Synthesis of highly doped silicon and germanium nanoparticles in a low-pressure plasma-reactor for thermoelectric and solar applications

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ABSTRACT

Microwave-plasma induced thermal decomposition of gaseous precursors like monogermane (GeH_4) and monosilane (SiH_4) is used to synthesize semiconductor nanoparticles for thermoelectric and solar applications. P- and n-doping can be achieved by mixing silane and germane with diborane (B_2H_6) and phosphine (PH_3), respectively. Adjusting the fraction of the respective precursor in the gas phase is used to control the dopant concentration. Steep temperature-time profile and kinetic control of particle formation enable for synthesizing spherical and loosely agglomerated nanoparticles with very high concentration of dopant beyond the solubility limit. The mean particle diameter can be tuned between 3 and more than 50 nm by variation of microwave-power, plasma-gas-flow, reactor pressure and precursor concentration. This enables us for producing tailor-made nanosized materials with respect to energy conversion in thermoelectrics and heterojunction solar-cells.

Keywords: silicon, doped, nanoparticles, synthesis, plasma

1 INTRODUCTION

Silicon is the most important semiconductor material and due to its very good availability and it is in the focus of a lot of solar or thermoelectric applications like heterojunction solar-cells [1] or thermoelectric generators [2,3]. There are several methods to synthesize e.g. silicon nanoparticles like solution phase synthesis [4,5], ion implantation [6] or multilayer CVD [7]. However, the gas phase synthesis has a significant scale-up possibility for industrial production. With this synthesis approach, nanoparticles with very high purity can be synthesized and it is a very cost effective method. With highly doped silicon nanoparticles one can ensure very good ohmic contacts on solar cells [8] and mixing of highly doped silicon and germanium nanoparticles is investigated to achieve high performance SiGe thermoelectric devices [9]. The structure of the nanopowder used for thermoelectric applications can be preserved during sintering to reduce thermal conductivity while the electrical conductivity of sintered samples can be adjusted with respect to dopant concentration.

2 EXPERIMENTAL

Doped as well as undoped silicon and germanium nanoparticles are synthesized in a low-pressure microwave plasma reactor. The pressure in the reactor is controlled in the range between 5 and 500 mbar (absolute) by a PID controller. Monosilane (SiH_4) or monogermane (GeH_4) is mixed with argon (Ar) and hydrogen (H_2) before being fed into the reactor. For optional n- or p-type doping, precursors like phosphine (PH_3) or diborane (B_2H_6) were added to the gas mixture, respectively. The precursor gas mixture is guided through a microwave-supported plasma ignited within a quartz gas tube that is located in the center of a microwave resonator. The microwave source is operated at a frequency of 2.45 GHz and enables a maximum microwave power of 6 kW. The composition of the precursor mixture can be adjusted in a wide range and enables for the synthesis of nanomaterials with doping concentrations ranging between 10^{16} and 10^{21} cm^{-3}. The gas temperature measured from the emission of the plasma by means of optical emission spectroscopy typically ranges between 900 and 1300 K depending on pressure, microwave power, and gas composition. The as-prepared particles are separated from the gas flow by means of a filter device and can be harvested under inert conditions to prevent them from oxidation. Figure 1 shows a brief sketch of the experimental setup used for the synthesis of the nanoparticles.

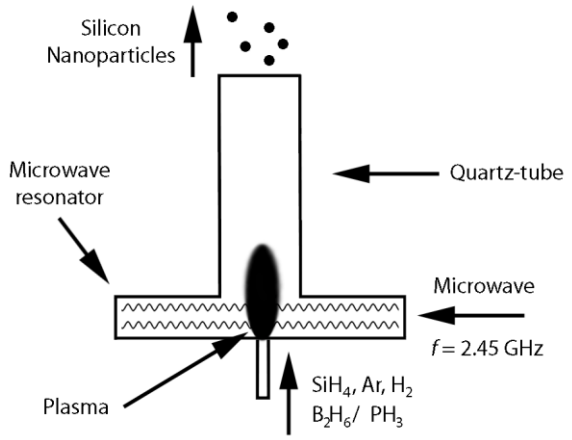

Figure 1: Schematic representation of the experimental setup for the synthesis of semiconductor nanomaterials.

3 RESULTS AND DISCUSSION

The size, shape and crystallinity of nanoparticles were analyzed by transmission electron microscopy (TEM) using a Philips CM12 at an accelerating voltage of 120 kV. The TEM specimens were prepared by ultrasonic dispersion of the nanoparticles in cyclohexane or methanol and dipping the carbon-coated Cu grids into the dispersion with subsequent drying. The mean size of the nanoparticles was investigated by means of gas-adsorption according to Brunauer, Emmett and Teller (BET) [10] using a Quantachrome Nova 2200 with N_2 as adsorption gas. The crystallinity and size of the nanoparticles were determined with a PANalytical X-ray diffractometer (X'Pert PRO) with Cu-K_α radiation and a subsequent Rietveld refinement with help of the MAUD program [11].

