Direct synthesis of silicon nanowires, silica nanospheres, and wire-like nanosphere agglomerates

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Elevated temperature synthesis has been used to generate virtually defect free SiO_2 sheathed crystalline silicon nanowires and silica (SiO_2) nanospheres which can be agglomerated to wire-like configurations impregnated with crystalline silicon. The SiO_2 passivated (sheathed) crystalline silicon nanowires, generated with a modified approach using a heated $Si–SiO_2$ mix, with their axes parallel to $\langle 111 \rangle$ are found to be virtually defect free. Modifications to the system allow the simultaneous formation of SiO_2 nanospheres ($d \sim 10–30$ nm) as virtually monodisperse gram quantity powders which form large surface area catalysts for the selective conversion of ethanol to acetaldehyde. © *2000 American Institute of Physics.* [S0003-6951(00)00717-8]

Semiconductor nanostructures, nanoagglomerates, and nanowires have attracted considerable attention because of their potential application in mesoscopic research, the development of nanodevices, and the potential application of large surface area structures. For several decades, the vapor-liquid-solid (VLS) process,[1,2] where gold particles act as a mediating solvent on a silicon substrate forming a molten alloy, has been applied to the generation of silicon whiskers. The VLS reaction generally leads to the growth of silicon whiskers epitaxially in the $\langle 111 \rangle$ direction on single crystal silicon $\langle 111 \rangle$ substrates.[1–3] More recently, Lieber,[4] Lee,[5] Yu,[6] and co-workers have extrapolated on the ideas entailed in the VLS technique to develop laser ablation of metal containing silicon targets,[4–8] obtaining bulk quantities of silicon nanowires. Lee *et al.*[5,9–12] have shown that oxides play a dominant role in the nucleation and growth of semiconductor nanowires be it by laser ablation, thermal evaporation, or chemical vapor deposition. In the present report, we apply the techniques of high temperature synthesis to modify the approach of Lee *et al.* and generate virtually defect free SiO_2 sheathed crystalline silicon nanowires and silica (SiO_2) nanospheres which can be agglomerated to wire-like configurations impregnated with crystalline silicon nanospheres.

The apparatus used for these experiments is depicted schematically in Fig. 1. Double concentric alumina tubes are heated to the desired temperature in a Lindberg Scientific tube furnace configuration. The inner tube is vacuum sealed by two water cooled stainless steel end pieces, attached and tightly lock-press fit against custom viton o-rings. At one end of the furnace, UHP argon enters through the upstream stainless steel end piece, passes through a matched set of zirconia insulators to the central region of the inner tube oven, and flows over a crucible containing the sample mixture of interest, either a silicon-silica (Si/SiO_2) mixture or powdered silicon monoxide, at a flow rate of 100 sccm.

The total tube pressure in the inner tube is typically ~225 Torr, controlled by a mechanical pump attached to the tube through the downstream stainless steel end piece. This end piece is mechanically attached to a ''water cooled'' cold plate, whose temperature is adjustable,[13] through a matching set of insulating zirconia blocks. Depending on the desired temperature range of operation, the crucibles used to contain the silicon/silicon oxide based mixtures were either commercially available quartz, alumina, or low porosity carbon. We observed the condensation of nanowires as dark brown deposits in a narrow region on the wall of the inner tube, close to the defining end points of the oven shell and corresponding to a temperature in the range 900–1000 °C. Large quantities of SiO_2 nanospheres were deposited on the temperature controlled cold plate.

Figure 2 corresponds to transmission electron micrographs (TEM) of the exemplary virtually uniform and straight nanowires, generated from a 50/50 Si/SiO_2 equimolar mixture heated to a temperature of 1400 °C at a total pressure of 225 Torr for 12 h. The central crystalline silicon core is ~30 nm in diameter whereas the outer SiO_2 sheathing is 15 nm in thickness. The high-resolution transmission electron microscopy (HRTEM) views in Figs. 2(b) and 2(c) demonstrate a number of distinguishing characteristics. Figure

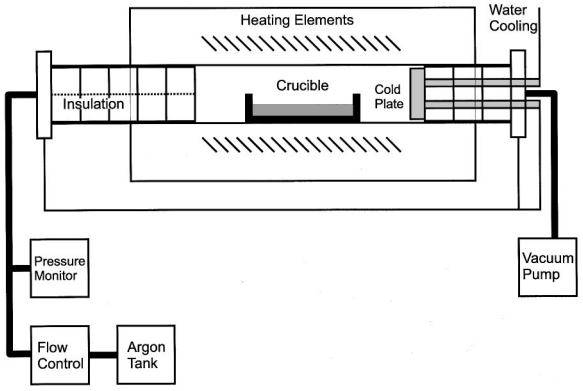

FIG. 1. Schematic diagram of high temperature oven system used for the synthesis of crystalline silicon nanowires and silica nanospheres.

