Copper-Nanoparticles as a Catalyst for InAs-Nanowire Growth during Molecular Beam Epitaxy

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1 Abstract

We study the usefulness of copper as a catalyst for the growth of InAs nanowires in a MBE-system. The project focuses on characterization of surface crystals using scanning electron microscopy. After first confirming that annealing causes a thin Cu-layer to form nanoparticles, growth is attempted at different temperatures on (111)B and (001) oriented surfaces. Finally, there is found no convincing proof of free-standing NWs, however onedimensional crystals are found growing horizonthally along the surface, with roughly the same dimensions as short nanowires.

2 introduction

Limitting the size of a semiconducting crystal in two dimensions to form a nanowire can have uses in different fields within modern physics[1][2].Physically, 1d and 2d structures confines conducting electrons so a more discrete set of energies are allowed. They are also characterized by a large surface compared to conductivity, which is practical for nano sensors.

Luckily, methods have been discovered, and are being refined, for creating nanowires with diameters less than 50 nm by epitaxial growth, where one can achieve both very high purity of the material as well as some control over the crystal structure of the wires[3].

The most common way to start such a growth is to deposit droplets, also called seed-particles, of a catalyst metal, usually gold, on a clean substrate, anneal the particles by heating them in a vacuum and then add the desired material either through chemical processes involving vapour as a carrying medium(for instance in metal-organic vapour epitaxy (MOVPE)) or as a beam of atoms(Molecular Beam Epitaxy, which was used in this project). Sometimes the anneal needs to take place within a flux of some of the materials of the substrate, to prevent dissipation, in particular arsenic is prone to dissipate at annealing temperatures.

The end result is wires standing as columns with heights, or lengths, up to many micrometers and diameters down to 10 nanometers. Oftentime the seedparticle remain at the top while the wire grows beneath it. A perceived similarity to standing hairs earned the wires the name nanowhiskers in some older litterature.

The growth process is not yet completely understood, however the Vapour-Liquid-Solid(VLS) model gives an explanation[4], where the gold particles are assumed to be liquid droplets at the growth temperature. Incoming particles from the vapour or beam will often diffuse along the substrate until they reach a droplet, where they might be absorbed. As a result the droplets becomes supersaturated with material, and the surplus can then pass to the solid phase, merging with the substrate below the droplet.

Apart from gold other metals such as silver and copper have been found to act as a catalyst for the VLS-proces[5][6]. Also, though not quite understood yet, catalyst-free "selfseeded" nanowires have been grown in recent years[7].

This project also serve as an introduction for me to some experimental methods, most importantly electron microscopy. The use of the plural first person throughout the text reflects the cooperation with my supervisor Jessica Bolinsson and others on the Qdev at NBI. My own contribution mainly consist in the examination and evaluation, while the actual growth were handled by more experienced staff. All pictures used were taken by me.

2.1 Seedparticles and Annealing

As mentioned most epitaxial growth of NW relies on nanoparticles of a certain metal, with diameters less than 100nm. They can either be deposited directly on the surface as aerosol, or created in-situ by heating a thin metal layer until it breaks up into islands. The latter method has the added bonus that the heating also anneals the seedparticles, removing impurities and oxygen by degassing and deoxidizing. Studies[8][9] have also shown that the annealing causes the catalyst metal to interact with the substrate, forming an ultrathin wetting layer with particles integrating into the substrate crystal structure. Another result of the annealing is reconfigurations of the surface, which can cause cracks and reefs that can interfere with particle diffusion and so inhibit NW growth. Usually the conditions can be adjusted to minimize the latter effect, but seeing as we are in unchartered territory with the copper, the reconfiguration played a major role in this project.

2.2 Substrates

NWs are usually grown both from and on very pure crystals of semiconducting elements. Silicon are often used, and so are III-V-group compounds, like GaAs or InAs. This is obviously part of the attractiveness of the field as the same substances are already used in sophisticated electronics.

