Electronic Supplementary Material (ESI) for RSC Advances.

Direct Electrochemical Deposition of Crystalline Silicon Nanowires at $T \geq 60°$ C

Luyao Ma,[1] Sudarat Lee,[1] Joshua DeMuth,[1] Stephen Maldonado*[,1,2]

1. Department of Chemistry, University of Michigan, Ann Arbor, MI 48109

2. Program in Applied Physics, University of Michigan, Ann Arbor, MI 48109

*To whom correspondences should be addressed

smald@umich.edu

S1. Contents

This document contains additional information that supports points made in the manuscript entitled "Direct Electrochemical Deposition of Crystalline Silicon Nanowires at $T \geq 60°$ C". Section S2 presents scanning electron micrographs of Si nanowires with Ga nanodroplets affixed at the tip. Si nanowires ec-LLS carried out at 4 different temperatures are shown in Section S3. An experiment to test the etching effect of $SiCl_4$ electrolyte on Ga nanoparticles is demonstrated in Section S4. Section S5 shows the transmission electron micrograph and energy dispersive X-ray (EDS) spectrum of a Si nanowire grown from EGaIn nanoparticles. Transmission electron micrographs, selected area electron diffraction patterns and the corresponding EDS spectrum of a Si nanowire grown from silica-coated EGaIn nanoparticles are shown in Section S6. Size correlation between Si nanowires and Ga nanodroplets are demonstrated in Section S7.

S2. Ga cap on Si nanowire

Si nanowire were prepared on n^+-Si(100) substrate *via* ec-LLS for 20 min. Hemispherical Ga caps were observed affixed to the tip of Si nanowires using scanning electron microscope.

