Size and shape controlled GaAs nanowhiskers grown by MOVPE

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Introduction

Whiskers can be grown as highly perfect one−dimensional nano−structures, suitable for basic physics investigations (nano−probes, transport physics…) as well as for potential applications in optical and electrical devices (LEDs, RTDs, waveguides, field emitters…). In most cases, the growth is initiated by the presence of Au−particles, which act as catalysts. In the classic description, the growth follows the VLS−mechanism (Vapour−Liquid−Solid) [1], although the details are still under debate. Very recently, the fabrication of whisker−based one−dimensional heterostructures has been reported and theirs functionality in resonant tunneling structures has been demonstrated [2]. Our previous attempts in whisker growth were based on CBE [3]. In this paper we report about our first results obtained in MOVPE.

Experiments

MOVPE for growth of GaAs and InAs whiskers was already done by Hiruma et al. [4], using evaporated Au films as catalyst, transforming into nanoparticles by annealing. In our approach size−selected aerosol−particles of Au (50−60 nm in diameter) were deposited at the semiconductor surface, which gives a better control over whisker−size and whisker−shape. The substrates used were (−1−1−1)B−oriented GaAs wafers. Before growth under low−pressure (100 mbar) MOVPE−conditions, the Au−particles were annealed at the surface for 10 minutes in a H_2 /AsH_3 −atmosphere at a temperature of 580 °C. After annealing we ramped down the temperature to the temperature T_G of whisker growth. A constant AsH_3 −pressure (a fraction of $5x10^{-4}$ in 6l/min H_2) and three different TMG−flows (trimethylgallium) were used, corresponding to As/Ga−ratios of 80, 40 and 27. The whisker growth time was kept constant at 2 minutes for all the experiments. A few experiments were done with an increased AsH_3 −, or alternatively an increased TMG−flow. It turned out that a higher AsH_3 −pressure had no significant effect on the whisker growth rate, whereas an increase of TMG led to a further increase. The whisker structures were characterized by SEM (scanning electron microscopy).

Results and discussion

Examples of whiskers grown in our MOVPE−experiments are shown in figure 1. All the whiskers are growing in <−1−1−1>B−direction, i.e., they are standing vertically on the (−1−1−1)As−surface. Whiskers grown at lower temperatures are rod−shaped with {110} 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. [4].

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°. The results of this evaluation are plotted in figure 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 450−470°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 lnR = f(1/T)−dependence decreases almost linearly, indicating kinetically limited growth with an Arrhenius energy of between 67−75 kJ/mol.

The reason for the decrease in growth rate towards higher temperatures is clearly the onset of competing growth on {110} side−facets (therefore the tapering) and on the (−1−1−1)B substrate surface. Towards lower temperatures at those surfaces almost no growth occurs. Growth under those conditions of kinetic hindrance happens therefore preferentially only at the Au/GaAs (−1−1−1)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 more rod−like, and the diameter of the whisker follows approximately the diameter of the Au−particle on top.

One remarkable observation is that the growth rate maximum is just peaking at temperatures where previous publications report the complete decomposition of TMG. Coming from lower temperatures it was found that TMG stepwise loses its methyl groups until at about 465 °C also the last CH_3 −group leaves the relatively stable monomethylgallium molecule [5]. It was also reported that this TMG decomposition, in contrast to the decomposition of AsH_3 , is not very sensitive to the presence of GaAs deposits or GaAs substrates in the reactor cell. 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 could be related to TMG decomposition as the limiting step. The slope of the lnR = 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