The crystal structure of the substrate can also be determining for the directions in which NW's wil grow. When using a cubic zincblende substrate the wires are often found to grow in the (111) direction[10]. The surface is therefore usually given a (111) orientation

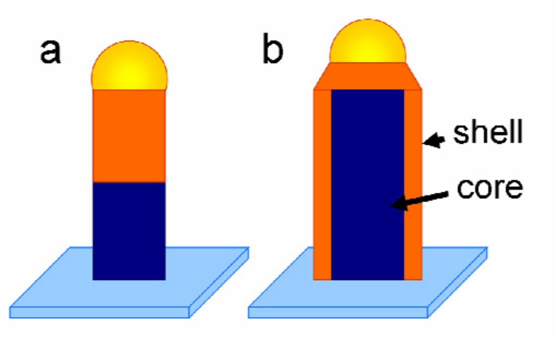


Figure 1: By using different materials, at different times and conditions, during epitaxy, it is possible to create NWs with axial (a) and radial (b) heterostructures[13].

to ensure the NWs stand straight.

2.3 Epitaxy

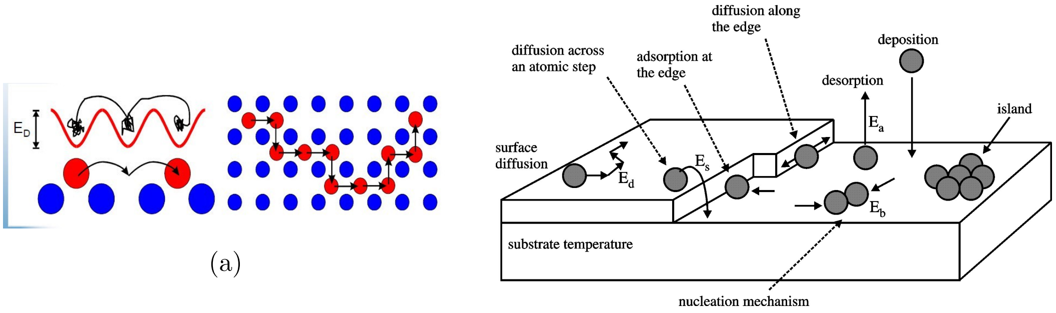
Epitaxy refer to an ordred deposition of new crystal layers. Several different methods for transferring new particles to the surface of the substrate. Molecular Beam Epitaxy works by heating a reservoir of the material to be deposited until particles take off as sublimation, and due to a high mean free path they can be directed to the sample, arriving as a beam. On the new surface the particles will then often diffuse to places where the change in Gibbs free energy is lower for a transistion back to the solid phase. Such places could be along edges or outcrops, but if the surface is smooth enough, a very fine film can also be formed.

An important aspect of the epitaxial growth is that it happens under circumstances where thermodynamical equilibrium cannot be assumed, making the process hard to describe with precision from theory, and the outcome hard to predict.

Epitaxy where only one compound is deposited is called homoepitaxy, in contrast to heteroepitaxy where the material to be deposited is changed at some points in time. Heteroepitxy allows the growth of crystals with different layers, for NWs it has been used to both vary the material along the length, axial heterostructures, and through the width of the NW, growing shells around a core, radial heterostructures.

2.4 Surface Diffusion

Atoms adsorped on the surface during epitaxial growth are called adatoms. Now if the lattices of the substrate and the adsorped material match each other, the adatoms will



(a)

(b)

Figure 2: Surface diffusion, (a) shows how the transistions across the surface can be considered a 2d random walk. The red circles are adatoms while the blue are atoms in the substrate. (b) shows how adatoms after a time will either settle at edges in the substrate or form clusters or islands.[14][15]

be bound to the crystal grid. The surface can be thought of as covered in potential wells[11], however as the adatoms usually are only bound to the lattice through a single nearest neighbour-atom in the surface, the wells are no deeper than the adatom might, given enough thermal energy, pass through a transistion state to another position on the surface. In places where the adatoms are bound to more neiughbouring atoms, such as at an edge or in a cavity, the potential well is deeper, and once an adatom is nestled at such a spot, it will be less likely to change its position or desorp again.

