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Growth of tin catalyzed silicon nanowires by electron beam evaporation

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ABSTRACT

Silicon nanowires were grown on tin (Sn) coated Si substrates using electron beam evaporation technique at a growth temperature of 350°C. The as grown Si nanowires were characterized by Field Emission Scanning Electron Microscope (FESEM), Transmission Electron Microscopy attached with Energy Dispersive X-Ray Analyser (TEM-EDX) for their morphological, structural, and compositional properties, respectively. The grown Si nanowires were randomly oriented on the substrate with a length of ~ 500 nm for a deposition time of 15 min. Silicon nanowires have shown tin nanoparticle (capped) on top of it confirming the Vapor-Liquid-Solid (VLS) growth mechanism responsible for Si nanowires growth. The nanowire growth rate was measured to be ~30 nm/min. Transmission Electron Microscope (TEM) measurements have revealed single crystalline nature of Si nanowires. The obtained results have indicated good progress towards finding alternative catalyst to gold for the synthesis of Si nanowires.

Keywords: Semiconductors; Si nanowires; electron beam evaporation; VLS growth mechanism; Sn catalyst; thin films.

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Introduction

The Vapour-Liquid-Solid (VLS) method is one of the most common synthesis used for Si nanowires (NWs) growth, which has been first proposed by Wagner and Ellis in 1964 **[1]**. In their investigation, a metal catalyst droplet has been alloyed and supersaturated with Si resulting in precipitation and an axial growth of nanowire beneath the droplet. The successful growth of Si NWs mainly relies on the use of gold (Au) as a catalyst **[2, 3]**. Although gold has several advantages such as good thermal stability, and chemical inertness, and can be deposited easily, attention has been given to alternate catalyst for Si NWs growth due to three different reasons **[4-7]**. First, Au is incorporated into the NWs during growth **[7]**. Since Au is a deep level impurity in semiconductors (Si, Ge) that degrades the optical and

electronic properties **[8, 9]**. Optical and electronic properties of NWs grown with alternate catalyst could be improved in principle **[10, 11]**. Second, nanowires growth with alternate catalyst can be done at low temperatures **[12-14]** when compared with the Au catalyzed NWs growth **[2, 3]**. This low temperature growth can be useful in microelectronic device fabrication. Third, high solubility of Si, Ge in Au does not result in abrupt hetro structures (Si/Ge or Si/GeSi) due to reservoir effect **[4, 15]**. The abrupt hetro structures can be possible with alternate catalysts due to low Si solubility in alternate catalyst **[4, 16]**. It is for this reason that an alternative metal to gold has been investigated for the synthesis of semiconductor NWs **[4-6]**. From this point of view, Tin (Sn) can be used as an alternative candidate because of its low eutectic point (232°C) **[17]**, low solubility of Si in Sn. Synthesis of Si NWs employing tin (Sn) as a catalyst has been recently achieved with the plasma enhanced CVD **[14, 18-21]**, supercritical fluid-liquid-solid (SFLS) **[22]** and Hydrogen radical assisted methods **[23-25]**. Recently, we have reported the growth of the Si NWs with alternate catalysts such as Indium (In), Bismuth (Bi) at low substrate temperatures of 280°C and 300°C respectively by e-beam evaporation method (EBE) **[12, 26]**. The advantages of e-beam evaporation are found elsewhere **[2]**. In the present investigation, the same method was now employed using Sn as a catalyst.

In the present investigation, we report the growth of Si NWs using tin (Sn) as a catalyst by EBE at a low substrate temperature of 300-350°C. For the first time, we are reporting the growth of the silicon nanowires with tin catalyst by EBE. As-grown nanowires were characterized by Field Emission Scanning Electron Microscope (FESEM), X-Ray Diffraction (XRD) and Transmission Electron Microscope (TEM) for their morphological and structural properties, respectively. The growth of Si NWs by EBE method using Sn catalyst can be further implemented with other alternate catalyst such as Ga as well.

Experimental

Materials

Silicon ingots (Balzers, 99.99%, USA) were used for Si nanowires growth. Tin ingots (Alfa Aesar, 99.99%, USA) were used for catalyst layer deposition. p-type Si (100) substrates (Silicon Valley Microelectronic, USA) were used as a substrates.

