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RESEARCH ARTICLE

1D nanostructures grown on GaAs and InP substrates

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Abstract

Nowadays nanoelectronics is a very promising and dramatically developing field for physics basic research and R&D activities. The most common material for nanoelectronic components are the semiconductor nanowires, carbon nanotubes and metal nanowhiskers. There are still many questions about the growth and synthesis of these 1D nanostructures and the true nature of the growth mechanisms is yet undiscovered. There are some growth theories but neither of them can describe the whole growth process without leaving unanswered questions. Nanowires can easily be grown on III–V semiconductor substrates. The key is the presence of some catalyst particles. According to one of the growth theories the particles (atoms, molecules) diffuse into the catalyst particle which is a gold seed with the approximate diameter of 100 nm *in our experiments. A crystallization phenomenon occurs after reaching the critical concentration in the gold seed. Consequently a cylinder-shaped nanowire will grow under the gold particle (Tip-type growth).*

We show a 3D FEM (Finite Element Method) time-dependent model of the gas-gold-substrate system from which we can determine the concentration of dissolved matter in the gold particle vs. time. This model is an extended version of previous solid-state diffusion (SSD) models. The FEM modelling was performed based on earlier results of TEM (Transmission Electron Microscopy), SEM (Scanning Electron Microscopy) experiments and EDS (Energy-Dispersive Spectroscopy) analysis.

Keywords

Atomic Force Microscope · III-V semiconductor · nanostructure · nanowire

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1 Introduction

Nanometer-sized structures are very important and promising fields of research. Originally the first material for 1D nanostructures was carbon and it is still the focus of attention. Among inorganic materials other important substances are metals and metallic compounds, III-V and II-VI semiconductors and elemental semiconductors (silicon and germanium).

Besides silicon, the III-V semiconductors are the most important base materials in electronics industry. There are numerous applications of III-V compounds, mainly in photonics. The GaAs and GaAlAs lasers form the basis of Optical Processing Units (OPUs) in optical data storage systems—in CD and DVD players. Moreover, GaN-based lasers are intensively researched due to the cutting edge optical drives (Blu-Ray and HD-DVD).

Since the manufacturing technology of III-V is well developed, it is obvious that these materials will provide interesting future possibilities in the future of micro- and nanoeletronic devices. There have been numerous papers about manufacturing basic circuit elements, diodes, transistors, etc. using III-V nanowires. Good examples of their use can be found in photonic devices [1], [4], [5] and [7]. Though the line production of nanowires has not been yet solved, we can be sure that the metal and semiconductor nanowires will be the electronic material of the future.

In this paper we introduce a simple method for III-V nanowire synthesis and summarize the theories about nanowire growth. We emphasize the main difference between the two common theories [11],[12] and present a numerical model based on the solid-state diffusion regime. We show that the model results are in line with our experiments.

2 Experimental analysis

2.1 Sample preparing

The n+ Sn-doped (100)-oriented GaAs substrates were covered with a 50 nm thick gold layer by vacuum sputtering after cleaning. GaAs and InP substrates were placed into glass capsules with an approximate length of 5 cm each. Total inner volume of the capsules was about 1 cm^3 and the total inner pressure was $p = 6 \times 10^{-1}$ mbar. This pressure was generated by a vacuum pump during the sealing process which was carried out using traditional gas flame.

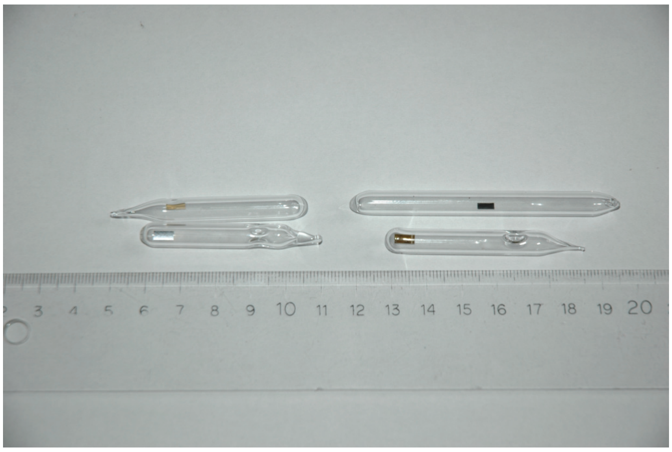

Fig. 1. Encapsulated GaAs and InP samples

2.2 Annealing process

The annealing was performed inside a silica oven. Typical temperature of the annealing were $T_{\mathrm{GaAs}} = 540\,^\circ\mathrm{C}$ in the case of GaAs and $T_{\mathrm{InP}} = 700\,^\circ\mathrm{C}$ in the case of InP.

