Electrical Properties of Functionalized Silicon Nanoparticles

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ABSTRACT

Silicon nanoparticles are a promising, non-toxic material with respect to printed electronics and quantum size effects. As silicon nanoparticles tend to form a native oxide shell when handled in air, a stable surface functionalization is required to make them applicable for semiconductor purposes. The most favorable way is the stabilization by means of alkylation and hydrosilylation. Therefore, the natural oxide of silicon nanoparticles was removed by etching the particles with hydrofluoric acid. In order to prevent the particles from re-oxidation, the surface of freshly etched particles was functionalized with different alkenes via thermal alkylation. The electrical conductivity of as-prepared, freshly etched, and functionalized Si-NPs was measured using impedance spectroscopy in the temperature range between 323 K and 673 K. The electrical properties of silicon nanoparticles stabilized with n-alkenes ranging from C_6 to C_{18} are investigated.

Keywords: silicon nanoparticles, functionalization, electrical conductivity

1 Introduction

The utilization of silicon nanoparticles (Si-NPs) for printable electronics like solar cells, sensor devices, light emitters and transistors requires highly stable, (semi)conducting materials. While bulk silicon is one of the key materials for microelectronics, it is not applicable for printed devices. Additionally, it is an indirect band gap semiconductor [1] which limits its utilization for optoelectronic applications. Decreasing the size of the particles below 10 nm results in an increased optical activity with luminescence properties approaching the visible [2]. Nevertheless, as-prepared silicon nanoparticles suffer from poor resistivity against oxidation resulting in poor optical and electronic properties. By removing the oxide layer with hydrofluoric acid, light emission as well as electrical conductivity can be improved but when leaving them in air, the oxide layer appears again limiting conductivity and photoluminescence [3,4]. To avoid the re-oxidation of freshly etched silicon nanoparticles, they must be covered with a stable shell e.g. consisting of organic molecules [5].

In this paper, we report on the electrical properties of silicon nanoparticles. A comparison between as-prepared, freshly etched hydrogen terminated, and silicon nanoparticles functionalized with different n-alkenes is given.

2 EXPERIMENTAL DETAIL

Phosphorous-doped as well as undoped Si-NPs with a mean particle diameter of about 50 nm were synthesized in a microwave plasma reactor by thermal decomposition of silane in the presence of hydrogen, argon and phosphine. The etching of Si-NPs was carried out using hydrofluoric acid, which removes the surface oxides and terminates the silicon surface with hydrogen. The quantitative removal of oxygen was verified by FT-IR spectroscopy. In order to prevent the particles from re-oxidation, the surface of freshly etched particles was functionalized with different alkenes (hexene (C_6), decene (C_{10}), dodecene (C_{12}), teradecene (C_{14}) and octadecene (C_{18})) via thermal alkylation as described [5].

Transmission electron microscopy (TEM) was performed to observe any change in size or morphology. It is found that – despite the removal of the native oxide shell – neither particle size nor particle morphology has changed significantly.

As-prepared, hydrogen-terminated and n-alkene-termi–nated particle powder were pressed into small discs with 5 mm in diameter applying a force of 1.02 GPa (see figure 1a and 1b).

a.) b.)

Figure 1a: Dried Silicon nanoparticle powder after synthesis and functionalization;
b: Mechanically stable disc for electrical measurements prepared from silicon nanopowder.

The mechanically stable discs were placed between two polished platinum electrodes inside the measurement cell for the electrical measurements (see figure 2).

The electrical conductivity of as-prepared, freshly etched, and functionalized Si-NPs was measured in hydrogen atmosphere using impedance spectroscopy in the temperature range between 323 K and 673 K using an impedance spectrometer (HP4192A) in the frequency range between 10 Hz and 10 MHz with 20 frequency points per decade. For a stepwise measurement of the temperature-dependent conductivity, heating ramps with a step size of 25 K were applied and the impedance was measured at each temperature point after the temperature has stabilized. After reaching 673 K the sample was cooled to 323 K and the measurements were repeated two times. Due to annealing effects occurring during the first heating cycle, these measurements usually differ from cycle two and three which are almost identical. Therefore, the data from the third cycle were used for further analysis

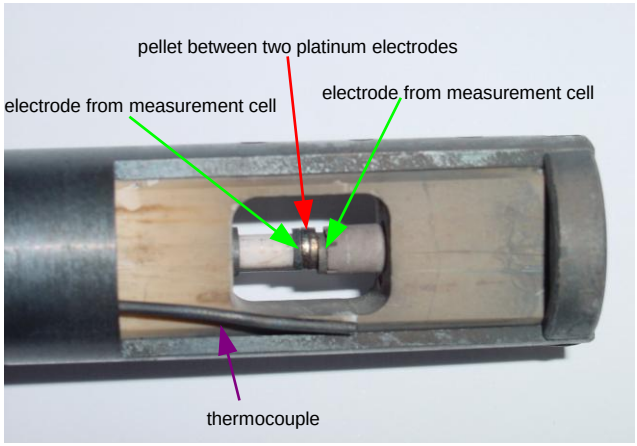

Figure 2: Compacted particles placed between two platinum electrodes of the measurement cell.