Methods

The experimental set up and experimental procedure of Si NWs growth with Sn catalyst is similar to the previous reports **[12, 26]** (See supplementary information). Pure Si ingots (99.99% Blazers) loaded into a water cooled graphite crucible have been used as a source for e- beam evaporation. p-type Si (100) wafers have been cleaned in an ultrasonic bath with acetone, followed by a (5%) dilute hydrofluoric acid (HF) solution for 3 min to remove the native oxide layer and then rinsed with de-ionised (DI) water, followed by isopropyl alcohol and finally blown dry with N_2 (99.999%) before loading in to e-beam chamber. E-beam chamber has been evacuated to a vacuum of 1×10^{-5} mbar using a diffusion and rotary pump combination. Initially, Sn thin film of thickness 20 nm is deposited on to the Si substrates by Resistive thermal evaporation of Sn at room temperature at a vacuum of 1×10^{-5} mbar. Without breaking the vacuum, Sn coated Si substrates have been annealed at growth temperature for 5 min prior to the Si NWs growth to get Sn catalyst droplets. The growth of Si NWs carried in a temperature window of 200-500 °C for a deposition time of 15 min at Si evaporation rate of 0.2 nm/s.

Characterization

The morphology of the grown Si NWs, formed Sn catalyst particles was examined by a Field Emission Scanning Electron Microscope (FESEM, FEI Sirion). Crystallinity of the Sn thin film was examined by X-Ray diffraction (XRD, D8 advacnce Bruker), the microstructure and compositional properties of the nanowires were characterized by Transmission Electron Microscopy (FEI, T-20).

Results and discussion

Characterization of tin nanoparticles

Fig.1(a) shows the formed tin catalyst particles on the Si substrate after annealing of the 20 nm Sn catalyst film at a temperature of 350°C for 5min. Silicon substrate surface has been uniformly covered by spherical tin droplets with a diameter in the range of 30-100nm. This formed Sn catalyst droplets used as a catalyst for Si NWs synthesis. **Fig. 1 (b)** shows the X-Ray diffraction pattern of Sn thin film deposited on Si substrates. The diffraction peaks at 2θ=30.68, 32.06 have been identified as the (200), (101) planes of the tetragonal crystal structure of Sn, which are very well coincided with JCPDS no. 04-0673.

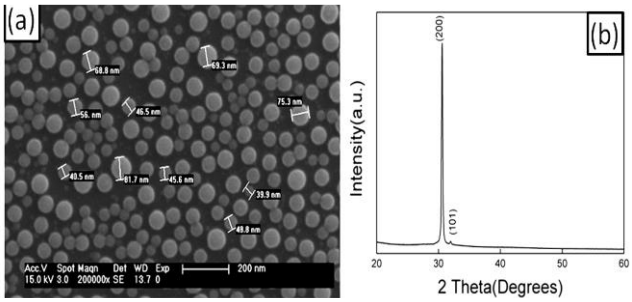

Fig. 1 (a) SEM image (b) XRD pattern of tin (Sn) nanoparticles formed on the Si (100) substrate at 350 °C substrate temperature for 5 min.

Characterization of silicon nanowires

Silicon NWs grown on Si substrates at different substrate (growth) temperatures of 300-480°C for 15 minutes have been shown in **Fig. 2 (a-d)**. No nanowire growth was observed on the bare Si substrates, eliminating the possibility of catalyst independent NWs growth. Nanowires growth was not observed below the eutectic temperature (231°C) according to the VLS growth procedure **[1]**. Upon increasing growth temperature above the 230 °C, initiation of nanowires growth observed (for brevity it is not shown in here). This (poor) nanowires growth behaviour is due to

slow absorption and diffusion of Si atoms into the Sn catalyst at temperature less than 300°C. Nanowires growth in the temperature range of 300-350°C becomes better and form dense nanowires on the substrates. Grown Si NWs morphology is similar to the reported Si NWs growth with alternate catalysts in the literature **[13, 14, 27, 28]**. These NWs have been randomly oriented with respect to the substrate, and each nanowire has tin (Sn) catalyst particle at its top and growth temperature is well above the eutectic temperature confirming the VLS growth of Si NWs **[6]**. High resolution FESEM images of the Si NWs grown at 350 °C shown in the **Fig. 2 (e-f)** (See supplementary material).