For NW growth diffusion is critical to understand why deposited material settle almost exclusively under the seedparticles. In the VLS-model the liquid droplet binds diffusing adatoms much better than the solid surface around it. It has also been found that even if the seedparticle is not liquid at the growth temperature, the interface between the seedparticle and the substrate is still a sufficiently beneficial area for the adatoms to nest, that NWs can be grown[10].
In the time an adatom spends on the surface before being desorped it will travel a random distance. The average distance travelled is known as the diffusion length. While a higher temperature makes transistions across the surface more frequent, it also makes the adatoms more likely to desorp, and so shortens the average time they stay on the surface. Therefore it has been found that for temperatures above a critical point, depending on the subtances used, the diffusion length decreases for higher temperatures, while below this point the diffusion length increases[11]. This also means that theoretically there exist a maximum diffusion length just below a critical temperature. In an experiment

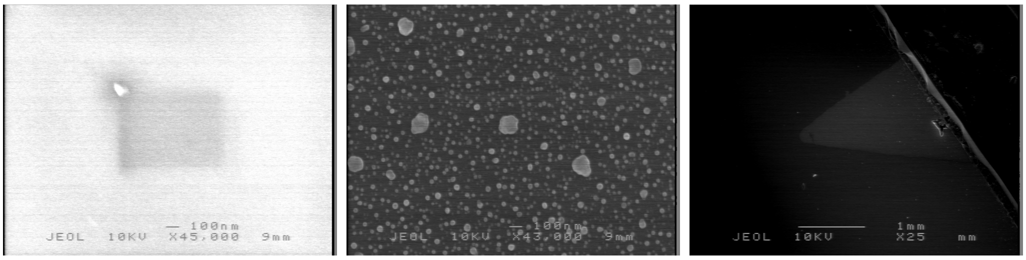
by Linus E. Jensen et al. InAs NWs were grown in a hexagonal pattern[17]. It was found that when the seperation between the NWs were less than the diffusion length (found to be a few μm) the NWs competed for material. The effect was that the growth rate of the NWs were proportional to the logarithm of the seperation distance.

2.5 Electron Microscopy

To observe structures with dimensions of less than 100 nm, visible light would be useless due to its relatively high wavelength and diffraction limit. We therefore rely on electron microscopy, either scanning (SEM) where a beam being probed over a region causes the surface to emit secondary electrons which can be detected to determine the obseved topography, or transmission (TEM) where electrons pass through the sample before reaching a detector. While TEM can achieve much higher resolution than SEM, it relies on the sample to be ultra thin and in a well defined position. For these reasons this project has used solely a SEM, allowing us to explore surfaces over some range of depth. The principle behind a SEM is not to different from an optical microscope, it involves a source of electrons which are sent through a set of magnetic component acting as lenses, directing the electrons onto a point, which can be down to a few nm across. For the electrons to reach the sample it is of course necessary that the process takes place in a vacuum. The focussed electron beam is scanned over the sample, and a detector catches secondary electrons, emitted from the surface. Some of the incoming electrons are also elastically back- scattered from the surface, and a portion of these can also be detected. The backscattered carry more information about the matter in the sample, more being scattered from heavy elemets than from light.

3 Annealing

Before we try to initiate growth, we need to know that the annealing causes the copperlayer to form into droplets of the appropriate size. The annealing is also used to degas and deoxidize the substrate, to ensure a low level of impurities. Five samples were prepared by deposting a 5 nm thick layer of copper on InAs(111b) substrates. The deposition were carried out using an AJA-system, which evaporated copper in a vacuum so it could condense on the sample. During the metaldeposition a mark is left by the clip holding the sample. This mark, where no copper is deposited, is later used as a control area to determine whether any effects are truly caused by the catalyst metal.
The first sample were left completely unannealed, as a control to study the effect without metal deposition. The second sample was only subjected to degasification at 250° C for



(a) S1 without any heating. (b) S2 only degassed. (c) Clipmark on S1.

