

# The preparation of a phosphorus doped silicon film from phosphorus containing silicon nanoparticles†

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Phosphorus containing and octyl-terminated silicon nanoparticles (NPs) are generated by a solution reduction route under room temperature conditions for the first time and characterized by TEM, HRTEM, EDX,  $^1\text{H}/^{13}\text{C}/^{31}\text{P}$  NMR, EPR, and PL spectroscopy, then annealed to form a thin film with phosphorus doping confirmed by microprobe elemental analyses.

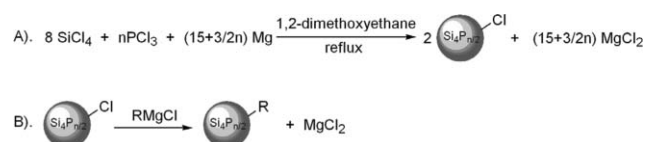
Nanoscaled materials have a range of properties different from their bulk or molecular counterparts. One attractive property of nanoparticles (NPs) is their substantially lower melting temperature in comparison to the bulk solid, due to their large surface area to volume and high surface energy. This makes NPs promising materials for film formation. Silicon is currently the mainstay of the electronics industry. Obtaining nanoscaled silicon and applying the property of a lower mp to form electronic-grade films by low cost techniques, such as ink- or laser-jet printing, may transform the way electronic devices are currently fabricated. Silicon NPs have been found to sinter together at temperatures as low as 162 °C and to form large areas of polycrystalline silicon at 350 °C.<sup>1</sup> The loss of lattice fringes in silicon NPs was evidence of melting when viewed in a transmission electron microscope (TEM) at temperatures that can be as low as 500 K for 2 nm nanoparticles.<sup>2</sup> The potential for surface modification of the NPs, tuning their solubility and stability, further enhance the ability of silicon nanoparticles in the practical formation of silicon thin films. This can be accomplished by deposition of Si NPs from solution, followed with annealing at relatively low temperatures.

To apply such films in the semiconductor industry, silicon nanoparticles are required to be doped first. Many techniques are available for the synthesis of silicon NPs doped with different elements. For instance, anodic etching of silicon wafers generates particles which are inherently doped with the elements present in the silicon wafer.<sup>3</sup> Phosphorus doped silicon NPs have been produced by sputtering,<sup>4,6</sup> and laser ablation<sup>7</sup> where phosphorus doped silicon nanocrystals are obtained in  $\text{SiO}_2$  glass. However, these techniques do not give control over the surface termination of the NPs. We report here the synthesis of phosphorus containing silicon NPs using a simple solution technique, amenable to scale-up, which also allows for control over the surface termination of the NPs. The two step procedure described in this paper allows for

control over the surface functionalization as well as composition. This is important for the solubility properties of the particles, their protection from oxidation, the growth of doped silicon films, and their possible application.

Phosphorus doped silicon NPs were produced in a process similar to that used to generate silicon nanoparticles in this group previously.<sup>8–10</sup> Silicon tetrachloride and phosphorus trichloride are co-reduced in a 1,2-dimethoxyethane (glyme) of 50 °C with finely divided magnesium (Scheme 1A).‡ The stoichiometry of the reaction was adjusted such that halide is left to cover the surface of the NPs, giving facile sites for reaction with terminating reagents. The resulting halide-capped NPs in a yellow suspension are then terminated with a Grignard reagent, octyl magnesium chloride, after an hour (Scheme 1B). The mixture was allowed to cool overnight and then filtered through a silica plug to remove salts. The solvent was removed under vacuum to give an orange oil. The residual volatiles were removed onto a liquid nitrogen cooled probe under vacuum with heating to 100 °C in a water bath. A viscous orange oil was obtained which is stable to air and moisture, and soluble in non-polar organic solvents, such as hexane. One drop of a chloroform solution of the silicon nanoparticles was placed onto a 5 mm square portion of germanium wafer. The solution was allowed to dry in air and then heated to 600 °C at 60 °C per hour *in vacuo*, and annealed at 600 °C for one hour. The wafer was then allowed to cool to room temperature at 60 °C per hour. A shiny black film was observed on the surface of the germanium wafer.

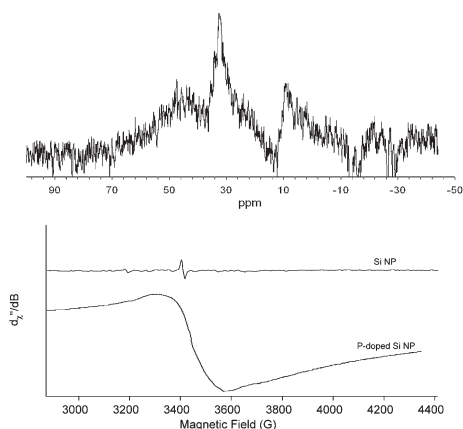
NMR spectra of samples in  $\text{CDCl}_3$  solution were obtained on a Varian 400 MHz spectrometer. Both the  $^1\text{H}$  and the  $^{13}\text{C}$  NMR spectra are consistent with octyl termination of the silicon NPs, and are provided as supplemental material.† In the proton NMR the protons of the  $-\text{CH}_2$  group closest to the silicon are observed at  $\delta$  0.58 ppm, which is in the expected region for alkyl silicon compounds. The resonance is much broader than that expected for a simple molecular species with a  $\text{Si}-\text{CH}_2$  moiety, consistent with the range of different environments present on the surface of the NPs, as well as their expected hindrance to free motion. This



**Scheme 1** A: Co-reduction of  $\text{SiCl}_4$  and  $\text{PCl}_3$  to give halide capped P-doped Si NPs; B: termination of the nanoparticles with alkyl magnesium halide Grignard reagent.

