compositional transition from pure silicon to pure germanium and vice versa with exponential and thus comparably sharp transition slopes. Based on these results not only Si–Ge heterojunctions seem to be possible using the vapor–liquid–solid growth process but also heterojunctions in optoelectronic III–V compounds such as InGaAs/GaAs or group III nitride compounds such as InGaN/GaN as well as axial p–n junctions in Si nanowires.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Due to their promising applications in nanoelectronics, biological sensing, nanoelectromechanical systems and photovoltaics [1–6], semiconductor nanowires (NWs) have become an intensively investigated research topic in recent years. Active electronic structures like transistors have also been prepared using NWs [7–10].

To realize such structures, heterojunctions in NWs are needed. Both radial [9–13] and axial [14–18] heterojunctions have been presented in the literature so far. In this paper, we focus on axial heterojunctions, which are promising due to the fact that they can be prepared in a continuous chemical vapor deposition (CVD) process. Furthermore, in the case of axial p–n junctions, a smaller depletion region can be realized compared to the case of radial junctions so that lower recombination losses at this interface can be envisaged.

The utilization of axial p–n junctions in SiNWs has been shown in single NWs by Kempa et al [14] to exploit the photovoltaic effect. The realization of an array of SiNWs that contain an axial heterojunction has been shown by Kim et al [17].

For the aforementioned applications, a reliable growth of abrupt heterojunctions is required to improve functionalities in devices and to extend the options of utilizing semiconductor NWs in active electronic device concepts.

In the present study, axial heterojunctions between Si and Ge were realized in NWs using a gold (Au) catalyzed vapor–liquid–solid (VLS) growth process [19]. The Si–Ge system gains interest due to the enhanced electrical properties [20] and the possibility of bandgap engineering [21]. Despite this, the system was chosen for the analysis of junction abruptness since it permits easy determination of composition by energy dispersive x-ray analysis (EDX). Physical vapor deposition (PVD)—here we apply pulsed laser deposition (PLD) [22] and electron beam evaporation (EBE) [23]—was chosen to permit one-dimensional NW growth only depending on the VLS mechanism that is based on the liquefying of the Au nanoparticles at low temperatures due to the low temperature...
The investigation of axial Si$_x$Ge$_{1-x}$ heterojunctions in NWs has been reported in the literature so far by several groups [16, 20, 29–32]. Whereas the authors in references [20, 29–32] report a maximum Ge content of about 30\% in the SiGe alloys, only in the most recent work [16], an initially sharp and complete heterojunction between pure Si and pure Ge has been realized. Wen et al [16] used a vapor–solid–solid (VSS) approach in their experiments. We, however, are the first to apply VLS growth in order to achieve a distinct transition between pure Ge and pure Si.

Li et al [33] provided a theoretical prediction for the width of the axial heterojunction between different components in a VLS NW growth process. The interfacial abruptness foreseen by Li et al [33] compared to our experimental results will be discussed in the present paper.

Scanning electron microscopy (SEM) as well as transmission electron microscopy (TEM) was used to characterize our samples regarding both structure and composition. Energy dispersive x-ray analysis (EDX) was utilized to investigate the chemical composition of the realized heterostructures composed of Si and Ge segments and an alloy transition region in NWs.

2. Experimental details

2.1. Growth of initial VLS NWs by PVD

The well-known gold catalyzed VLS NW growth mechanism [19] was used to realize epitaxial growth of one-dimensional nanostructures, i.e. NWs on Si(111) substrates. This process for bottom-up realization of NWs uses an Au nanoparticle to drive one-dimensional NW growth. This Au nanoparticle forms a eutectic with Si and Ge. The growth species are supplied in the gas phase and supersaturate in the liquid Au droplet. Excess Si or Ge atoms crystallize at the interface between Au droplet and Si substrate or later the Si or Ge NW itself in the form of an NW.

Two different types of specimen were realized: (i) NWs with a Ge and (ii) NWs with an Si bottom segment directly at the interface with the Si(111) wafer. The bottom segment of either Si or Ge composition of the NWs was grown using PVD. The PVD process was chosen for the initial NW growth as it guarantees well-separated, straight and comparatively thick NWs which usually grow straight along a (111) direction perpendicular to the Si(111) wafer surface [23, 34].

