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Characterization of III-V semiconductor nanoparticles using TEM techniques

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Abstract. Nanoparticles of GaAs and InP have been prepared by aerosol techniques and characterized by electron microscopy methods. Through variation of the reaction temperature, it has been possible to follow how the reaction proceeds when the group-III aerosol reacts with the group-V precursor to form III-V semiconductor nanoparticles. The reaction can be followed both by the measurement of the change in particle size and the determination of the increase in the group-V element content in the particles.

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1 Introduction

The search in recent years for monodisperse, structurally and compositionally well-defined nanoparticles has involved various preparation techniques. These include methods ranging from solution chemistry to physical deposition techniques. The nanoparticles involved in this study have been prepared using a method that has been given the name aerotaxy [1] because it involves a self-organized growth in an aerosol phase. By this method, it is possible to prepare monodisperse bielemental nanoparticles that can be deposited on a wide variety of surfaces. The preparation technique is based on the generation of an aerosol of a group-III metal. The aerosol droplets are size-selected, and the monodisperse aerosol is then allowed to react with a group-V precursor resulting in nanoparticles of the III-V semiconductor.

This paper is focused on the characterization of III-V semiconductor nanoparticles prepared by aerotaxy. Through the use of transmission electron microscopy (TEM) techniques, it has been possible to follow the generation of the stoichiometric nanoparticles. Characterization of these particles has been made with respect to both composition and structure. Analysis of the average composition, as well as of the composition of single particles, has been made by energy-dispersive X-ray spectrometry (EDS). To study the atomic structure and the shape of the particles, high-resolution transmission electron microscopy (HRTEM) has been applied.

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2 Experimental

2.1 Preparation of particles

The semiconductor particles were prepared by an aerosol-based technique. A group-III metal is evaporated in a tube furnace to produce an aerosol consisting of sufficiently small droplets. The droplets in the aerosol stream are size-selected, and the monodisperse aerosol is mixed with a group-V precursor. The mixture is passed through a reaction furnace where the reaction can take place. This way, an aerosol of III-V semiconductor particles is created. The formation of the final product can be controlled by control of the temperature in the reaction furnace. In this study, the characterization of GaAs and InP particles prepared in this way is described. The GaAs particles were achieved by the reaction of Ga aerosol with AsH_3, and the InP particles by the reaction of an In aerosol with PH_3. More information about this technique is given in [1, 2].

2.2 Electron microscopy

The structural and compositional characterization of the nanoparticles was accomplished by the use of TEM techniques. Elemental analysis of the particles was done using a conventional TEM (JEM-2000FX) equipped with an X-ray spectrometer. The smallest electron probe size possible with this setup is ≈ 30 nm. This is not dedicated microanalysis equipment, but it is still possible to focus the beam on single particles and do the measurements. This way, the average composition in each sample can be compared with the local composition of single particles.

To study the structure and morphology of the particles, HRTEM was used. The experiments were done using a 400 kV TEM (JEM-4000EX) with a structural resolution of ≈ 0.17 nm. This enables us not only to examine the shape of the particles but also to draw detailed conclusions about the internal atomic structure (e.g., stacking faults and twin planes).

The size determination of the particles was made from electron microscopy negatives that were scanned and then measured. Such measurements can generate various parameters related to the shape and size of the particles. In this paper, we will use the average diameter and the circularity to describe the particles. To extract these parameters, we marked the perimeter (manually) for each particle and from that, calculated the desired parameters. Since the diameter measurements are only valid for spherical particles, it is necessary to relate the diameter determination to a measure of how closely the particle resembles a sphere. Since the electron micrographs give only projected information, all diameter measurements are in two dimensions. As a consequence of this, we have used the circularity of the particles as an indirect way to measure the sphericity. The circularity measurement gives a relative value of how well the projected perimeter of the particles fit with a circle. The formula used for this calculation is $(4 \cdot \pi \cdot \text{area})/(\text{perimeter}^2)$. This gives the value 1 for a perfect circle.

As a complement to the compositional analysis, so that the formation of III-V semiconductor particles could be confirmed, electron diffraction was used.

3 Results

3.1 HRTEM

For both investigated material systems, we took samples from experiments using different reaction furnace temperatures in order to follow how the creation of the III-V nanoparticles proceeded.

To exemplify these measurements, the InP particles were chosen. During the experiments, samples were taken in a temperature range from room temperature to 530 °C. We chose the upper temperature limit to ensure that the cracking of phosphine was kept to a minimum [3]. In order to simplify the compositional analysis of single particles, an initial In droplet size of approximately 22 nm was chosen, although it is possible to fabricate particles with sizes below 10 nm.