Figure 3: The mark in the middle on figure (a) is made by focusing the SEM on and area for a few minutes and then zooming out. It's used to show that the surface is in focus. (c) Is an overview of the mark left behind by the clipholder when copper was deposited on the rest of the sample. (Notice the different scale bar for (c))

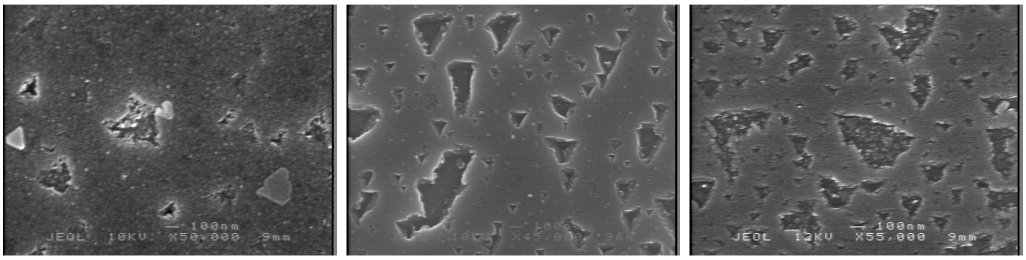
one hour under As flux. The remaining three samples were degassed likewise before the temperature was brought up to 550^o and held there for different amounts of time. Our interest is how the difference in time for the last step will affect the samples.

sample Id	degasification	deoxidization
S1	-	-
S2	250^o C for 60 min	-
S3	250^o C for 60 min	550^o C 0 min
S4	250^o C for 60 min	550^o C 5 min
S5	250^o C for 60 min	550^o C 15 min

Table 1: Annealed samples. S1 is the control, left unannealed. The degassing took place under an As-flux. When we write that S3 was heated for 0 min, we mean that the temperature was brought right down again, after 550^o was reached. Notice that all five samples have (111)B surface orientation.

The samples are inspected with a scanning electron microscope(SEM). The unannealed sample displays a smooth, bright surface, whilst after the preannealing the copper clearly seems to have formed into droplets ranging in size approx 20-200 nm.

Looking at the annealed samples, we notice that the size and concentration of nanoparticles diminishes and that the surface around the droplets have changed, forming cavities, which tend to be triangular and aligned in the same direction. Focusing on the surface left smooth between the cracks, we found that there were no particles left at S5, possibly because all the copper had dissipated into the substrate. For the other samples,



(a) S3 (b) S4 (c) S5

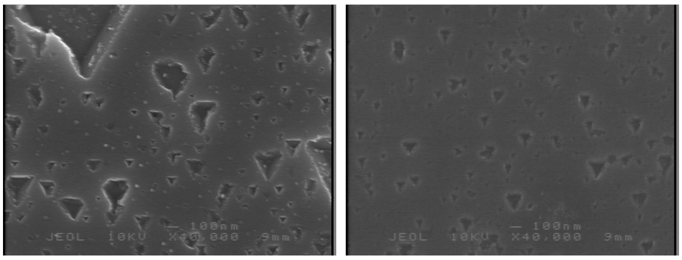
Figure 4: Annealed samples. The surface of all three has begun to form cavities, which fills a larger part of the surface for longer annealing times.

I used the program ImageJ to heighten the contrast, but due to the edges and cracks the program could not distiguish the particles, so I had to count by hand, and measure the area of each picture to get an estimate of the particle density. I found it to be 40 μm^{-2} for S3 and 20 μm^{-2} for S4.

However, S3 also had a higher concentration of surface crystals, which might inhibit diffusion, wherfore S4, although containing fewer droplets seemed like the best candidate for NW growth.

