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Vapor–liquid–solid growth of silicon nanowires using organosilane as precursor†

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Utilizing monophenylsilane as the precursor and liquid injection chemical vapor deposition (LICVD) as the fabrication method offers a novel synthetic approach for the facile, ambient pressure, and continuous vapor–liquid–solid (VLS) synthesis of high quality Si nanowires.

The promise of silicon (Si) nanowires as building blocks for the preparation of nanoelectronics such as field-effect transistors, chemical and biosensors, photovoltaic devices, and logic gates has drawn intense attention in the past decade.[1] Gas-phase chemical vapor deposition (CVD) combined with Au-seeded vapor–liquid–solid (VLS) growth has become the common way to produce Si nanowires with single crystalline, long length (over 30 μm), and tunable p- or n-type electrical properties.[2] Choosing suitable Si precursors for VLS nanowire growth is quite challenging since Si is extreme sensitive to oxidation and Si's precursor decomposition kinetics usually involves in complicated chemical pathways which could disrupt nanowire growth. Currently, the widely-used oxygen-free Si precursors are mainly silanes (*e.g.*, monosilane and disilane) and chlorosilanes (*e.g.*, $SiCl_4$ and Si_2Cl_6). Silanes readily decompose to Si at relatively low temperatures (~ 400 °C),[3] but cause spontaneous combustion upon contact with air due to their pyrophoric nature.[4] Experiments associated with silanes require strict formal procedures for safe operation and emergency response so as to prevent potential hazards such as lab fires and explosions. On the other hand, chlorosilanes, though safer to handle, produce hydrochloric acid in the presence of H_2 and the resulting acid could unselectively etch the substrate, the reactor wall, and the processing equipment. High synthetic temperatures (> 800 °C) needed to thermally decompose chemically stable chlorosilanes result in agglomeration of liquid eutectic droplets because of the Ostwald ripening effect, and consequently, nanowires with large diameters (several hundreds of nm) are often obtained.[5] In addition, the CVD-VLS synthetic method is generally equipped with high-cost instrumentation composed of complicated configuration. Metal nanocrystals are pretreated on a substrate, thus limiting the nanowire growth on the substrate surface, and this batch-type reaction has made the conventional CVD-VLS process extremely low yielding and impossible for continuous production.

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Organosilanes are promising precursors for Si nanomaterial synthesis, and have been explored for Si thin film deposition by CVD,[6a] Si nanocrystal synthesis by reduction methods,[6b,c] and Si nanocrystal and nanowire synthesis under supercritical conditions.[6d,e] Herein, we report using monophenylsilane (MPS), an organosilane, as precursor for VLS growth of Si nanowires. We chose MPS since it is a low toxic, inflammable, hydrophobic, and liquid organosilicon compound exhibiting superior chemical stability under ambient conditions.[7] MPS generates sufficient Si atoms for nanowire growth at relatively low temperatures since its pyrolysis temperature is around 450 °C. We apply liquid injection CVD (LICVD) as the fabrication method for nanowire synthesis (Fig. 1). LICVD allows MPS and dodecanthiol-coated Au nanocrystals to disperse well in solution prior to transportation, and precisely control the injection rate of reactant solution. No gases, such as N_2 or H_2, are used; instead, toluene serves as both the solvent and the carrier gas to transport the gaseous reactants. Reactions are carried out in ambient pressure, so no vacuum pump system is needed.

Briefly (see supplementary information for detail†), a 10 mL stainless steel reactor containing a cleaned Si substrate inside was placed in a nitrogen-filled glove box to make the reactor free of oxygen. The reactor was removed from the glove box and heated to 480 °C. 10 mL of precursor solution containing 630 mM MPS and 3.9 nm dodecanethiol-capped Au nanocrystals (see Fig. S1 and S2 for Au nanocrystals TEM image and size distribution†) at a Au/Si mole ratio of 1 : 6000 in toluene, was prepared in the glove box and loaded into a 10 mL loading loop (see Fig. S3 for precursor solution appearance†). The loaded reactants were injected by an injection pump at a flowing rate of 0.05 ml min^{-1} to proceed a LICVD-VLS nanowire reaction. Reactants were vaporized in the preheated region at temperatures around 220 °C (MPS: bp 120 °C; toluene: bp 110 °C), and transported into the reactor where the nanowire reaction occurred at elevated temperatures.
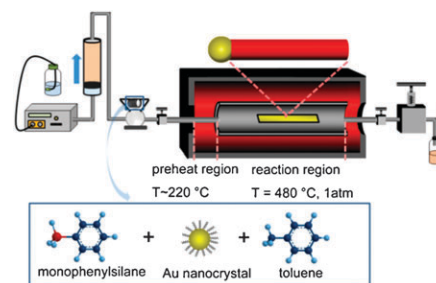

Fig. 1 LICVD system for VLS growth of Si nanowires using mono-phenylsilane as precursor and dodecanethiol-capped Au nanocrystals as seeds.