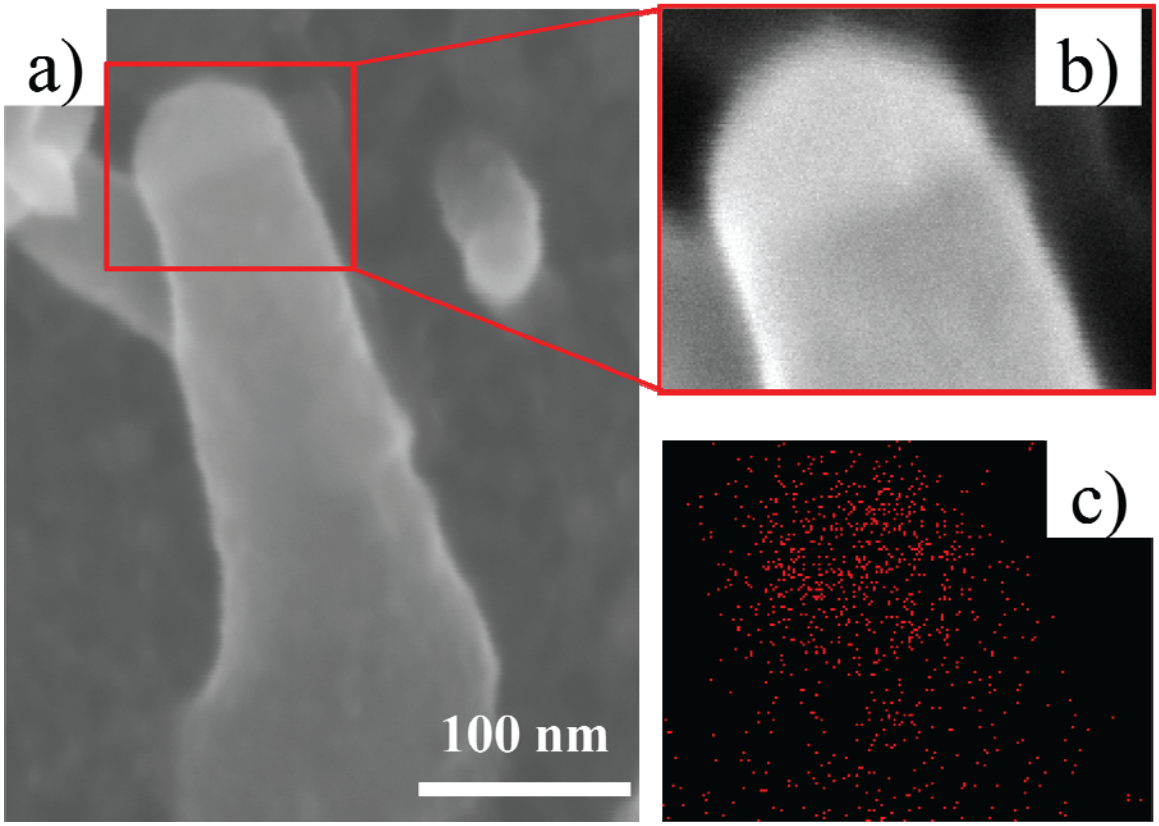

Figure S1. (a) Scanning electron micrograph of a Si nanowire prepared by 20 min ec-LLS electrodeposition at 120 °C. (b) Enlarged SEM image of the region indicated in (a). (c) EDX spectroscopic elemental mapping of Ga content in the cap of nanowire as shown in (b).

S3. Si Nanowire ec-LLS Temperature Dependence

Figure S2 shows scanning electron micrographs of Si nanowire films deposited at several process temperatures.

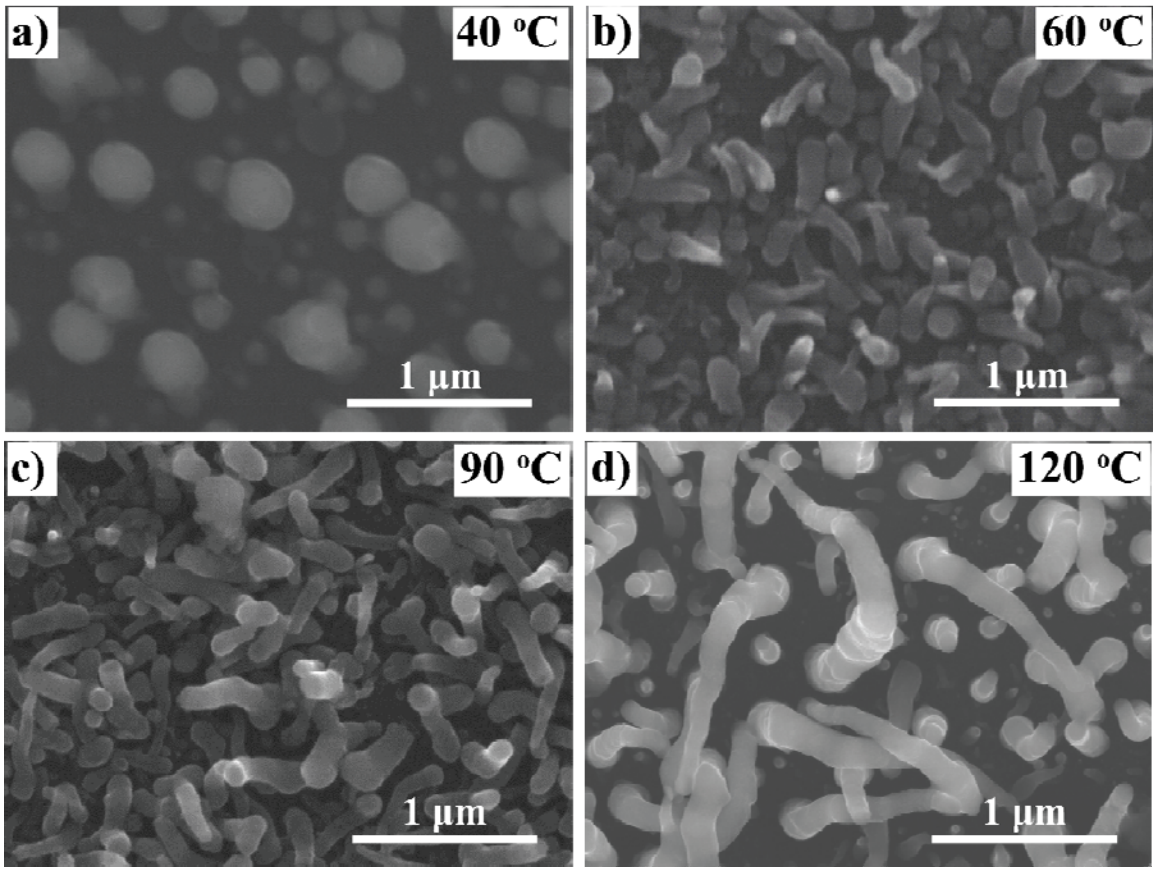

Figure S2.

