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Report on the status of the different NIL based techniques

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Executive Summary

In this deliverable, the work related to the patterning of metal nano-particles as catalyst arrays for the highly defined nanowire growth on III/V substrates is described. As patterning technique we are evaluating different nanoimprint lithography (NIL) toolings and processes as well as one alternative technique, namely micro-contact printing (µCP). As metallisation technique both physical vapour deposition and electroplating are tested. The quality of the realised catalyst arrays is evaluated first using scanning electron microscopy (SEM) and atomic force microscopy (AFM). After the following step of epitaxy (work package 2: III/V nanowire growth), the quality of the catalyst arrays is rated with respect to optical properties PL energy and luminescence intensity.

We reproducibly imprint 2” wafers with Au metal particles in a matrix of 200 nm diameter holes and a hexagonal pitch of 500 nm, optimised for light absorption in InP NW arrays. NIL is a working method for large scale economically viable patterning.

Introduction and Motivation

The nanowire growth on III/V InP substrates requires the highly defined patterning of catalyst metal nanoparticles. As patterning technique within the Nano-Tandem project, we are investigating different nanoimprint lithography (NIL) techniques as well as a closely related technique, the so-called micro-contact printing (µCP). In NIL, a resist is molded mechanically using a structured stamp [1]. In µCP, a stamp is applied to transfer a very thin patterned monomer layer onto a substrate [2]. Both techniques can be used to realise patterned gold particles as they are needed as catalyst for the nanowire growth and sub-100 nm resolution was already demonstrated [1,3].

At the University of Lund as well as the Fraunhofer ISE, there are different toolings for NIL processes. Also different resist and stamp materials are applied. Therefore, one task is the evaluation of the processes at each location. The successful nanowire growth requires very well defined dimensions of the gold nanoparticles. Thickness, diameter and shape of the particles have to be realised in a very precise way. Another driving force setting the pattern parameters is the application of the nanowire array as photovoltaic device. There, it has been shown that a period of 500 nm and a diameter of 200 nm are best from the point of maximising absorption within the wire. Given these two parameters the target thickness for the gold particles is about 65 nm.

The activities in work package 3 are closely related to the epitaxy done in work package 2 as the quality of the particle arrays mainly can be evaluated after the subsequent nanowire growth. Therefore additionally to the microscopic evaluation of patterned catalyst arrays, we are presenting results for measurements of life time of carriers and PL energy and luminescence intensity of realised nanowires. These measurements confirm that the grown nanowires are of high quality and are very well suited and are right on track for the further works and aims within the NanoTandem project of realising high efficiency tandem solar cells.

Patterning of catalyst arrays

Nanoimprint Lithography (NIL)

At Fraunhofer ISE elastomeric stamps made-off polydimethylsiloxane (PDMS) were applied to pattern a UV-curable resist layer (mr-UVCur06 from Micro Resist Technology). As test pattern a crossed grating structure with a period of 300 nm and a hole diameter of approx. 150 nm was used. Figure 1 shows the resulting resist structure after imprint as well metal dots after subsequent plasma etching of the residual layer, sputter coating of metal and lift-off. The patterned area was 5 x 5 cm². It can be seen, that even for smaller structures than the target ones this process chain is working in principle; however, the thickness of the particles did not yet meet the required 45 nm but was 30 nm and the quality of the lift-off process was not fully successful (see also Figure 1). Master structures used for these tests were fabricated using interference lithography.