The reaction solution was kept injecting for continuous production of Si nanowires. Unreacted reactants and byproducts were condensed to the pipe line connected to the end of the reactor, collected in a glass reservoir, and disposed into a waste barrel. After the reaction ceased, the micro-controlled valve was closed, and the injection pump and the heater were turned off. The reactor cell was cooled by fresh room temperature air until the cell reached room temperature and the obtained nanowires collected on the Si substrate were kept for further characterization.

Fig. 2 shows the reaction product produced from injecting the precursor solution into anhydrous toluene vapor at 480 °C in the presence of dodecanethiol-capped Au nanocrystals. SEM and TEM images (Fig. 2a, b and 3a) show large quantities of nanowires as the primary reaction product with very little particulate byproduct. These wires are over 40 μm in length with an average diameter of approximately 47.6 nm. The measured average nanowire diameter does not match with the original size of colloidal Au nanocrystals (3.9 nm), which is most likely attributed to the agglomeration of colloidal Au nanocrystals. X-Ray powder diffraction of the obtained products shows three peaks in agreement with the (111), (220), and (311) peaks of diamond cubic Si (JCPDS card no. 27-1402) which confirms that the nanowires are crystalline with a diamond cubic structure. Fig. 3b shows a high-resolution TEM (HRTEM) image of 20 nm Si nanowires with single crystallinity. Most of the obtained Si nanowires exhibit a ⟨111⟩ growth direction (Fig. S4†), consistent with previous work in VLS growth of Si whiskers.[8] Few (<2%) nanowires grow in a ⟨112⟩ growth direction and exhibit lamellar {111} twins along their length (Fig. S6†).[8] The surface of the Si nanowires has a 1–3 nm thick amorphous layer, which most likely is attributed to surface oxidation of wires exposed to air or side-deposition of Si or C on the nanowire surface during the nanowire growth. There appears to be a nanocrystal attached to the end of a Si nanowire showing darker contrast relative to the nanowire body (Fig. 3c). Energy-dispersive X-ray spectroscopy (EDS) collected with the electron beam focused on the tip reveals that Au is the major component of the seed particle, confirming the nanowire growth *via* the VLS mechanism.[9] The Cu signal comes from the copper grid and the O signal originates from the surface oxidation of Si surface after being exposed to air.

The synthetic temperature of 480 °C, higher than 364 °C of the Au/Si eutectic point, allows Au promoting Si nanowire growth *via* the VLS scheme. The reaction region was uniformly heated to thermally decompose gas reactants. Since the total pressure was kept around 1 atm, the gas-phase reactions are taken into account in the rate determining step for the overall reaction kinetics.[10] MPS can undergo biomolecular disproportionation reactions to form silane and diphenylsilane *via* the exchange of a hydrogen atom and a phenyl group between two monophenylsilane molecules.[11] The disproportionation rate is proportional to temperature and the phenyl group migrates readily at temperatures above 300 °C.[12] Although the detail of the monophenylsilane disproportionation reaction has not been well studied, Coutant and Levy proposed that the disproportionate reaction is *via* a four-center activated transition state.[13] Perhaps the
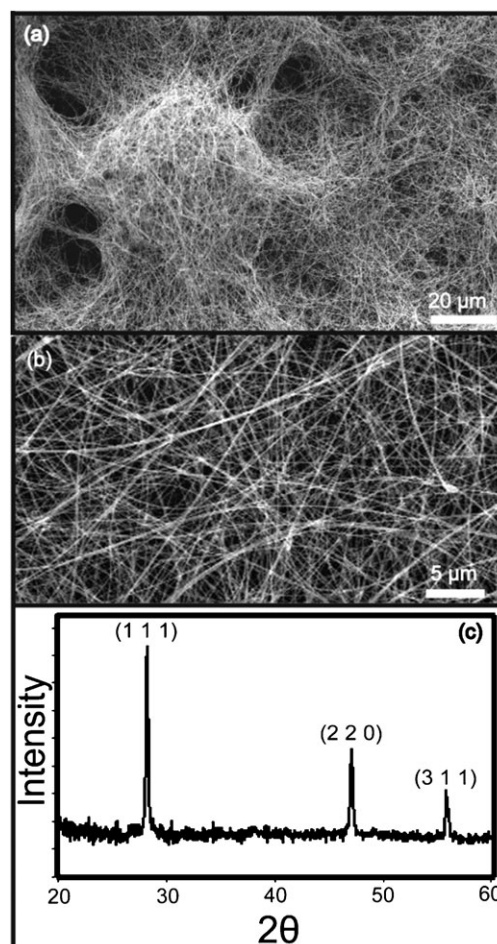