2.3 Microscopy

It is a well-known fact [2] that a continuous gold layer with thickness of about 10–100 nm will be ripened during an annealing process. This process will provide the precursor particles for nanostrucure formation.

In the course of the present investigations, Scanning Probe Microscopy (SPM) was carried out on the ripened gold surface and tapping-mode atomic force microscopy mode for topographic imaging. The size of the formed gold particles is typically between 50 nm and 200 nm but it heavily depends on the parameters (temperature, duration) of the annealing.

The measurements were performed by Veeco SPM system (diInnova) in the laboratory of Veeco GmbH, Mannheim, Germany.

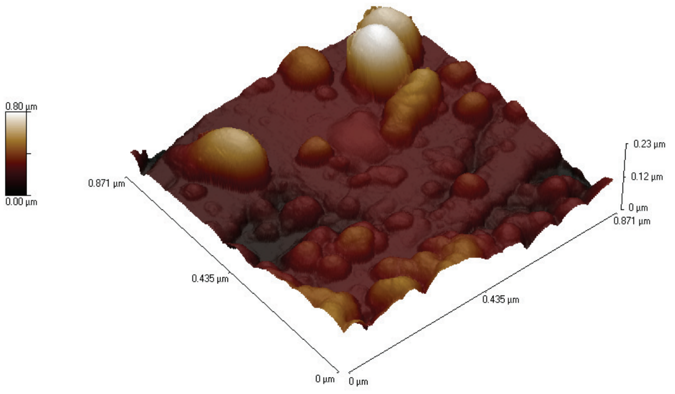

Fig. 2. AFM image of ripened gold surface on GaAs substrate.

In Fig. 2 hemisphere-shaped gold particles can be seen, which serve as seeds for nanostructure growth (note the different marker sizes in x, y and z direction). The typical aspect ratio of these particles is 1:1. Consequently in the FEM model (see Section 4) the approximation of the gold particle with a hemisphere is reasonable.

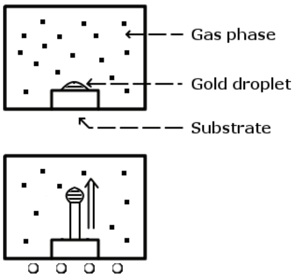

Fig. 3. Three steps of VLS crystal growth

It is not obvious from this figure that the gold surface forms a fractal-like structure, but the 2D grayscale topography image shows patterns with definite fractional dimensions. Analysis of fractal-like gold surfaces will be a main topic of a forthcoming paper.

3 Theories on growth mechanism

3.1 Vapor-liquid-solid growth

One of the oldest explanation of nanowire growth is the vapor-liquid-solid (VLS) mechanism and since its first mention [12] in literature in 1964, it has been widely used for growing low-dimension structures; since the discovery of 1D nanostructures (nanowires and nanotubes) a whole family of nanostructure growth is easily explained by this theory.

Regime of VLS method is based on catalyst-assisted[1] crystal forming. Semiconductor nanowires contain a catalyst droplet (usually some sort of metal or alloy, e. g. gold or titanium, depending on the chemical properties of the substrate). During an annealing process this catalyst particle is in a liquid phase and atoms or molecules from vapor phase are being dissolved in this droplet. Crystal growth begins when the droplet becomes supersaturated (see Fig. 3). It follows that the prerequisite of VLS mechanism crystal growth is a suitable solubility of a solid component in the liquid phase. In case of single-component nanowires, VLS theory can be a simple and efficient explanation of the growth phenomena.

VLS mechanism provides us a fairly simple explanation of single crystalline nanowire growth. Unfortunately there are some phenomena which cannot be reasonably explained.

3.2 Theory based on solid-state diffusion (SSD model)

According to the classic description of diffusion, if the particle flux is time-dependent, the following Partial Differential Equation (PDE) holds for particle concentration (Fick's

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[1] The word "catalyst" should not be interpreted in the chemical sense here: the catalyst particles do not have reaction accelerating role, they serve as condensation nuclei and initialize the wire growth.

