

A Novel Catalyst-free Synthesis of Vertically Aligned Silicon Nanowire-Carbon Nanotube Heterojunction Arrays for High Performance Electron Field Emitters

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Supporting Information:

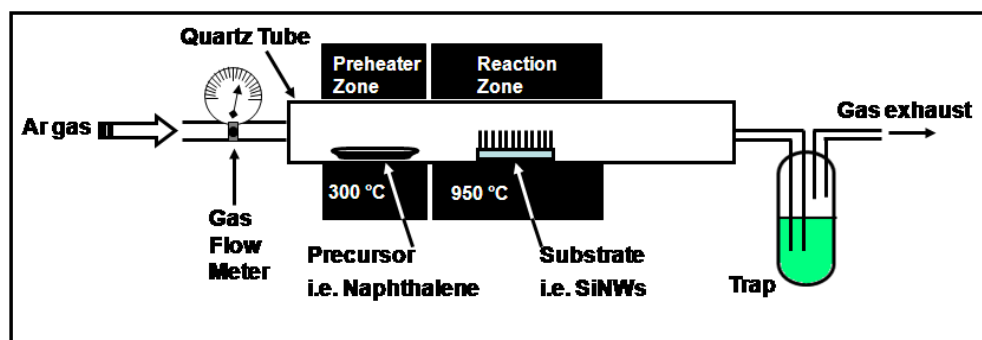
I- Experimental:

SiNWs Synthesis: A 1 x 1 cm² piece of phosphorus doped, n-type Si (100) wafer (0.001-0.002 Ω.cm, Wafernet Inc.) is cleaned sequentially with Acetone, Isopropanol and De-Ionized (D.I) Water (18.2 MΩ.cm) by ultrasonication for 5 min each. Then the native oxide layer on Si wafer is removed by treatment with boiling piranha solution (80 °C) i.e. 98 % H₂SO₄ : 30 % H₂O₂ (3:1 in volume) for 20 min and then washed with D.I. water and dried with Ar flow.

The cleaned Si wafer is then kept in a Polytetrafluoroethylene (PTFE) vessel containing etching solution of 4.6 M HF and 0.04 M AgNO₃ (1:1 in volume) and is heated up to 55 °C for 10 min. After the reaction, the sample is washed with D.I. water and then kept in a mixture of HNO₃: HCl: H₂O (1:1:1 in volume) overnight in order to remove Ag. As prepared SiNW arrays are then dipped into 5% HF solution for 1 min. This is rinsed with water immediately, dried in an Ar flow and used for the synthesis of va-SiNW-CNT heterojunction arrays.

Nano-heterojunction Synthesis: The va-SiNW-CNT nano-heterojunction arrays are synthesized by an in-house fabricated CVD set-up, capable of attaining 1200 °C (with a dual zone). The end of the main (reaction) zone is connected to the exhaust system through a cooling condenser, where the unreacted hot gases are trapped. In the beginning, quartz tube (inner diameter 34 mm and length 108 mm) is cleaned with ethanol several times, followed by air blowing. Then, a stream of argon (Ar) is passed through the quartz tube at 100 standard cubic centimetres per minute (sccm) to expel all the impurities. This quartz tube is kept horizontally

inside the dual zone electric furnace as shown in experimental setup. Naphthalene is used as the precursor for carbon and is kept in the preheater zone of the dual furnace, maintaining the temperature at 300 °C to ensure complete sublimation of naphthalene. The sublimed precursors are then passed into the main (reaction) zone by means of Ar as a carrier gas at 500 sccm where SiNW arrays are heated at 950 °C. The temperature of the reaction zone is programmed in such a way that it attained 950 °C when precursor zone is at 300 °C. The reaction is continued for 60 min to ensure the complete growth of CNTs on SiNW arrays; the Ar flow rate is maintained at 500 sccm to minimize the oxygen contamination during the reaction. The heating rate of furnace is 20 °C min⁻¹.



Schematic representation of in-house built dual zone CVD set-up

II-Characterization:

Scanning electron microscopy (SEM) images of samples are taken on Quanta 200 3D FEI instrument. The TEM and HRTEM images were taken by a TECNAI-T 30 model instrument operated at an accelerating voltage of 300 kV. Samples for TEM imaging were prepared by scratching a SiNW-CNT arrays from Si wafer by sharp razor blade and dispersed in ethanol and placed a drop of sample onto a carbon-coated Cu grid (3 nm thick, deposited on a commercial copper grid for electron microscope), dried in air and loaded into the electron microscopic chamber. Atomic Force Microscope (AFM) (Model: MMAFMLN, Veeco Digital Instruments, Santa Barbara, CA, USA) images are taken at tapping mode. Raman analysis of samples was performed on a JASCO confocal Raman spectrometer using 532 nm green laser (NRS 1500 W). Thermogravimetric Analysis (TGA) is performed on a SDT Q600 TG-DTA analyzer under Air atmosphere at a heating rate of 10 °C min⁻¹. The samples for TGA were collected in powder form by scratching the SiNWs and SiNW-CNT arrays from Si wafer.