S4. Etching of Ga nanoparticles in $SiCl_4$ electrolyte

Ga nanoparticles were electrodeposited on n^+-Si(100) substrate from $Ga(NO_3)_3$ aqueous solution as shown by the scanning electron micrographs (Figure S2a). The Ga coated Si substrate was then immersed in an organic electrolyte containing 0.5 M $SiCl_4$ and 0.2 M TBACl dissolved in propylene carbonate and heated to 100 °C. The Si substrate coated with Ga was then taken out of the electrolyte after immersion for 1 hour, rinsed, dried and taken into a scanning electron microscope for characterization. As shown by Figure S2b, after being immersed in $SiCl_4$ electrolyte for 1 hour, the sizes of Ga nanoparticles decreased significantly, which is a result of etching by H^+ form after $SiCl_4$ hydrolysis with trace amount of H_2O in organic electrolyte.[1]

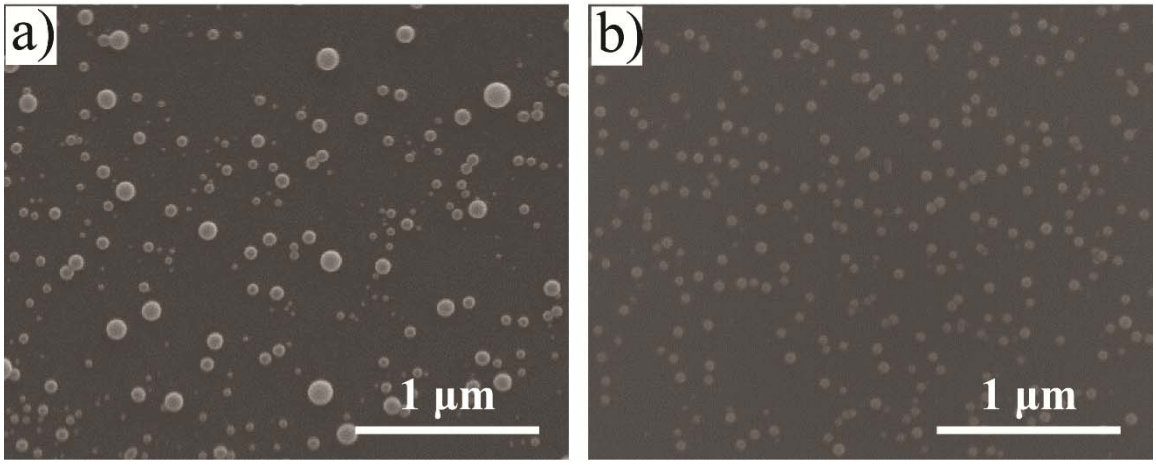

Figure S3. Ga nanoparticles on Si substrate formed by electrodeposition (a) before and (b) after immersing in 0.5 M $SiCl_4$ electrolyte for 1 hour at 100 °C.

