

Control of Silicon Nanowires Crystallinity using Metal Assisted Chemical Etching of Silicon and Porous Silicon Substrate

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Abstract: Control of crystallinity is a vital aspect while synthesizing silicon nanowires (SiNWs). Solar photovoltaic devices need a highly crystalline phase, while lithium-ion battery anodes require a highly amorphous phase. The possible solution lies in the choice of substrate, either a silicon or porous silicon. Metal-assisted chemical etching is a low-cost method used for fabricating silicon nanowires using an electrolyte solution (hydrofluoric acid, metal salt, and hydrogen peroxide) at room temperature. Various combinations of substrates and electrolyte compositions are studied to control the morphology of synthesized nanowires such as length, strain, hydrophobicity, and crystallinity. Microscopic and spectroscopic study of the synthesized nanowires is carried out to explain the presence of the amorphous phase and strain in the SiNWs. The Si+M_{II} combination produces the highest crystallinity (i.e., 84.91%) and length of SiNWs (i.e., 23.3 μ m), which is more suitable for solar cell application compared to other combinations. The PSi+M_{II} combination results in the highest amorphous Si phases (i.e., 35.79%), suitable for lithium-ion battery anode.

Keywords: Metal-assisted chemical etching (MACE); Silicon nanowires (SiNWs); Amorphous Si; Superhydrophobicity; Current-Voltage measurement.

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1. Introduction

Indirect bandgap and small binding energy of crystalline silicon (c-Si) limit its use in optoelectronic devices [1]. The use of low-dimensional Si nanostructures overcomes the limitations of c-Si, as spatial confinement in Si nanostructures relaxes the k-selection rule [2]. Semiconductor nanowires (NWs) are quasi-one-dimensional (1-D) materials with diameter ranges from 10 nm to 100 nm, and has a length up to few

microns. Being a 1-D nanostructure, silicon nanowires (SiNWs) are gaining continuous attention due to their technological prospects by allowing the engineering of phonons, electrons, and plasmons. The SiNWs show a higher surface-area to volume Si ratio and the porous surface nanostructure, which produces a quantum confinement effect (QCE) on optical and electronic properties [3]. The design of SiNWs enhance the

lifetime of traditional electronics fabricated on Si by achieving higher performance, lower power consumption as well as lower cost [4], and scalable device applications ranging in various technological areas such as photovoltaic [5, 6], lithium-ion battery (LIB) [7, 8], sensor [9], field-effect transistor [10], and biosensor [11].

The SiNWs based solar cells are low-cost and have superior anti-reflection and light trapping properties [5] compared to conventional methods. Light befalls to NWs in various ways depending on the light wavelength, NW diameter, NW composition, and the dielectric discrepancy between the NW and the neighborhood media [5]. A previous study [12, 13] reports that reflection in the solar cell decreases for a higher length of the SiNWs. The amorphous Si (a-Si) solar cell exhibits lower efficiency because of poor electron transport properties and hence lower carrier diffusion length compared to c-Si solar cells [14]. Therefore, a higher length and crystallinity of the SiNWs show enhanced efficiency when used in solar cell fabrication.

Another potential application of the SiNWs is lying in the synthesis of the LIB battery anode. The capacity of the LIB enhances $\sim 4200 \text{ mAhg}^{-1}$ when the graphite is replaced by Si anode [15, 16]. A volume change of $\sim 300\%$ during charging and discharging gives rise to capacity fading of the LIB [15, 16]. The nanostructure of Si is a suitable candidate to avoid such capacity fading problems and improve cyclic stability. A previous study [17, 18], using thin-film a-Si, suggests that the a-Si exhibits higher cyclic stability compared to c-Si. Therefore, a higher amorphous phase in the SiNWs exhibits improved cyclic stability when used in the anode fabrication of LIB. A core-shell structure of SiNWs enhances cyclic stability as well as the performance of the LIB when used in anode

fabrication [19]. The core-shell structure of SiNWs also finds numerous applications as sensing [20], and optoelectronic [21] devices.

Fabrication of the SiNWs includes thermal evaporation, molecular beam epitaxy, laser ablation, chemical vapor deposition, and metal-assisted chemical etching (MACE). The MACE [22] achieves the unique advantages of low-cost fabrication and control over the size of SiNWs. The MACE is an electroless etching technique that takes place at the interface of Si and metal. The fabrication of porous SiNWs by MACE proceeds through the use of highly doped Si substrate and etching temperature [23–25]. The metal particles act as a cathode, and the surface of Si substrate behaves as an anode, resembling electrochemical etching for porous Si (PSi) fabrication [26]. The metal particles are crucial in the technique to promote H_2O_2 decomposition and form electron-hole pairs into the Si surface. During this process, the Si dissolves by HF to fabricate nanostructures on the surface.