The results from measurements of particles produced at increasing reaction furnace temperature show a moderate change in diameter up to 300 °C (Fig. 1). Above this temperature, the diameter drastically increases until it reaches a maximum. After that, the diameter decreases to around 33 nm. It should be pointed out that the onset temperature of the reaction is dependent on the size of the initial In droplets; i.e., the values in Fig. 1 are only valid for this particular particle size.

The maximum at approximately 400–450 °C can be attributed to the difficulty in measuring the diameter of non-

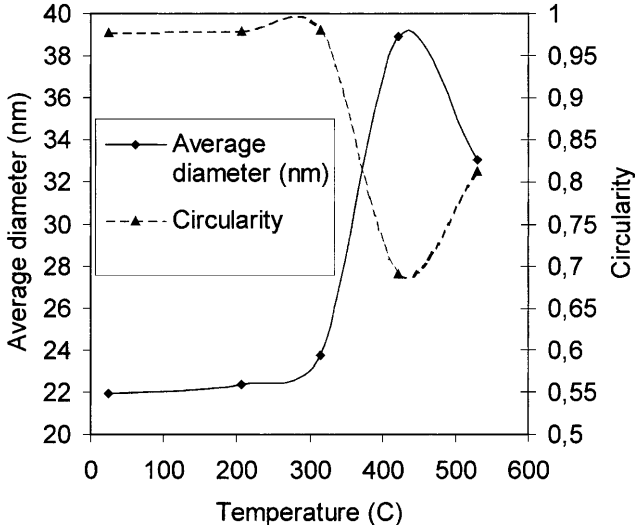

Fig. 1. The average diameter and the circularity as a function of the reaction furnace temperature for the preparation of InP nanoparticles.

circular particles. The average diameter is a parameter only relevant for close to circular or spherical objects. Since it is our goal to prepare spherical particles, we still use the average diameter as the size-determining parameter. From a plot of the circularity in the same diagram as the measured diameter (Fig. 1), this relationship is obvious. A sample with circularity of around 0.9 or above will appear reasonably circular to the eye. This means that at the higher temperature, full circularity is not achieved for this initial particle size. A higher reaction furnace temperature would increase the circularity, but this would also result in phosphine cracking with phosphorous contamination as a consequence. For smaller particles, the upper temperature is enough to produce spherical particles (see Fig. 7).

The actual shape of the particles generated at 400–450 °C indicates that the reaction is taking place in a preferred direction, giving elongated particles. This elongation is the explanation for why the nonspherical particles cause the maximum in the diagram.

The increase in particle diameter is to be expected when In reacts to form InP. If we use the density and the molecular weight of In and InP, it is possible to estimate the theoretical increase in diameter if spherical particles are assumed. This would give a diameter ratio of 1.26 for InP/In. The measurements show a higher value than expected (1.5). This can be attributed to the noncircular shape of the imaged particles. As has been pointed out, the measurement only gives information about two dimensions. Any deformation of the particles in the third dimension when deposited on a surface is not taken into account. Complementary studies by EDS and electron diffraction confirm the formation of InP particles.

Similar measurements were performed for the preparation of GaAs particles. The results are equivalent to the InP measurements showing the increase in diameter and the elongated particles.

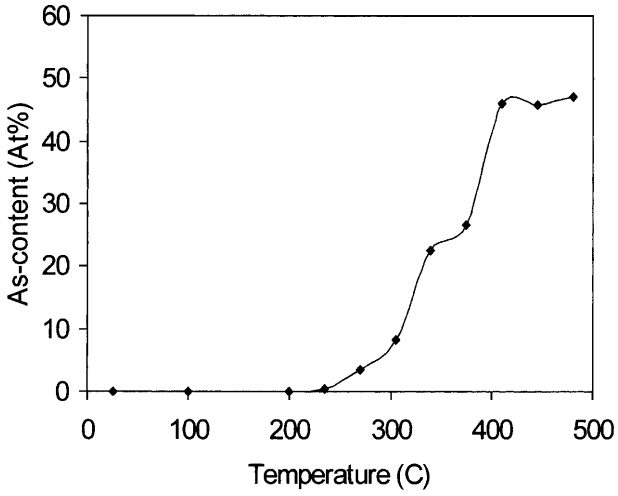

Fig. 2. Arsenic content (in atomic percent) as a function of reaction furnace temperature for the preparation of GaAs nanoparticles.