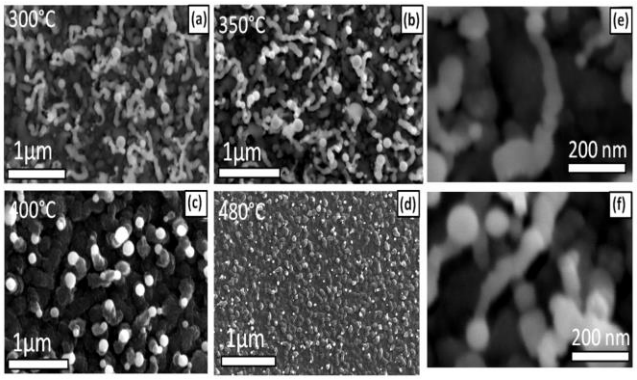

Fig. 2. SEM images of Si nanowires grown on tin nanoparticles as nucleation growth at different growth temperatures of (a) 300 (b) 350, (c) 400, (d) 480°C. (e)-(f) High resolution SEM image of the Si NWs (at 350°C).

These NWs have a length of approximately 500-600 nm. We could not measure accurately the diameter of the nanowires because of the tapering of the NWs. The Si NWs growth rate has been measured and found to be ~30 nm/min. From SEM images, the areal density (number of NWs per unit area) has been calculated and is found to be around 2-3 NWs/µm^2. As the growth temperature is increasing from 350 to 400 °C nanowires growth turned out to be nanorods growth and more un-catalyzed deposition on the nanowires, finally at growth temperature greater than 450°C nanowires growth is completely suppressed. This nanowires growth behaviour with temperature is well supported by experimental and theoretical works on nanowires growth by physical vapour deposition (PVD) methods such as EBE and MBE **[29, 30]**. The nanowires growth is explained by two processes. The evaporated atoms fall on the substrate as well as on the catalyst particle. The atoms which fall on the catalyst particle eventually supersaturate and precipitate as a nanowire according to the VLS principles. The atoms which fall on the substrate and nanowires sidewalls will diffuse towards the catalyst particle and contribute to the nanowire growth **[29]**. The adatoms contribution to the nanowire growth is a temperature dependent phenomenon. Nanowires length is increases with temperature (300-350 °C) initially due to increased diffusion of ad atoms that contribute to the axial growth. As temperature increases (350-450 °C), adatoms contribution to the nanowires gradually decreases results in thin film (2D) deposition dominates over the nanowires (axial) growth. This was clearly evidenced in the **Fig. 2(d).** The advantage of current approach of Sn catalyzed Si nanowires is simple process, cost effective and low temperature growth of Si nanowires compared to the other methods such as hydrogen radical assisted method **[23,25]**, plasma enhanced CVD **[14, 21]** (see supplementary material). In hydrogen radical assisted method, plasma enhanced CVD additional plasma pre-treatment is required to get Sn catalyst particles but in the current report no such treatment is required. High vacuum deposition of catalyst layer in the present report is useful for avoiding the oxidation of catalyst layer. Avoiding the catalyst layer oxidation is greatly enhances the nanowires growth probability.

Bright filed TEM image of a single Si nanowire grown by EBE at substrate temperature of 350°C for 15min has been shown in **Fig. 3(a)**. It has been clearly identified in **Fig 3(a)** that tin nanoparticle located at the end of (capped) the Si nanowire, implying that a tin (Sn) catalyst assisted VLS mechanism growth in Si NWs formation. The High resolution TEM recorded over the nanowire has clearly shown a high degree of crystallinity with a clear crystal lattice as shown in **Fig 3 (b).** The lattice spacing in the HRTEM in **Fig. 3(b)** has been found to be 0.31 nm, which corresponds to the "d " spacing of the (111) plane of Si.

