

Hot-wire synthesis of Si nanoparticles

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Abstract

The viability of producing silicon nanoparticles using the HWCVD process is investigated. A system is assembled and particles are produced from silane at pressures between 0.2 and 48 mbar, with hydrogen dilutions of 0–80%, at a total flow rate of 50 sccm and with a tungsten filament maintained at 1650 °C. The as-prepared powder varies in colour from yellowish to dark brown and is deposited on all surfaces inside the reaction chamber. The material is a highly porous agglomeration of nanoparticles of primary size in the order of 40 nm, with a narrow size distribution. The nanoparticles produced are mostly amorphous, hydrogenated and have a partially oxidised surface.

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1. Introduction

Nanoparticles are considered as fundamental building blocks of nanotechnology. Likewise, the size-tunable optical and electronic properties of silicon nanoparticles make them interesting candidates for a wide spectrum of high-end applications, including light emitting diodes (LED), quantum dot lasers, chemical sensors and molecular electronics. Further low-end applications include printed electronics and flexible solar cells [1] as well as luminescent materials and composites [2]. These applications are expected to benefit social as well as industrial use. Historically nanoparticles have been manufactured by top–down approaches such as milling, laser ablation or etching, and bottom-up synthesis such as colloidal chemistry and gas phase pyrolysis. The chemical processes in the latter are generally equivalent to those in the chemical vapour deposition of compact films. In the case of silicon deposited by hot-wire chemical vapour deposition (HWCVD), powders formed by gas phase reactions and nucleation are often an unwanted by-product [3]. Furthermore, the charge cluster model that suggests nanometre size clusters are formed in the gas phase and become the deposition unit for thin films [4], leads us to believe that thermal catalytic pyrolysis, based on established HWCVD

techniques, is a viable process for Si nanoparticle (powder) synthesis. The objective of this research is to produce Si nanoparticles in sufficient quantities while maintaining control of the important properties namely size, size distribution, composition and crystallinity.

2. Experiment

Silicon nanoparticles were synthesized inside a stainless steel cylindrical chamber with inner diameter of 150 mm and a volume of 2.65 l. A water cooled carousel supported 6 substrates at a distance of 50 mm from the filament and allowed selective deposition per substrate. Filaments are constructed from a 30 mm long 0.5 mm diameter tungsten wire of 99.95% purity wound into a 6 mm diameter coil. The gas feed pipe ends 30 mm above the centre of the filament.

The base pressure achieved by the rotary vane pump was 4×10^{-3} mbar. The coiled tungsten wire filament was fixed at 1650 °C, while the total flow rate was 50 sccm. The temperature of the stainless steel substrates, in the carousel, did not exceed 70 °C. Si nanoparticles were produced with silane as precursor and hydrogen dilutions ranging from 0 to 80% and at operating pressures of 0.2 to 48 mbar. For each hydrogen dilution ratio, 5 substrates were loaded into the carousel and particles were produced with the same filament, but with the pressure being increased in 8 min intervals. Upon completion of the synthesis, the system was flushed with nitrogen for 4 min and samples were stored at atmosphere.

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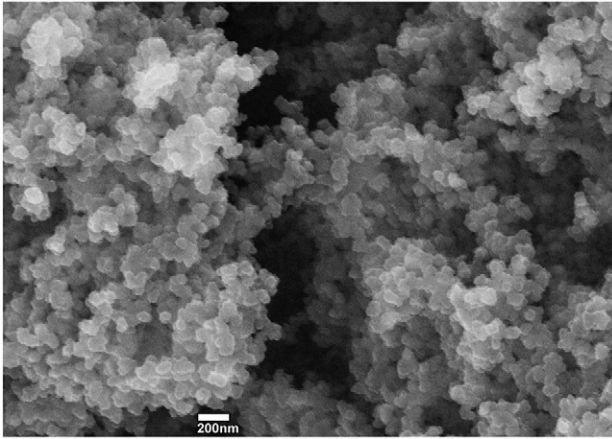


Fig. 1. a-Si:H nanoparticles produced at 48 mbar and 40% H₂ dilution.