II. Law):

$$\frac{\partial c}{\partial t} = -\nabla \mathbf{j} = \nabla \left(D \nabla c \right), \qquad (1)$$

where D is the diffusion constant, c is the particle concentration, and $\mathbf{j}$ is the particle flux. This equation was implemented in an FEM model in 3D (see Section 4).

Initial and boundary conditions are quite simple for our FEM model:

- *Inital value:* can be described by the gallium concentration at time $t = 0\,\mathrm{s}$.
- *Boundary conditions on the surface of the hemisphere:* We assume that thermal equilibrium holds for the surface of the gold particle. It means that the gallium flux through the surface is proportional (with the proportionality factor k) to the difference between concentrations in gas and solid phases:

  $$-\mathbf{n} \cdot \mathbf{N} = k \left(c^{g}_{\mathrm{Ga}} - c^{s}_{\mathrm{Ga}} \right), \qquad (2)$$

  where $\mathbf{n}$ is the surface normal, $\mathbf{N}$ is the particle flux; c^{g}_{Ga} and c^{s}_{Ga} denote the gallium concentration in the gas and the solid phase, respectively (von Neumann type boundary condition).
- *Boundary condition on the circle between gold particle and substrate:* We assume that the material of the nanowire will be built up by a chemical reaction. One of the reactants is gallium, the other reactant depends on the components in the gas phase (e. g. arsenic, oxygen etc.). We can also assume pseudolinear reaction, where for the reaction rate we can write:

  $$r = -k' c_{\mathrm{Ga}} c_{\mathrm{As}}, \qquad (3)$$

  which in practical terms means an outward flux towards the substrate.

A solid-state diffusion model for nanowire growth is introduced in [11] including the previously mentioned initial and boundary conditions. In this paper we show an extended model based on this work. The main difference between the previously cited paper and our work is that we used time-dependent 3-dimensional FEM modelling for determining the concentration of soluble component in the gold droplet over time.

3.3 Comparison of VLS and solid-state diffusion mechanisms

To summarize the main differences between VLS and solid-state diffusion mechanism and our extended solid-state diffusion models (XSSD), we have constructed the following table, which includes the main physical principles, the field of validity and typical material systems.

4 FEM modelling

FEM modelling was performed in order to determine the distribution of concentration in the gold droplet especially vs. time. (The basis of the Finite Element Method is not to be discussed here.) Our FEM model was used for solving Eq. (1) regarding the boundary conditions.

Gold particles on the surface of substrate were modelled by a hemisphere with a given diameter. During growth, this particle was the catalyzing seed. The growing wire was considered to be a cylinder with the same diameter as the hemisphere. (In the actual model, we did not take into consideration that the neck region has smaller diameter than the gold particle.) In the FEM model the substrate is an infinite two-dimensional plate. The geometrical 3D model of this structure can be seen in the following figure:

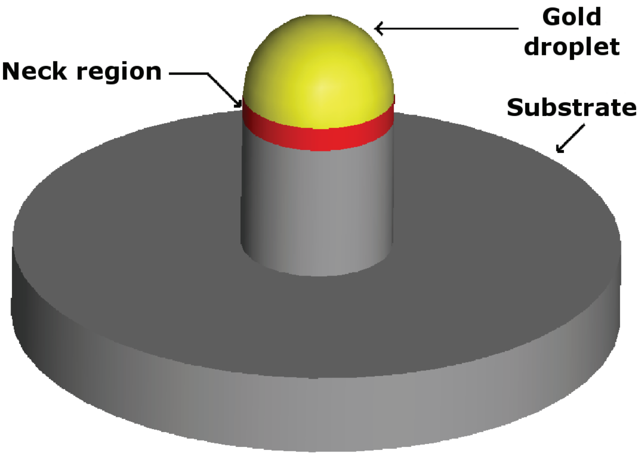

Fig. 4. Geometrical model of Au-GaAs system. The chemically active region is marked in dark gray

The physical model is fully described by Eqs. (1), (2) and (3). We implemented these bulk PDE and boundary conditions in a full 3D model by using a commercially available FEM software, based on [3].