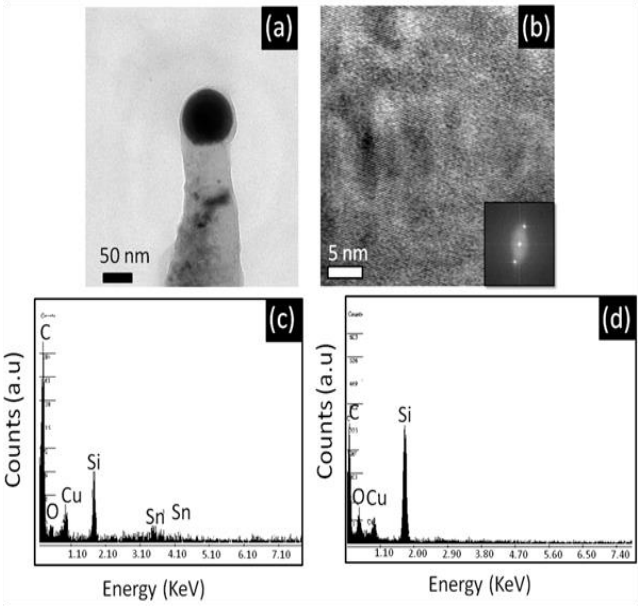

Fig. 3. (a) TEM image of the single Si nanowire, (b) HRTEM recorded on the Si nanowire (inset FFT pattern), (**c**) EDX spectrum recorded on the catalyst particle and (d) EDX spectrum recorded on the nanowire.

EDX spectra recorded on the Si NWs at the tip and the stem of the Si NWs during analysis have been shown in **Fig. 3 (c)** and **(d)**, respectively. The EDX spectra have revealed that the tip of the nanowire contains both Si and Sn, whereas the base or stem of the nanowire contains only Si. The other peaks, such as Cu and O, have also been detected attributing to the effect of TEM grid (Cu, O) and also oxide layer formed on the as grown Si NWs due to exposure of sample to the atmosphere during sample preparation. These results have indicated that the as-synthesized Si NWs by e- beam evaporation technique are single crystalline in nature without any impurities.

Conclusion

Tin catalyzed Si NWs were grown by the electron beam evaporation method under a high vacuum (1×10^{-5} mbar) on a Si substrate at a temperature of 300-350°C. FESEM studies show that the grown nanowires were randomly oriented with respect to the substrate, having an average length of 500-600 nm. Each NW is capped with a tin nanoparticle and growth temperature well above the eutectic temperature confirming the VLS growth of the Si NWs and the nanowires growth rate was measured to be ~ 30 nm/min. The TEM study on the nanowires shows that the grown nanowires were single crystalline in nature. It is observed that a narrow temperature window from 300°C to 350°C for the Si nanowires growth with Sn catalyst.

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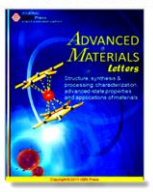
Reference