The material was characterised for morphology, bonding configuration and crystallinity using field emission scanning electron microscopy (FESEM), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Raman spectroscopy, respectively. A Mettler AX 205 mass balance with an accuracy of 10 μg was used to determine the weight of the powder deposited on each substrate. The surface area of each substrate and the resulting production rate was calculated in $\mu\text{g mm}^{-2} \text{min}^{-1}$. The morphology of the nanoparticles was investigated using a LEO 1525 FESEM, operated at a potential differential of 3–10 kV. FTIR spectra were collected in transmission mode, using a Nicolette Nexus 470 FT-IR spectrometer in the 400–4000 cm^{-1} range, with an energy resolution of 2 cm^{-1} . Raman spectroscopy was performed on a Dilor XY Raman spectrometer with a Coherent Innova 300 Argon laser (green line at 514.5 nm) with a beam intensity of 50 mW at source. For XRD characterization a Phillips PW 1830, operating at 45 kV and 40 mA was used with Copper K α radiation with a wavelength of 1.5406 \AA . The diffraction pattern

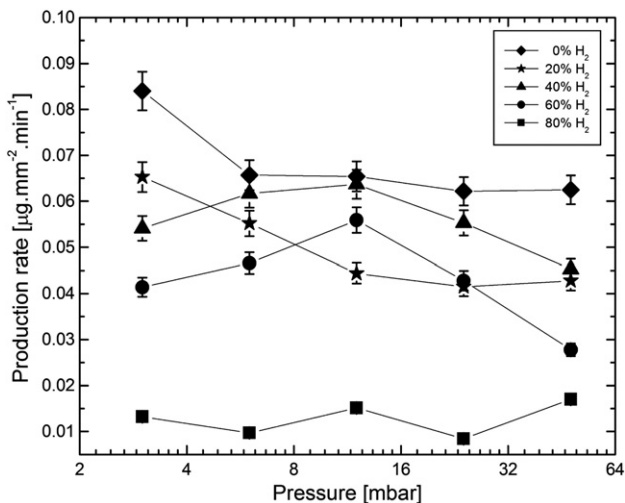


Fig. 2. Production rates at varying hydrogen dilutions and pressures.

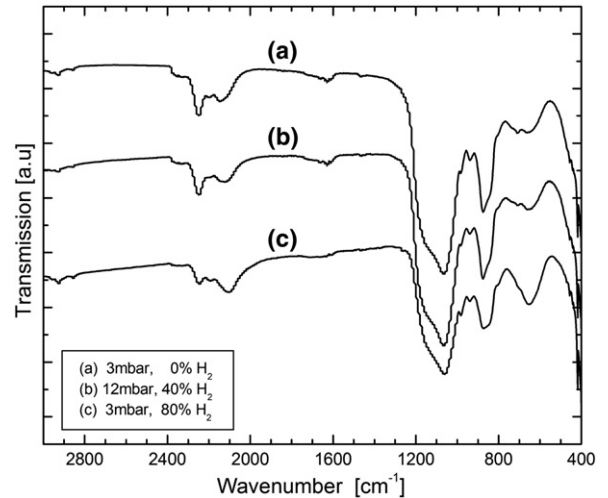


Fig. 3. FTIR spectra of a-Si:H nanoparticles produced at (a) 100% silane gas, (b) 40% hydrogen and (c) 80% hydrogen dilution.

was recorded from 5° to 90° in 2θ , with a step size of 0.02°, and 1 s step time.

3. Results and discussion

The as-prepared powder varies in colour from yellowish to dark brown and is deposited on all surfaces inside the reaction chamber. The material is a highly porous agglomeration of nanoparticles (Fig. 1). The primary size, of the smallest particles produced, determined from the micrographs, is in the order of 46 nm with a size distribution of about 20 nm.

As expected, the production rate shown in Fig. 2, in general, increases with decrease in hydrogen dilution and at first increases with increasing pressures, followed by a decrease after 8 min of production. This decrease can be ascribed to the accelerated ageing of the filament under high pressure conditions [5].

Fig. 3 shows the stacked FTIR spectra of the material produced at different operating pressures. The absorption bands at wave numbers 2250, 1070 and 460 cm^{-1} indicate a partial

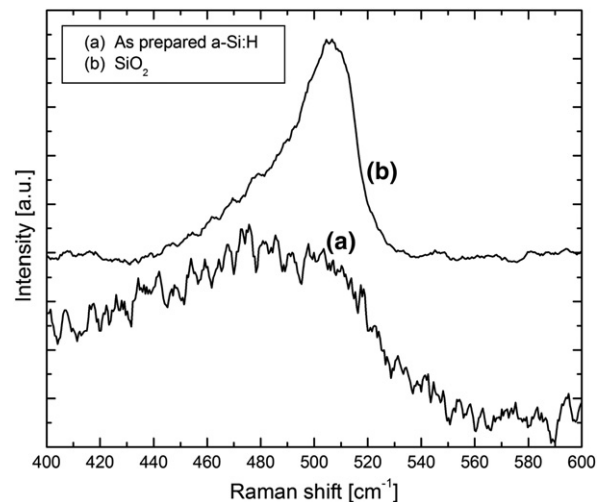


Fig. 4. Raman spectra of as-produced powder (a), and silicon oxide (b), after laser induced oxidation.