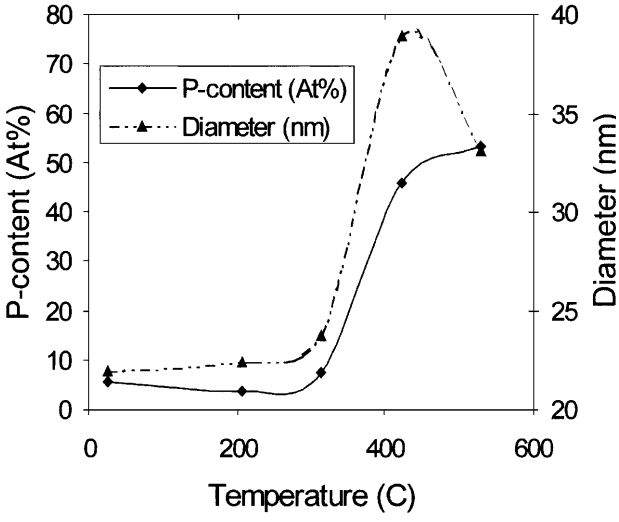

Fig. 3. Phosphorous content (in atomic percent) as a function of reaction furnace temperature for the preparation of InP nanoparticles. The dotted line indicates the particle diameter for the same furnace temperatures.

3.2 EDS

All samples were investigated by EDS, both for average and local composition. The average composition was in good agreement with the local (single particles); this indicates a homogeneous sample. Figures 2 and 3 show the content of the group V element as a function of the reaction furnace temperature. For the low-temperature part of both measurements, the concentration of As and P respectively was very low. When the reaction furnace temperature is increased, the group-V element content gets higher, indicating that the reaction has started. The increase in the group-V content levels out slightly above 400 °C for both cases. At this stage, the P content in the InP experiment was 53% and the As content in the GaAs experiment was 47%. This is in close agreement with the formation of a stoichiometric compound.

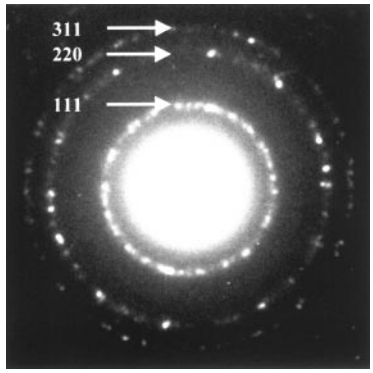

Fig. 4. Electron diffraction pattern from an area including several GaAs particles. The indices of the rings of reflections are given in the image.

In Fig. 3, the composition curve is complemented by a curve showing the average particle diameter. It is clear from the two curves that the increase in diameter is directly related to the increase in phosphorous content.

3.3 Electron diffraction

To further confirm the formation of GaAs and InP, electron diffraction studies were made. The limited size of the particles makes conclusive diffraction studies of single particles virtually impossible, but it is still possible to record diffraction patterns from areas covered by the nanoparticles. Such diffraction patterns will give average structural information. During these studies, all significant reflections could be attributed to GaAs and InP respectively. An example of a GaAs diffraction pattern is given in Fig. 4.

Calculated diffractograms from HRTEM images of single particles also support the formation of InP and GaAs.

4 Discussion

The TEM and EDS measurements clearly show that nanoparticles of GaAs and InP have been formed. After the completed reaction, the composition of both materials can be regarded as stoichiometric. Slight deviations from exact stoichiometry can be expected, since single particles might be influenced by the electron beam during the time of measurements (several minutes for each EDS analysis), and since we have not applied any theory for the termination of the particle surface.

The change in shape of the particles is apparent when examining the micrographs (Fig. 5). The low-temperature experiments only create droplets of indium or gallium, i.e., no reaction takes place. These particles are spherical. When the reaction starts, the growth rate appears to be higher in the direction perpendicular to the crystallographic {111} planes. From vapor phase epitaxial growth, it is known that the highest growth rate is to be expected on the (111)A planes [4]. This is in agreement with the results