A question that might come to mind is whether all the copper that was originally deposited has formed into nanoparticles. To use a handwaving estimate, we'll assume that all the droplets are semispherical with a radius of 20 nm and consists of pure copper. For a concentration of 20 pr μm^2 this gives an amount of approx $3.35*10^{-4}$ μm^3 Cu pr μm^2 of surface. As we deposited a 5 nm thick Cu layer, this leaves around $4.65*10^{-3}$ μm^3 Cu pr μm^2, or around 93%, unaccouted for. Presumably the missing copper has either formed a wetting layer between the droplets, or sunk into the substrate. Som of it might also have condensed in pure form at the edges of holes. Comparison with the clipmark makes the last possibility seem likely, based on the difference in brightness of the edges.

In any case, it was confirmed that the annealing did leave behind Cu-droplets, which answered the primary question. To determine whether the cavities in the substrate also were caused by the copperlayer, we investigated the clipmarks on the samples. Here the same pattern of triangular holes were seen, although the mean size were somewhat smaller. So while the copper weren't the cause for the change, it might have accelerated it in some areas. In conclusion, annealing at 550° C forms nanoparticles, but the concentration decreases for longer times. We therefore decide to anneal the growth samples for a little less than 5 minutes.



(a) (b)

Figure 5: The surface of S4 is dominated by aligned triangular holes, (a) is outside and (b) is inside the clipmark.

4 Growth

We prepared six new InAs substrates. This time though three samples had (111)B and three had (001) surface orientations. We again deposited a 5nm layer of copper and left clipmarks for control. The six substrates are glued two and two to the same wafer so each of three samples actually contain two sub-samples, one of each orientation. All three are initially degassed at 250° for one hour under As-flux, and annealed at 550° C for 3 minutes before the MBE-system is used to deposit InAs for the growth. During the final step the temperature is lowered, with different temperature for each sample.

sample id	growth temperature
S6	425° C
S7	475° C
S8	525° C

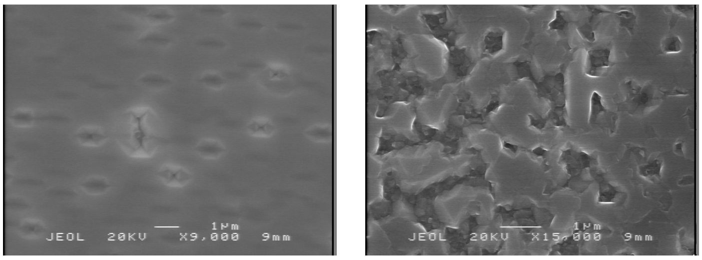
Table 2: Growth samples

4.1 S6 (425° C)

The sample with the lowest temperature showed no signs of NW growth on either substrate, neither were there any particular difference between the surface outside and inside the clipmark. A remarkable difference can be seen between the two configurations.

4.2 S7 (475° C)

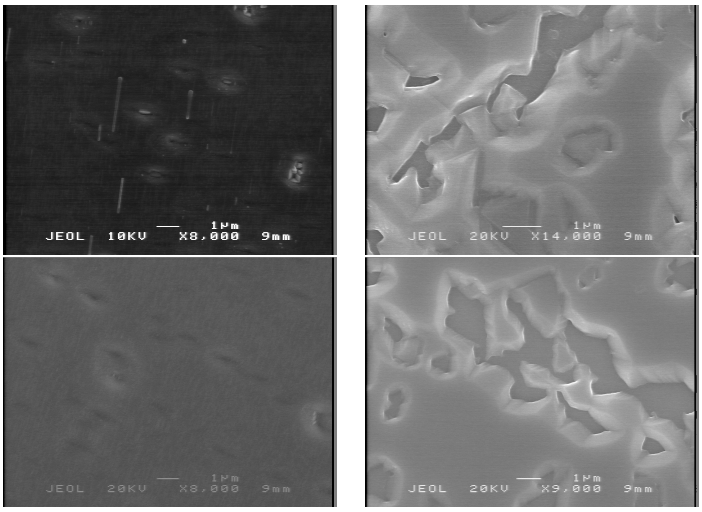
The difference between the (001) and the (111)B orientations are seen even more clearly on these sample, and on the former a clear difference is also seen between the copper-