Here the fabrication of SiNWs proceeds using Si and PSi substrate through two electrolyte compositions of MACE. The four combinations of substrates and electrolyte compositions are studied in detail to determine the suitable combinations for diverse applications of the SiNWs. The objective is to study and compare the property of SiNWs fabricated from the four combinations for two applications, i.e., higher length of SiNWs used in a solar cell enhances the anti-reflection property, as well as efficiency and higher content of amorphous phases in SiNWs used in the fabrication of LIB anode, enhances its cyclic stability. The core-shell structure of porous SiNWs obtained from MACE imparts special attention in the LIB due to the presence of amorphous phases in the shell. We used the term “etched-Si” to indicate both the SiNWs as well as PSi after MACE.

2. Materials and Methods

The SiNWs are fabricated from cleaned Si (p-type, (100), $0.01\text{--}0.02 \text{ }\Omega\cdot\text{cm}$, boron-doped, $275\pm 25 \text{ }\mu\text{m}$ thick, 2” diameter), or PSi substrate. The PSi substrates are synthesized from the cleaned Si by anodization [26–28], where the anodization current was 0.6 A, anodization time was 10 minutes, the electrolyte was (HF : Ethanol - 1 : 2). Fig. 1 shows, in the method I (M_I), dipping of substrates in an electrolyte solution, comprising of 4.8M HF (make: Across Organics) and 0.02M AgNO_3 (make: Sigma-Aldrich) for one minute, deposits Ag particles

followed by deionized (DI) water to withdraw surplus Ag^+ ions. Then the Ag deposited substrates are dipped inside another electrolyte solution, including 4.8M HF and 0.1765M H_2O_2 (make: Fisher Scientific) for 60 minutes at room temperature, fabricates SiNWs. In method II (M_{II}), dipping of the substrates in a single electrolyte solution, comprising of 4.8M HF, 0.02M AgNO_3 , and 0.1765M H_2O_2 , for 60 minutes at room temperature, fabricates the SiNWs. The SiNWs sample thus formed (i.e., both from Si and PSi



substrate) was cleaned with DI water followed by HNO_3 (30% [29]) solution for a few minutes to take out the excess Ag particles. Dipping the samples in HF removes the strong oxide layer formed on SiNWs during HNO_3 treatment [30]. Further, rinsing with DI water removes the remaining Ag particles.

High-resolution transmission electron microscopy (HRTEM) (make: FEI Technique, G20 F30), field emission scanning electron microscopy

(FESEM) (make: NOVA NANOSEM 450, FEI), Raman spectroscopy (make: SpectraPro HRS 300), contact angle (make: DSA 4-software), current-voltage (make: Keithley 6487, Picoammeter/voltage source) characterization studies the high-resolution image, cross-sectional view, peak shift, superhydrophobicity, and current-voltage (I-V) characteristics of etched-Si, respectively.

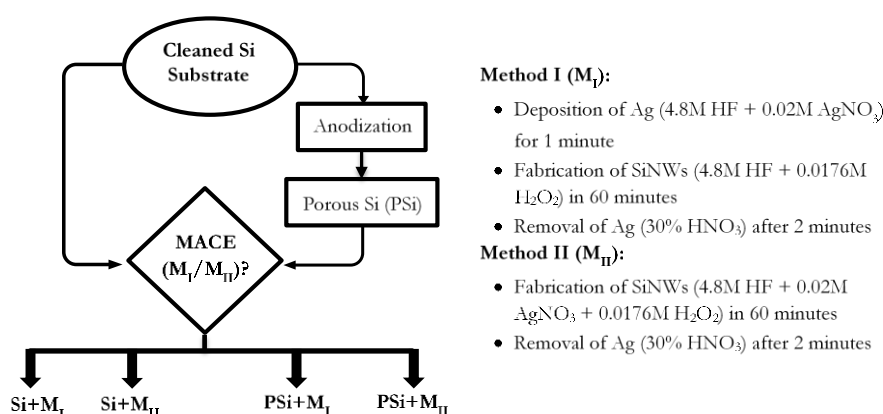


Figure 1. Flowchart of SiNWs fabrication through two methods of MACE using Si and PSi substrate.

3. Results and Discussion

The anodization fabricates PSi having an average porosity of $46 \pm 1\%$ from cleaned Si wafer. Fig. 2 (a) shows the surface view of PSi having pore diameter ranging from 60 nm to 150 nm. Fig. 2 (b) shows the cross-sectional view of PSi having an average thickness of $13.5 \pm 0.3 \mu\text{m}$.

