

**Deposition of Gold particles on the side walls of InP nanowires**  
FFFN35F

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# Introduction

Nanowires are a field of extensive research due to their various applications in energy [1] and optics [2]. In this work we will grow InP nanowires using a Metal-Organic-Vapor-Phase-Epitaxy (MOVPE) process and pursue the growth branched structures from the sidewalls of nanowires. These structures are interesting for making LEDs in which the active region is outside of the p-n junction. Branched nanostructures have been previously grown using Au aerosol particles [3], but in this project we want to try growing branched structures with a different method, since in aerosol deposition it is difficult to control their deposition position. The objective in this work is to perform experiments by dipping the nanowires in a Au solution with a concentration of 1mM for different times and observe if Au deposits on the side walls of nanowires.

# Theory

Growth of nanowires with MOVPE is done via Au assisted catalysis. The gold seeds (GD) are created using a technique called Nanoimprint Lithography (NIL). NIL uses a master nickel stamp to transfer a nanostructured pattern to an intermediate polymer stamp (IPS). IPS is employed as stencil to transfer the original pattern of the master stamp to the underlying material.

As shown in Figure. 1, IPS is firstly placed on the top of the master stamp and heated, below the substrate, above its glass transition temperature. After that, a high pressure is applied on the top of IPS to force the polymer to take the form of the underlying pattern of the master stamp. If this step is performed properly, IPS takes the form of the negative master stamp pattern, which resembles an array of pillars. After the stencil (IPS) is generated, the wafer is coated by a double-layer resist, top and bottom layer, respectively. The IPS is placed on the substrate before heating the substrate at a temperature above the glass transition temperature of the top layer resist; at this point, pressure is applied on the top of IPS. In this way, the top layer resist takes the shape of the IPS pattern and voids are created. The top layer remains in order to separate the IPS and the bottom layer resist. Then, IPS is uncoupled from the top layer after treating (photocuring) the top layer resist surface with UV light. The residual layer at the bottom of the holes are removed by  $O_2$ -plasma in a reactive ion etcher (RIE). A wet chemical etchant is applied to partially dissolve the bottom layer and obtain the holes where gold is evaporated to form the seed particles for the growth process. The excess of resist and gold are removed by a lift-off process, and only gold particles remain on the wafer surface. [4]

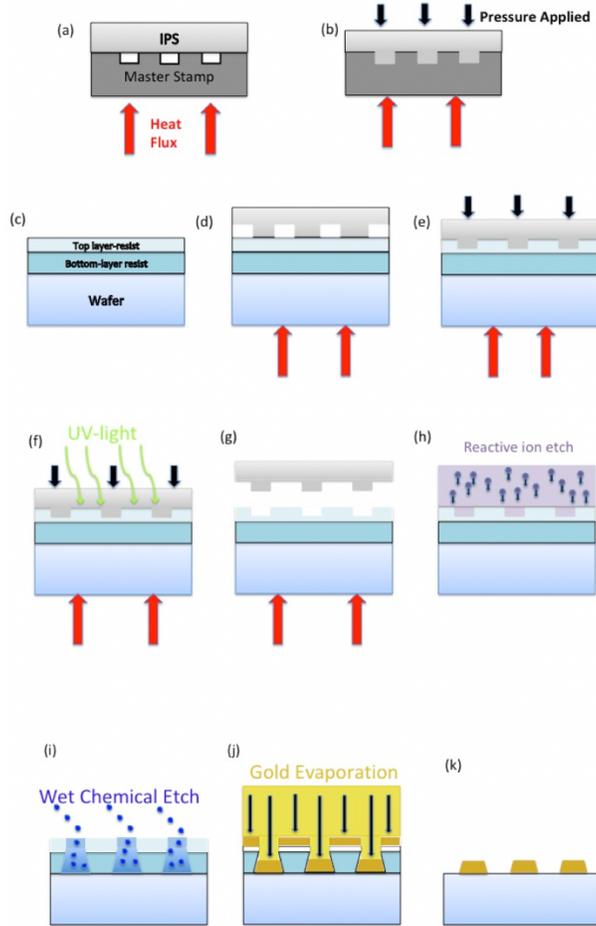


Figure 1: Schematic representation of all the steps necessary to create the gold particle seeds on the sample where it is necessary to grow nanowire or nanostructure.