(a) (001)
(b) (111)B

Figure 6: S6

covered areas and the clipmark. The basic surface structure is the same, but outside the clip we find rodlike crystals of length up to a few μm. These are seen only on the (001)-substrate.



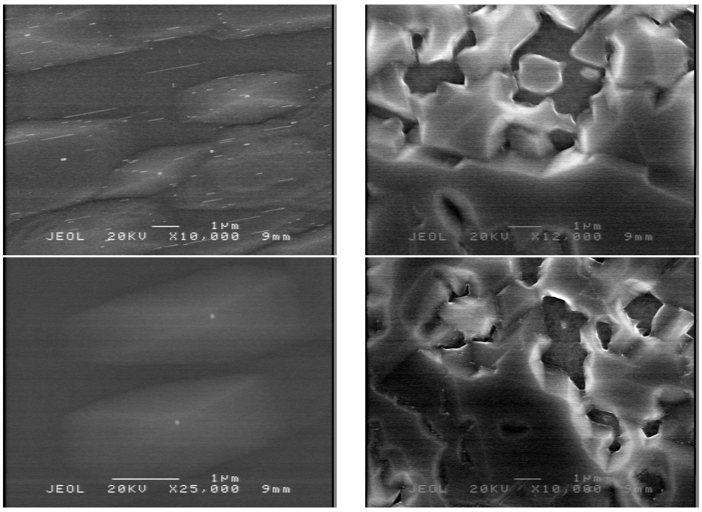
(a) (001)
(b) (111)B

Figure 7: S7. The top pictures show the ordinary surfaces while the bottom two shows the surface in the clipmark.

At a glance the crystals on the (001)-oriented sample might resemble NWs growing out at an angle(since they're visible from an angle completely orthogonal to the surface). However by tilting the sample up to 45° we saw that they did not change in length or orientation in comparison to the underlying structures. This indicates that they're growing along the surface instead of up from it. There's more on this in the discussion.

4.3 S8 (525° C)

The basic patterns are the same as from the previous, with no growth whatsoever on the (111)b and rodlike crystals on the (001). Unlike for S7 these rods are only seen on a limited region, approximately a quarter, whilst the rest of the sample is indistinguishable from the surface in the clipmark. The rods are somewhat thinner, and with less definition at the edges than the ones seen on Qdev 214.



(a) (001) (b) (111)B

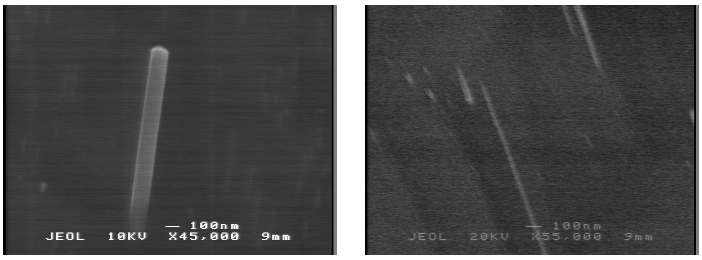
Figure 8: S8. The top pictures show the ordinary surfaces while the bottom two shows the surface in the clipmark.

Again tilting reveals that the rods are probably lying along the surface. They range in length up to 1.5 μm and are almost exclusively around 50 nm wide.