3 RESULTS AND DISCUSSION

3.1 Structural Properties

Transmission Electron Microscopy (TEM) images of as-prepared silicon nanoparticles show agglomerated and highly crystalline silicon particles with an oxide shell of about one to two nanometers in thickness. After etching and functionalization the particles are still crystalline but no oxide shell was observable and the agglomeration was broken resulting in single particles.

The XRD measurements analyzed with Rietveld refinement [6] show crystalline silicon nanoparticles with a diamond cubic structure. Before and after functionalization the crystallinity, the type of crystal lattice and the size of the crystals do not change. In figure 3, a Scanning Electron Microscopy (SEM) image of the surface of compacted silicon nanoparticles is shown illustrating the existence of porous silicon nanoparticle network.

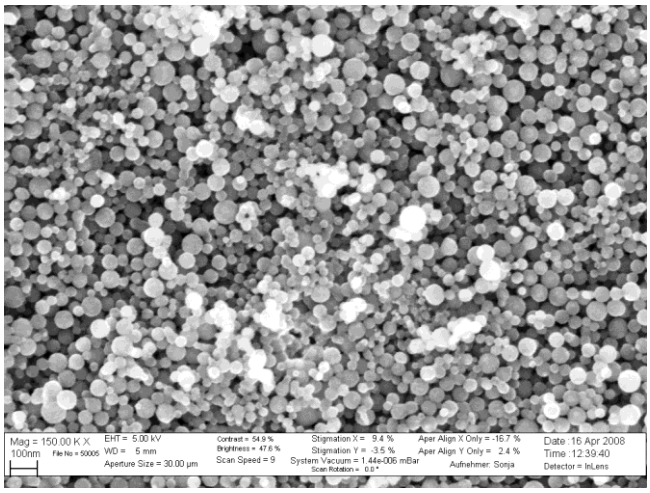

Figure 3: SEM picture of compacted silicon nanoparticles.

3.2 Electrical Properties

The conductivity of as-prepared silicon nanoparticles was measured in hydrogen atmosphere at different temperatures and compared to those, who were etched and functionalized. The resistivity of as-prepared Si-NPs decreases going to higher temperature which is typical for semiconducting materials and the activation energy is found to be in the range of 1.2 eV.

The freshly etched Si-NPs showed a very large increase in conductivity (about 4 orders of magnitude for measurements performed at 323 K) compared to the respective as-prepared samples (see fig. 4). With surface functionalization, the conductivity changes depending on the length of the alkenes used for stabilization.

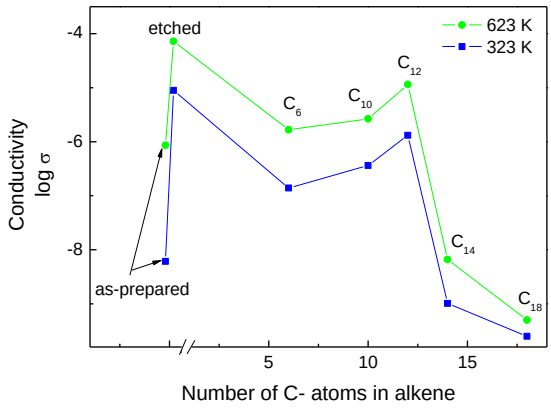

Figure 4: DC-conductivity of as-prepared, etched and functionalized silicon nanoparticles measured at 323 and 623 K.

Freshly etched as well as the functionalized samples show ntc conduction behavior as it is typical for semiconducting materials. Interestingly, conductivity increases from C_6 to C_{12} and is higher compared to the as-prepared materials. In contrast, samples functionalized with C_{14} and C_{18} show very poor conductivity. Particles functionalized with C_6 - C_{10} show a lower conductivity than C_{12} but still a better one than C_{14} and C_{18}. While FTIR-spectroscopy indicated that surface functionalization with C_6 - C_{10} is not very stable due to a creeping re-oxidation, dodecene (C_{12})-terminated nanoparticles showed the highest conductivity, even after storage in ambient conditions for half a year. We attribute the poor conductivity of C_{14} and C_{18} terminated Si-NPs to a large tunneling barrier caused by a thick organic layer which is expected to consist of well-aligned hydrocarbon chains perpendicular to the nanoparticle surface.

From our measurements we conclude that the conductivity of silicon nanoparticle ensembles is dominated by inter-particle transport rather than by the transport properties within the silicon core itsself. Therefore, engineering of the particle surface is the most important challenge for a useful application of silicon nanoparticles in printable electronics e.g. ink jet printed films.

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