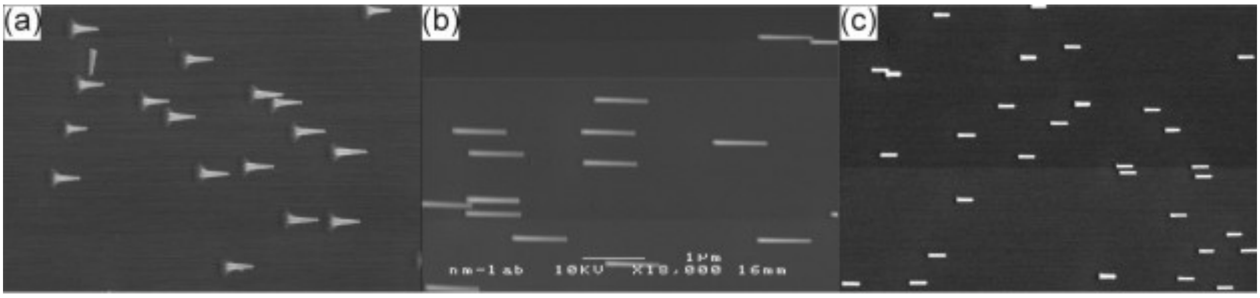

Fig.1: SEM images of whiskers grown with a TMG molar fraction of $1.85x10^{-5}$ at different temperatures, (a) 520 ºC, (b) 450 ºC and (c) 400 ºC. The substrate is (−1−1−1)B GaAs, tilted by 45 ° towards the e−beam. The scale is indicated in figure 1b).

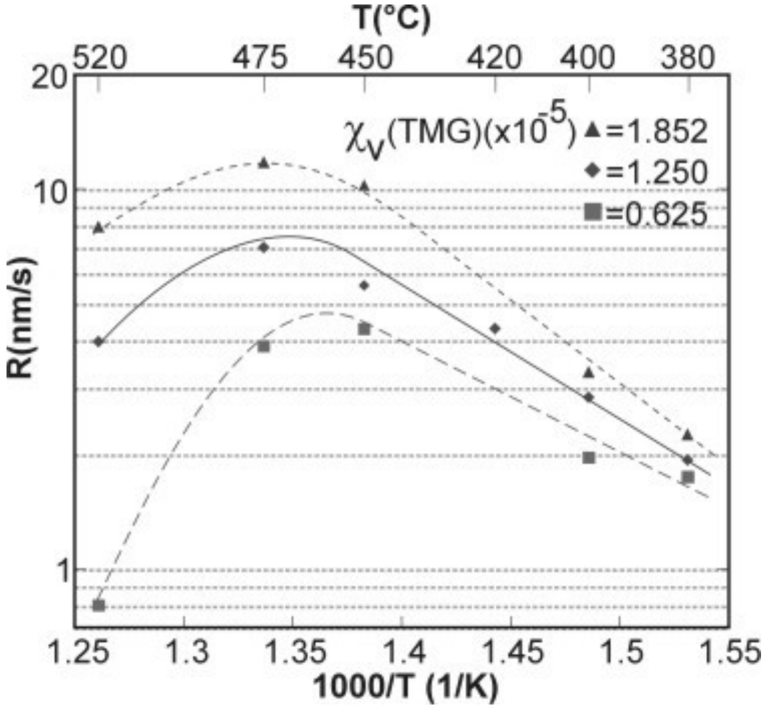

Fig. 2: A plot based on the medium whisker lengths obtained, growth rate versus 1/T for respective TMG molar fraction, x_v (TMG). Lines are guidelines for the eye.

for the overall GaAs low−temperature MOVPE−process [6]. Within this view, obviously, the Au−particles have no influence on the overall−kinetics of the MOVPE process. The function of the Au−particle is to act as a local catalyst by collecting the decomposition products and enabling locally a liquid−phase−epitaxy−like deposition process at the GaAs/Au, Ga−interface. In fact, due to the high local concentration of Ga (we estimate 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.

Summary and conclusions

We have investigated the Au−catalyzed growth of GaAs <−1−1−1>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 (−1−1−1)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 lnR = f(1/T)−plot. The slope 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_3 . Our results indicate, therefore, that it is not the reaction at the (−1−1−1)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 an only local catalyst and as a collector for the reactants, enabling a liquid−phase−epitaxy−like growth with high growth rates at the (−1−1−1)B/Au, Ga interface.

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