Synthesis and optical properties study of GaAs epitaxial nanoparticles on silicon

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Abstract. The integration of direct bandgap III-V materials on Si is one of the main tasks on the way to the development of cheap and highly effective optoelectronic devices. The goal of this work is to study the morphology and optical properties of GaAs nanoparticles grown on Si(111) by molecular beam epitaxy (MBE). Nanostructure morphology is studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). Optical properties are studied by photoluminescence (PL) and Raman spectroscopy. Interestingly, despite large lattice mismatch between the silicon substrate and GaAs no sufficient change of Raman spectra was observed for both continuous layer and nanoparticles indicating that they are relaxed. The room temperature PL signal in the red spectral range was obtained from the epitaxial structure. It is demonstrated that high pump optical excitation of the nanostructures can lead to sufficient change of the PL signal typical for photo-oxidized GaAs.

1. Introduction
Epitaxial nanostructures based on semiconductor III-V compounds are promising elements for the creation of nanoelectronics, photonics and photovoltaic devices [1,2,3,4]. Small interface area and the high surface-to-volume ratio of epitaxial nanoparticles and nanowires contribute to a low concentration of structural defects even in lattice-mismatched systems (GaAs and Si have a 4.2% lattice mismatch) [5], which allows monolithic integration of direct-gap III–V semiconductors on silicon [6].

Vapor-liquid-solid (VLS) formation mechanism of III-V nanowires (NWs), especially within the self-catalytic approach [7], which does not allow to independently control the group III and V supersaturation [8], limit the ability to independently tune axial and radial growth rates and thus control the NWs size and aspect ratio [9,10]. Thus the diameter of the self-catalytic GaAs nanowires usually does not exceed 100-150 nm [5,9], while for realizing functional light-emitting or photoconverting structures, nanostructures of a given morphology with a lateral size scale which is close to the working wavelength are required. At the same time ability to control the morphology of self-organized epitaxial nanostructures is also limited as it largely determined by surface and interfacial energies [11]. Thus, it is necessary to develop growth techniques to control the morphology
of nanostructures in a wide range, for example, multi-stage techniques that allow to independently control the density of the array and the rate of radial and axial growth.

2. Experimental

GaAs nanostructures were grown using Veeco GEN-III MBE setup on Si(111) substrates. Before loading into MBE setup the substrates were chemically cleaned by boiling in CCl4, isopropanol and 3:1:1 H2O–H2O2–NH4OH solution. Prior to the loading into the MBE chamber native silicon surface oxide was removed in diluted HF. The substrate temperature was measured by both thermocouple and pyrometer. After loading and degassing the substrate temperature was ramped directly to the growth temperature 550°C, which is much lower than needed for the SiOx thermal decomposition [12]. Ga flux was kept constant and equivalent to the GaAs growth rate of 0.4 ML/s, calibrated by reflection high energy electron diffraction (RHEED) oscillations during planar GaAs/GaAs(001) growth. As flux was set to be four times higher than stoichiometric value, determined by the observation of As-rich (4x2) to Ga-rich (2x4) surface phase transition during planar GaAs/GaAs(001) growth at 550°C [13].

The structure and morphology of the synthesized heterostructures were studied by scanning electron microscopy (SEM) (Zeiss SUPRA 25-30-63) and atomic force microscopy (AFM) (INTEGRA Aura NT-MDT). To study the optical properties of the structure the Raman scattering (RS) and photoluminescence (PL) spectra were obtained in backscattering geometry at room temperature (300K) on a Horiba LabRam HR800 Raman spectrometer equipped with a CCD detector and a laser with the excitation wavelength $\lambda = 532$ nm (2.331 eV).

