Investigation of Sn particle formation on InAs substrate

Introduction

MOVPE

Metal-organic Vapor Phase Epitaxy (MOVPE) is an epitaxial crystal growth technique used for growing III/V nanowires and other high quality single crystalline thin films of different materials on different substrates.
As shown in Fig. 1, we can divide the MOVPE into two mainly parts, one is the gas mixture introducer and the other is the reactor. In the first introducer part, the precursors are usually metal-organic compounds stored in the bubblers in the liquid phase. A Mass Flow Controller (MFC) is used to control the gas flow from the bubbler. Hydrogen gas is usually supplied to take the organic part away in the reactor. The substrate is hold by the susceptor in the reactor system. The heating lamps control the reaction temperature, which will cause the precursors to decompose, leaving the metals on the substrate. Finally, the waste product will go through the exhaust pipe.

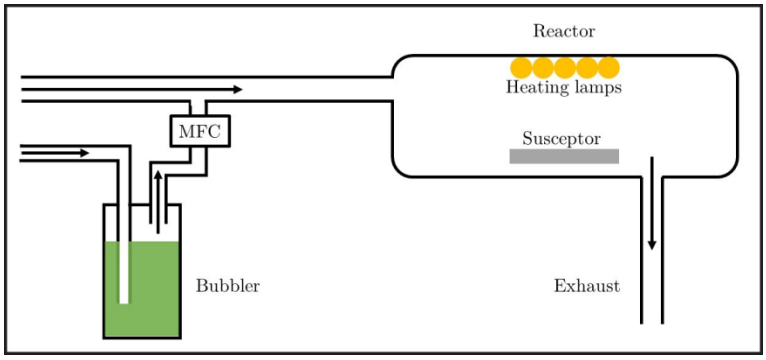

Figure 1 - A simple schematic view of MOVPE [2]

Uses of tin particles – alternative seed particles /nanowires

Most of the III/V semiconductor nanowires are grown by a catalyst assisted vapor-liquid-solid (VLS) mechanism. The pre-deposited atoms used as the catalysts are also named as seed particles. The gold is commonly used seed particles, which works well in many kinds of substrates. However, the alternative seed particles are expanded, because the gold seed particles are not compatible with the silicon industry. When growing the nanowire, the gold is easily integrated into the Si based semiconductor substrate. In this project, we study the Sn particle nucleation and formation on InAs substrate.

Theory

Particle nucleation and formation

Generation

Decomposition of precursor material

Pyrolysis is the process in which the precursors decompose into pure metals. It happens in the MOVPE reactor through the temperature control. In general, nucleation is a phase transformation, which may take place via density fluctuations.

Surface diffusion

Here, the surface diffusion is a process that the added Sn particles move on the InAs substrate. This motion is promoted process with rates changes when vary the reaction temperature. Usually, the surface diffusion rates and mechanisms are affected by a variety of factors such as the strength of the surface-adparticle bond, orientation of the surface lattice, attraction and repulsion between surface species and chemical potential gradients.

Ostwald ripening

Ostwald ripening is the phenomena that smaller particles in solution dissolve and redeposit on large particles in order to reach the thermodynamically stable state. The unstable surface molecules often go into shrinking the particle over time and increasing the number of free molecules as show in figure 2. As a result, this shrinking and growing of particles will make a large mean diameter of a particles size distribution.

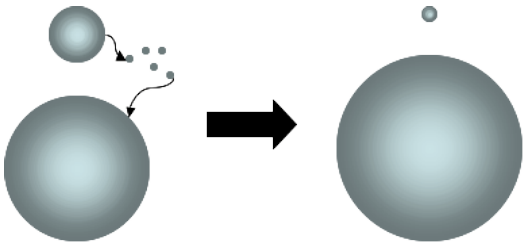

Figure 2 - Basic schematic of the Ostwald ripening process [3]

Experimental setup

Experiments were performed at a fixed flow of arsine and tin precursor. Only the temperature was varied for each of the samples. A set of six samples with the temperatures 525-625C were produced and analyzed in this project.