We employed an Au nanoparticle-mediated VLS process on an Si(111) wafer. The Au droplets were prepared by annealing a 2 nm thick gold layer at a temperature of 800 °C for 1 h.

For NWs with an Si bottom segment, the NW growth starts homoepitaxially on Si wafers, deposited by EBE of Si in a home-built EBE system. This growth is carried out at a temperature of 650 °C and has been discussed in detail in [23].

For NWs with a Ge bottom segment, the NW growth is heteroepitaxial and strained on the Si(111) wafer. Ge was deposited by PVD using PLD of Ge targets (slices of undoped Ge delivered by Crystec GmbH). This PLD VLS growth process of Ge NWs is carried out by ablating Ge targets using a pulsed KrF excimer laser (Lambda Physik LPX300CC) operated at a wavelength of 248 nm and a repetition rate of 70 Hz. The NWs grow on a heated substrate at approximately 540 °C. For Ge NW growth a Ge target is ablated by the pulsed laser beam using an off-axis approach shown in figure 1(a).
2.2. Growth of heterostructures within NWs

For the growth of axial heterostructures in NWs on Si(111) substrates, we used two different approaches:

(i) The growth of NWs with a bottom Ge segment was realized by combining the mentioned PLD growth of Ge with CVD growth of Si on top. After the PLD Ge growth step, the sample was unmounted from the PLD set-up. It was immediately transferred to a cold wall CVD chamber for growth of the Si segment through ambient air without further treatment. We carried out the CVD process using a mixture of 4 sccm Ar and 3 sccm SiH₄ and a pressure of 0.5 mbar. The NWs were grown at a temperature of 660°C[5]. This growth of a Ge segment on an Si(111) wafer followed by CVD growth of an Si segment is schematically shown in figure 2(a).

(ii) Figure 2(b) illustrates the growth of a Ge top segment by PLD on an Si bottom segment on an Si(111) wafer. The Si homoepitaxy on the Si(111) wafer was this time realized by EBE [23, 36]. The Si(111) wafer with initial VLS Si NWs is etched in 5% HF(aq.) to remove the native oxide formed on the NWs’ surface during storage in air. This oxide removal step is important to achieve heteroepitaxy between segments of NWs. The substrate was subsequently installed in the PLD reaction chamber. After the evacuation of the chamber, the Ge segment was deposited by PLD as described before but at a temperature of 700°C.

2.3. Analysis of the realized heterostructures in NWs

The different VLS-grown NWs were investigated using SEM, bright-field TEM and EDX in the TEM. We used a JEOL 6300F field emission microscope for SEM imaging. TEM investigations were carried out in a Philips CM 20 FEG field emission electron microscope (TEM/STEM) operated at 200 kV and equipped with an EDX detector (IDFix-system, SAMx, Germany). Cross-sectional samples were prepared using conventional gluing, grinding and ion milling with the wires embedded in the glue.

The TEM set-up used in this work tends to overestimate the junction width due to a 15° tilt of the sample for the EDX analysis. The measured transition region widths may therefore be larger than the ones actually achieved; thus they are to be seen as an upper limit.

3. Results and discussions

Aiming at the growth of segmented NWs, we used a two-step process as described in section 2. This means the growth of initial NW segments by PVD and a subsequent processing of a second segment by either PVD or CVD to achieve the heterojunctions.

3.1. Initial NW segments

Initial NW segments were synthesized by a PVD process that is EBE of Si or PLD of Ge. The diameters of the gained PVD NWs range between 100 and 300 nm depending on the Au layer’s thickness, the PVD growth parameters such as temperature, flux, time, etc, and of course substrate orientation and substrate preparation [37].

Typical NWs achieved in the PVD process are shown in figures 3(a) and 5(a). In a PVD process, the entire substrate is coated with the growth species; thus next to the one-dimensional NW growth a two-dimensional (2D) layer forms between the NWs as visible in the cross-sectional TEM micrographs in figure 3. The reason for NWs to grow faster than the 2D layer is the metal catalysis in VLS growth that enhances growth velocities.