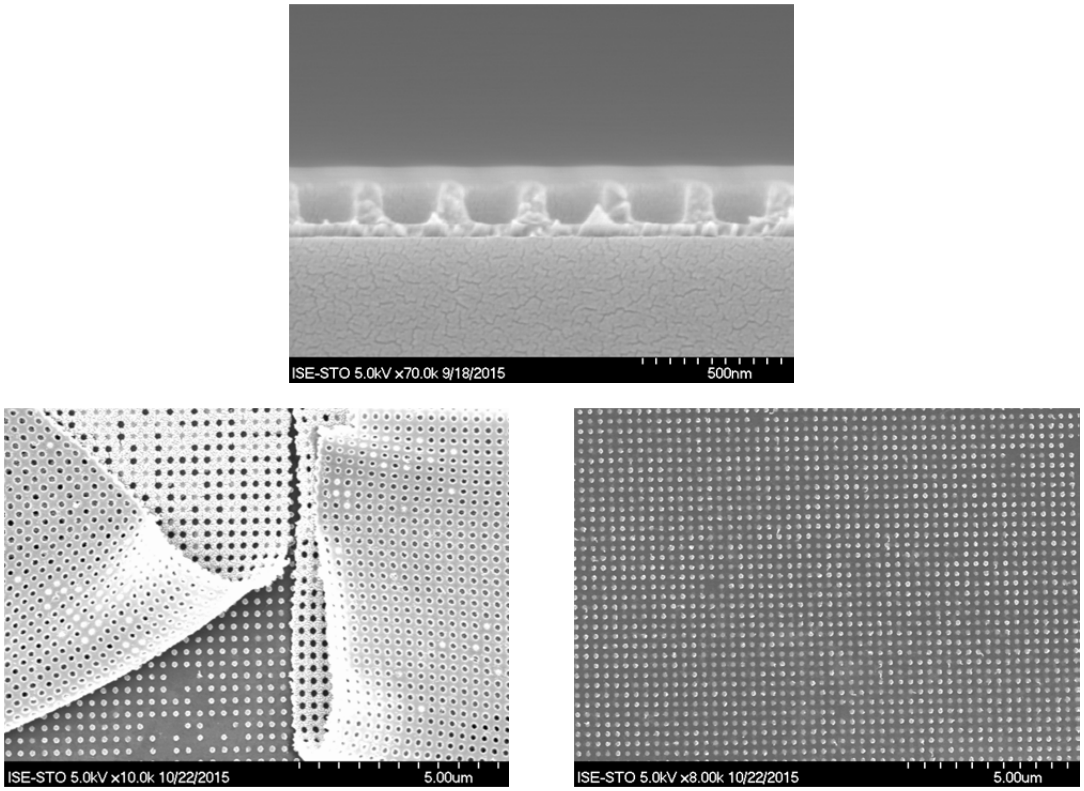

Figure 1: Scanning electron microscopy (SEM) micrographs of the NIL processing route to originate gold nanoparticles at Fraunhofer ISE. Top: Imprinted resist mask. Bottom: Resulting structure after lift-off. On the left hand side the lift-off is incomplete and the resist mask partially remained on the substrate. On the right hand gold nanoparticles of a diameter of approx. 150 nm can be seen after a successful lift-off.

At University of Lund, master structures realised using electron beam lithography having the target dimensions of a period of 500 nm and a hole diameter of 200 nm were applied. As stamp and resist materials, proprietary chemicals from the company Obducat were used. The metallisation was realised using Au evaporation on full 2” wafers after imprint. As the movement or merger of gold particles during the high temperature process of epitaxy is very critical for the arrangement and the successful growth of nanowires, a research focus was placed on measures to reduce these effects. To this end, the influence of heat treatment prior to and after the NIL processing as well as an embedment of the nanoparticles into a silicon nitride mask was evaluated.

Results for different types of heat treatment (before NIL and after lift-off) are shown in Figure 2. We found that these anneal steps improved the resulting quality in nanowire growth.

