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Borgström, Magnus

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# Size- and shape-controlled GaAs nano-whiskers grown by MOVPE: a growth study

M. Borgström, K. Deppert, L. Samuelson, W. Seifert\*

*University of Lund, Solid State Physics, Box 118, S-221 00 Lund, Sweden*

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## Abstract

We have investigated the Au-catalyzed GaAs  $\langle \bar{1}\bar{1}\bar{1} \rangle$ B whisker growth under low-pressure metal-organic vapour phase epitaxy conditions. By varying the growth temperature we found a maximum in the whisker growth rate at about 450–475°C. With increasing temperature the growth rate decreases due to competing growth at the  $(\bar{1}\bar{1}\bar{1})$  substrate surface and at the  $\{110\}$  whisker side facets, which leads to significant tapering of the whiskers. For low temperatures, the growth rate  $R$  in the  $\ln R = f(1/T)$ -plot results in an Arrhenius activation energy of about 67–75 kJ/mol, a value which is in agreement with activation energies reported for low-temperature planar growth of GaAs from TMG and AsH<sub>3</sub>. The Au acts as a local catalyst and as a collector of reactants, enabling a liquid-phase-epitaxy-like growth with high growth rates at the GaAs  $(\bar{1}\bar{1}\bar{1})$ B/(Au,Ga) interface.

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## 1. Introduction

Whiskers can be grown as highly perfect one-dimensional nano-structures, suitable for basic physics investigations (nano-probes, transport physics, etc.) as well as for potential applications in optical and electrical devices (LEDs, RTDs, waveguides, field emitters, nano-probes, etc.). In most cases, the growth is initiated by the presence of metal particles, which act as catalysts. In the

classical description, the growth follows the vapour–liquid–solid (VLS) mechanism [1], although details are still under debate. Metal-organic vapour phase epitaxy (MOVPE) for growth of GaAs and InAs whiskers was already used by Hiruma et al. [2], with evaporated Au films, transforming into catalytically active nanoparticles by annealing. Very recently, the fabrication of whisker-based one-dimensional heterostructures has been reported [3–5] and their functionality in resonant tunneling structures has been demonstrated [6]. However, there are still many open questions to be answered before whiskers can be used as versatile building blocks

\*Corresponding author. Tel.: 46462227671;  
fax: 46462223637.

E-mail address: [werner.seifert@ftf.lth.se](mailto:werner.seifert@ftf.lth.se) (W. Seifert).

in nanostructure devices. We focus in this paper on investigating the growth mechanisms, with special emphasis on effects of growth temperature and reactant pressures on growth rate and the development of the shape of the whiskers.

## 2. Experimental procedure

In our approach, size-selected aerosol-particles of Au (surface density in the order of  $10^8$  particles/cm<sup>2</sup>) were deposited randomly at the GaAs ( $\bar{1}\bar{1}\bar{1}$ )B surface [7]. The diameter of the Au particles defines, in a first-order approximation, the diameter of the growing whisker. Before growth under low-pressure (10 kPa) MOVPE conditions, the Au particles were annealed at the surface for 10 min in a H<sub>2</sub>/AsH<sub>3</sub> atmosphere at a temperature of 580°C. During this annealing step surface oxide will be desorbed and Au will be alloyed with GaAs, primarily by an up-take of Ga in the Au droplet. After annealing, the tempera-

ture was ramped down to the temperature  $T_G$  of whisker growth.  $T_G$  was chosen between 380°C and 520°C. Whisker growth started when TMG (trimethylgallium) was supplied to the reactor cell. A constant AsH<sub>3</sub> pressure (a fraction of  $5 \times 10^{-4}$  in 6 l/min H<sub>2</sub>) and three different TMG flows were used, corresponding to As/Ga ratios of 80, 40 and 27. The whisker growth time was kept constant at 2 min for all the experiments. A few experiments were done with an increased AsH<sub>3</sub> flow, or an increased TMG flow. It turned out that a higher AsH<sub>3</sub> pressure had no significant effect on the whisker growth rate, whereas an increase of TMG led to a further increase of the growth rate. The whisker structures were characterized by scanning electron microscopy (SEM).