SEM imaging

The samples were analyzed in a SEM to image the particles. As the samples were conducting there were

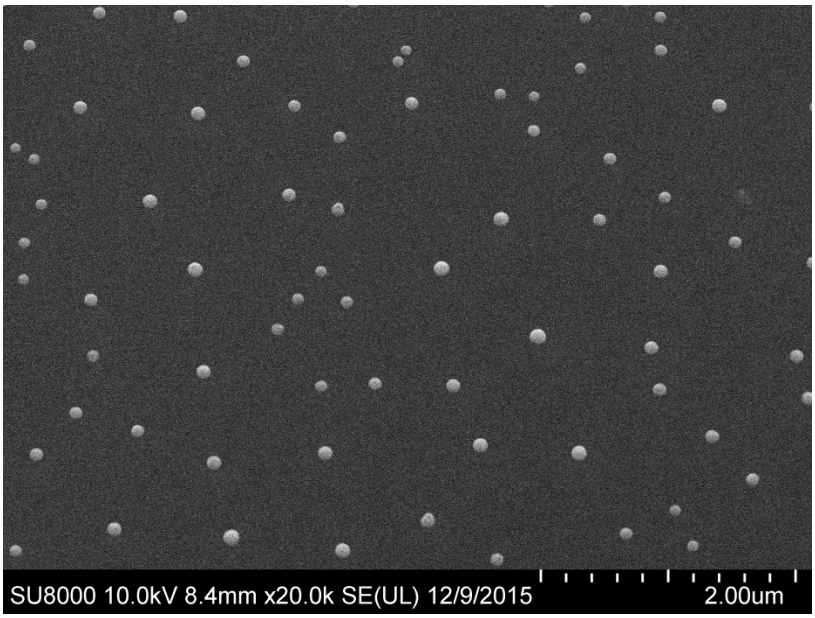

Figure 3 – Tin particles on InAs substrate

no need for any further samples preparation. A set of 5 images were captured for each samples at a fixed magnification. Brightness and contrast were optimized for image analysis of the particles, i.e. high contrast between the particles and background, and sharp edges of the particles without losing any particles with low contrast, example in Fig. 3.

Image analysis

The SEM images were analyzed in ImageJ [4]. Identification and measurements of the particle size were performed by applying a set of median and Gaussian filters before thresholding the image as in Fig. 4. After thresholding the built-in Analyze particles were used to segment and measure. Several parameters in the segmented particles could be measured but as the interesting properties in this project were all related to the radius, only the area was considered.

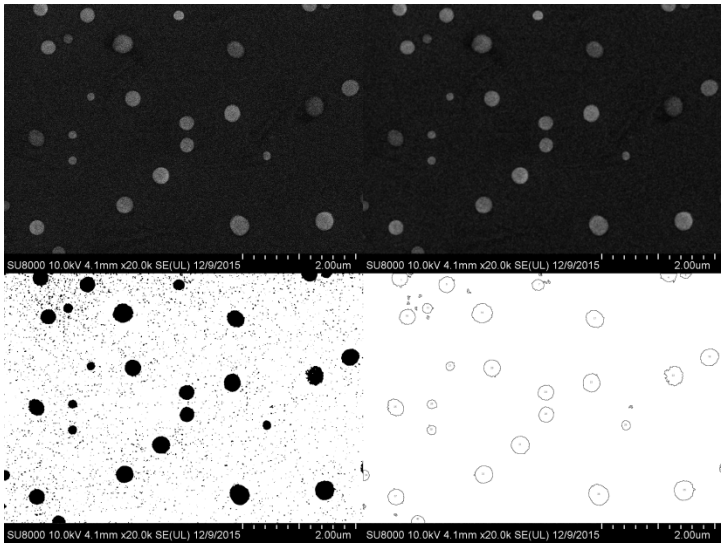

Figure 4 – Original SEM image, filtered image, thresholded image, segmented and labeled.