The nanoparticles exhibit very high crystallinity and almost every sphere consists of one single crystal (see fig. 2 and 3).

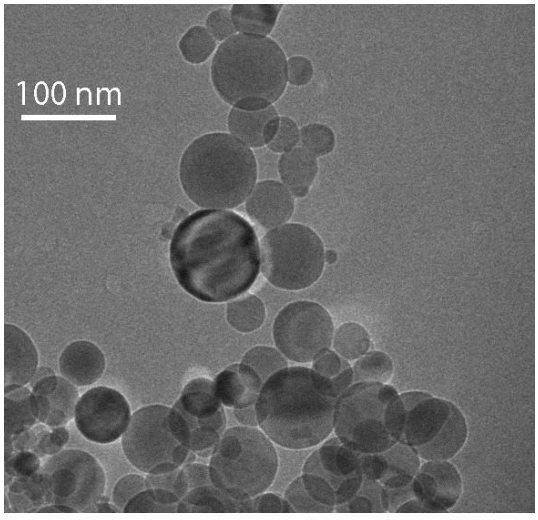

Figure 2: Single crystalline silicon nanoparticles from microwave plasma synthesis.

The results from BET analyses regarding the mean diameter of the particles comply with measurements from TEM and XRD (data not shown). With respect to synthesis conditions, parcels ranging from 3 to more than 50 nm in size are accessible. While low pressure (about 10 mbar) and low precursor concentration in the range of a few thousand ppm result in very small particles with a few nm in diameter, higher pressure as well as higher precursor concentration are necessary for the formation of bigger ones. Due to a limited residence time of the gas mixture within the hot reaction zone, the maximum particle size levels around 100 nm.

When the particles come into contact with the atmosphere the surface of the nanoparticles oxidizes. As an example, we show the HRTEM image of silicon nanoparticles as shown in figure 3. The lattice fringes clearly demonstrate that the particles are highly crystalline and that they are covered with an amorphous oxide layer. Elemental analysis of the as-prepared materials ensured that — despite the oxygen covering the particle surface — the chemical composition of the product is identical to what is expected from the gas-mixture introduced into the reactor.

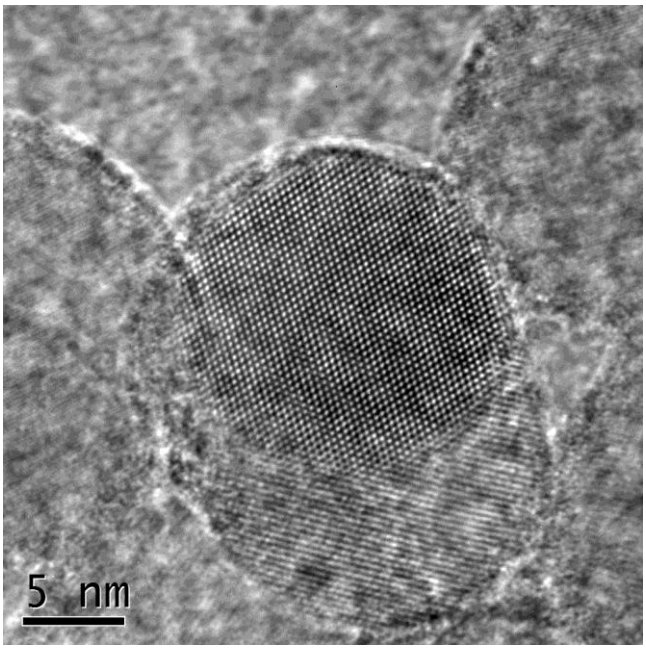

Figure 3: High resolution TEM image illustrating the crystallinity of the particles.

4 SUMMARY

We synthesized silicon and germanium nanoparticles by thermal decomposition of silane or germane in a microwave induced plasma reactor. The nanoparticles can be doped with phosphine or diborane by adding the dopant into the gas flow and the reactor enables for a quantitative decomposition of the precursor material. The nanoparticles were characterized by using BET, TEM and XRD. These

particles form an oxide layer on their surface under ambient conditions. The mean diameter of the particles can be controlled by varying the microwave power, the pressure and the temperature in the reactor. The doping concentration can be precisely controlled by adjusting the gas flow of dopant inside the reactor chamber.

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