## 3. Results and discussion

Examples of whiskers grown in our MOVPE experiments are shown in Fig. 1. All the whiskers

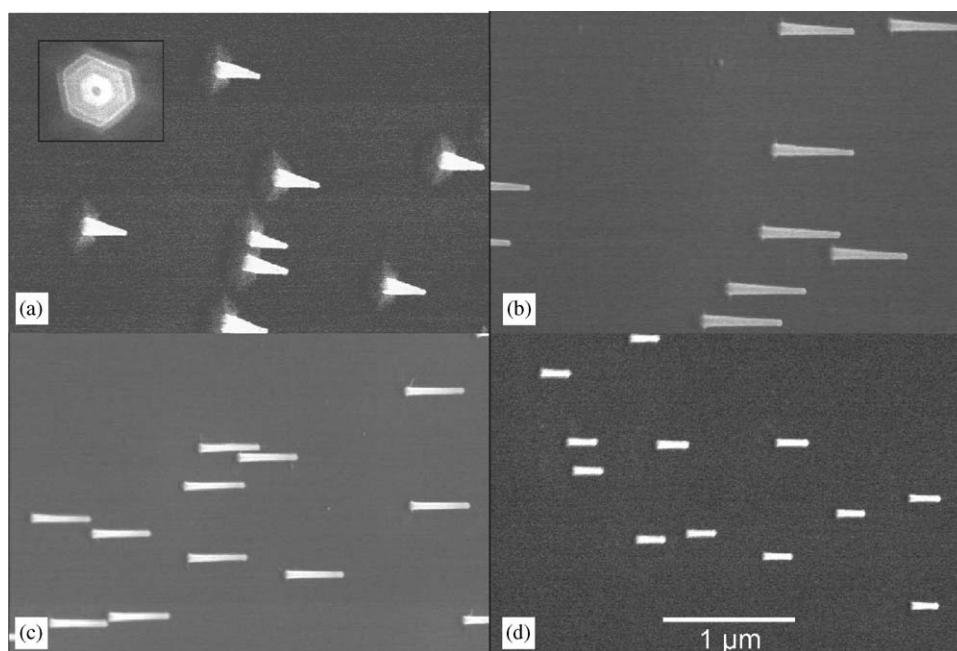


Fig. 1. SEM images of whiskers grown at different temperatures: (a) 520°C, (b) 475°C, (c) 450°C and (d) 400°C. The substrate is ( $\bar{1}\bar{1}\bar{1}$ )B GaAs, tilted by 45° towards the e-beam. The length bar is indicated in (d) and the magnification of the images was 33 000. The inset in figure (a) shows a whisker seen from the top, visualizing the hexagonal cross-section with the  $\{\bar{1}10\}$  side facets. The pyramids at the bottom develop a trigonal symmetry with facets of  $\{\bar{1}00\}$  and  $\{\bar{1}\bar{1}0\}$ .

are growing in  $\langle \bar{1}\bar{1}\bar{1} \rangle_B$  direction, i.e., they are standing vertically on the  $(\bar{1}\bar{1}\bar{1})$  As surface. In addition, also on  $\{011\}$  cleavage planes, which were exposed to Au deposits, whiskers were growing. On such surfaces the whiskers are also oriented in one of the  $\langle \bar{1}\bar{1}1 \rangle_B$  direction which forms a  $109^\circ$  angle with the  $\langle \bar{1}\bar{1}\bar{1} \rangle_B$  on the  $\langle \bar{1}\bar{1}\bar{1} \rangle_B$  surface. Whiskers grown at lower temperatures are rod-shaped with  $\{\bar{1}10\}$  side facets. There is a clear tendency that with increasing growth temperature, the whiskers get increasingly tapered with the thicker end at the base of the whisker. These trends are in agreement with observations of Hiruma et al. [2].