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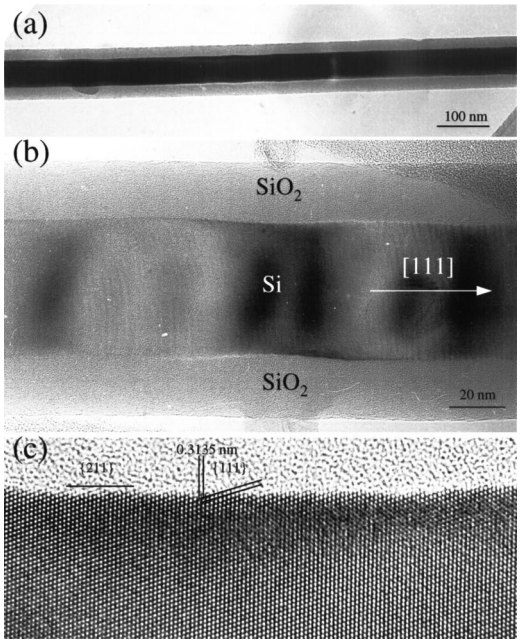

FIG. 2. TEM of (a) SiO_2 sheathed crystalline silicon nanowire, (b) closer view showing (1) slight wire undulations and stress patterns which are apparent in a virtually defect free nanowire, and (c) closer view showing crystalline core axes parallel to ⟨111⟩ direction. Synthesized @ 1400 °C from 50/50 Si/SiO_2 mix (P_{Total}=225 Torr, flow rate 100 sccm of UHP argon).

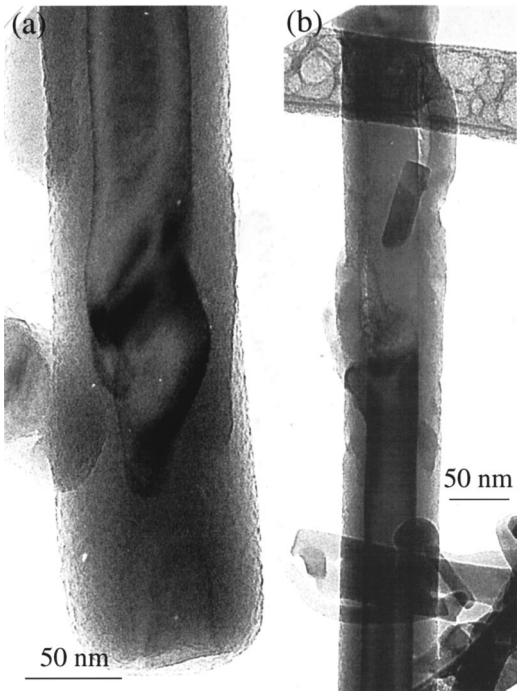

FIG. 3. TEM closeup view of (a) end of SiO_2 sheathed crystalline silicon nanowire showing pinch off of inner crystalline core at the end of the formation process and (b) opposite end of SiO_2 sheathed crystalline silicon wire showing strength of SiO_2 sheath. Conditions as in Fig. 2 earlier.

2(c) demonstrates that the axes of the SiO_2 clad crystalline silicon nanowires are parallel to ⟨111⟩. This is distinct from the results obtained by Lee *et al.*[5] whose wires have their axes parallel to ⟨112⟩ as they display twinning, high order grain boundaries, and stacking faults. At the $Si–SiO_2$ interface [Fig. 2(c)] the crystal planes are best described as {211}. The wire which is depicted in Fig. 2 appears virtually defect free. As Fig. 2(b) suggests, the inner crystalline silicon core undulates slightly. However, the fluctuations in the shading that are apparent in the HRTEM micrograph indicate that the wires are of sufficient quality that the detailed strain due to slight bending above the TEM mount can be readily observed in the TEM.

Figure 3(a) and 3(b) demonstrate further distinguishing characteristics of the nanowires generated in this study. Figure 3(a) demonstrates the pinch off of the crystalline silicon core at the beginning of the wire growth, suggesting a distinctly different formation mechanism than that suggested by Lee *et al.*[5] for their wires generated using a similar source and by Lieber *et al.*[4] for their iron catalyzed wire formation from Fe/Si mixtures generated using laser ablation. While Lee *et al.* find evidence for a growth mechanism along ⟨112⟩ with which they associate a complex process involving Si_xO formation, the observed structure in Fig. 3(a) would suggest at least a close analogy to the VLS mechanism albeit with an apparent self-assembly of the silicon in the absence of a metal catalyst. Further, the data in Fig. 3(b), which shows the opposite end of the same nanowire, suggests a significant strength for the outer SiO_2 sheath. Finally, a comparison to the TEM micrographs of Lieber *et al.*,[4] which show the clear termination of their nanowires at larger–nearly spherical $FeSi_2$ nanoclusters, offers yet an additional contrast, suggesting further alternate mechanisms for the wire formation.