After the description of NIL principle, we move on to describe the basic principle regarding MOVPE growth. Epitaxy is referred to an ordered growth of single layer crystalline material on top of the substrate, crystalline material as well, where the substrate governs the atomic arrangement of the growing material. This process is widespread and important in semiconductor technology. The term “Metal Organic Vapor Phase” is due to the fact that atoms for growing the crystal are provided by metal organic molecules in vapor phase.

The growth conditions are set in the MOVPE reactor, where the substrate temperature, chamber pressure, flow of precursor and gas carriers are under control to facilitate the growth. The gas is usually supplied at room temperature (RT), whereas the sample is heated at the bottom of the substrate, as depicted in Figure. 2, within 400-1000 °C.

The passage from the atoms in vapor phase to the atoms organized in a crystal structure, requires minimizing the Gibbs free energy  $G$  of the system when chemical potential equilibrium is reached, at constant temperature and pressure. The chemical potential is expressed as follows [4]:

$$\mu = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_j} \quad (1)$$

where  $T$  is temperature,  $P$  pressure and  $n_i$  is the number of moles of component  $i$ .

It is relevant to mention that a system in thermodynamic equilibrium is in its lowest energy state, as consequence, even the chemical potential between vapor and solid phase is the same. Hence, the transition from one phase to another changes the total energy of the system, thus the MOVPE is a non-equilibrium process where the chemical potential of the vapor phase is higher than the crystal phase,  $\mu_v > \mu_c$ .

To initialize the growth process it is necessary that the chemical potential of the vapor,  $\mu_v$ , is increased by adding material through the precursor gas; this causes a supersaturation (a concentration which is higher than the equilibrium one) of the vapor. The difference in chemical potential between vapor and crystal (solid) is the thermodynamic driving force of the reaction. The MOVPE technique enables to keep the thermodynamic driving force necessary for the growth of the crystalline layer, by regularly supplying precursor gas during reaction. The elements in group III and V of the periodic table, such as Indium (I) and Phosphorus (P), are usually supplied as compounds such as phosphine ( $PH_3$ ) and trimethyl Indium (TMIIn); pyrolysis (thermal decomposition) is therefore needed to decompose the compounds to atoms before the layer growth.

Supersaturation is the key role which drives the material to be supplied rapidly to the sites, till completion of the nanostructures. The process of moving growth species from vapor to solid phase is made in two steps, kinetics and mass transport process, respectively. Kinetic processes entail, through pyrolysis (thermal decomposition), the release of precursor atoms from precursor molecules i.e. the migration of growth material onto the crystal surface which bring to nuclei formation called nucleation. The mass transport process involves the migration of the precursor molecules in gas phase to the growth interface, which occurs via diffusion through a boundary layer close to the interface. The diffusion is governed by the concentration gradient between the carrier gas and the substrate. The kinetic process is temperature-dependent (hence, higher temperatures increase the kinetic step); the growth rate of the crystal layer is related to the mass transport.

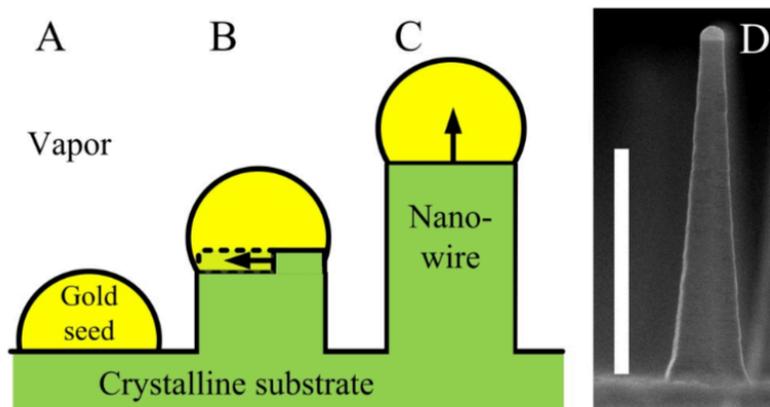


Figure 2: Schematic representation of different steps of a nanowire growth. (A) Gold seed particle. (B) Process of growth occurring at the interface between the seed particle and the substrate. (C) By supplying material (or growth species) the nanowire grows until completion. (D) SEM image of a InP nanowire [5]

# Experimental procedure and Results

Results from the initial growth process described in the section above are presented in Figures 1a), b), c), d). In Figure 1a and 1b a top view of the substrate with nanowires is shown. We observe that the pattern we wanted is reproduced with a high accuracy, expect for a few defects, where different gold droplets have merged to form a bigger droplet. By tilting the stage to 30° we can observe the nanowires and measure their length and diameter, shown in Figure 1c and 1d. We observe that our nanowires have a length of about  $1.4\mu\text{m}$  and thickness of about 210 nm.