X-ray Photoelectron Spectroscopic (XPS) measurements were carried out on a VG Micro Tech ESCA 3000 instrument at a pressure of $> 1 \times 10^{-9}$ Torr (pass energy of 50 eV, electron take off angle 60° and the overall resolution was ~ 0.1 eV).

All contact angle measurements were performed on a GBX model (DIGIDROP contact angle instrument) using Windrop software at room temperature (27°C).

Electron Field Emission Studies: Field electron emission measurements on blank SiNWs and SiNW-CNT arrays are carried out in planar diode configuration under ultra high vacuum. A vacuum in the order of 1×10^{-7} mbar and below is routinely obtained and maintained in the field emission system with the help of sputter ion pump and titanium sublimation pump. The current-voltage (I-V) characteristics are recorded using a high voltage power supply (0-40 kV, Spellman, USA) and a picoammeter (Keithley 614) at room temperature. Fowler-Nordheim (F-N) plots are obtained from the recorded I-V data. The cathode-anode separation is kept at ~ 1.5 mm for both the samples. All field emission experiments were carried out under identical conditions and are repeated at least three times and the results are found to be highly reproducible.

Calculation of Field Enhancement Factor (β): The FE current-voltage characteristics are further analyzed using the Fowler-Nordheim (F-N) equation,

$$J = (A \beta^2 E^2 / \Phi) \exp(-B \Phi^{3/2} / \beta E) \quad (1)$$

$$\ln(J/E^2) = \ln(A \beta^2 / \Phi) - B \Phi^{3/2} / \beta E \quad (2)$$

Where A and B are constants with values of 1.54×10^{-6} A (eV) V^{-2} and 6.83×10^3 $\text{V} \mu\text{m}^{-1}$ $\text{eV}^{-3/2}$, respectively, J is the current density, β is the field enhancement factor, E is the applied field, and Φ is the work function of the emitting materials.

The actual enhanced field can be estimated from the equations as follows,

$$\beta = [-6.8 \times 10^3 \Phi^{3/2}] / m \quad (3)$$

where, ' β ' is field enhancement factor and ' Φ ' is the work function of the emitter material in eV and ' m ' is the slope calculated.

β for blank SiNWs is calculated to be 2267 by taking the work function of elemental Si as $\Phi = 4.1$ eV with slope 'm' as calculated from respective graph of F-N plot Fig 4 (b) in main text.^[1]

and β for SiNW-CNT arrays is calculated to be 6010 by taking the work function of CNTs as $\Phi = 5.0$ eV with slope 'm' as calculated from respective graph of F-N plot Fig 4 (b) in main text.^[2]

AFM imaging:

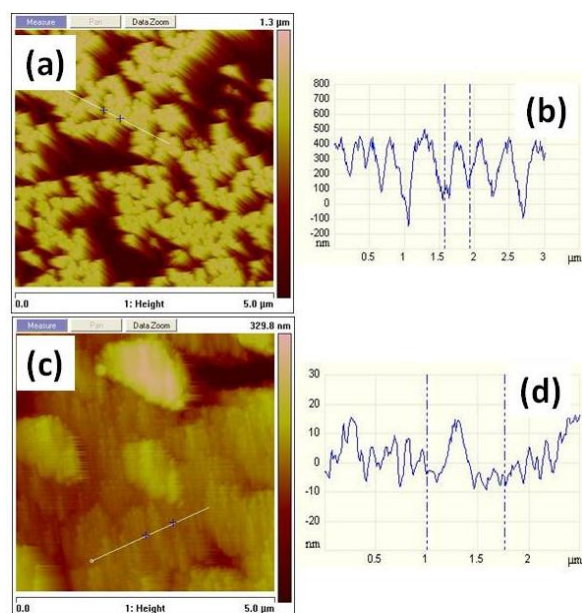


Fig S1: (a) is the height profile AFM image of blank SiNWs of $5 \times 5 \mu\text{m}^2$ area and (b) the linear cross section graph of the marked line in Fig S1 (a); Similarly (c) is the height profile AFM image of SiNW-CNT arrays of $5 \times 5 \mu\text{m}^2$ area and (d) the linear cross section graph of the marked line in Fig S1(c).