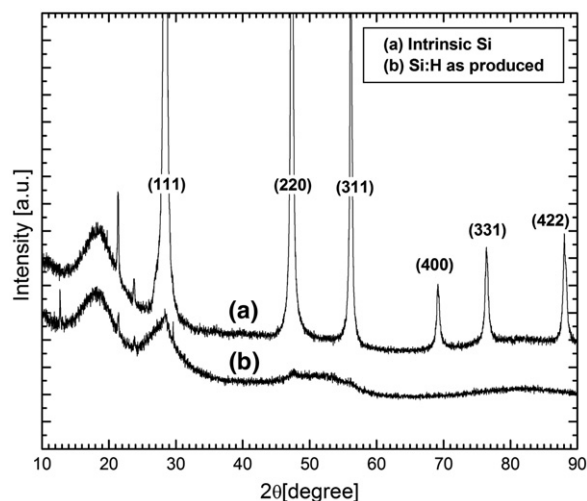


Fig. 5. XRD spectra of (a) commercial intrinsic silicon nanoparticles and (b) material collected from the shutter, produced at 6 mbar and 'substrate' temperature exceeding 120 °C.

surface oxidation [6], most likely caused by contact with air upon removing the powder after production [7]. The absorption bands at 2140, 2100, 880 and 640 cm^{-1} indicate the presence of Si–H_x mono- and polyhydride bonds, indicative of hydrogen surface passivation and possibly micro voids [8], which can be interpreted as the voids between particles, in the porous structure. It is noted, in Fig. 3, that the ratio between the Si–O peak at 2250 cm^{-1} , and the Si–H peak at 2142 cm^{-1} , changes with a change in hydrogen dilution. These peaks indicate surface bound oxygen and surface bound hydrogen, respectively. When the production conditions exclude hydrogen (Fig. 3(a)), the Si–O peak is dominant, but when the hydrogen dilution is increased to 80% (Fig. 3(c)), the Si–H peak is dominant. This domination of Si–H bonds at high hydrogen concentrations are due to the increased hydrogen passivation of the silicon surface of the nanoparticle, thereby reducing available sites for surface oxidation, upon introduction of the sample to atmosphere.

The presence of the Si–H peak at 2142 cm^{-1} in sample (a) in Fig. 3, with 0% hydrogen dilution, is an indication of the release of hydrogen from the dissociation process of silane at the filament.

To determine crystalline fractions, Raman spectroscopy was performed on the particles produced. However, the collection of spectra proved difficult. Upon laser radiation of the sample, the sample would "burn" or "glow out". Depending on the material, this "burning" would occur in a fast flash of orange light over the whole sample ($\sim 8 \text{ cm}^2$), or in the form of many tiny bright orange "balls of light", propagating from the laser point, resulting in white coloured powder.

This process can be ascribed to the release of surface bound hydrogen caused by the laser energy and subsequent oxidation of the silicon nanoparticle surface. Due to the high surface area of the silicon nanoparticles, the process is exothermic, resulting in a partial or complete oxidation of the powder.

One successful spectrum (Fig. 4(a)), of particles produced with 100% silane at 0.2 mbar, shows a broad peak, centred around 480 cm^{-1} , consistent with generally amorphous material. Upon exothermic oxidation of the same sample, as described above, a second spectrum (Fig. 4(b)) was collected, resulting in a narrower peak, centred at around 510 cm^{-1} .

The XRD spectrum of commercial intrinsic silicon nanoparticles (Fig. 5), produced by laser pyrolysis and used as a benchmark, displays clear crystalline peaks, with their respective lattice planes [9] indicated in the figure. Our darker brown material, deposited on the wall of the reaction chamber where temperatures exceed 120 °C, has a corresponding broad peak at the position of the (111) reflection at $\sim 28.5^\circ$. There is also a second broad between 47° and 56°, with a suggestion of the (200) crystalline peak at $\sim 48^\circ$. Taken together these observations are indicative of a generally amorphous material with some crystalline order.

4. Conclusion

The experiments have demonstrated that thermal catalytic pyrolysis (HWCVD) can produce a-Si:H nanoparticles with size <50 nm. The particles are mostly amorphous, but small crystalline fractions can be detected in particles produced at substrate temperatures higher than 120 °C. The particles are hydrogenated and surface oxidation is present. Although the production rate increases with increasing pressure and silane concentration, the filament deteriorates at an accelerated rate. Production of Raman spectra proved difficult, due to spontaneous oxidation initiated by the laser.

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