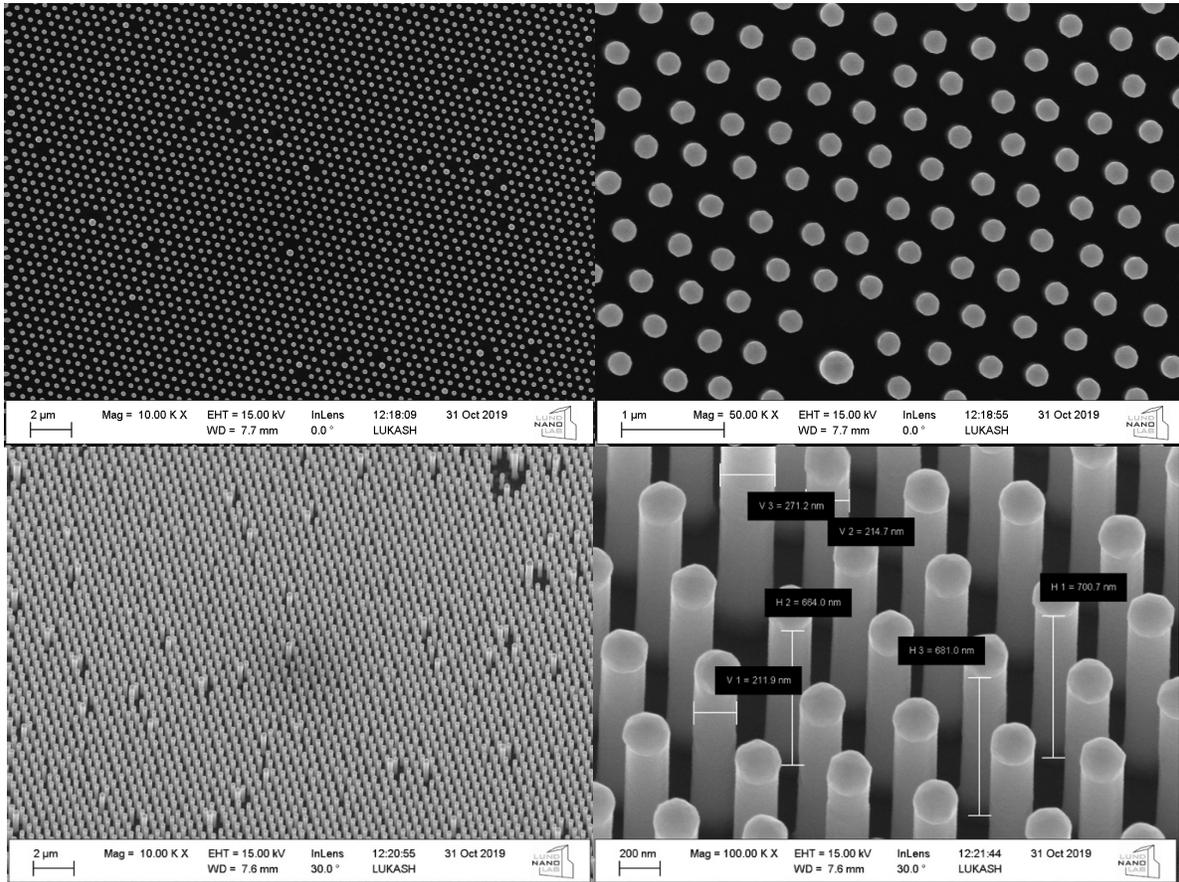


Figure 2: a-b) SEM image of the top view of grown InP nanowires. c-d) Tilted SEM image of InP nanowires.

In this work we make use of  $\text{HAuCl}_4 \times 3\text{H}_2\text{O}$  for depositing gold nanoparticles on the side walls of the nanowires. First, we prepare a solution of 1mM  $\text{HAuCl}_4 \times 3\text{H}_2\text{O}$  in deionized water. The molar mass of our chemical is 394 g/mol. By knowing the molar mass, we can calculate the amount of the chemical we need to put in 50 ml of water to make our solution:

$$1\text{mM} = \frac{1\text{mM}}{L} * 0.05\text{L} * \frac{394\text{g}}{\text{Mol}} = 0.0197\text{g} \approx 20\text{mg}$$

After preparing the solution, we pour it in a beaker and put it in a hotplate which is heated at 70°C. Then we put our substrate with nanowires in the solution and wait for a certain amount of time. In this work, 3 tests have been done by dipping the substrate in the solution for a time of 5, 10 and 15 minutes. Afterwards the substrates are rinsed in water 2 times and dried with  $\text{N}_2$ .