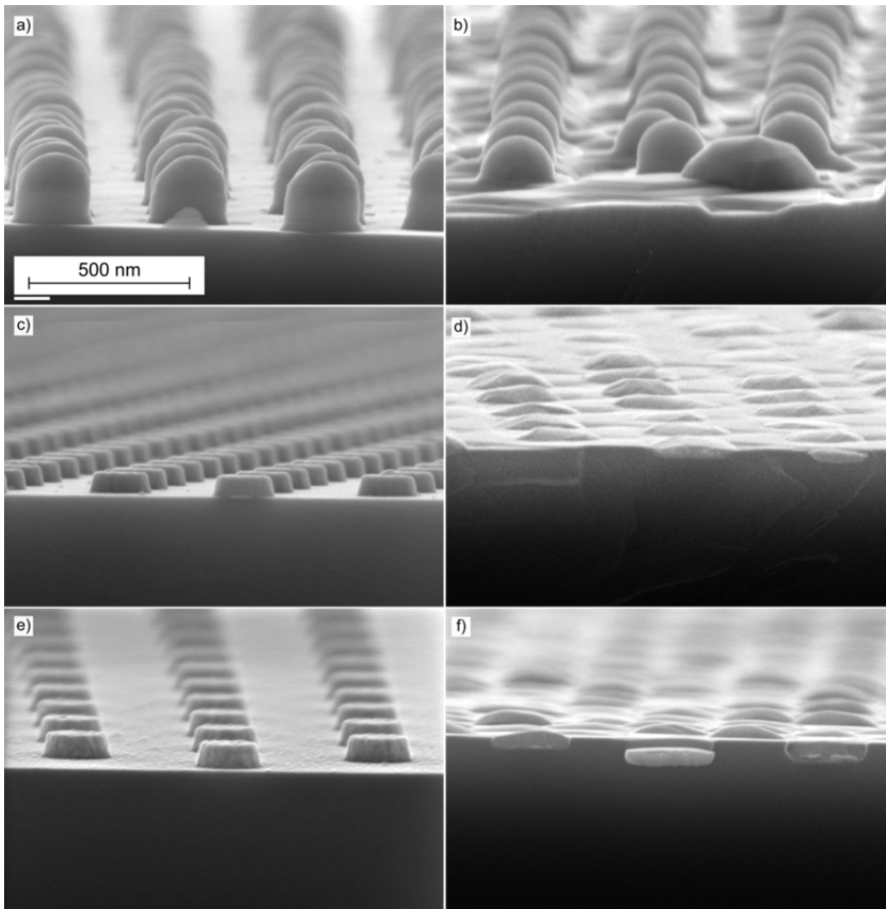

Figure 2: Cross-section SEM images of sample after a) pre-anneal nucleation at 420 °C only, b) pre-anneal nucleation at 420 °C and annealing at 550 °C, c) pre-anneal nucleation at 280 °C only, d) pre-anneal nucleation at 280 °C and annealing at 550 °C, e) imprint, and f) after annealing at 550 °C only. Pre-anneal nucleation lasted for 1 min, with χTMIn = 5.9×10-5, χDEZn = 9.2×10-7 and χPH_3= 6.9×10-3. Annealing lasted for 10 min at 550 °C, with χPH_3= 3.5×10-2.

Although we see great improvement in yield and reproducibility of pattern preservation when implementing the pre-anneal nucleation step in our growth procedure, some imperfections are still present. To take full control of this issue we added a patterned SiN_x layer as growth mask to the substrate surface [4–6]. With this growth mask in place, we achieve 100% pattern preservation with 100% vertically grown NWs over all sampled areas from different substrate pieces cleaved from the 2” imprinted wafer. The use of such a growth mask has the additional benefits of preventing parasitic substrate growth, as well as facilitating use of electrodeposition of gold to reduce material consumption and make reuse of the growth substrate possible [5].

Microcontact printing (µCP)

As an interesting alternative route for the fabrication of gold nanoparticles, we evaluated µCP as masking technique. The basic processing sequence and chemical recipes are taken from Ref. [7] and were slightly adopted to our requirements. In µCP the gold layer is deposited on full area, a very thin (~2 nm) polymeric mask is transferred from a patterned PDMS stamp onto the gold layer and finally the

unmasked gold is etched wet chemically (aqueous solution of ferric nitrate ($Fe(NO_3)_3$), thiourea ($SC(NH_2)_2$) and HCl to set a pH value of 2). Figure 3 shows AFM micrographs of the printed etching mask as well as the resulting gold nanoparticles after the etching process.

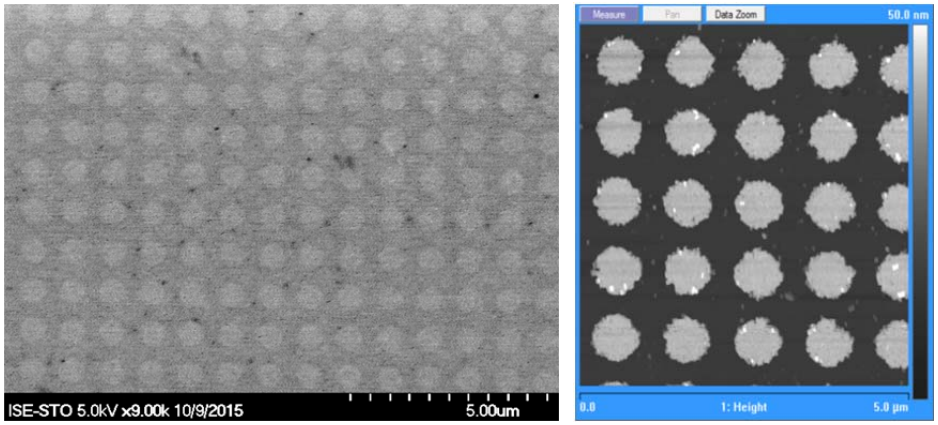

Figure 3: Left: SEM micrograph of the printed alkanethiol etching mask. The thickness of this monolayer is just about 2 nm. Right: AFM micrograph of isolated gold particles. In both cases the pitch is 1 µm and the diameter is approx.. 500 nm.