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† Electronic supplementary information (ESI) available:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are provided. See DOI: 10.1039/b513330k



**Fig. 1** (Top)  $^{31}\text{P}$  NMR of the phosphorus doped silicon nanoparticles in  $\text{CDCl}_3$  solution; (bottom) EPR of undoped and phosphorus doped silicon nanoparticles.

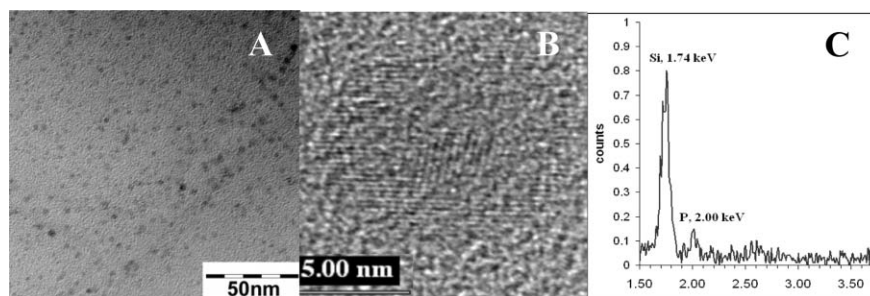
broadened resonance also suggests the attachment of terminal groups to the silicon core. The integrals of the resonances are correct with the triplet observed at  $\delta$  0.90 ppm and the broad resonance centered at  $\delta$  1.28 ppm, corresponding to the protons of the terminal  $-\text{CH}_3$  of the alkyl chain and the protons of the remaining alkyl  $-\text{CH}_2$  groups respectively. In the  $^{13}\text{C}$  APT NMR all eight carbons can be clearly distinguished, although the resonances, especially that of the  $\text{Si}-\text{CH}_2$ , are broader than would be expected for a simple molecular species containing an octyl moiety. This is again consistent with different environments for the alkyl groups on the surface of the NPs.  $^{31}\text{P}$  NMR (Fig. 1, top) shows the presence of phosphorus with a broad and complicated peak centered at  $\delta$  30 ppm. This is lower than the reported  $65 \pm 10$  ppm for phosphorus doped polycrystalline silicon,<sup>11</sup> in which phosphorus was found to be at the boundaries between silicon grains. In our material, given the relatively low reaction temperature, the phosphorus atoms may not have enough energy to overcome the thermal barrier to segregation. There are also additional broad peaks that might be attributed to phosphorus at the surface. There are also additional broad resonances both above and below 30 ppm that might be consistent with some of the phosphorus at the surface or in multiple sites in a solid. The NMR is not consistent with a molecular impurity or pure phosphorus nanoparticles.

CW-EPR spectra were collected at a temperature of 5 K with a Bruker ECS106 X-band spectrometer equipped with an Oxford

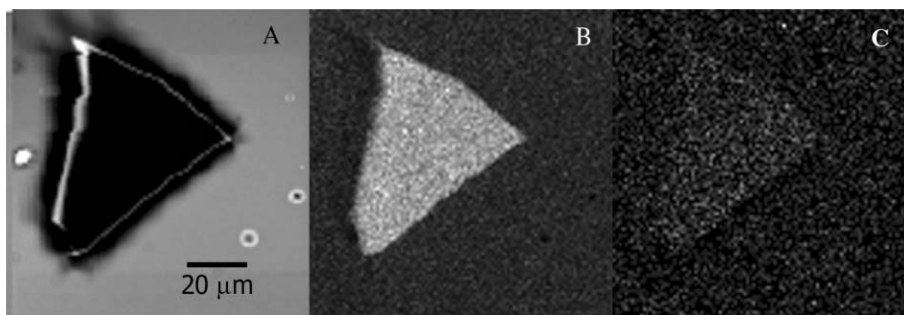
ESR900 liquid helium cryostat and an ITC503 temperature controller. A Bruker dual mode cavity in perpendicular mode at 9.68 GHz, field modulation of 8 G, microwave power of 0.25 mW and a gain of  $1.00 \times 10^4$  were used. Six scans were averaged to obtain each spectrum. Fig. 1, bottom, shows the results of the undoped (upper) and phosphorus containing (lower) silicon NPs. The undoped NP show a narrow symmetric line shape with  $g = 2.0060$  and a peak-to-trough line width of  $\sim 11$  G. This signal is characteristic of silicon dangling bonds from non-bonding electrons on three-coordinated silicon atoms.<sup>12–15</sup> The P-doped NP spectrum shows a significantly broader and more intense asymmetric line shape with an effective  $g = 2.0080$  and a peak-to-trough line width of  $\sim 312$  G. While the increased signal intensity and broadening is consistent with material doping (P, As, B),<sup>16</sup> the extent of each and the observed effective  $g$  value are unprecedented. Possible explanations for the observed line shape are inhomogeneous broadening from  $g$ -anisotropy and broadening from “spin-spin” interactions of direct bonds between phosphorous atoms (high phosphorus content). Further studies as a function of phosphorus concentration are necessary to fully characterize the local environment of the phosphorus in this NP system.