4.4 discussion

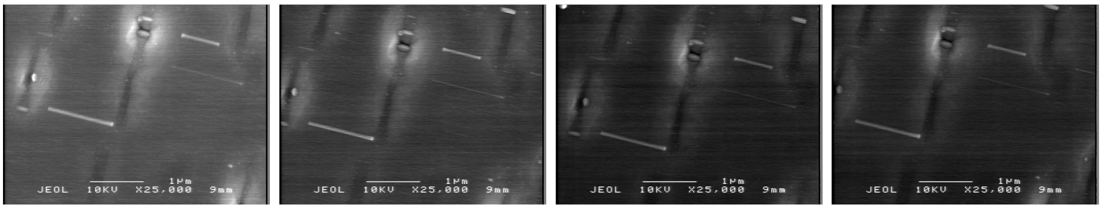
It certainly seems interesting how consistently (001) and (111b) substrates react quite differently in the MBE. Seeing how aligned in one direction the rods on the (001) samples are, their growth is very likely linked to the underlying crystal lattice, although whether they themselves have the same structure as the substrate have not been detemined in this study, but might be worth examining in the future..

to study the directions of the rods relatice to the surface plane, it is possibly to tilt the sample within the SEM. It's only possible within a range of 10° without removing and reinserting the sample, so only within these limits can a specific point on the surface be kept under observation during the tilting.



(a) S7 (001) (b) S8 (001)

Figure 9: The crystalrods on the surface of the two samples. The average thickness were higher on S7, while in some areas the concentration were higher on S8.



(a) 0^o tilt (b) 3^o tilt (c) 7^o tilt (d) 10^o tilt

Figure 10: Pictures taken on S7 with different tilt. The tilting happens around an axis that points toward the top of this page. Measurements were also made with the sample rotated 90 degrees in the same plane.

The length of the rods, or at least their projection on the pictures, can be measured by the program ImageJ, which counts the pixels. This has an uncertainty of more than ten nm, as the direction to measure along has to be put in by hand. No remarkable change in the length of the rods were found as the sample was tilted, although some of the longer might have been shortened with up to 20 nm at 10^o. This is however to small a change that we can be sure it really happened.

Assuming the rods started in the horizonthal plane, the relative difference in length one should expect at 10^o is:

$$1 - cos(10) \cong 0.015$$

.

Which for a length of 1 micrometer would equal 15 nm. In other words it seems quite likely that the rods are growing horizontally. We also found that objects on the surface do not change their internal positions during tilting, indicating that the surface itself is approximately flat.

The difference in the surface between samples with (001) and (111)B surface orientation might actually be the reason for why ordered growth can only be found on the (001) surfaces. The cavities that covered part of the surface of the simply annealed samples in the former section could have shortened the distance of diffusion on samples with (111)B orientation (recall that the annealing study only used (111)B and no (001)). In hindsight, or as a subject for future research, it might therefore have been worthwhile to also have studied the effect of annealing on (001) oriented surfaces. Judging by the samples which has been subjected to epitaxial growth, the (001) surface would be smoother, and the particles could have a larger chance of reaching the site of a seedparticle(Notice though that the only indication that the rods even grew from seedparticles are their absence in the clipmark).

In a study[16] by Vogel et. al. where chemical beam epitaxy were used in conjunction with Ag-seedparticles to grow InSb(111)B wires it was found that at temperatures higher than 380° C the growth rate of a parasitic film on the surface started to approach the growth rate of the NWs. It's dubious whether this result is relevant for our samples, where both epitaxy and catalyst are different, but assuming it holds it could explain the behaviour of the (111)B samples during growth: The seedparticles could have been swallowed up by a layer of InAs growing straight on the substrate. In favour of this hypothesis it can be pointed out, that the cavities we saw were created on (111)B substrates by annealing could have stopped deposited particle's diffusion across the samples, causing broad crystal-layer growth.

5 conclusion

Apparently NWs do not form from Cu-seed particles under a molecular beam of InAs. However highly aligned onedimensional surface crystals did form, and only in areas on which there had been copper. These were not seen at the lowest growth temperature of 425° C, and neither on the (111)b substrates.

6 acknowledgements

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