Fig. 3 (a) shows the HRTEM image of SiNW fabricated using $\text{PSi}+M_{II}$ combination, where the average length and diameter are $3.44 \mu\text{m}$ and $0.22 \mu\text{m}$, respectively. Fig. 3 (b) shows the HRTEM images of Si nanocrystal (e.g., Si quantum dots, QDs) having (100) and (111) planes [23]. Fig. 3 (c) shows a core-shell structure of SiNWs, where the core consists of nanocrystalline Si, such as porous Si, Si QDs, and that of the shell consists of a-Si. Ghosh et al. [31] reported that sidewall etching of SiNWs by the metal particles produces QCE. At higher resolution image, as shown in Fig. 3 (d), the core-shell structure is distinguished, where the average diameter of the porous SiNWs is $0.12 \mu\text{m}$ in which the average Si core diameter is $0.09 \mu\text{m}$, and that of the average shell depth of a-Si is 15 nm. Fig. 3 (e) shows the SEAD pattern of SiNWs, indicating amorphous phases, and polycrystalline

phases, i.e., for various crystalline planes observed from the different diameter of the ring. Our previous study [23] revealed the formation of (111) plane along with (100) plane during the fabrication of porous SiNWs using both the diffraction pattern and the XRD calculation. An oxide layer (SiO_x) of thickness varied from $2 \text{ \AA}$ to $3 \text{ \AA}$ [32, 33], covers the surface of the etched-Si under ambient atmosphere, in an HF containing solution. Fig. 3 (f), Fig. 3 (g), and Fig. 3 (h) show the high-angle annular dark-field (HAADF) image, elemental mapping, and elemental mapping contents in a porous SiNW. Fig. 3 (g) clearly shows that the oxygen is present all over the SiNWs irrespective of nature, which indicates the formation of the oxide layer in the outer part, i.e., on the surface of the a-Si shell structure. The oxygen content should be as low as possible to avoid the formation of the SiO_x layer that hinders the flow of charge during the device applications.

Therefore, in the core-shell structure of porous SiNWs, the core consists of Si nanocrystal (e.g., QDs). The shell consists of a-Si, and as the outer surface area of the a-Si shell structure is exposed to ambient atmosphere, an oxide layer was formed.

The oxide layer mainly consists of amorphous phases due to which the SEAD pattern shows both crystalline and amorphous phases. During the fabrication of SiNWs for LIB anode, special care should be taken (e.g., inert atmosphere) to reduce the amorphous SiO_x formation. However, the controllable fabrication of amorphous phases in SiNWs is possible using the PSi substrate, which helps to enhance the cyclic stability as well as the performance of LIB when used in anode synthesis.

The MACE fabricates the SiNWs using Si substrate in both M_I and M_{II} , as shown in Fig. 4 (a) and Fig. 4 (b), respectively. However, using the PSi substrate, in M_I , a high porosity layer (HPL) and a low porosity layer (LPL) were formed instead of SiNWs, as shown in Fig. 4 (c). Further, MACE produces SiNWs using PSi substrates in M_{II} , as shown in Fig. 4 (d). Table 1 summarizes the observed length of SiNWs fabricated using the four combinations. The Si+ M_{II} combination achieves the highest length of SiNWs. The PSi+ M_I combination does not produce SiNWs may be due to the lesser etching capacity of Ag particles present on the surface of PSi. Fig. 5 (a) and Fig. 5 (b) show the Raman peak shift of etched-Si using Si and PSi substrate, respectively, at room temperature. The Raman peak of etched-Si downshifts compared to the c-Si peak, and asymmetric line-shape ranging from 470 cm^{-1} to 480 cm^{-1} for all samples revealing amorphous-like structure (not shown here). The Raman intensity of etched-Si is much higher compared to the c-Si (not shown here) because of multiple scattering takes place in the etched-Si [34]. Yogi et al. [35] suggested that the enhanced Raman intensity is due to decreased crystallite size. The downshift in the Raman peak for the SiNWs fabricated using Si+ M_{II} , as shown in Fig. 5 (a),

indicates the formation of the nano-crystallites, i.e., the sidewalls become porous with lower pore diameter. However, the upshift in the Raman peak for the etched-Si fabricated using PSi+ M_{II} , as shown in Fig. 5 (b), is mainly because of the formation of the oxide layer on the larger surface area of the porous SiNWs. The formation of Si QDs on the core of porous SiNWs downshift the Raman peak, and at the same time, the oxide layer formed on the outer part of the a-Si shell structure upshifts the peak. The larger surface area of the porous SiNWs and the remanence of Ag nanoparticles on the sample creates an oxide layer dominate over the formation Si QDs, which pulls the Raman peak in the upward direction.

