# Dispersing, Stabilizing and Functionalizing Silicon Nanoparticles

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## ABSTRACT

Silicon particles were dispersed in organic solvents using a variety of methods. Morphology, particle size and structure of untreated and dispersed silicon nanoparticles (SiNP) were examined using high-resolution transmission electron microscopy (HRTEM), dynamic light scattering (DLS) and X-ray diffraction (XRD). The amorphous $SiO_x$ of the SiNP was removed by hydrofluoric acid (HF) etching. The resulting hydride (H) terminated SiNP surfaces were functionalized with styrene via hydrosilylation of phenyl acetylene. Evidences of a successful functionalization of the SiNP were obtained from diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), solid state $^{13}C$ nuclear magnetic resonance (NMR) and HRTEM.

## 1. INTRODUCTION

Future progress in electronics requires the development of more powerful and compact integrated circuits and nanometer-sized devices. In the bottom-up approach the building blocks are proposed to be formed by semiconductor nanoparticles via surface-controlled self-organization processes. Since nowadays all microprocessor chips in electronic products are still built on crystalline silicon wafers, the development of printing techniques using semi-conducting silicon nanoparticles (SiNP) promises inexpensive manufacture of electronic devices on flexible substrates. The fabrication of inorganic thin film transistors out of a solution of either CdSe or PbSe nanocrystals has been already reported in literature [1, 2]. The untreated SiNP however are nearly insulating because of their native passivation shell that is composed of amorphous $SiO_x$. Hence, SiNP surfaces which enable interfacial charge transfer do not only require the complete removal of the insulating oxide layer but also have to be functionalized with organic monolayers that achieve both, the protection against oxidation and the support of the charge carrier transport. To this end, silicon surface chemistry is of fundamental importance for potential applications of nanostructured silicon in modern technology and has become an area of intense research interest.

The Si-C linkage is both, kinetically and thermodynamically stable, due to the high strength and low polarity of the bond. Hence, the most successful approach for an organic functionalization of Si surfaces is accomplished via hydrosilylation of 1-alkynes or 1-alkenes yielding surface (Si-C) bound vinyl and alkyl groups, respectively. Hydrosilylation requires hydride-terminated Si surfaces as involving the insertion of the unsaturated C-C bond into the Si-H group so that Si-C bonds are formed. For efficient functionalization of porous Si with unsaturated organic compounds Buriak and coworkers developed more than five wet chemistry syntheses towards Si-C formation on porous Si surfaces [3, 4]. Since the purification of SiNP is very difficult, the least contaminated products are expected to be obtained directly via thermally or photochemically induced hydrosilylation of 1-alkenes or 1-alkynes on hydride-terminated Si surfaces.

As a subproject of the Research Training Group 1161/1 "Disperse Systems in Electronics", in close cooperation with Degussa, this work focuses on the dispersion of SiNP and subsequent functionalization of the particle surfaces with phenyl acetylene. The main impetus is to achieve an in-depth insight into the alteration of the surface morphology of the oxide-passivated SiNP occurring in the course of the HF etching procedure and the subsequent thermally induced hydrosilylation reaction. To this end, solid-state $^{13}C$ NMR and DRIFT spectroscopy measurements were conducted to obtain unambiguous evidence for surface-bound styrene molecules. Valuable information on size, bulk and surface structure of untreated, ground and functionalized SiNP were obtained from high-resolution transmission electron microscopy (HRTEM).

## 2. EXPERIMENTAL

A suspension of 20 wt.% silicon particles in 1-butanol was dispersed for 6 h with a stirred media mill (Netzsch PE 0785). The temperature of the milling chamber was kept constant at 15°C, and the revolution velocity of