4.1 Results of numeric simulations and comparison with experiments

We studied the rate of nanowire growth in our FEM model. The main difference between our investigations and those in earlier papers was the time-dependent behaviour of wire sythesis. We took into consideration that the concentration in gas and vapour phase (exponentially) depended on the temperature during the annealing process.

We also determined the maximum concentration of the soluble component (i. e. gallium in the following example). This $c_{\max}$ concentration showed an exponentially saturating dependence over time. This is not surprising: diffusion-type problems in a therodynamic equilibrium state often result in a saturating behaviour. The main question is to determine the characteristic time of this saturation.

The final result can be seen in the following figure. The boundary and initial conditions have been discussed earlier. The fitted curve has the following expression:

$$c_{\max}(t) = c_0 + A \exp\left(\frac{t}{t_1} \right), \qquad (4)$$

Tab. 1. Comparison of actual growth theories

Model	Main physical principles	Grown from	Controlled by	Character of the main process	Time dependence
VLS	Surface tension solubility	liquid	material flow in liquid	non-equilibrium	yes
SSD	diffusion	solid	diffusion	near equilibrium	no
XSSD	diffusion	solid	diffusion	near equilibrium	yes

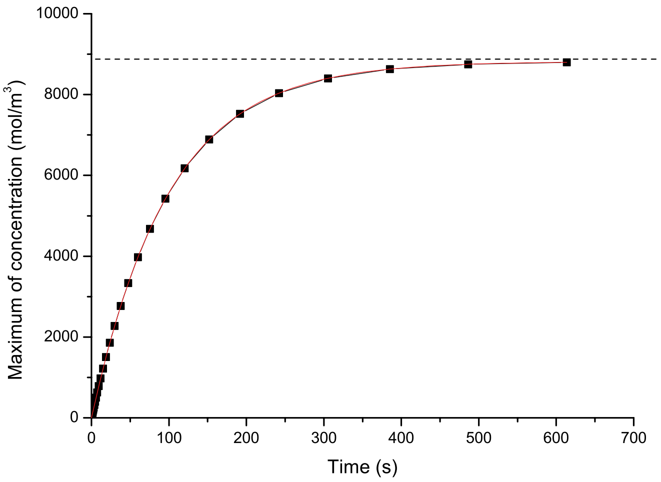

Fig. 5. Maximum of gallium concentration in gold droplet vs. time

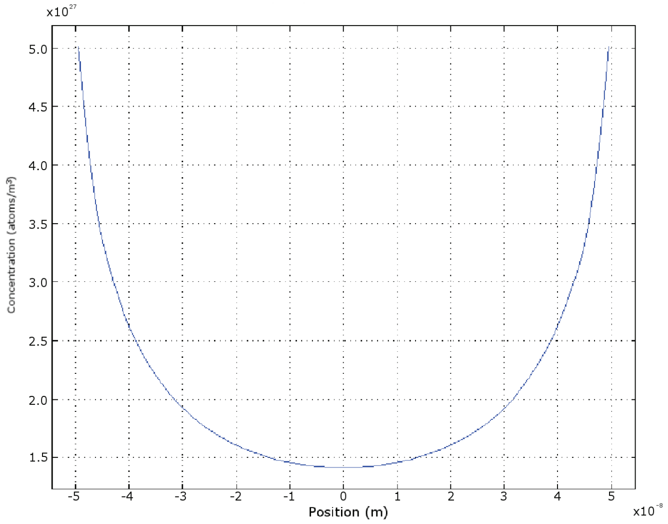

Fig. 6. Gallium concentration in the neck vs. radius

where c_0 is the initial concentration ($c_0 = 0\ \frac{\text{mol}}{\text{m}^3}$ in our model), $A \left[\frac{\text{mol}}{\text{m}^3}\right]$ and t_1 [s] are fitting parameters.

As it can be seen here, it takes about 10 minutes to reach the saturated gallium concentration in the gold droplet. After that time, wire growth can be initiated. It is a very good quantitative agreement with the experiments on GaAs substrates, where less than 10 minutes of annealing does not lead to wire synthesis. Papers published earlier [11] predicted faster condensation and growth, which were not compatible with our experiments.

Another important outcome from the FEM model is the soluble component distribution in the gold droplet, mainly in the neck region. The reaction kinetics determine the nanowire synthesis through the concentration and for that very reason is this distribution the main object of our investigations. Fig. 6 contains a cross-sectional plot of gallium concentration c_{Ga} in the neck. This graph was plotted in the state of thermal equilibrium.

