MBE growth of GaAs and InAs nanowires using colloidal Ag nanoparticles

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Abstract. Ag colloidal nanoparticles were used as a catalyst for molecular beam epitaxy of GaAs and InAs nanowires on the Si(111) substrates. The scanning electron microscopy measurements revealed that nanowires obtained are uniform and have small size distribution.

1. Introduction

During recent years, semiconductor nanowires (NWs) attract great attention due to their distinctive optical and electronic properties. On the practical side, semiconductor NWs are very attractive for direct integration of III-V materials on Si, which provide new opportunities for the design and fabrication of numerous applications, including solar cells [1], light emitting diodes [2], field-effect transistors [3]. For a large number of devices, it is essential to fabricate NWs with well-controlled dimension, orientation, structure, phase purity and density on the surface. Nanowire size and shape are important parameters that have to be considered. At these scales quantum mechanical effects play a key role; even small variations in size of NWs can influence on overall device performance. Up to now, the most common technique for nanowire synthesis is vapor-liquid-solid growth using Au metal seed particle, which acts as a catalyst to initiate the growth. However, the use of Au can result in unwanted effects, such as formation of deep-level defect states and Au migration on the semiconductor surface. This leads to deterioration of own NW optical and electrical properties [4]. To solve this problem, emerging methods based on self-catalyzed [5] or template-assisted growth of NWs [6] can be used. In addition, the use of foreign metals as a catalyst (e.g. Ag [7]) is also of great interest.

The position and size control of seed can be achieved by patterning the substrate using lithographic technique, e.g. electron beam lithography [8], nanoimprint lithography [9] and subsequent Au deposition using physical vapor deposition. However, lithographic processes are intrinsically wasteful, not suitable for large scale-production and challenging for the deposition of small-diameter catalyst particles. Other methods based on nanosphere lithography [10] and laser interference lithography [11] remain quite complex to deal with.

Ag colloidal nanoparticles can potentially overcome the above-mentioned limitations. Nowadays colloidal nanoparticles have gained widespread acceptance in different areas (markers and biosensors [12], optoelectronic applications [13], etc.) due to their properties, withal they are commercially available in a wide range of different sizes and shapes. Therefore, they are an attractive alternative to use as a catalyst of NW growth.

In this study we present MBE growth of GaAs and InAs nanowires arrays using Ag colloidal nanoparticles.
2. Experiment
The investigations were carried out using epi-ready silicon (111) oriented p-type substrates. The substrate surface was covered with a native oxide layer. We used Ag colloidal nanoparticles with 20 nm diameter, which were obtained from BBI Solutions. Deposition of Ag nanoparticles was performed by placing a drop of colloidal solution directly on the silicon surface. The typical deposition time was about 30s. Then the solution remnants were blown away and the substrates were dried with N\textsubscript{2} gas.

For the growth experiments Compact 21 MBE system was used. MBE system consist of the main chamber equipped with standard Ga, In effusion cells and As cracking cell, and additional high vacuum connected chamber, which allows to perform the annealing of the samples at the temperatures up to 950\textdegree C. The process of NWs growth was monitored in situ by the reflection high energy electron diffraction (RHEED). RHEED was also used to calibrate material growth rate. The deposition rates of GaAs and InAs were set at 0.7 and 0.3 ML/s, respectively.

A Zeiss Supra 24 field emission scanning electron microscope (SEM) was used to investigate the morphology and dimensions of the Ag seeds and NW arrays.

3. Results and discussion
Pregrowth Ag nanoparticles distribution on the Si (111) substrate is shown in Figure 1a. As it was expected, Ag nanoparticles are randomly distributed, but they homogeneously cover the whole silicon surface.

The substrates with deposited Ag nanoparticles were loaded into additional chamber of MBE system. An annealing step at a set temperature of 850\textdegree C was carried out for 5 min to remove surface contaminants and native oxide (see Figure 1 b). Then the temperature was decreased, the samples were transferred to the growth chamber. After reaching the growth temperature, group III metal flux and As shutters were simultaneously opened. The GaAs and InAs NWs growth temperatures were set at 580\textdegree C and 400\textdegree C, respectively. In situ RHEED observation showed that pattern changes appeared after 10-20 seconds of the growth. According to the RHEED patterns NWs have mixed wurzite/zinc blende phases. This effect has been previously found experimentally for most III–V NWs [14]. The growth was terminated by switching off the group III metal flux while maintaining the As flux until the substrate temperature dropped to below 300\textdegree C. Total growth time for GaAs and InAs NWs was equal to 15 and 20 min, respectively.

![Figure 1](image_url)

**Figure 1.** (a) - SEM image of the silicon surface with deposited Ag nanoparticles, (b) - schematic illustrations of the temperature sequence for annealing process and the subsequent InAs, GaAs nanowire growth.

Typical arrays of NWs formed under conditions described above are shown in Figure 2. The result obtained demonstrate than both GaAs and InAs NWs can be grown using colloidal Ag nanoparticles by MBE. InAs and GaAs nanowires exhibit prevalent vertical directionality, indicating a direct relationship to the underlying Si(111) substrate. Moreover, no droplets related to the group III element (i.e. Ga or In) rich phase could be resolved at the individual nanowire tips by SEM. As can be seen also, the
temperature where InAs NW formation was observed strongly differ from that for GaAs NWs (see Figure 1 b). This is in good agreement with other reports [15, 16] and connected with different solubility of group III elements in the Ag catalyst. It is noteworthy, that temperatures ranges are much narrower; no NW formation was observed at temperature changes greater than 30°C.

Figure 2. SEM images of (a) – GaAs, insert shows the shape changes of NWs along the growth direction; (b) – InAs NWs grown on Si(111) using Ag nanoparticles.

The cross-sectional SEM images were used to determine the mean NW height and diameter by making a statistical average over about 10 wires. As it was expected, GaAs NWs have small size distributions. They have typical 6.8 μm length. However, the diameters of these NWs are irregular, NWs smoothly tapered from 80 nm at the base to sub-30 nm at the top (see insert in Figure 2 a). It could be caused by the limitations of Ga adatom diffusion length. Besides, there are significant amount of low-tier NWs with length of about 3 μm and 40 nm diameter. The size distribution of the InAs NWs also have no discernible differences, they have 1.2 μm length and 100 nm diameter, which is constant along the growth direction. It can be seen that average GaAs NWs growth rate is about 7 times higher than InAs growth rate (7.5 nm/s versus 1 nm/s). This could be explained by the different temperatures of the substrates during the growth experiments (Figure 1 b).

According to the top-view SEM images (see Figure 3), NWs in both arrays have hexagon-shaped geometries. GaAs NWs grown on Si using Ag nanoparticles have higher surface density than InAs NWs. It is likely that low-tier GaAs NWs are obtained by the self-catalyzed method, i.e. Ga droplets were formed and acted as additional catalyst for the NW growth [5]. But this question requires an additional clarification.

Figure 3. Top-view SEM images of – GaAs, (b) – InAs NWs grown on Si(111) using Ag nanoparticles. Inserts show the shape of NWs.
4. Conclusion
In summary, the GaAs and InAs NWs have been obtained by molecular beam epitaxy using Ag colloidal nanoparticles as a growth catalyst on the Si(111). The majority of the NWs have preferential growth direction along <111>. The NWs obtained are uniform and have small size distribution. The ability to prepare uniform nanowires on Si substrates may provide new opportunities for studying their size-dependent physical properties and fabrication promising nano- and optoelectronic devices.

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