the SiC stirrer was set at 1000 min-1. Beads of yttrium stabilized ZrO2 with diameters between 0.25 and 0.4 mm were used as grinding media. For the sake of safety the oxygen concentration was kept below 7% during the milling process. Every hour four drops of suspension were taken from the milling chamber and diluted with 5 ml 1-butanol. These samples were used to examine the evolution of the particles size distribution during the milling process by dynamic light scattering. After 6 h of dispersing the milling beads were separated from the SiNP by sieving and a stable suspension of SiNP in 1-butanol was received. 1-Butanol was removed from the SiNP suspension by distillation. 15 g of the ground SiNP material were redispersed by stirring in 40 ml ethanol. H termination of the SiNP was acquired by adding 50 ml of aqueous 40 wt. % HF solution and by heating the mixture at 60°C under $N_2$ for 1 hour. The etching was stopped by removing the HF solution through distillation. The H-terminated SiNP were dried in a $N_2$ stream. Styrenyl functionalization was started by immersing the H-terminated SiNP in 100 ml phenyl acetylene. The yellow suspension was refluxed under $N_2$ atmosphere at ca. 150°C for 7 hours. Unreacted phenyl acetylene was decanted. The styrenyl-functionalized SiNP were washed 6 times with toluene and subsequently 20 times with ethanol. Finally the SiNP were dried by evaporation of ethanol. The solid-state TOSS (total suppression of spinning sidebands) ^{13}C NMR experiments were carried out on a Jeol Alpha 500 MHz spectrometer (1H = 500 MHz) operating at 125.79 MHz for 13C. DRIFT spectra of the SiNP were recorded on a Varian FTS 3100 FTIR spectrometer equipped with a Pike Technologies EasiDiff accessory. The TEM and HRTEM images were obtained using a Phillips CM 30 T/STEM microscope and a Philips CM 300 UltraTwin microscope, respectively. The measurements were carried out at an acceleration voltage of 300 kV in the bright-field mode. A Siemens D 500 diffractometer equipped with a graphite secondary monochromator was used to measure the XRD spectra.

## 3. RESULTS AND DISCUSSION

The size, bulk structure and surface morphology of the untreated silicon particles were examined using XRD and HRTEM. The XRD spectrum (Fig.1) shows diffraction peaks that unambiguously identify lattice planes of crystalline bulk silicon. As obvious from the TEM image in Fig.2 the SiNP have nearly spherical shapes and a primary particle size of approximately 100 nm. They are interconnected via sinter bridges so that µm-sized agglomerates are formed.

The SiNP obtained from Degussa Creavis were fabricated by gas phase synthesis in a hot-wall reactor. The solid bridges are expected to result from sintering or surface growth in the course of the synthesis.
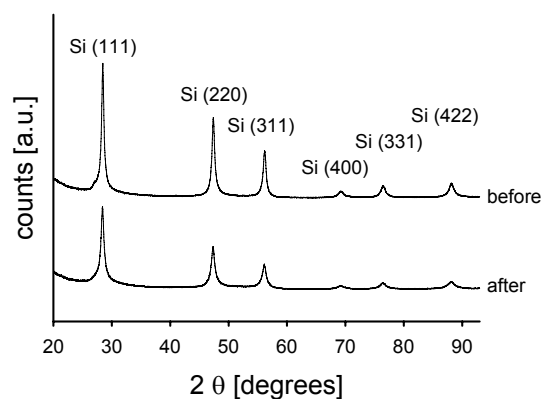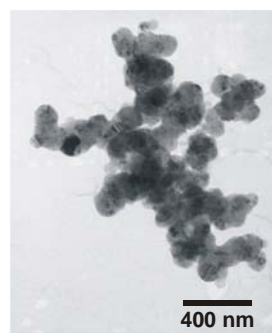


Fig. 1 XRD of untreated and disp. SiNP.



Fig.2 TEM image of untreated SiNP.

Fig. 3 displays a high-resolution TEM (HRTEM) image of a part of a single SiNP. The occurrence of equally spaced fringes, arising from the interference between the diffracted and undiffracted electron waves, indicates the crystalline bulk of the SiNP. On the other hand, the amorphous (i.e. disordered) shell with a thickness of about 5 nm is ascribed to the $SiO_x$ passivation layer.
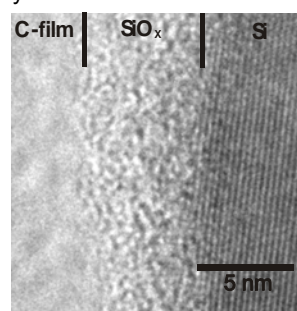


Fig. 3 HRTEM image of a part of an untreated SiNP.

The SiNP do not generate stable suspensions while dispersing with ultrasound or ultraturrax due to the formation of µm-sized agglomerates during the gas phase synthesis. Hence, successful processing requires methods with a high specific energy input e.g. a stirred media mill. To this end, the SiNP powder was wet-ground with 1-butanol as described before. The

temporal evolution of the volumetric SiNP mean size ($x_{1,3}$) during the milling process was determined using dynamic laser scattering (see Fig.4). The mean size $x_{1,3}$ decays exponentially with a time constant of 32 min and reaches a value of 166 nm after 6 h milling. For longer dispersing times the mean size $x_{1,3}$ stays nearly constant due to the equilibrium of breakage, agglomeration and desagglomeration [5, 6].
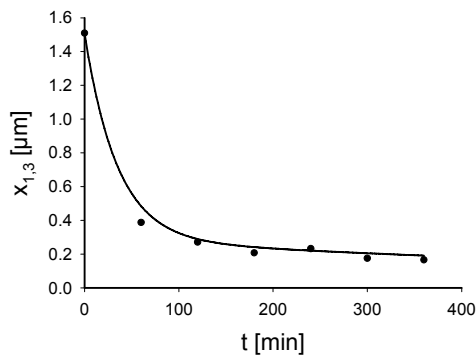


Fig. 4 Evolution of $x_{1,3}$ with disp. time.