We have measured the length of the whiskers by evaluating the SEM images. For this purpose the substrates were tilted against the e-beam by  $45^\circ$ . The results of this evaluation are plotted in Fig. 2. Each measurement point represents an average over about 40–100 whiskers, selected from areas of high whisker homogeneity. There is a maximum in growth rate at a medium temperature of about  $450\text{--}470^\circ\text{C}$  for all three TMG flows. Towards higher temperatures the growth rate decreases, the lower the TMG flow the more pronounced the effect. Towards lower temperatures the  $\ln R = f(1/T)$ -dependence decreases almost linearly, indicating kinetically limited growth with an Arrhenius energy of between 67 and 75 kJ/mol.

The reason for the decrease in growth rate towards higher temperatures is most probably the onset of competing growth on  $\{\bar{1}10\}$  side-facets (therefore the tapering) and on the Au-free  $(\bar{1}\bar{1}\bar{1})_B$  substrate surface. Towards lower temperatures almost no growth occurs at those surfaces. Growth under those conditions of kinetic hindrance happens therefore preferentially only at the whiskers Au/GaAs  $(\bar{1}\bar{1}\bar{1})_B$  interface. This interface acts as the sink at the surface where the supersaturation can be diminished. Consequently, towards lower growth temperatures the whisker shape gets rod-like, and the diameter of the whisker will approximately be defined by the diameter of the Au particle on top. Note that the whisker growth could also be affected by slight temperature-dependent composition and geometry changes of the Au droplet, an effect, however, which we consider to be negligible for our situation.

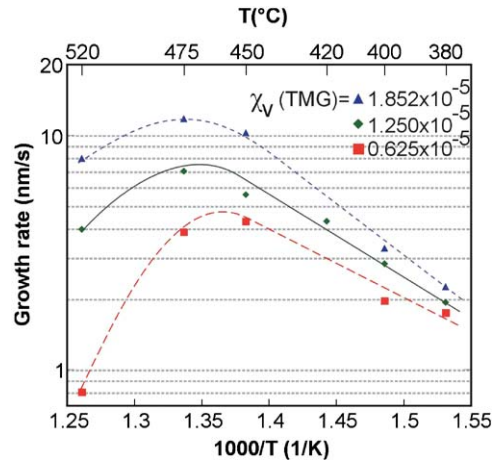


Fig. 2. A plot of the whisker growth rate versus  $1/T$  for three different TMG molar fractions,  $\chi_V(\text{TMG})$ . Lines are guidelines for the eye. The slope of the low-temperature branches results in Arrhenius activation energies between 67 and 75 kJ/mol for the low and the high TMG flow, respectively.

One notable observation is that the growth rate maximum is peaking at temperatures where previous publications report the complete decomposition of TMG [8]. Coming from lower temperatures, it was found that TMG stepwise loses its methyl groups until at about  $465^\circ\text{C}$  also the last  $\text{CH}_3$  group has left the relatively stable monomethylgallium molecule. In Ref. [8], it was also reported that this TMG decomposition, in contrast to the decomposition of  $\text{AsH}_3$ , is not very sensitive to the presence of GaAs deposits or GaAs substrates in the reactor cell. In a later investigation, however, it was found that especially at GaAs  $\langle \bar{1}\bar{1}\bar{1} \rangle_B$  surfaces, in the absence of  $\text{AsH}_3$  and at temperatures above  $460^\circ\text{C}$ , Ga globules were formed and that in this case the TMG decomposition was enhanced by the Ga on the surface [9]. We assume that complete decomposition is a precondition for dissolution of Ga within the Au droplet on top of the whisker. Therefore, the decrease in whisker growth rate with decreasing temperature is most probably related to TMG decomposition as the limiting step. The slope of the  $\ln R = f(1/T)$  dependence approximately fits to an Arrhenius activation energy  $E_A$  between 67 and 75 kJ/mol, a value which is in agreement with  $E_A$ -values found