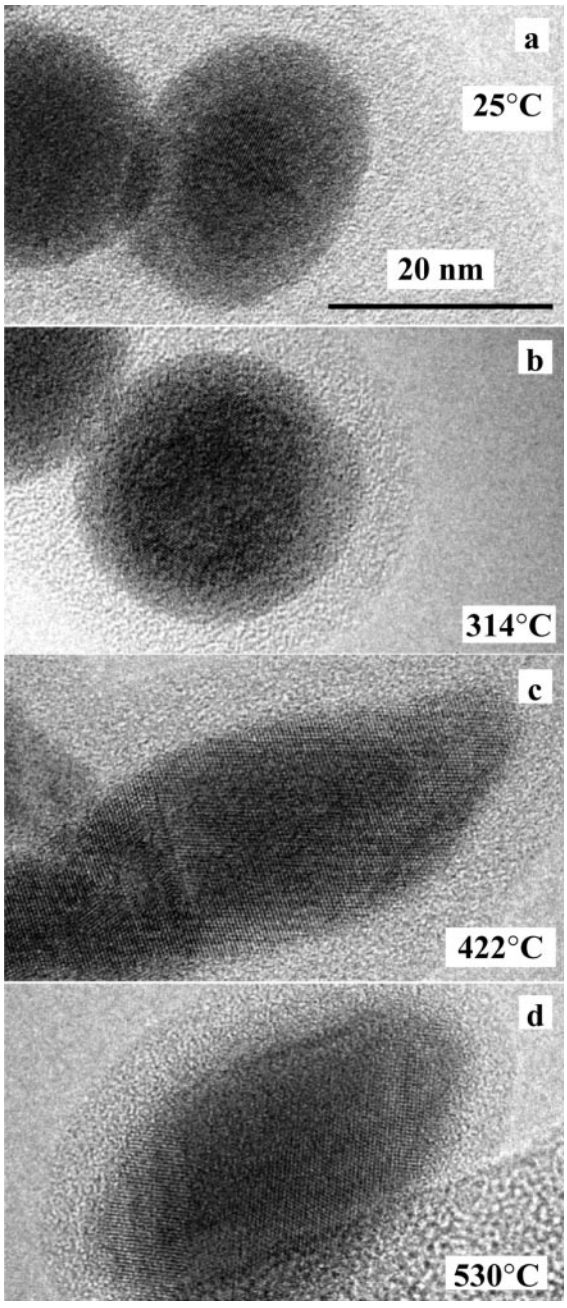

Fig. 5. In/InP particles prepared using different reaction furnace temperatures. The particles in (a) and (b) contains almost no P, whereas the particle in (d) is almost pure InP. The samples have been exposed to the atmosphere prior to investigation, hence some surface contamination should be expected. For this particular particle size, 530 °C is not enough to create spherical particles and to remove structural defects that can be seen in (c) and (d).

from the TEM studies of the InP and GaAs nanoparticles (Fig. 6).

The elongation of the particles gradually disappears when the reaction furnace temperature is increased. An example is given in Fig. 5d, though the particle is not perfectly spherical. For smaller particles, the sintering process

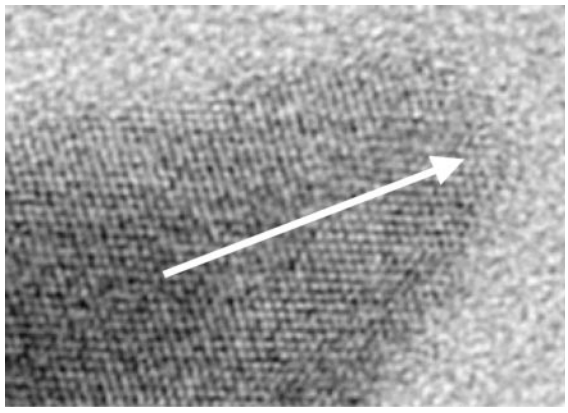

Fig. 6. This is an enlargement of the upper right corner in Fig. 5c. The elongation direction is given by the white arrow. From high resolution image it can be seen that the elongation is perpendicular to the crystallographic {111} planes.

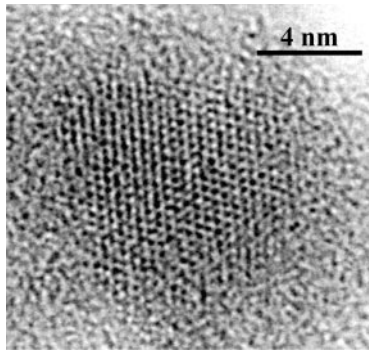

Fig. 7. A HRTEM image of an InP particle with a diameter of approximately 9 nm. The particle appears to be spherical and has a good crystallinity.

(the formation of spherical, single crystalline particles) is faster and takes place at lower temperatures. An example of a 9 nm InP particle is given in Fig. 7.

From the results, it is clear that nanoparticles of InP and GaAs have been formed by this preparation technique. For the sizes presented here, the final particles have not reached total sphericity, but smaller particles prepared the same way will be spherical and have a well-defined crystal structure (zinc-blende).

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