The processing using µCP has some potential advantages compared to the NIL route. For example the amount of chemicals used as masking material is virtually nothing and the interface between InP and gold can be of very high quality as the gold is deposited onto the clean surface without any contaminations. Another benefit might be that the etched gold can be recycled [8]. However, it was found that this approach is especially challenging concerning reproducibility. The quality of resulting particles was not as high as for the NIL approach.

Conclusions

Although the µCP approach could be very well suited for the patterning of the catalyst nano-array, it seems that the NIL approach is by far more mature and reliable. This is crucial for the application pursued within the NanoTandem project. As next steps we want to intensify the in-depth comparison of different NIL approaches, tools and materials at Fraunhofer ISE and University of Lund. To this end, we chose demanding test structures which will be replicated in both institutions (period 1µm, pillars with a diameter of only 100 nm) in order to ensure a tolerance to processing errors in the process which then will be transferred to the 200 nm diameter, 500 pitch stamp.

Evaluation of nanowire quality after epitaxy

In Figure 4 a)-c), top-view SEM images of NWs grown with three different pre-anneal nucleation temperatures are shown. This highlights the positive effect of thermal treatments on the fixation of gold particles and thus an improvement on the nanowire growth. At 320 °C, no missing NWs are observed in the pattern. The evaluation of missing NW density as a function of different pre-anneal nucleation temperature, ranging from 280 °C – 420 °C, is shown in figure 3d). The missing NW density decreases from 1.1 to 0.0 μm^{-2} (1.4 μm^{-2} without the use of pre-anneal nucleation) by a decrease in pre-anneal nucleation temperature from 420 °C, with excellent preservation for pre-anneal nucleation temperatures below 320 °C. Slight shifts of the exact NW position compared to the imprinted pattern can still be observed, but no

thick NWs resulting from merged seed particles could be observed on the investigated areas.