Estimation of particle properties

The radius of the particles was estimated from the total area by assuming projected spheres which for most particles holds true. A majority of the particles were next to circular which makes the error in the assumption small. Particles with low contrast in the raw image will sometimes turn out as slightly deformed after the thresholding leading to an under estimation of the radius.

The surface number concentration were simple a sum of the identified particles over the total analyzed area. Uncertainties in the homogeneity of the sample might induce an error in this measure but as the selected areas were chosen in a random fashion this error would be minimized in the analysis.

Mass concentration of the particles were estimated from the two previous properties and by assuming pure tin with bulk density and spherical particles.

Results and Discussion

Number of particles/area

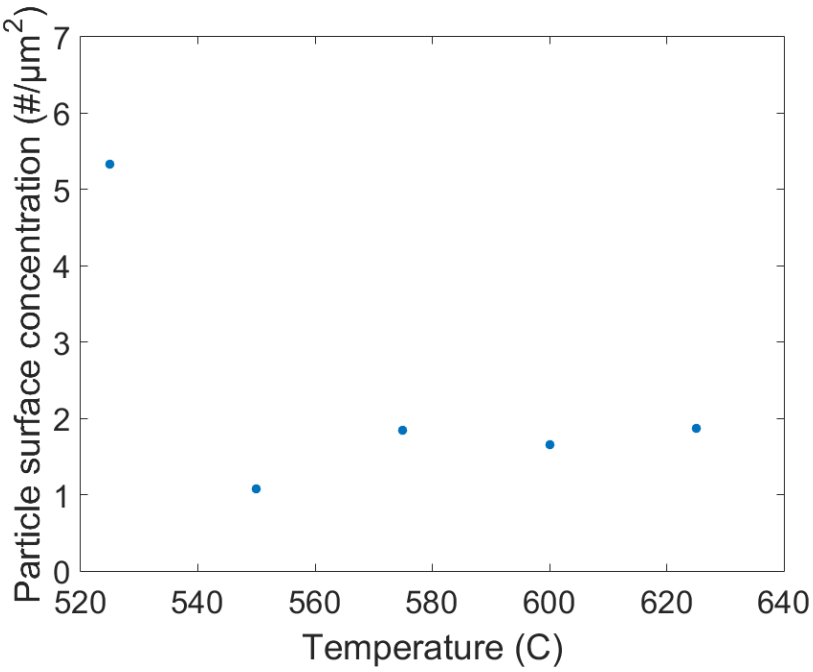

Figure 5 - Particle surface concentration

As can be seen in fig. 5, the number of particles per area decreases as the temperature increases. This can be explained by the way that the particles are formed. Particles nucleate at random on the surface. The initial particles will not be stable as the high vapor pressure over the highly curved surface of the small particles promotes the evaporation of material. Without a high overpressure of, in this case, tin the particles won't have a chance to form on a homogenous surface. The size of the particles will eventually reach a point where they become stable. This critical size will be same across the sample which will make all the initial particles the same size. The formation of these particles will also hinder the formation of new particles on the surface as the energy required to nucleate are far greater compared to incorporating onto an already existing particle surface.

As more material is added the particles will grow but as can be seen in fig. 5, the number of particles decreases. This is a result by surface diffusion and coalescence of existing particles on the surface. Small particles will diffuse faster, have a higher rate of evaporation compared with the larger one. This will in practice lead to larger particles effectively consuming the smaller ones leading to a lower surface concentration of the number of particles. Once the particles have grown the diffusion rate will diminish and the coalescence rate will decrease.