1. Wagner, R. S.; Ellis, W. C. *Appl. Phys. Lett.* **1964,** *4*, 89. **DOI:** 10.1063/1.1753975
2. Irrera, A.; Pecora, E. F.; Priolo, F. *Nanotechnology*. **2009**, *20*, 135601. **DOI:** 10.1088/0957-4484/20/13/135601
3. Xu, T.; Sulerzycki, J.; Philippe, J.; Patriarche, G.; Grandider, B.; Stevenard, D. *Nanoscale. Res. Lett.* **2011**, *6*, 113. **DOI:** 10.1186/1556-276X-6-113
4. Ross, F. M. *Rep. Prog. Phys.* **2010**, *73*, 114501 **DOI:** 10.1088/0034-4885/73/11/114501
5. Ross, F. M.; Wen, C. Y.; Kodambaka, S.; Wacaser, B. A.; Reuter, M. C.; Stach, E. A. *Philo. Mag.* **2010**, *90*, 2807. **DOI:** 10.1080/14786431003745583
6. Schmidt, V.; Witterman, J. V.; Senz, S.; Gosele, U. *Adv. Mater.* **2009**, *21*, 2681. **DOI:** 10.1002/adma.200803754
7. Hannon, J. B.; Kodambaka, S.; Ross, F. M.; Tromp, R. M. *Nature.* **2006**, *440*, 69. **DOI:** 10.1038/nature04574
8. Valdinoci, M.; Colalongo, L.; Pellegrini, A.; Rudan, M. *IEEE Transctions. on Electronic. Devices.* **1996,** *43*, 2269. **DOI:** 10.1109/16.544420
9. Perraud, S.; Poncet, S.; Noel, S.; Levis, M.; Faucherand, P.; Rouviere, E.; Thony, P.; Jaussaud, C.; Delsol, R. *Solar. Energy. Mater. Solar Cells.* **2009**, *93*, 1568. **DOI:** 10.1016/j.solmat.2009.04.009
10. Gunawan, O.; Guha, S. *Solar. Energy. Mater. Solar Cells.* **2009**, *93*, 1388. **DOI:** 10.1016/j.solmat.2009.02.024,
11. Kayes, B. M.; Filer, M. A.; Putnam, M.C.; Kelzenberg, M. D.; Lewis, N. S.; Atwater, H. A. *Appl. Phys. Lett.* **2007**, *91*, 103110. **DOI:** 10.1063/1.2779236
12. Kumar, R. R.; Rao, K. N.; Phani, A. R. *Mat. Lett.* **2012,** *66*, 110. **DOI:** 10.1016/j.matlet.2011.08.064
13. Alet, P. J.; Yu, L.; Patriarche, G.; Palacin, S.; Cabarrocas, P. R. I. *J. Mat. Chem.* **2008,** *18*, 5187. **DOI:** 10.1039/b813046a
14. Yu, L.; Alet, P. J.; Picardi, G.; Maurin, I.; Cabrrocas, P. R. I. *Nanotechnology*. **2008**, *19*, 485605. **DOI:** 10.1088/0957-4484/19/48/485605
15. Li, N.; Tan, T. Y.; Gosele, U. *Appl Phys A: Mater. Sci. Process.* **2008**, *A90*, 591. **DOI:** 10.1007/s00339-007-4376-z
16. Wen, C. Y.; Reuter, M. C.; Tersoff, J.; Kodambaka, S.; Stach, E. A.; Ross, F. M. *Science*. **2009**, *326*, 1247. **DOI:** 10.1126/science.1178606
17. Olesinski, R. W.; Abbaschian, G. J. *Bull. Alloy. Phase. Dia.* **1984,** *5*, 273. **DOI:** 10.1007/BF02868552
18. Cho, J.; Donnell, B.O.; Yu, L.; Kim, K. H.; Ngo, I,; Cabarrocas, P. R. I. *Prog. Photovolt: Res.Appl.* **2013**, *21*, 77. **DOI:** 10.1002/pip.1245
19. Donnell, B. O.; Yu, L.; Foldyna, M.; Cabarrocas, P. R. I. *J. Noncrys. Solids.* **2012,** *358*, 2299. **DOI:** 10.1016/j.jnoncrysol.2011.11.026
20. Parlevliet, D.; Jennings, P. *J. Nanopart. Res.* **2011**, 13, 4431. **DOI:** 10.1007/s11051-011-0478-9
21. Rathi, S. J.; Jariwala, B. N.; Beach, J. D.; Stradins, P.; Taylor, P. C.; Weng, X.; Ke, Y.; Redwing, J. M.; Agarwal, S.; Collins, R T. *J. Phy. Chem. C.* **2011**, *115*,3833. **DOI:** 10.1021/jp1066428
22. Chockla, A. M.; Klavetter, K. C.; Mullins, C. B.; Kargel, B. A. *Chem. Mater.* **2012,** *24*, 3738. **DOI:** 10.1021/cm301968b
23. Jeon, M.; Uchiyama, H.; Kamisako, K. *Mater. Lett.* **2009, 63**, 246. **DOI:** 10.1016/j.matlet.2008.10.005
24. Jeon, M.; Kamisako, K. *Mater. Lett.* **2009,** *63*,777. **DOI:** 10.1016/j.matlet.2009.01.001
25. Jeon, M.; Kamisako, K. *Curr. Appl. Phys.* **2010**, *10*, 5191. **DOI:** 10.1016/j.cap.2009.11.056
26. Kumar, R. R.; Rao, K. N.; Phani, A. R. *Ma.t Lett.* **2012**, *82*, 163. **DOI:** 10.1016/j.matlet.2012.05.090
27. Hernandez, M. J.; Cervera, M.; Ruiz, E.; Pau, J. L.; Piqueras, J.; Avella, M,; Jimenez, J. *Nanotechnology*. **2010**, *21*, 455602. **DOI:** 10.1088/0957-4484/21/45/455602
28. Yu, L.; Donnell, B. D.; Alet, P. J.; Boj, S. C.; Peiro, F.; Arbiol, J.; Cabarrocas, P. R. I. *Nanotechnology*. **2009**, *20*, 225604. **DOI:** 10.1088/0957-4484/20/22/225604
29. Artoni, P.; Pecora, E. F.; Irrera, A.; Priolo, F. *Nanoscale. Res. Lett.* **2011**, *6*, 162. **DOI:** 10.1186/1556-276X-6-162
30. Duborovskii, V.G.; Sibirev, N. V.; Cirlin, G. E.; Harmand, J. C.; Ustinov, V. M. *Phy. Rev. E.* **2006**, *73*, 021603. **DOI:** 10.1103/PhysRevE.73.021603