Figure 4 corresponds to a TEM micrograph of the nearly monodisperse SiO_2 nanospheres of diameter 30 nm which can be generated as a deposit in gram quantities on the cold plate depicted in Fig. 1. These nanospheres were generated in the same experiment that produced the nanowire of Fig. 2. By adjusting the flow parameters and temperature, it is possible to generate nanospheres ranging in diameter to at least 10 nm in virtually monodisperse distributions. It is possible to generate these nanospheres not only from Si/SiO_2 mixtures but also from SiO powders albeit at somewhat higher temperatures.

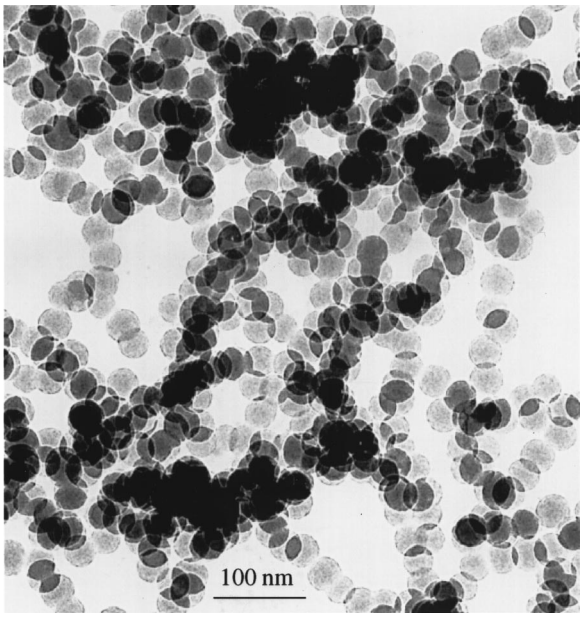

FIG. 4. TEM of virtually ''monodisperse'' SiO_2 nanospheres 30 nm in diameter.

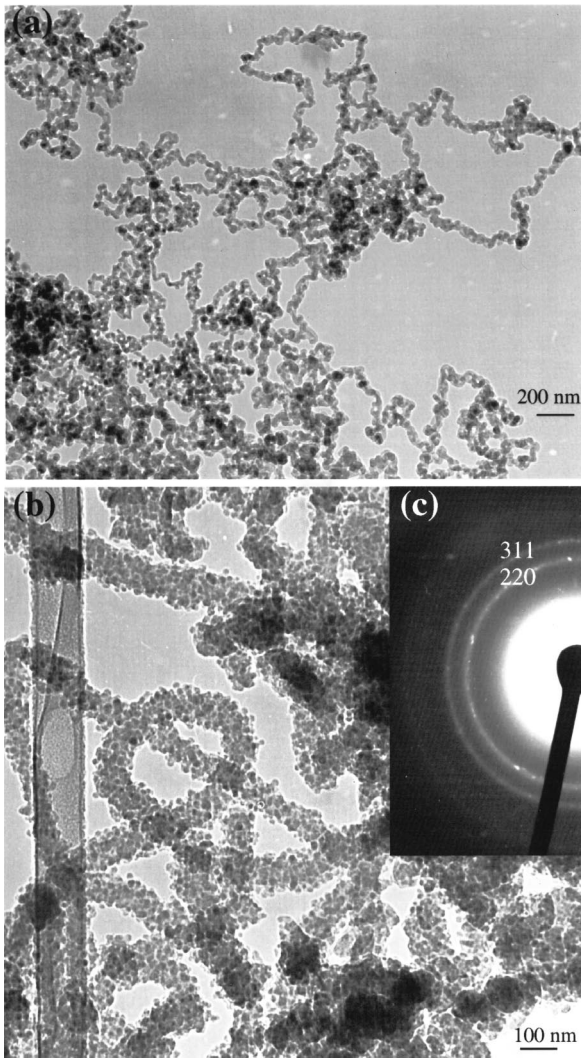

FIG. 5. TEM micrographs of (a) SiO_2 nanospheres agglomerating into wire-like groupings and (b) closer view showing crystalline silicon nanoclusters (see diffraction pattern inset) impregnating the SiO_2 wire-like agglomeration.

With additional adjustments of flow rates and temperature gradients, it is possible to agglomerate the nanospheres into the wire-like configurations depicted in Fig. 5(a) which, on closer view, correspond to wire-like SiO_2 nanosphere agglomerates impregnated by crystalline silicon nanoclusters [Fig. 5(b) and inset].