Mass/area

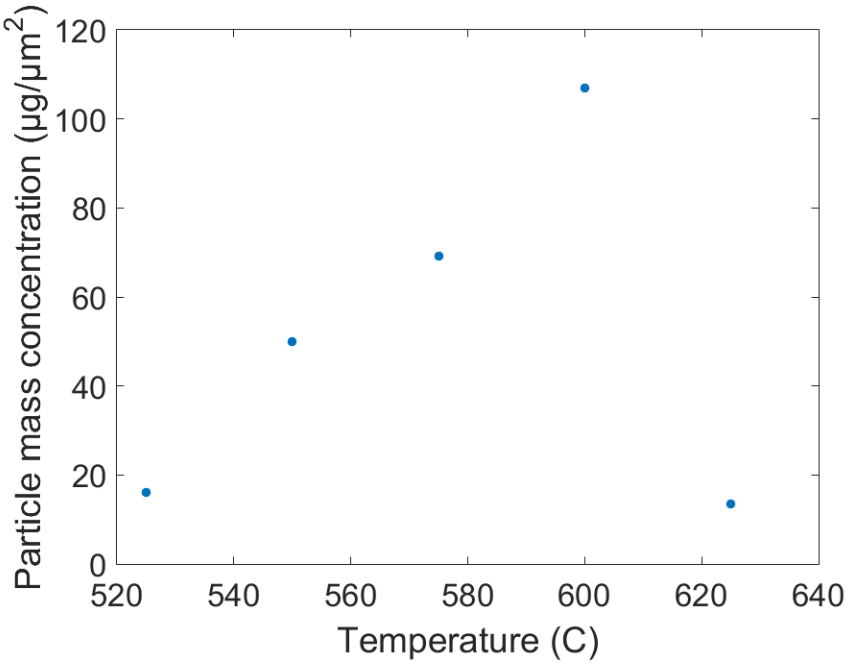

Figure 6 - Particle mass surface concentration

The total mass or mass concentration per area of the sample is steadily increasing with the temperature as expected, Fig. 6. A higher temperature should result in a higher decomposition rate of the precursor gas. It is evident that the highest temperature results in a lower mass concentration which might be counter intuitive. This might have an explanation in that the material is evaporating faster from the particles then its added which would result in a lower growth rate of the particles.

Median radius of the particles

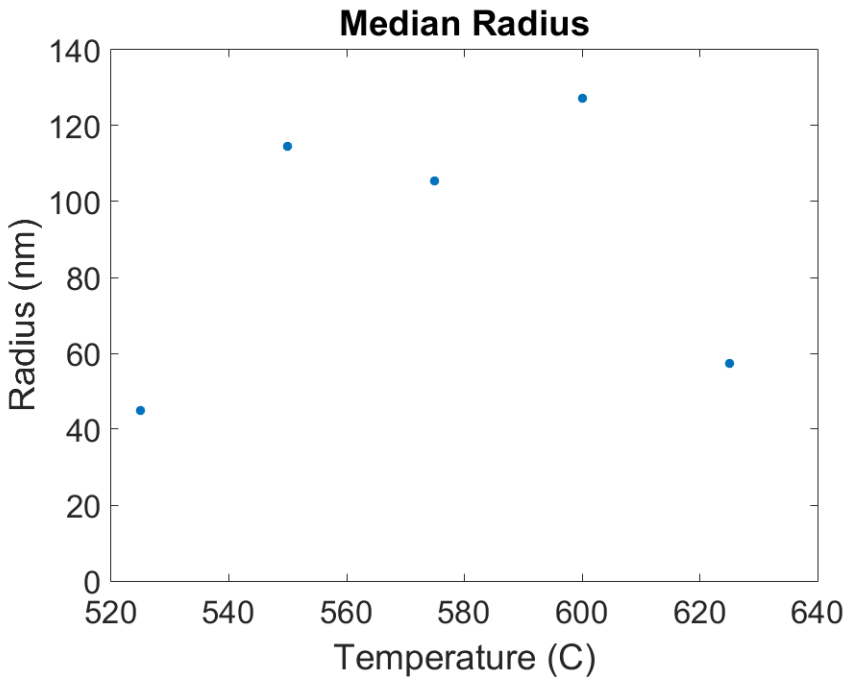

Figure 7 - Median particle radius

The median radius of the particles is reaching a plateau for the intermediate temperature, although as will be seen in the next section will have a quite different distribution. The small radius of the low temperature sample follows from the same reasoning as for the surface number concentration, many small initial particles which with increased time or temperature coalesce. The drop in particle size for the highest temperature gives the impression that the material either doesn't reach the particles in the same rate as before, or as stated previously is losing material more rapidly as the equilibrium vapor pressure increases with the temperature.