3.2. Heterostructures with a Ge bottom segment

Figure 3(a) shows an XTEM micrograph of an initial PLD-grown Ge segment before the growth of an Si top segment.
Figure 3. Cross-sectional TEM investigation of epitaxial VLS NWs with Si and Ge segments on Si(111) wafers as schematically shown in figure 2(a); (a) a PLD-grown VLS Ge NW is shown; the NW clearly resides within a 2D Ge layer on top of the Si(111) substrate; the Si substrate appears brighter than the Ge 2D layer and NW due to materials’ contrast in the bright-field TEM micrograph. (b) Chemical element distribution mapping of the NW shown in (a) using EDX; the NW is composed of a pure Ge shaft (yellow) and an Au nanoparticle cap (purple), typical of the VLS growth process. (c) TEM cross-sectional view of a segmented Ge/Si VLS NW on an Si(111) substrate being composed of an initial PLD-grown Ge segment (darker in materials’ contrast) and the Si segment with the Au cap. (d) The EDX mapping of the segmented NW shown in (c) proves this composition.

The EDX mapping in figure 3(b) proves this NW to consist of pure Ge. An XTEM micrograph of the NW after the growth of an Si segment by CVD on top of the Ge shaft is given in figure 3(c). Figure 3(d) shows an EDX mapping of the same NW, indicating the pure Ge and Si nature of the different segments. This proves we were successful in realizing a complete transition between Si and Ge using a VLS process. These mappings show the junction abruptness as well.

The slight tilt seen at the heterojunction in the Si/Ge NW in figures 3(c) and (d) is probably due to a preferred ⟨112⟩ growth direction for SiNWs grown by CVD using SiH₄ at the partial pressure used in our experiments. The dependence of the growth direction on the SiH₄ partial pressure has been described by Lugstein et al. A second possibility that cannot be excluded is that the GeNWs do not grow perpendicular to the substrate surface in one of the symmetrically equivalent ⟨111⟩ directions but in one of the ⟨112⟩ directions and just the CVD-grown Si NW part follows a ⟨111⟩ direction. Due to the 2D layer which is deposited on the Si(111) substrate it is hard to distinguish between the two aforementioned cases. Selected-area electron diffraction (SAED) clearly shows that both parts of the nanowires, the Si as well as the Ge segment, are single crystalline. A statistically relevant number of SAED investigations, however, are required to get more information on the crystal orientations of Si and Ge segments in the nanowires.

In the EDX line scan along the NW axis presented in figure 4, the Ge, Si and Au profiles are clearly visible. In the line scan, the slopes of the Si and Ge content are exponential, with the junction width being of the order of the NW diameter. This result is in good agreement with the junction profiles predicted based on theoretical considerations by Li et al. for VLS growth of NWs. The experimental data of Clark et al. which were measured by HAADF-STEM (high angle annular dark-field STEM) on axial heterojunctions between pure Si and SiₓGe₁₋ₓ also showed a transition region width of the order of the diameter of the NW, as is visible in our results. In contrast to their results, however, we realized a complete transition from pure Ge to pure Si. Additionally, Clark et al. reported residual Ge in the catalyst droplet even after growing several 100 nm of pure Si, whereas in our experiments EDX analyses suggest that no residuals of the initial growth species can be found in the catalyzing Au droplet on top of the NW. This proves complete de-mixing of the NW growth mediating Au droplet and the growth species in our experiments as is predicted in the model of Li et al.

3.3. Heterostructures with an Si bottom section

Figure 5(a) shows an SEM image of Si NWs synthesized by EBE before the growth of a Ge top segment. XTEM imaging (figure 5(c)) and EDX mapping (figure 5(d)) show the Ge segment grown on top of the Si NW.