S5. Si nanowire grown from EGaIn nanoparticles

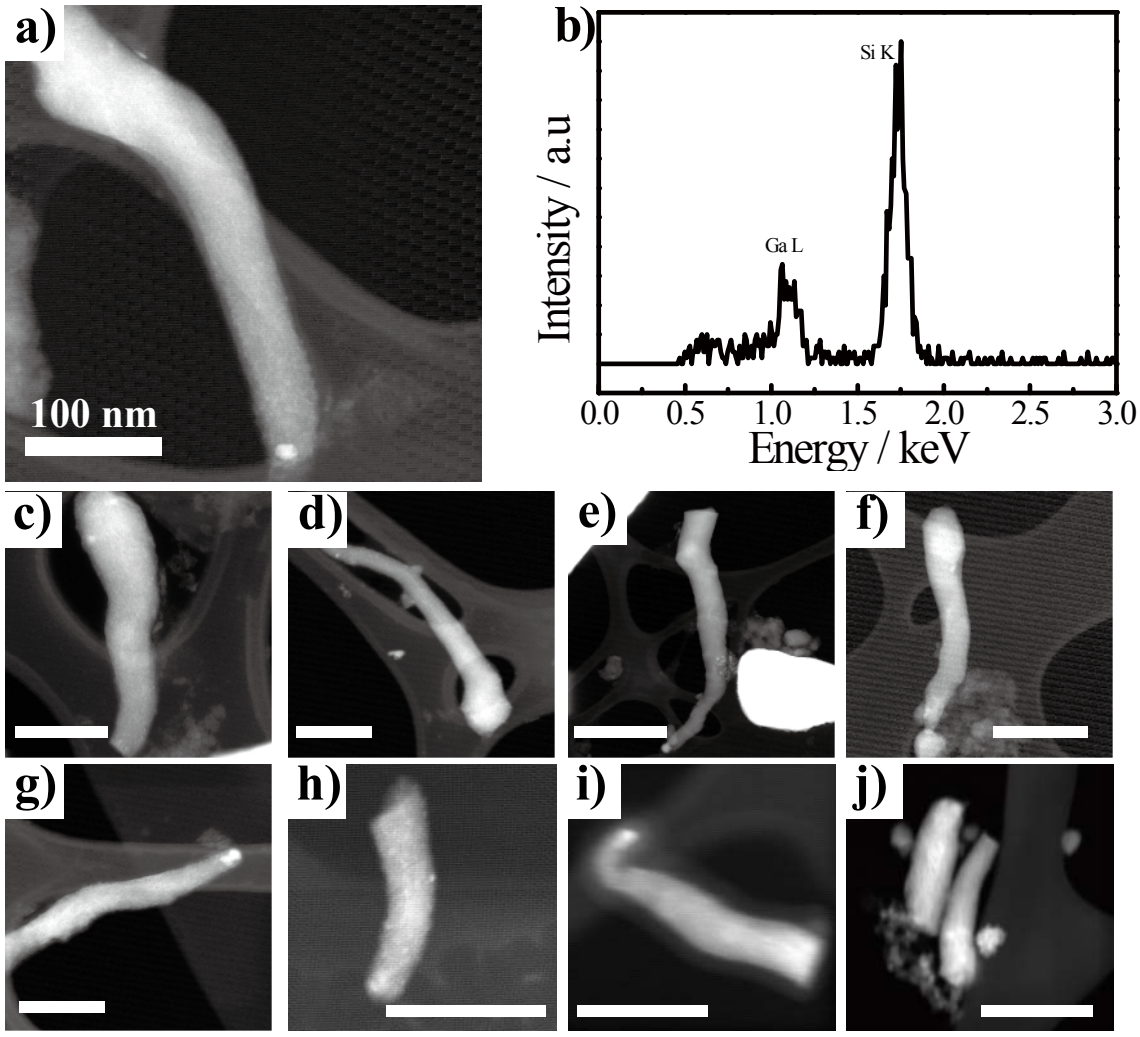

Figure S4. a, c - j) Transmission electron micrographs of Si nanowires grown from EGaIn nanoparticles taken under scanning transmission electron microscopic mode. b) Energy-dispersive X-ray spectrum of the nanowire in a).

S6. Si nanowires grown from silica coated EGaIn nanoparticles

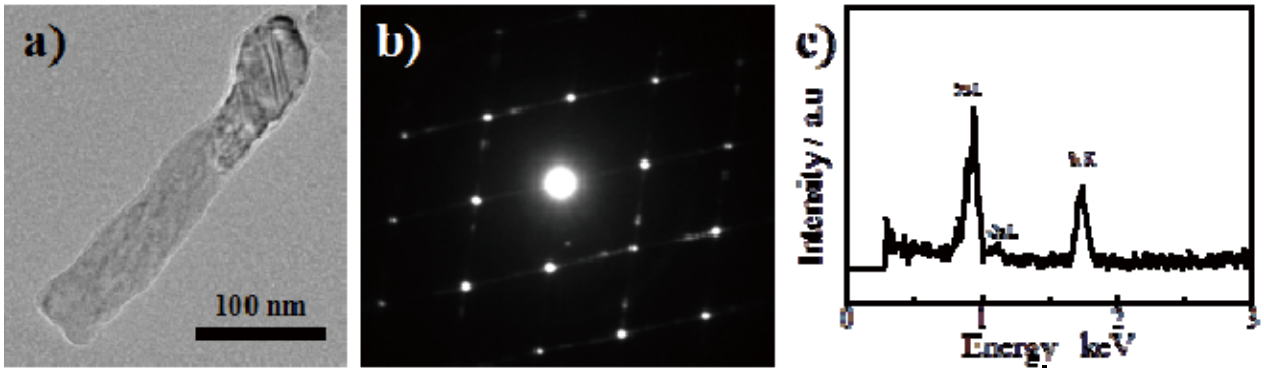

Figure S5. a) Transmission electron micrograph of a Si nanowire grown from silica coated EGaIn nanoparticles. b) selected area electron diffraction pattern of the Si nanowire in a). c) Energy-dispersive X-ray spectrum of the nanowire in a).