Size distribution

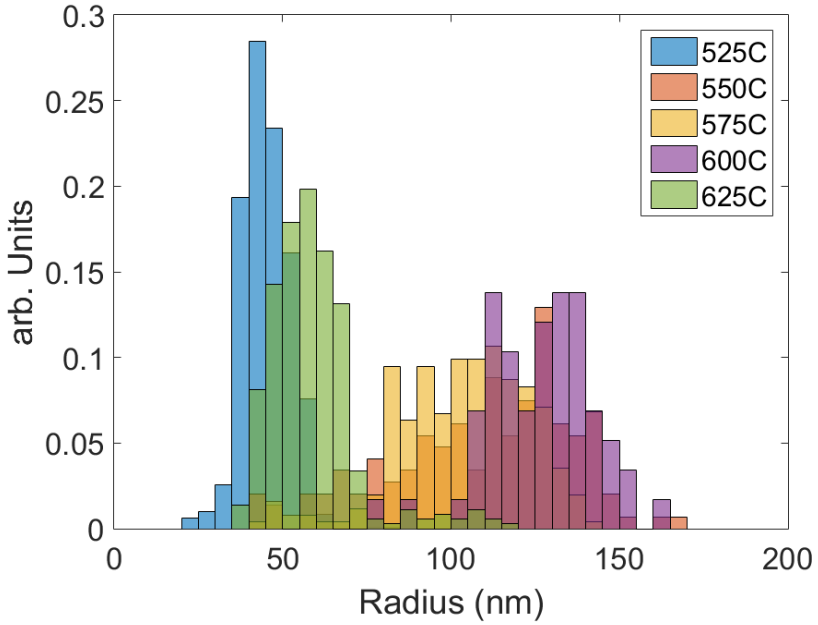

Figure 8 - Particle radius distribution

Fig. 6 shows the distribution of the radii of the particles in all samples. The height of the samples is normalized to sum up to one for each sample. A high bars in a sample indicates a more narrow size distribution. It is clear that the samples falls into two groups as were seen already in Fig. 5. The two extremes in temperature does not only have a smaller radii but also a more narrow size distribution.

Error analysis

As the analysis of the particles are based on an automatic detection the bias in identifying the particles are removed. However this introduces another error, the thresholding of the images will generate a slight miss-cut in what is determined to be a particle if the raw image is not sharp. This error will be small as the resolution of the images is sufficient to accept a miss-cut of ± a few pixels. With the settings used this will equate to an error of about ± 2nm in diameter of the particles. A grater error is introduced by not analyzing enough particles or areas. In this project a total of about 200 particles per sample were analyzed which will make the measurements sensitive to statistical errors as one image of an area with a significantly different particles would impact the whole of the sample properties. An improvement of the experiments would be to simply increase the number of imaged particles. In terms of the results of the project, further investigations of the drastic changes in particle number and diameter would be needed in order to better estimate when these transitions occur.

Conclusions

In situ particle generation provides many advantages compared to pre-produced particles. The possibility to do all things in one process limits the errors introduced in moving the sample and exposing the sample to air. The change in particle size with temperature could be a useful way to in situ vary the particle size to enable growth of nanowire of different diameters.

Reference:

[1]. http://pssnicomp.com/definitions/ostwald-ripening#lightbox[auto_group]/0/

[2]. Lund University Master Thesis, Author: Erik Mårtensson, December 2014.

[3]. https://en.wikipedia.org/wiki/Surface_diffusion

[4] Rasband, W.S., ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, http://imagej.nih.gov/ij/, 1997-2015.