At 6 h the milling process was stopped, the yttrium stabilized $ZrO_2$ beads were removed by sieving and a stable suspension of SiNP was received. In Fig. 5 the TEM image of ground SiNP is depicted. Obviously, the adhesion forces of the particles are sufficiently strong so that the SiNP organize as aggregates during evaporation of the solvent on the carbon film. However, instead of solid sinter bridges weaker physical interaction forces act between neighboured SiNP. The zeta potential of ground SiNP dispersed in 99:1 butanol-water mixture reaches a value of -46.6 mV that resembles the zeta-potential of silica in 99:1 butanol-water mixture with a value of -45 mV [7]. This result shows that the surface potential of SiNP is predominately determined by the electronic properties of amorphous $SiO_x$.
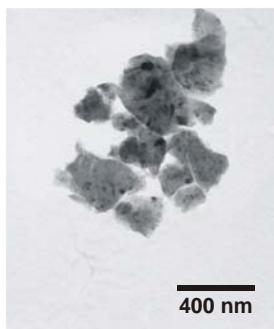


Fig.5 TEM image of aggregated ground SiNP.

The $SiO_x$ passivation shells of ground SiNP were removed by HF etching, and the resulting H-terminated surfaces were functionalized via hydrosilylation with phenyl acetylene. Fig.6 presents a HRTEM image of a part of a single styrenyl-terminated SiNP. In comparison with the untreated SiNP the 5-nm thick amorphous passivation layer is now substituted by styrenyl groups yielding a surface covering thinner than 0.5 nm. The styrenyl termination of the SiNP significantly decreases the value of the zeta potential to -22.36 mV. This indicates to significant electronic and structural changes of the SiNP surfaces arising from the substitution of $SiO_x$ by surface-bound styrene.
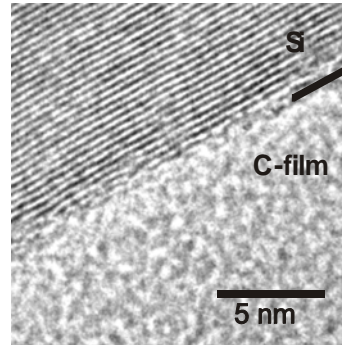


Fig. 6 HRTEM image of a functionalized SiNP.

The DRIFT spectrum of styrenyl-terminated SiNP (Fig.7) contains the characteristic vibrational spectrum of styrene consisting of bands at 700 cm$^{-1}$ (1), 1448 cm$^{-1}$ (7), 1492 cm$^{-1}$ (8), 1598 cm$^{-1}$ (10) with a shoulder at 1592 cm$^{-1}$ (9), 3029 cm$^{-1}$ (14) and 3061 cm$^{-1}$ (15) [8]. While aromatic in-ring $v_{(C-C)}$ stretches give rise to the bands at 1448 cm-1 and 1492 cm$^{-1}$, the vibrational bands at 1598 cm$^{-1}$ and 1592 cm$^{-1}$ presumably originate from the overlap of the $v_{(C=C)}$ stretching mode of the vinyl group with that of the phenyl ring [9]. The band at 700 cm$^{-1}$ is assigned to the $\delta_{(C=C-H)}$ bending mode of the vinyl group. The vinylic and aromatic $v_{(C-H)}$ stretching modes produce bands at 3027 cm$^{-1}$ (11) and 3061 cm$^{-1}$ (12), respectively. The appearance of the typical styrene bands in the DRIFT spectrum may be taken as an indirect evidence for styrenyl-terminated SiNP surfaces. The clear indication of the Si-C bond by the $v_{(Si-C)}$ stretching mode predicted to occur (600 – 800 cm$^{-1}$) in the IR spectrum is very difficult to obtain, since Si-H, Si-Si and Si-O vibrational modes appear in the same spectral range [10]. Fortunately the broad peak at 803 cm-1 (3) may be unambiguously assigned to the $\delta_{(Si-O)}$ bending mode so that the sharper one at 761 cm$^{-1}$ (2) should emerge from the stretching mode of the Si-C bond. The observation of both, the vibrational spectrum of styrene and the Si-C stretch at 761 cm$^{-1}$ indicates to styrenyl functionalization. The broad band between 3200 and 3500 cm$^{-1}$ (16), the peaks between 2930 and 2966 cm$^{-1}$ (13) and band at 1376 cm$^{-1}$ (6), as being characteristic for the O-H stretching, the alkane C-H stretching and C-H rocking modes, respectively, originate from either ethanol used for the washing procedure or 1-butanol used for the milling procedure. The pronounced band at 1100 cm$^{-1}$ (5) is due to the $v_{(Si-O)}$ and $v_{(Si-O-Si)}$ stretching modes of residual $SiO_x$, whereas the band at 930 cm$^{-1}$ (4) is generated by the $\delta_{(Si-OH)}$ bending mode [11]. Residual H termination of the SiNP are responsible for vibrational structures at , 2100 cm$^{-1}$ (11) and 2261 cm$^{-1}$ (12) which are assigned to stretching modes [12].
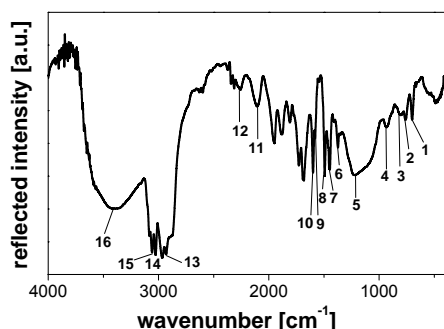
Fig. 7 DRIFT spectrum of styrenyl-terminated SiNP.