The present study, in concert with the results obtained by Lee *et al.*[5] and Lieber *et al.*,[4] would suggest that there are several exciting possibilities for the synthesis of useful silicon based nanowires and nanostructures. We have adopted a configuration similar to that reported by Lee *et al.*[5] to generate SiO_2 passivated (sheathed) crystalline silicon nanowires using a $Si–SiO_2$ mix heated to temperatures between 1300 and 1500 °C. We have found that the judicious manipulation of this high temperature system including mixture stoichemistry, flow conditions (kinetics), and temperature range, yields more than would have been previously anticipated. The current results would seem to suggest that additional mechanisms which are analogs not only of the VLS mechanism[1–3] on the nanoscale but also represent some crystalline silicon self-assembly, may be operative. Further, Lee *et al.*[5] produce a jumble of uniform SiO_2 coated crystalline silicone nanowires of various sizes which, when straight, have their axes parallel to ⟨112⟩. These wires, however, display twining, high order grain boundaries, and defect sites (stacking faults). As we modify their approach to produce wires whose axes are parallel to the ⟨111⟩ direction we find that these wires can be made virtually defect free and demonstrate no twining. Given the high temperature synthesis of alternate combinations of metal/metal oxide nanowire configurations, the current techniques would appear to be well suited to photonic waveguide applications.[14]

We are attempting to extend newly developed techniques in our laboratory[15] which we have successfully applied to the electroless metallization of PS, to fabricate gate all around nanotransistors[16] constructed from the silicon nanowires. The SiO_2 nanospheres which are now generated in gram quantities suggest the possibility (with metallization) of forming novel extremely high surface area catalysts. In fact, we have now used these powders as a means of developing large surface area Cu/SiO_2 catalysts which are selective to the conversion of ethanol to acetaldehyde.[17] The synthesis of these nanoparticles might well be used to replace the present techniques for making fumed amorphous silica with a process that is environmentally safer.[18] The now widely applied process for making fumed silica burns silicon tetrachloride to make silica and HCl; however, the current process eliminates the need to handle the tetrachloride and does not produce the acid gas.

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[1] R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. **4**, 89 (1964).
[2] E. I. Givargizov, J. Cryst. Growth **32**, 20 (1975).
[3] G. A. Boostma and H. J. Gassen, J. Cryst. Growth **10**, 223 (1971).
[4] See for example, J. Hu, T. W. Odom, and C. M. Lieber, Acc. Chem. Res. **32**, 435 (1999), and references therein.
[5] See for example, S. T. Lee, N. Wang, Y. F. Zhang, and Y. H. Tang, Mater. Res. Bull. **August**, 36 (1999), and references therein.
[6] D. P. Yu, Z. G. Bai, Y. Ding, Q. L. Hang, H. Z. Zhang, J. J. Wang, Y. H. Zou, W. Qian, G. C. Xiong, H. T. Zhou, and S. Q. Feng, Appl. Phys. Lett. **72**, 3458 (1998).
[7] Y. F. Zhang, Y. H. Zhang, N. Wang, D. P. Yu, C. S. Lee, I. Bello, and S. T. Lee, Appl. Phys. Lett. **72**, 1835 (1998).
[8] A. M. Morales and C. M. Lieber, Science **279**, 208 (1998).
[9] N. Wang, Y. H. Tang, Y. F. Zhang, D. P. Yu, C. S. Lee, I. Bello, and S. T. Lee, Chem. Phys. Lett. **283**, 368 (1998).
[10] N. Wang, Y. F. Zhang, Y. H. Tang, C. S. Lee, and S. T. Lee, Appl. Phys. Lett. **73**, 3902 (1998).
[11] N. Wang, Y. H. Tang, Y. F. Zhang, C. S. Lee, and S. T. Lee, Phys. Rev. B **58**, 16024 (1998).
[12] N. Wang, Y. H. Tang, Y. F. Zhang, C. S. Lee, I. Bello, and S. T. Lee, Chem. Phys. Lett. **299**, 237 (1999).
[13] Using appropriate slush baths the cold plate temperature can be adjusted to well below room temperature as a means of modifying condensation rates.
[14] C. Summers (private communication).
[15] J. L. Gole, L. Seals, and P. Lillehei, J. Electrochem. Soc. (submitted).
[16] See for example, K. Morimoto, Y. Hirai, K. Yuki, and K. Morita, Jpn. J. Appl. Phys., Part 1 **35**, 853 (1996).
[17] J. L. Gole and M. G. White, Chem. Mater. (submitted).
[18] We refer to the synthesis of fumed amorphous silica produced by the Cabot Corporation (Cab-O-Sil).