Fig. 2 Au-seeded VLS-growth of Si nanowires produced from pyrolysis of MPS in anhydrous toluene at 480 °C by LICVD: (a, b) SEM; (c) XRD.

resonance effect of the benzene ring lowers the activation energy and stabilizes the transition complex for the disproportionation reaction. In contrast, alkylsilanes disproportionate slowly and cannot generate sufficient Si atoms for high quality Si nanowire growth, which might be because the alkyl group does not give rise to a resonance effect.[11] Silane generated from phenylsilane disproportionation could decompose to Si at temperatures above 350 °C.[14] Si atoms are continuously fed into a Au/Si liquid droplet, and after supersaturation, crystalline nanowires are nucleated from the droplet/Si interface in the form of nanowires. Scheme 1 shows the schematic of the overall nanowire growth. To achieve high quality Si nanowire reactions, MPS decomposition must balance nanowire growth and avoid side-reactions such as homogeneous Si-particle nucleation. Our results reveal that MPS provides suitable Si atom supply for sustainable nanowire growth and yields nanowires in lengths up to several tens of micrometres.

In conclusion, we have demonstrated that using MPS as a Si precursor combined with LICVD synthetic configuration offers a safe, facile, low cost, ambient pressure, and continuous VLS synthesis of high quality Si nanowires. MPS exhibits suitable reactivity for Au-seeded VLS nanowire growth. Handling MPS for synthesis prevents potential personal and equipment
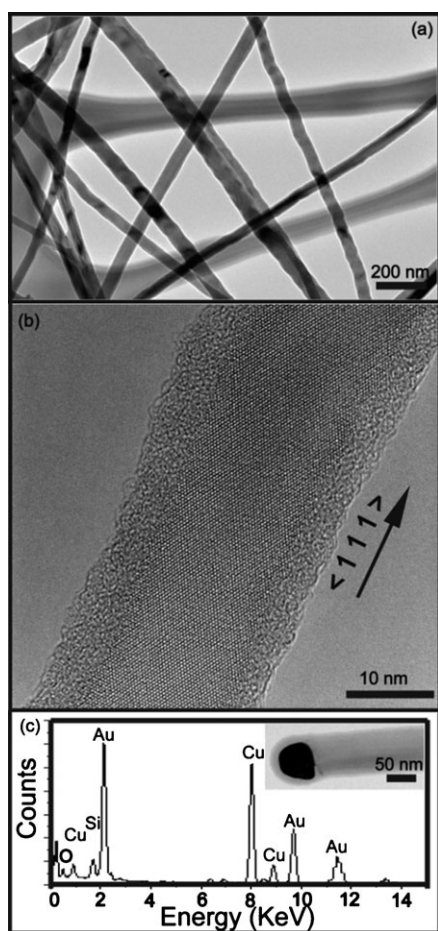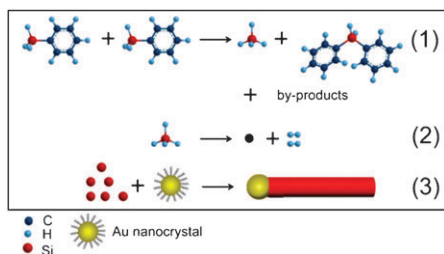
Fig. 3 (a, b) TEM image of Si nanowires obtained by thermal decomposition of MPS in anhydrous toluene at 480 °C by LICVD (c) EDS collected from the tip of a Si nanowire (inset).

Scheme 1 Schematic of monophenylsilane as precursor for gas-phase Si nanowire synthesis: (1) bimolecular disproportionation of mono-phenylsilane, (2) thermal decomposition of silane to Si (3) Au-seeded VLS Si nanowire growth.

damage which is usually caused by corrosive and hazardous precursor gases. In contrast to the conventional CVD-VLS method,[5] the synthetic design of the LICVD-VLS process achieves technical simplicity since there is no need for sophisticated gas installations, vacuum pumps, bubblers and vaporizers, and lowers the cost of fabrication equipment. We believe that our approach could be adapted for the preparation of nanowires

of numerous materials. The new synthetic scheme outlined here could be further extended to scale-up synthesis, nanowire doping, and surface passivation plus a variety of permutations for future synthetic design toward commercialization. Furthermore, the variability, with respect to the choice of organosilanes, offers an additional degree of freedom for optimization.

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