Supporting information

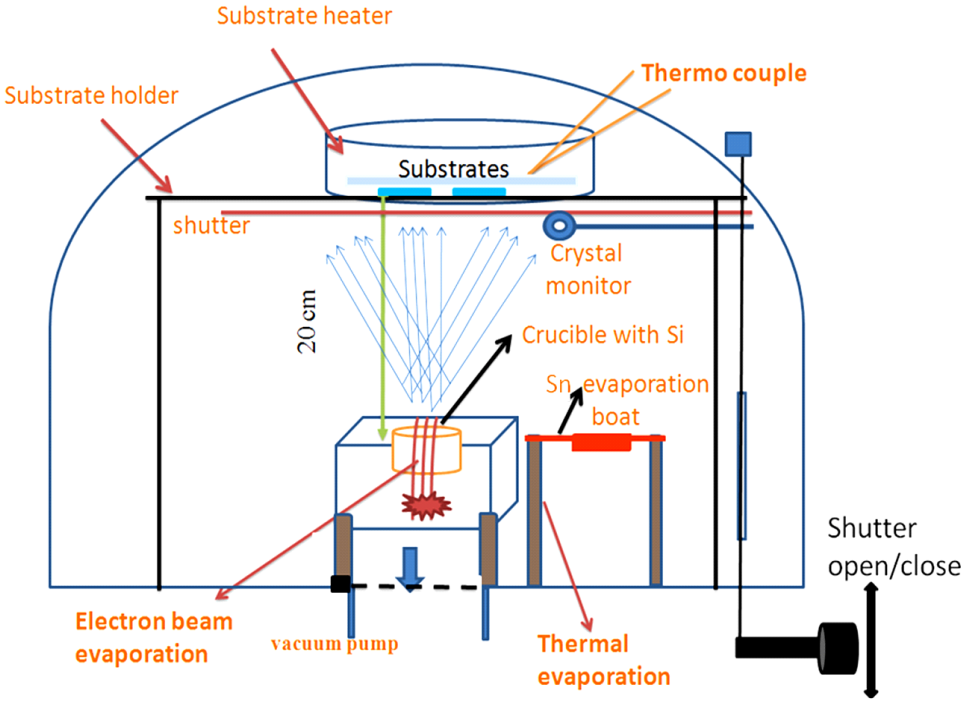


Fig. S1. Schematic of the Si nanowires growth system.

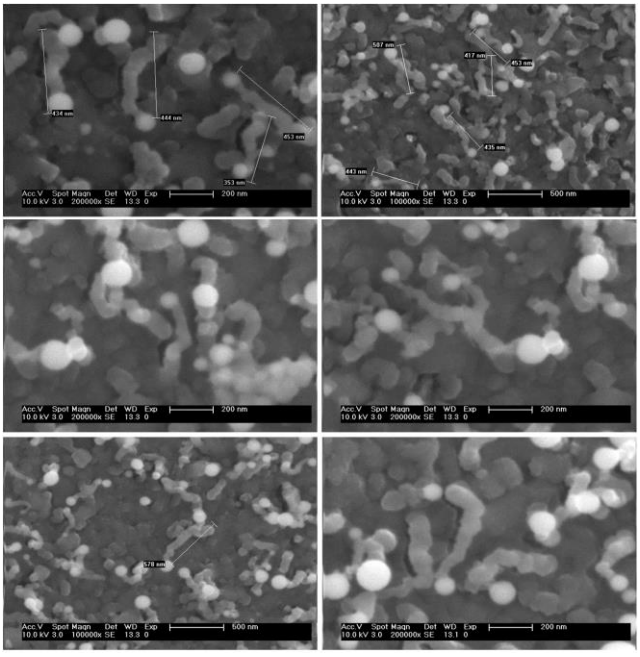


Fig S2. High resolution FESEM images of the Si NWs grown at 350°C.

Table S3. Literature review of mostly used method for Si nanowires growth with Sn catalyst.

S.No.	Growth Method	Growth temperature	Catalyst film Pre-treatment	Ref.
1.	Hydrogen radical assisted deposition	400 °C	Hydrogen radical treatment	1
2.	Hydrogen radical assisted deposition	400 °C	Hydrogen radical treatment	2
3.	Plasma Enhanced CVD	600 °C	Plasma treatment of catalyst film	3
4.	Plasma Enhanced CVD	400 °C	Plasma treatment of catalyst film	4