Figures 2a) and 2b) are SEM images which present the results after dipping the substrate in the solution for a period of 5 minutes. In Figure 2a) we notice that many gold particles have been deposited throughout the entire length of the nanowire. The particles are quite varying in size, with a general trend of particle size changing from bigger to smaller particles when you look from the top to the bottom of the nanowire. There is also another feature that can be observed in the SEM image of Figure 2a). The particles seem to deposit in an aligned fashion and same distance between each other. Reason for this behavior is still under investigation to obtain a better understanding. On the other hand, in Figure 2b) we also observe structures which we would like to avoid in our experiment, such as gold particles agglomerating on top of the gold particles used for the initial growth of nanowires.

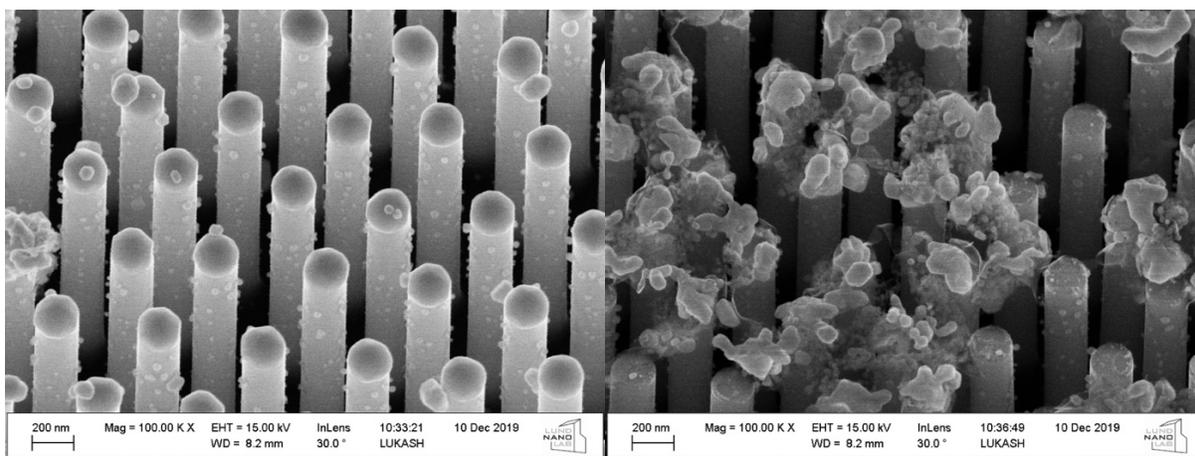


Figure 3: a) SEM image of InP nanowire with Au particles deposited on the side walls. b) InP nanowires with Au particles agglomerated at the top of the nanowire

The second test was to perform the experiment by dipping the substrate for 10 minutes in the solution and to observe any changes compared to the first experiment. Figures 3a) and 3b) show the results obtained from the experiment. A clear noticeable trend is that the amount of deposited gold particles has increased with increase of time. The particles are still scattered throughout the length of the nanowire, but it is noticeable that there are gold particles deposited also on the substrate. The particle size is bigger close to the tip of the nanowire, possibly due to agglomeration in the vicinity of the catalytic gold particle.