S7. Size correlation between Ga nanodroplets and Si nanowires

Statistical analysis of the sizes of Ga nanodroplets and Si nanowires were conducted using ImageJ for measurement of features on SEM images. 100 Ga nanodroplets and 100 Si nanowires were measured for analysis. The diameters of both Ga nanodroplets and Si nanowires are 150 ± 30 nm.

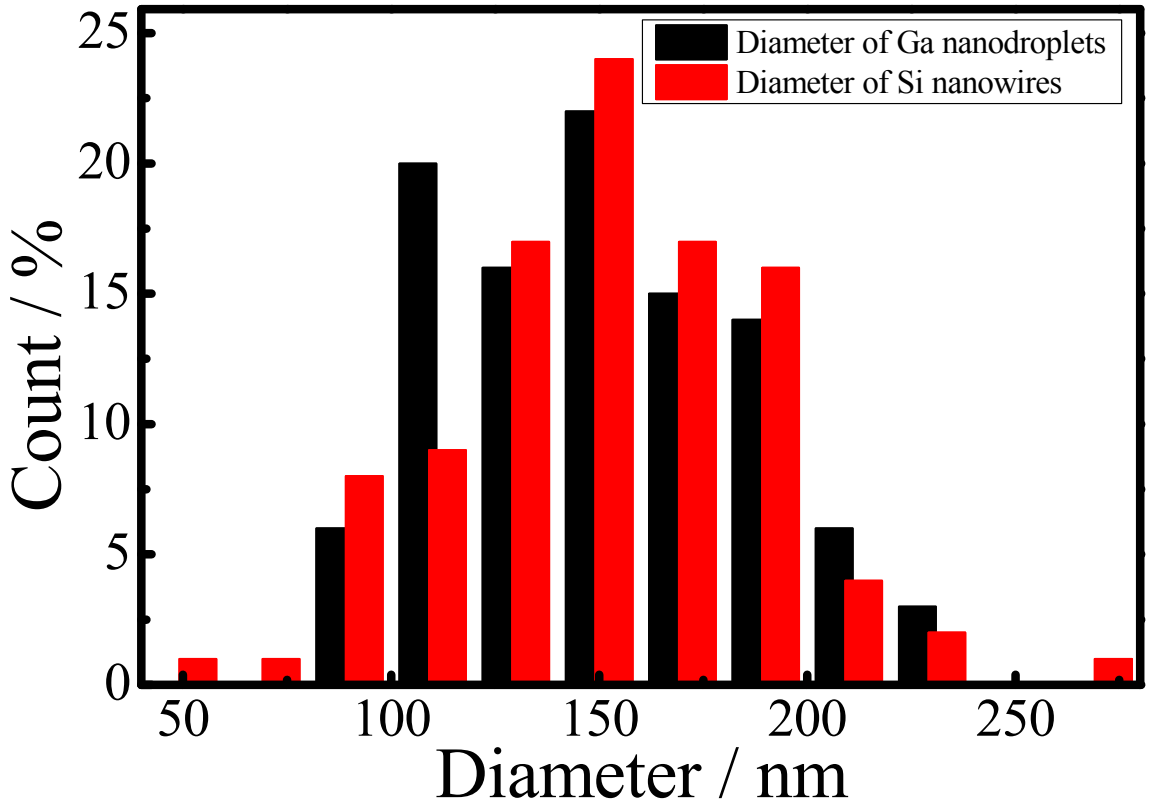

Figure S6. Size distribution of the diameters of Ga nanodropletss and Si nanowires shown in Figure 3a, b.

S.8 References

[1] T. Munisamy, A. J. Bard, *Electrochimica Acta* **2010**, *55*, 3797.