3. GaAs nanoparticles

SEM images of the two samples grown at the same conditions for a different period of time of 10 and 30 minutes are presented in figure 1. It can be seen that both continuous layer and three-dimensional nanoparticles are formed at chosen growth conditions. Epitaxial nanoparticles and continuous layers tend to be separated by a circular area with diameters up to 1200 nm free from deposited material and visible as a dark contrast on SEM images. As can be seen from the close-up SEM image (figure 2) centered on the single nanoparticle, it is faceted by the inclined planes, while the surrounding continuous layer tends to be planar. One can find that the continuous layer is formed by coalesced nanoislands. It can be suggested that nanoparticles and nanoislands were nucleated with an opposite polarity, namely (111)B and (111)A top surfaces correspondingly. The (111)A planes are energetically favorable and thus nanoislands can form the continuous planar layer during coalescence [14]. Flat (111)A facets are clearly can be seen in the AFM image presented in figure 3.

![Figure 1](image1.png)

**Figure 1.** Plane view SEM images of GaAs nanoparticles on Si substrate is grown for 10 (left) and 30 minutes (right)
Figure 2. Close-up plane view SEM images of GaAs nanoparticle on Si substrate

From the comparison of structures grown for 10 and 30 minutes, one can find that nanoparticle density (from 0.08 to 0.007 μm$^{-2}$) decreases due to the overgrowing of the nanoparticles with a continuous layer during the growth.

Figure 3. AFM images and height profiles of GaAs nanoparticles on Si substrate is grown for 10 (left) and 30 minutes (right)

The diameter of the nanoparticles doesn’t change much at shown growth time range, indicating that island growth period is shorter than sample growth time, and one can suggest that observed GaAs
nanoparticles are formed by VLS mechanism and their growth rate significantly reduces after droplet consumption and adatoms are predominantly embedded in the continuous layer. According to the AFM images for the sample grown for 10 minutes, epitaxial nanoparticles are several times larger in height than the continuous layer, however, particles which are started to be overgrown by continuous layer in the sample grown for the 30 minutes are having heights which are equal or smaller to continuous layer. This observation pointing out that material which forms GaAs nanoparticles tend to be redistributed during their overgrowth by GaAs with the (111)A polarity to minimize surface area and form the continuous layer.

4. Optical properties
PL spectra of the nanoisland array, a single nanowire and the continuous layer at 300 K are presented in figure 4. Integral PL and RS measurements were conducted with an excitation power density of $\sim 6 \times 10^2$ W/cm$^2$ and laser spot diameter $\sim 10$ μm, while microspectroscopy of a single nanoparticle was conducted with an excitation power density of $\sim 6 \times 10^4$ W/cm$^2$ and laser spot diameter $\sim 1$ μm. It can be seen that PL spectra measured from the array and micro-PL signal from the nanoparticles are rather different. The broad peak centered at 870-880 nm (1.42 eV), which corresponds to the band-gap transition of the GaAs material [15] dominates in the PL signal obtained from the array, while a broadened peak located at a shorter wavelength range of 650-800 nm becomes dominant in micro-PL spectra. This signal can be attributed to the gallium oxide formed due to the GaAs decomposition and oxidation at high excitation density during micro-PL measurements [16].

![Figure 4. Room-temperature PL spectra of the GaAs nanoparticle array (left), a single nanoparticle and the continuous layer (right).](image)

RS spectra of GaAs nanoparticles and the GaAs continuous layer on Si(111) substrate measured at backscattering geometry are presented in figure 5. Even though GaAs and Si have a 4.2% lattice mismatch, there’s no considerable position shift of the GaAs TO and LO peaks for nanoparticles and continuous layer, indicating stress relaxation of the structure [17]. There is no evidence of a gallium oxide or an As layer at the presented RS spectra at chosen excitation pump density [16].
Figure 5. Room-temperature RS spectra of a single GaAs nanoisland and the continuous layer.

5. Conclusions
GaAs nanoparticles were grown on silicon (111) substrates by MBE. It was found that the growth rate of epitaxial nanoparticles significantly reduces after they reach a certain size and incoming adatoms are starts to be mostly consumed by continuous layer which leads to the overgrowth of nanoparticles with the continuous layer. AFM study indicates a liquid-like character of coalescence during overgrowth. Analysis of PL spectra from GaAs nanoparticles showed a tendency to photo-oxidation at high excitation densities. RS spectra study showed the stress relaxation of the GaAs nanoparticles and the GaAs continuous layer.

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