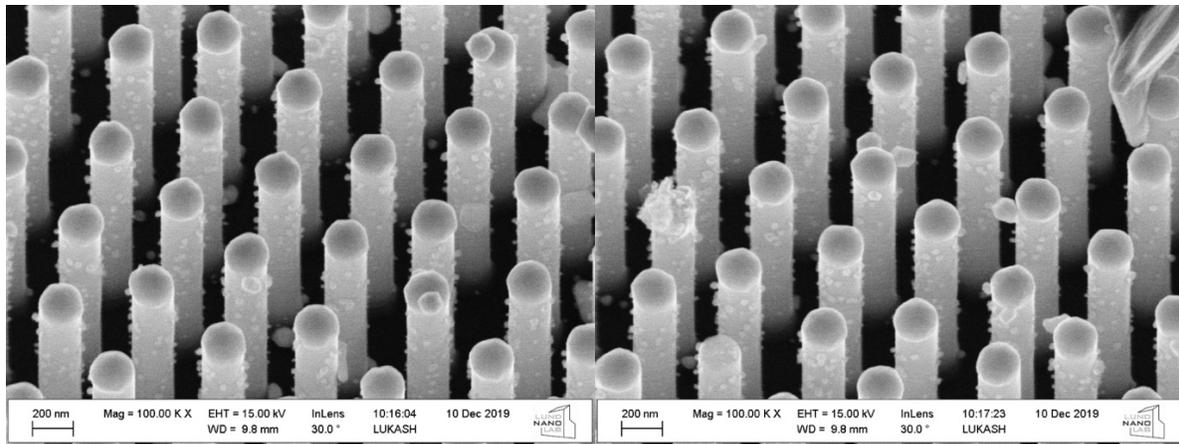


Figure 4: a-b) SEM image of InP nanowires with Au particles deposited on the sidewalls.

The last experiment performed was dipping the substrate in the solution for a period of 15 minutes. This time the results are quite different from before. Figure 4a) and 4b) are SEM images of the experimental results. In Figure 4a), a top view of the substrate is shown. We can observe many gold particles agglomerated and deposited in the substrate. In Figure 4b), showing a tilted image, we also observe that gold particles have agglomerated at the top of the nanowires and there are very few particles deposited on the sidewalls of the nanowires. Reason for this can be from the longer time that the substrate was dipped in the solution. Gold particles first deposit on the side walls and with time, since more particles get deposited, they start agglomerating and move towards the gold particle used for the initial growth of the nanowires.

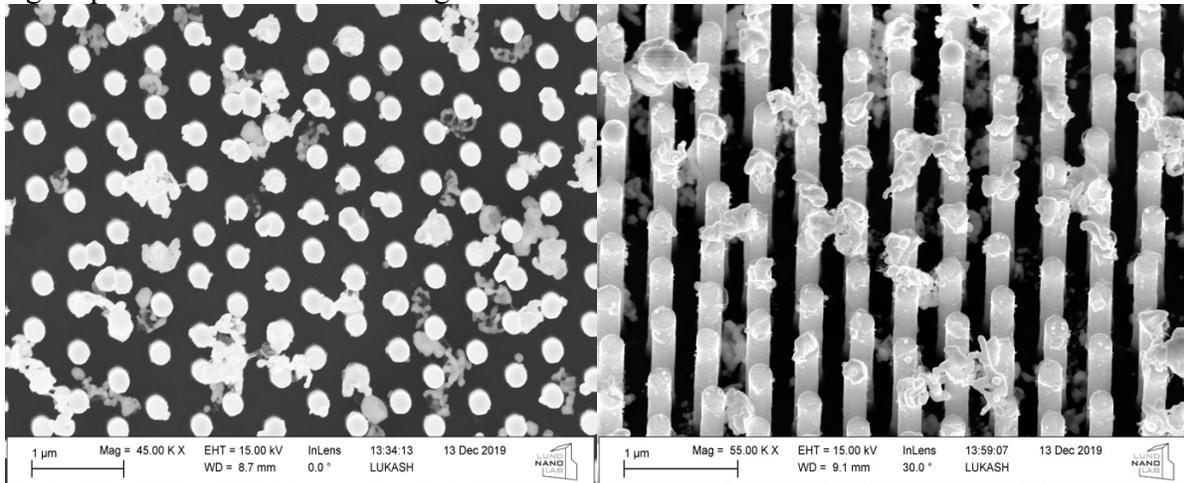


Figure 5: a-b) Topview SEM image of InP nanowires and Au particles deposited on the substrate and agglomerated on the tip of the nanowire

There are several ways to move forward currently in the project. One would be to first remove the gold particle used for catalysis before dipping the substrate in the solution and repeat the same experiments and compare the results. Another possibility is to cover the current substrates with a resist and then remove the gold particles on top. The latter would still leave the gold particles deposited in the substrate which can affect growth results.

## Conclusions

In this work, the growth process of InP nanowires was performed. Starting from the process of NIL to create the pattern in our wafer and deposit gold particles that act as catalyst for nanowire growth, we then grew InP nanowires in an MOVPE machine. With the grown nanowires, experiments were performed to deposit gold particles to the side walls of the nanowires with the purpose of growing secondary wires and form branched structures. The experiments gave promising results with many gold particles deposited on the side walls for dipping periods of 5 and 10 minutes, but for the process lasting 15 minutes the outcome is very different. The next step in this work would be to try growing nanowires from the deposited gold particles and observe the results.

## References

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