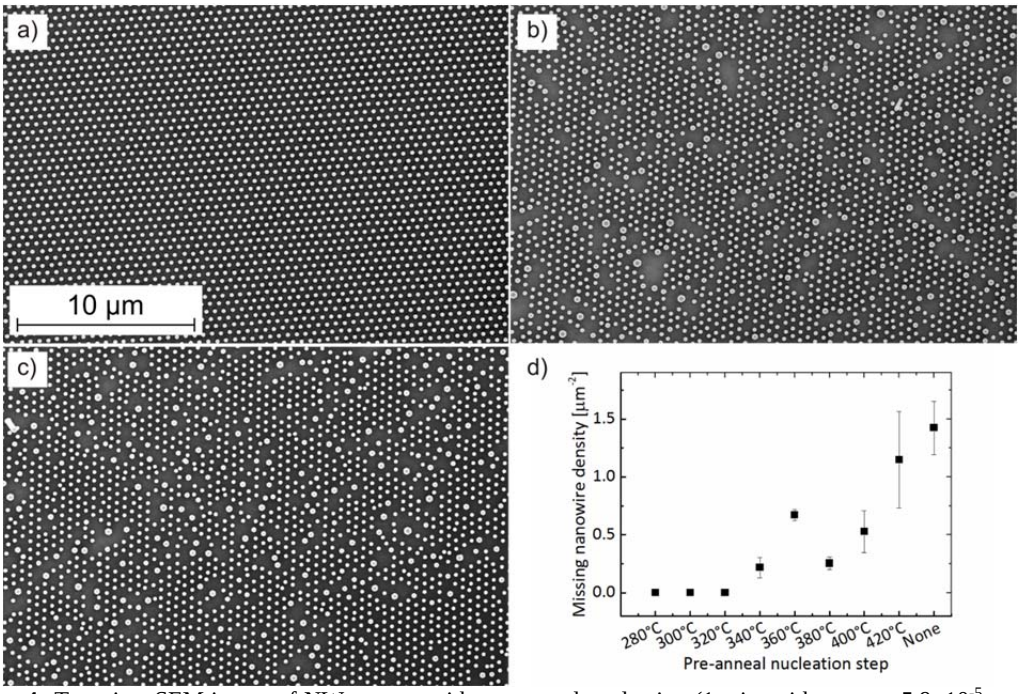

Figure 4: Top-view SEM image of NWs grown with pre-anneal nucleation (1 min, with $\chi_{TMIn} = 5.9\times10^{-5}$, $\chi_{DEZn} = 9.2\times10^{-7}$ and $\chi_{PH_3} = 6.9\times10^{-3}$) at a) 320 °C, b) 360 °C and c) 420 °C. d) The density of missing NWs after growth as a function of different pre-anneal nucleation temperatures. "None" indicates that no pre-anneal nucleation step was included in the growth procedure.

In order to investigate the resulting nanowire materials quality as a function of pre-anneal nucleation temperature, PL characterization was performed on single InP NWs taken from samples grown with pre-anneal nucleation at 280 °C, 320 °C, 380 °C and 420 °C, as well as from the reference sample grown without any pre-anneal nucleation. Four to five single NWs were measured from each sample. All NWs from all samples show multiple sharp peaks corresponding to optical transitions at energies lying between the bandgap of ZB (1.42 eV) and WZ (1.49 eV) InP which is commonly seen in InP NWs with mixed crystal structure and twin planes distributed along the length of the wire [9]. A sum of all single NW spectra taken from each sample is shown in Figure 5. All samples show similar luminescence behaviour. A small exception is the sample where pre-anneal nucleation was performed at 320 °C, where the luminescence spectrum is smoother and less evenly distributed between the bandgaps of the two crystal phases. Overall however, there is no clear change in the optical properties depending on the pre-anneal nucleation conditions.

Thus, the electrical properties of the nanowires are only little influenced by the thermal pre-treatment; however, the regularity induced by the pre-annealing will be beneficial for the solar cell structure i.e. the contacting and the formation of the tandem device.

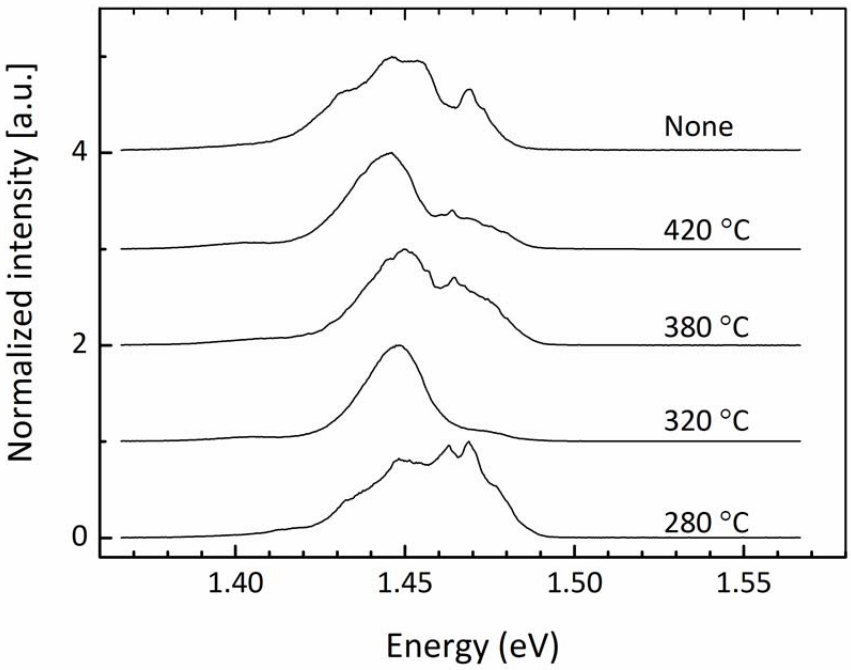

Figure 5: PL spectra from samples grown with different pre-anneal nucleation conditions. Each spectrum shown is a sum of the spectra from 4-5 single NWs. NWs were measured at 5 K, with an excitation wavelength of 532 nm.

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