for the overall GaAs low-temperature MOVPE process [10]. This agreement covers even the slight differences in  $E_A$  found for different V/III-ratios: with increasing input V/III  $E_A$  slightly decreases. Within this view, obviously, the Au/Ga-particles have no influence on the overall-kinetics of the MOVPE process. The function of the Au/Ga-particle is to act as a local catalyst by collecting the decomposition products and enabling a liquid-phase-epitaxy-like deposition process at the GaAs( $\bar{1}\bar{1}\bar{1}$ )/(Au,Ga)-interface. In fact, due to the high local concentration of Ga (we estimate less than about 20% Ga within the Au-droplet) the whisker growth rates come well in the order of growth rates typically observed for liquid phase epitaxy [11].

A few experiments were carried out with a doubled  $\text{AsH}_3$ -flow in the kinetically controlled, low-temperature range, with the result that this had no significant effect on the whisker growth rate. This means that within the range of the chosen growth parameters, with V/III-ratios between 27 and 80, the availability of As at the growing interface is not a growth limiting factor.

We also performed a few experiments with an increase of the TMG flow by a factor of 1.5 in relation to our higher TMG flow. This increase had a significant effect on the growth rate, whereby only a very weak trend towards saturation is visible, see Fig. 3. This means that within the range of chosen growth parameters we do not yet reach the upper limit of growth rates at the whisker ( $\bar{1}\bar{1}\bar{1}$ )B surface.

#### 4. Summary and conclusions

We have investigated the Au-catalyzed growth of GaAs  $\langle\bar{1}\bar{1}\bar{1}\rangle$ B whiskers under low-pressure MOVPE-conditions. Varying the growth temperature, we found a maximum in the whisker growth rate at about 450–475°C. With increasing temperature, the growth rate decreases due to competing growth at the ( $\bar{1}\bar{1}\bar{1}$ )B substrate surface and at the  $\{110\}$  whisker side facets, which leads to significant tapering of the whiskers. For low temperatures, the growth rate decreases almost linearly in the  $\ln R = f(1/T)$ -plot. The slope

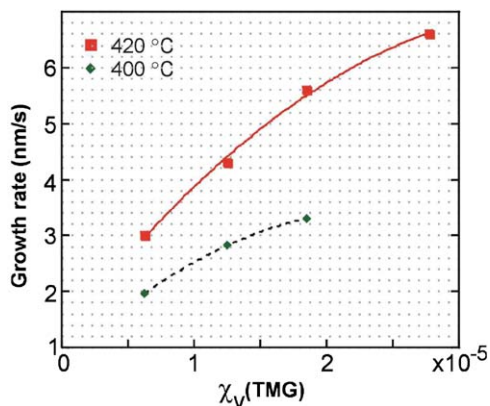


Fig. 3. A plot of the whisker growth rate versus the molar fraction of TMG,  $\chi_V(\text{TMG})$ , with the  $\text{AsH}_3$  molar fraction of  $\chi_V(\text{AsH}_3) = 5 \times 10^{-4}$ . Lines are guidelines for the eye. Note that there is only a weak tendency to reach saturation with increasing TMG flow.

results in an Arrhenius activation energy of about 67–75 kJ/mol, a value which is in agreement with activation energies reported for low-temperature planar growth of GaAs from TMG and  $\text{AsH}_3$ . Our results indicate, therefore, that it is not the reaction at the ( $\bar{1}\bar{1}\bar{1}$ )B/(Au,Ga)-interface which limits the whisker growth rate, but the processes outside the Au droplet. The Au on top of the whiskers does not affect the activation energy of the global deposition process. It acts as a local catalyst only and as a collector for the reactants, enabling a liquid-phase-epitaxy-like growth with high growth rates at the ( $\bar{1}\bar{1}\bar{1}$ )B/(Au,Ga) interface.

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