Again, the slopes and the width of the transition regions were analyzed by an EDX line scan along the NW axis. This scan is shown in figure 6. We see an exponential decrease of
Figure 5. Scanning (a), (b) and transmission electron microscopy studies (c), (d) of pure VLS Si NWs deposited by EBE on Si(111) substrates and segmented Si/Ge NWs as shown in the schematic in figure 2(b). (a) SEM image of EBE-deposited SiNWs. Note the smooth 2D Si layer. (b) SEM image of the same sample after Ge deposition by PLD. The Ge deposited on the substrate forms triangular islands on the 2D silicon layer. This can be attributed to strain relaxation. (c) Cross-sectional TEM analysis of the EBE Si NW after additional PLD deposition of a Ge segment. (d) EDX mapping of the segmented NW showing the Si substrate as well as the homoepitaxial Si NW segment (green) and the Ge segment of the NW as well as the 2D layer that forms on the Si wafer surface (yellow) followed by a purple gold droplet at the very tip of the NW. Note that Ge decoration is visible on the Si NW segment. This finding indicates that Ge surface diffusion does probably not occur to a large extent. The Ge segment in the NW is of comparable thickness to the 2D Ge layer on the Si wafer surface.

the initial component (Si) and a rising content of the second material (Ge). This result is in good agreement with modeling results shown in [33]. However, the Ge segment grown in this case is not long enough to completely exchange the Si content in the Au nanoparticle. Thus, an Si content still remained in the lower part of the nanoparticle in the EDX line scan. The short length of the Ge segment is due to a limitation in deposition time caused by our experimental set-up.\footnote{The window where the laser light is introduced into the PLD chamber is also coated with the growth species. This causes the laser fluence to diminish during the PLD run. We compensated for this issue by controlling the laser power, but when exceeding a specific amount of material on the window, the fluence cannot be maintained.}

Note that, despite this fact, the nanoparticle consists of pure Au after cooling down to room temperature and, based on EDX measurements, no growth species remain in the Au nanoparticle after finishing the VLS growth processes. This again is in contrast to the results reported in [39].

A comparison between the thickness of the two-dimensional layer deposited on the substrate during the PLD process and the thickness of the Ge layer on top of the NW shows both to be roughly identical (cf figure 5(d)), whereas in the case of Ge NWs grown directly on the Si substrate, the deposited layer on the substrate is only half as thick as the length of the grown NW (cf figure 3(b)). This clearly shows that, in the case of Ge NW growth directly on the substrate,

Figure 6. EDX line scan along the axis of the segmented Si/Ge NW; the inset shows the EDX mapping of the segmented NW and scan lines show the relative intensities of the different elements, i.e. Si, Ge and gold; the slope of the Si decay and the Ge increase are both exponential giving an interfacial abruptness of the order of $\sim 100$ nm. Surface material is incorporated both by diffusion and direct absorption of the growth species in the nanoparticle whereas diffusion is inhibited in the case of growth on top of an Si NW.

The growth of a Ge segment with a thickness equivalent to that of the Ge layer on the substrate clearly proves the growth by direct incorporation at this point.
The SiNW sidewalls are seen to be decorated with Ge. This Ge deposition is due to the PLD process, which coats all surfaces. The Ge deposited on the SiNW sidewalls is subject to islanding. This can be attributed to Stranski–Krastanov growth of Ge on the SiNWs [40]. The presence of these deposits on the NW sidewalls again shows that the growth species were not incorporated into the Au nanoparticle by surface diffusion.

Upon deposition of Ge onto the sample which already contained SiNWs, it can be seen that the Ge layer deposited on the substrate between the NWs is discontinuous and rather forms triangular islands (cf figure 5(b)). This island formation is due to the strain between Ge and Si that can be relaxed elastically by three-dimensional island formation [41, 42]. It is worth mentioning that the two-dimensional Si layer stays intact and no intermixing between Si and Ge layers takes place.

In the NWs, however, strain-related effects such as plastic relaxation by extended lattice defects such as dislocations or stacking faults [43] cannot be found. This is most probably due to elastic strain relaxation in one-dimensional NW structures due to their large free surface area [44].

Although the Au-catalyzed VLS growth of NWs has already been investigated in detail, still, the initial phase of NW nucleation is not fully understood. There is a controversy if the eutectic droplets form during annealing of an Au layer by incorporating material from the substrate or if the material’s incorporation from the gas phase in the initial phase of NW growth liquefies the Au nanoparticle. There are several reports on an ‘incubation time’ for NW growth, which means that the NW growth starts with a characteristic time delay after the supply of precursor gas is turned on. This time is attributed to be required for forming the eutectic and supersaturating the Au nanoparticle by incorporating growth species from the gas phase [45, 46].Kim et al [47, 48] showed this incubation time for NW growth in an in situ TEM experiment: however, they used SiN as a diffusion barrier, thus preventing Si incorporation from the substrate.