The photoluminescence spectrum of the samples was measured on a Jobin Yvon Fluoramax-P spectrophotometer. In the photoluminescence emission spectrum a maximum emission for the NPs at 400–430 nm was observed at an excitation of 270–300 nm. This is consistent with that observed for the octoxyl-capped NPs prepared by this route previously.<sup>10</sup> Anthracene remaining from the preparation of the finely divided magnesium was also detectable in the photoluminescence spectrum in the same region, preventing a detailed analysis of the spectrum. However, it may not interfere with the further preparation of silicon films due to the relatively high vapor pressure of anthracene.

The nanoparticles were visualized using a transmission electron microscope (TEM), Phillips CM-12, at 100 keV accelerating voltage. High resolution TEM (HRTEM) images were obtained from a Phillips CM200 operating at 200 keV at the National Center for Electron Microscopy. The TEM image of the NPs dispersed onto a holey carbon grid from a hexane solution shows them to be discrete crystallites of between 5 and 12 nm in size (Fig. 2A). At higher magnification the NPs are observed to have lattice fringes with a 3.1 Å lattice spacing, as expected for diamond crystalline silicon (Fig. 2B). Energy dispersive X-ray spectroscopy (EDX) of the NPs shows the presence of both silicon and



**Fig. 2** A: TEM of phosphorus doped silicon nanoparticles dispersed on a holey carbon grid; B: HRTEM showing lattice fringes consistent with that of crystal; C: EDX spectrum of nanoparticles. Only the phosphorus and silicon region is shown. Peaks corresponding to both phosphorus (at 2.00 keV) and silicon (at 1.74 keV) are clearly visible.



**Fig. 3** Microprobe images of a section of the phosphorus doped silicon film. A is the backscattered electron image, while B and C are the silicon and phosphorus energy filtered maps, respectively.

phosphorus (Fig. 2C), consistent with elemental analysis (Si : P ratio = 1 : 0.056). This ratio suggests that the amount of phosphorus is significant ( $\sim 6\%$ ), consistent with the interpretation of the broad NMR signal suggesting multiple sites and the broad EPR line width, suggesting phosphorus–phosphorus interactions.

In order to more fully investigate whether or not the phosphorus might be homogeneously distributed in all NPs, the NPs were used as a precursor to a film. The film was grown by annealing a suspension of the NPs that was simply dropped onto on a p-type germanium wafer and heated *in vacuo* at 600 °C. The obtained black reflective film could be removed from the surface of the wafer. Microprobe measurements were made on a Cameca SX100 instrument operating at 15 kV and 20–40 nA. Fig. 3 gives microprobe images of a small section of the film on the germanium wafer. Fig. 3A is the backscattered electron image (BSE) of the film, while 3B is the energy selected silicon image and 3C is the energy selected phosphorus image. In the BSE image the black triangular region is the film while the rest is the germanium wafer. In the two energy selected images lighter shades represent a higher concentration of the selected elements while darker shades represent a lower concentration. It can be seen that the film is predominantly silicon, with a small but significant concentration of phosphorus. The phosphorus appears evenly dispersed throughout the sample to the resolution of the instrument.

In conclusion, we have shown it is possible to generate phosphorus containing silicon NPs with a reduction technique under mild conditions. These NPs are crystalline, capped with octyl groups and are soluble in organic solvents such as hexane. When these particles are annealed at 600 °C under vacuum, a phosphorus doped silicon film is obtained. Further studies with EPR and NMR on a series of phosphorus containing silicon NP samples would be important for determining where the phosphorus resides, in the crystal lattice or on the surface, and more detailed investigations are important for further optimization of this reaction.

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## Notes and references

‡ All manipulations were carried out under an inert atmosphere of either argon or nitrogen. The solvent, 1,2-dimethoxyethane, was distilled over potassium then Na/K alloy before use. Finely divided magnesium was prepared by the thermal decomposition of magnesium anthracenide to strongly pyrophoric black powder, at 210 °C under vacuum for 12 h. The  $^1\text{H}$  NMR spectrum of a  $\text{C}_6\text{D}_6$  extraction of this powder showed the presence of a small amount of residual anthracene, which may facilitate the reduction reaction, acting as a phase transfer catalyst. All other reagents were used as obtained from standard sources. Chemical analysis was obtained from Galbraith Laboratories.

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