Not surprisingly the distribution over a diameter of the gold droplet is symmetrical which generates a cylindrical wire. Maximum of gallium concentration is more than $5 \times 10^{27}\ \frac{1}{\text{cm}^3}$ and at minimum is about $1.5 \times 10^{27}\ \frac{1}{\text{cm}^3}$. Theoretically, this shows not so much a solid wire but a tube. It is a virtual inconsistency between the experiments and calculations. An explanation of this paradox may be found in the preparation of our sample and the annealing process. During our numeric calculations we assumed thermal equilibrium and we took only one soluble component into consideration. The annealing process is very far away from ideal: there are impurities due to the remaining gas in the capsules as one example. We did not use aimed atomic beams (like in HBE methods). Our model results were proved in literature by [6], that could fabricate GaN[2] nanotubes under very strict puritiy conditions.

5 Summary

We have introduced a time-dependent model for 1D nanowire growth in this paper. Our model was based on a solid-state diffusion mechanism, which assumed the presence of a catalyst particle. We used fine structures of an Ostwald-ripened gold surface for condensation seeds. The proofs of the hemisphere-shaped gold seed formation were tapping-mode AFM measurements.

Quantitative correspondence was found between our numerical model and experiments. The main advantage of our time-dependent model against other models was accuracy over time.

References

1 **Agarwal R, Lieber C M**, *Semiconductor nanowires: optics and optoelectronics*, Appl. Phys. A **85** (2006), 209–215, DOI 10.1007/s00339-006-3720-z.

2 **Beszeda I, Gontier-Moya E G, Imre Á W**, *Surface Ostwald-ripening and evaporation of gold beaded films on sapphire*, Appl. Phys. A **81** (2005), 673–677, DOI 10.1007/s00339-005-3254-9.

3 **Brenner S C, Scott L R**, *The Mathematical Theory of Finite Element Methods*, Springer-Verlag, 2002. second edition.

4 **Duan X, Huang Y, Cui Y, Wang J, Lieber C M**, *Indium phosphide nanowires as building blocks for nanoscale electronic and optoelectronic devices*, Nature **409** (2001), 66–69, DOI 10.1038/35051047.

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[2] GaN, GaAs and even β-Ga_2O_3 have similarly gallium as soluble component, we assume that our model is also valid for all these materials

5 **Duan X, Huang Y, Agarwal R, Lieber C M**, *Single-nanowire electrically driven lasers*, Nature **421** (2003), 241–245, DOI 10.1038/nature01353.

6 **Goldberger J, He R, Zhang Y, Lee S, Yan H, Choi H J, Yang P**, *Single-crystal gallium nitride nanotubes*, Nature **422** (2003), 599–602, DOI 10.1038/nature01551.

7 **Gudiksen M S, Lincoln J, Wang L J, Smith D C, Lieber C M**, *Growth of nanowire superlattice structures for nanoscale photonics and electronics*, Nature **415** (2002), 617–620, DOI 10.1038/415617a.

8 **Gupta R P, Khokle W S, Wuerfl J, Hartnagel H L**, *Diffusion of gallium in thin gold films on GaAs*, Thin Solid Films **151** (1987), 121–125, DOI 10.1016/0040-6090(87)90145-3.

9 **Huang M. H., Mao S, Feick H, Yan H, Wu Y, Kind H, Weber E, Russo R, Yang P**, *Room-Temperature Ultraviolet Nanowire Nanolasers*, Science **292** (2001), 1897–1899, DOI 10.1126/science.1060367.

10 **Iván I, Pécz B, Kökényesi S, Mojzes I, Misák S, Szabó I**, *Nanowire growth on GaAs and InP crystal surfaces*, Proc. SEMINANO 2005, 10–12 September, 2005, pp. 23–26.

11 **Persson A I, Larsson M W, Stenström S, Ohlsson B J, Samuelson L, Wallenberg L R**, *Solid-phase diffusion mechanism for GaAs nanowire growth*, Nature Materials **3** (2004), 677–681, DOI 10.1038/nmat1220.

12 **Wagner R S, Ellis W C**, *Vapor-liquid-solid mechanism of single crystal growth*, Appl. Phys. Lett. **4** (1964), 89–90, DOI 10.1063/1.1753975.