In contrast with these results, in the case of the heterojunctions in NWs presented here, the eutectic is formed by remelting the top of the initial NW as can be seen by interpreting the transition region.

If the eutectic formed by incorporating material from the gas phase, no material from the NW bottom section should be found in the transition region. So in this case, the heterojunction should be rather sharp like is known for a VSS process [16]. We, however, observe a transition region with the content of the material in the lower section of the NW diminishing exponentially and thus in line with the model by Li et al [33]. This model actually describes a non-interrupted VLS process with the droplet staying liquid during the entire growth time.

The absence of a sharp heterojunction in our results therefore proves that the gold droplet was already liquid after heating the sample for the second growth step.

Although the two-dimensional Ge layer deposited on the substrate makes EDX analysis of the NW–substrate interface difficult, the slope seen at the NW–substrate interface in figure 4 implies that this melting behavior also occurred at the NW–substrate interface. We therefore conclude that the Au nanoparticles liquefied by incorporation of material from the substrate into the nanoparticle.

The incubation times for the start of NW growth on a silicon substrate without a diffusion barrier layer reported by Clement et al [46] thus represent the time required to supersaturate the already molten Au nanoparticle beyond equilibrium.

In addition, this result shows that sharper heterojunctions than those obtained here cannot be formed by an Au-catalyzed VLS process.

Wen et al showed the growth of heterojunctions between Si and Ge with a very small region of intermixing [16]. This was assumed to be possible due to a VSS process catalyzed by a solid Au–Al alloy. Whilst enabling the better heterojunction abruptness, the use of a VSS process decreases the growth velocity and the yield of the grown NWs. Therefore, a VLS process like the one shown in our work may have advantages for technological applicability even if it cannot reach the interface abruptness realized by VSS processes.

4. Conclusions

A combination of PVD and CVD techniques was successfully used to realize comparably abrupt axial heterojunctions between pure Si and pure Ge in NWs using a gold-catalyzed VLS approach. For the first time reported in the literature, a complete axial transition between Si and Ge was realized using the VLS approach.

The interfacial Si–Ge alloy region is of the order of the NW diameter as predicted by a model derived by Li et al [33]. This model was developed for uninterrupted CVD growth of VLS NWs. Our good agreement of junction abruptness and junction width with predictions by Li et al indicates that their modeling is valid not only for CVD but for PVD VLS growth as well.

Even the growth interruption which takes place when moving the sample between the different growth chambers for Si and Ge segment deposition obviously does not disturb the epitaxial VLS process. This includes the fact that the 1D NW growth-mediating Au nanoparticle solidifies when the sample is moved between processes and is remolten in the second growth step.

We proved that the Au nanoparticles saturate with semiconductor material (Si, Ge) initially from the underlying substrate material and are supersaturated from the gas phase thereafter, a fact which has been a controversy in the literature so far.

Lattice strain between Si and Ge in 2D layers usually results in the formation of extended lattice defects such as dislocations or stacking faults or even islands form to relax lattice strain elastically. Neither observation could be found between the NW segments in our Si–Ge NW growth experiments. Presumably this is due to effective elastic strain relaxation in 1D structures of nanoscale dimensions as proposed by Dailey et al [44]. However, lattice strain is found in TEM studies to result in strain-induced defect formation and islanding in the 2D PVD Ge layer between NWs on the lattice-mismatched Si growth substrate.
The PLD technique used for the deposition of the Ge segment of the NWs can be applied to grow NW segments of a wide variety of materials. We already reported on the realization of doped SiNWs using this approach [22]. Other materials systems, e.g. compounds such as InGaAs/GaAs or even quaternary compounds, might also be used in a PLD set-up just by the choice of the ablation targets. Therefore, axial p–n junctions as well as heterojunctions between various materials in NWs can be possibly realized using this versatile growth technique which has the advantage not to require the use of any poisonous gases.

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