Solid-state TOSS $^{13}$C NMR provides complementary information of the Si-C linkages founding the styrenyl termination of the SiNP. The $^{13}$C NMR spectrum (Fig.8) exhibits a prominent peak at δ= 127.76 ppm and a smaller, broadened peak centered at δ = 143.34 ppm with a shoulder at 138.2 ppm.


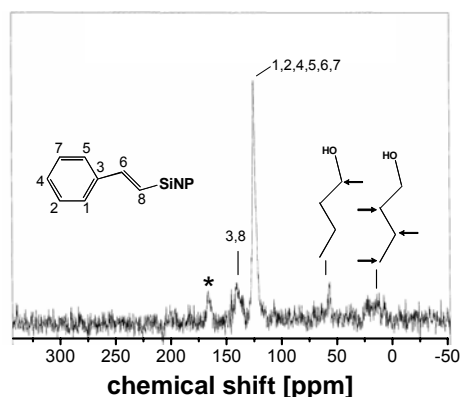
Fig. 8 Solid-state TOSS 13C NMR spectrum of styrenyl-terminated SiNP.

While the prominent peak results from the superposition of the $^{13}$C resonances of five aromatic carbon atoms (1, 2, 4, 5, 7) as well as of one olefinic carbon atom (6), the maximum (δ=143.34 ppm) and shoulder (δ=138.2 ppm) of the smaller peak are assigned to one aromatic carbon atom (3) and to the other olefinic carbon atom (8) that is bound to the SiNP surface, respectively. In particular, the assignment of the shoulder at δ=138.2 ppm to the Si surface-bound olefinic carbon (8) is corroborated by a simulation of a $^{13}$C NMR spectrum of β-trimethyl-silylstyrene, where the trimethylsilyl-bound carbon atom exhibits a $^{13}$C resonance at 134.57 ppm.

## 3. CONCLUSIONS

Since the untreated SiNP as received by Degussa Creavis are interconnected via sinter bridges and thus form µm-sized agglomerates, the SiNP were dispersed

in 1-butanol using a stirred media mill. A stable suspension of SiNP was obtained after the milling procedure. Subsequently the SiNP were functionalized with phenyl acetylene via hydrosilylation. Morphology, size and bulk structure of untreated, ground and styrenyl-terminated SiNP were examined using HRTEM, DLS and XRD. XRD data and HRTEM images of untreated and functionalized SiNP manifest the crystallinity of the SiNP. Additionally HRTEM revealed information of the amorphous SiO$_x$ shell of the untreated SiNP and the alteration of the surface morphology during the functionalization process. Evidence for the styrenyl termination of the SiNP was provided by solid-state TOSS $^{13}$C NMR and DRIFTS measurements. While the $^{13}$C NMR spectrum contains the $^{13}$C resonance of the olefinic carbon atom that is bound to the SiNP surface, there are vibrational bands in the DRIFT spectrum that are characteristic for styrene and for the Si-C linkage.

## ACKNOWLEDGEMENTS

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