The height profile AFM image of blank SiNWs of $5 \times 5 \mu\text{m}^2$ area which is the same area as in Fig 1 (a) of the main text shows that the nanowires occur in bundles. Fig S1 (b) is the linear section height profile of marked line in Fig S1 (a). The roughness of the bundles of nanowires is ~ 500 nm which acts as the platform for the growth of CNTs.

Similarly, Fig S1 (c) is the height profile AFM image of SiNW-CNT arrays of $5 \times 5 \mu\text{m}^2$ area which is same as in Fig 1 (c) of the main text shows that the growth of CNTs are also occur in bundles. Fig. S2 (d) is the linear section height profile of marked line in Fig S2 (c). The roughness of bundles of CNTs is upto 30 nm. The significant change of surface roughness from

500nm of blank SiNWs to 30 nm of SiNW-CNT arrays is due to the growth of CNTs on SiNW arrays.

Energy Dispersive X-ray (EDX) Analysis:

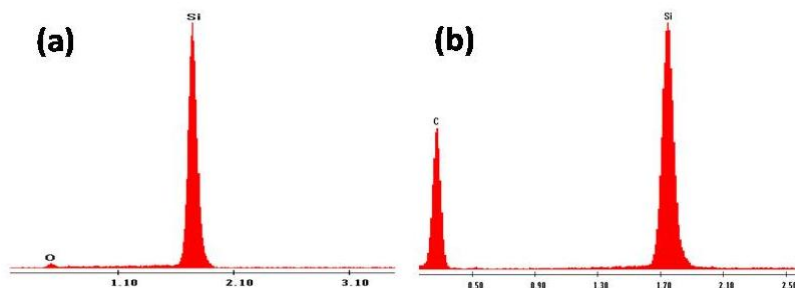


Fig S2: Energy Dispersive X-ray analysis of (a) blank SiNWs and (b) SiNW-CNT arrays.

EDX analysis clearly indicates that carbon is not present in blank SiNWs while in SiNW-CNT arrays have ~ 43 % of carbon and remaining ~ 57 % of silicon.

Water Contact Angle Measurements:

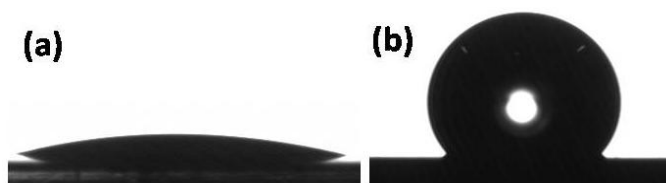


Fig S3: Water Droplet Contact Angle image of (a) blank SiNWs (b) SiNW-CNT arrays.

The water droplet contact angle obtained for blank SiNWs is 6° whereas that obtained for SiNW-CNT arrays is 130° . This drastic change in water contact angle by virtue of surface changes indicates the formation of CNTs on SiNWs.

Thermogravimetric Analysis (TGA):

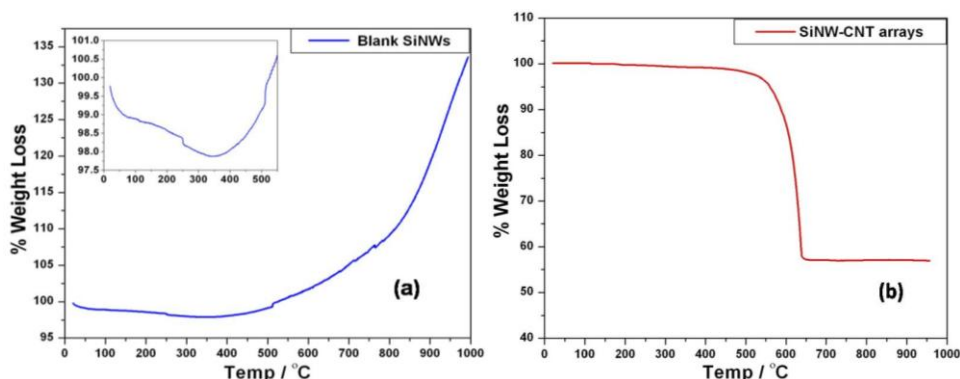


Fig S4: TGA profile obtained in air from room temperature to 1000 °C for (a) blank SiNWs; inset of fig (a) shows the enlarged portion showing the initial weight loss followed by the weight gain of SiNWs (b) SiNW-CNT arrays.

Since it is well-known that the electronic properties of Si and SiO₂ are extremely different and also Si is prone to form SiO₂, it is important to confirm whether the nano-heterojunction is formed on Si or SiO₂. Thermogravimetric analysis (TGA) is carried out to confirm this perplexity. Fig S4. shows TGA of (a) blank SiNWs and (b) SiNW-CNT arrays from room temperature to 1000 °C in air. Both the samples are collected by scratching from the surface of silicon wafer. It is found that there are distinct differences in the TG profiles of the two samples. Fig S4 (a) which corresponds to the TGA profile of blank SiNWs shows slight initial weight loss upto 350 °C followed by a continuous weight gain. This weight gain indicates that ~ 97.8 % of the SiNWs is Si and only ~2.2 % is in the form of SiO₂. Inset of Fig S4 (a) is enlarged portion of it upto 550 °C which clearly confirms the continuous weight gain of the major portion of the SiNWs. TGA profile of SiNW-CNT arrays in Fig S4 (b) indicates the initial weight loss starting from 500 °C upto 650 °C corresponding to CNTs on SiNWs. The weight loss is considerably 43%, illustrating that the growth of CNTs on SiNWs is uniform and covering all SiNWs surface as can be seen from SEM and AFM images also. The remaining 57% is SiNWs. This confirms that the CNTs are grown on the tips of Si instead of SiO₂ from SiNWs, which is further supported by XPS analysis.

X-ray Photoelectron Spectroscopy (XPS) analysis: High resolution (0.1 eV) XP spectra are recorded to identify the chemical states of blank and heterojunction samples. The core level binding energies were referenced to the C 1s neutral carbon peak at 285.0 eV, to compensate for the effect of surface charging.

It can be seen (Fig S5) from the close spectral inspection of the C1s region of the samples of (a) blank SiNW and (b) SiNW-CNT arrays showed peaks for C-C at 285.1 eV. A new peak at 284.5 eV in SiNW-CNT sample refers to the formation of C-Si bond; it also inform that carbon is present C in graphitic phase and consequently confirms formation of CNTs on SiNWs. Peaks at higher binding energy can be attributed to other functional groups like -OH or adventitious chamber impurities.

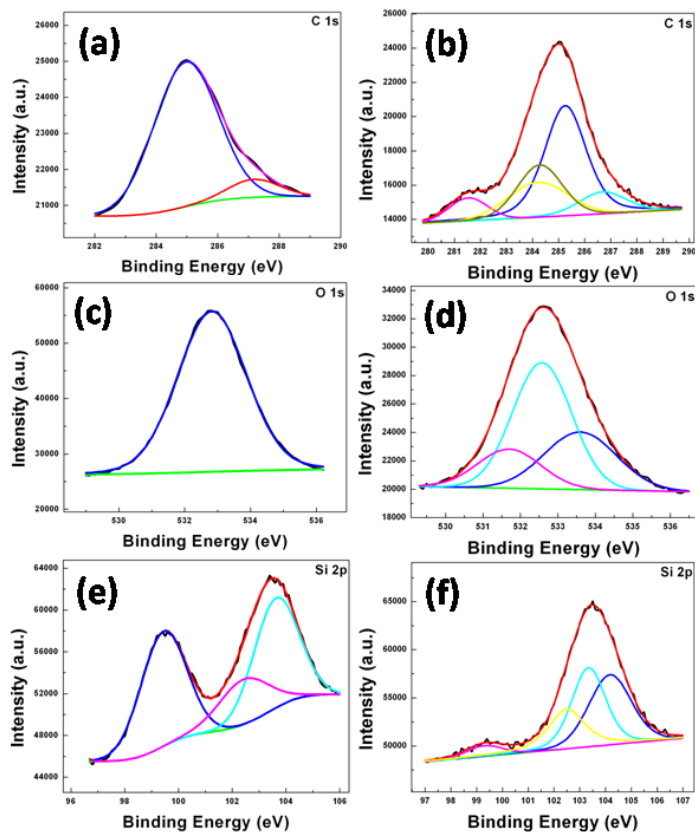


Fig S5: The high resolution XPS spectra of (a) C 1s, (c) O 1s and (e) Si 2p levels for blank SiNWs and (b) C 1s, (d) O 1s and (f) Si 2p levels for SiNW-CNT arrays.

High resolution O 1s peak analysis showed that both (c) blank SiNW and (d) SiNW-CNT are having peaks at 532.6 eV corresponding to O-Si bond. However in SiNW-CNT arrays intensity of O-Si peak is decreased and a new peak appearing at 531.5 eV indicates formation of O-C bond.

The Si 2p electron orbital spectra are shown for (e) blank SiNW and (f) SiNW-CNT. Peaks at 103.6 eV and 99.6 eV correspond to Si-O and Si-Si bond respectively with decreasing intensity of later in SiNW-CNT arrays. A new peak at 102.5 eV in SiNW-CNT arrays corresponds to Si-C bond.