The fabrication of SiNWs induces strain (ξ) as well as changes the crystallinity (ρ_c) for all the combinations, calculated using [36] from Raman spectra. The responsible parameters for inducing strain on the SiNWs are processing technique [37, 38], oxidation of NWs shell, i.e., a variation of oxide layer thickness on the porous SiNWs [37, 39–41], and variation of lattice constant [36]. Samanta et al. [42] reported that during the growth of SiNWs, the rigid boundary of the 1-D system develops tensile strain in the vicinity of pores of the porous SiNWs. Table 1 suggests that the strain becomes higher for higher length or thickness of etched-Si. A possibility of lower-dimensional pore size (nano-crystallites Si, i.e., QDs) in the sidewalls of the SiNWs and higher strain downshift the Raman peak of Si+ M_{II} combination more compared to Si+ M_I . An oxide layer on the surface of the SiNWs fabricated in PSi+ M_{II} combination upshifts the Raman peak more compared to PSi+ M_I .

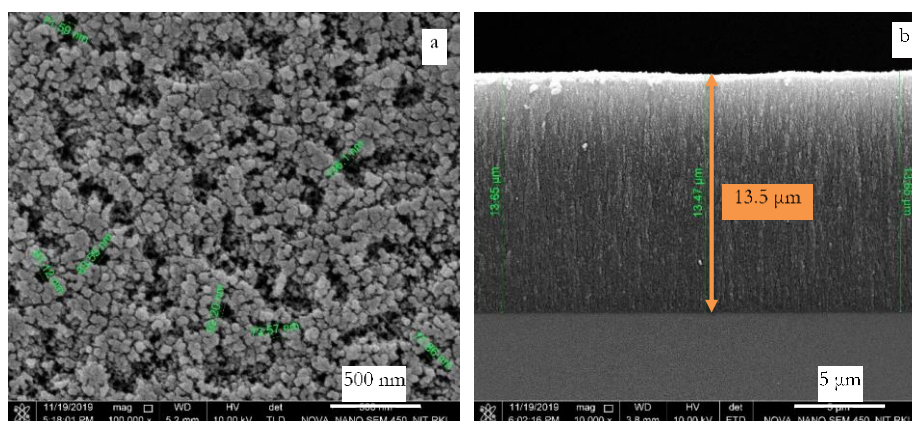


Figure 2. FESEM image of PSi fabricated by anodization (a) surface view and (b) cross-sectional view.

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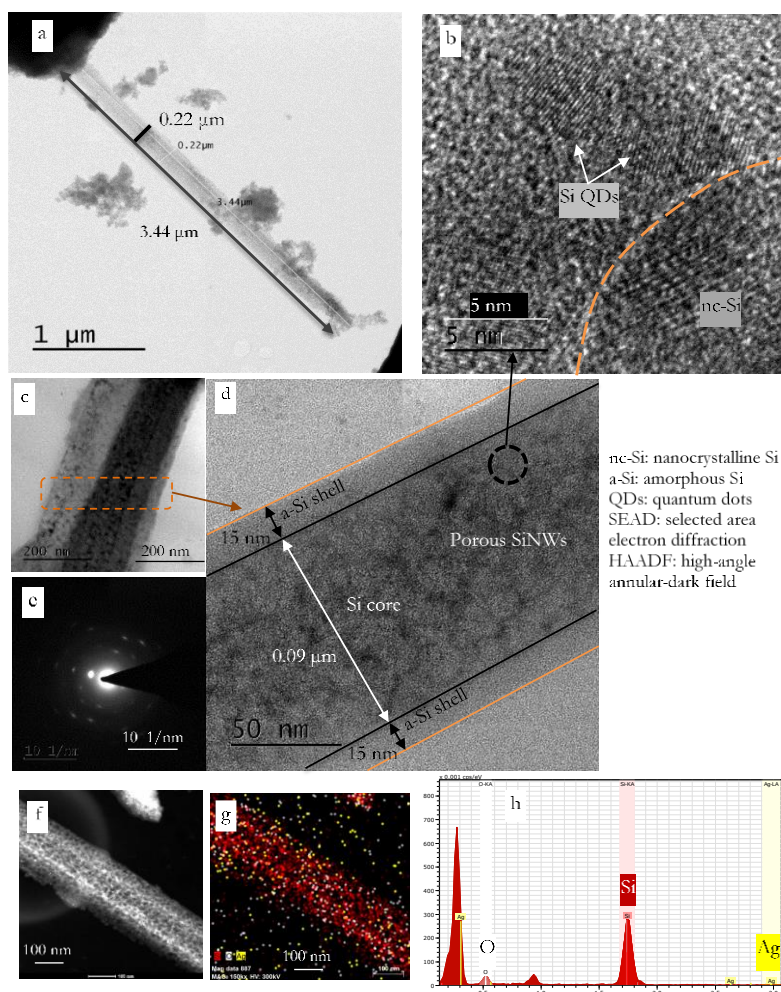


Figure 3. (a) HRTEM image, (b) nanocrystalline Si core, (c, d) core-shell structure, (e) SEAD pattern, and (f, g, h) HAADF image, mapping element and pattern of SiNWs fabricated using PSi+M_{II}.

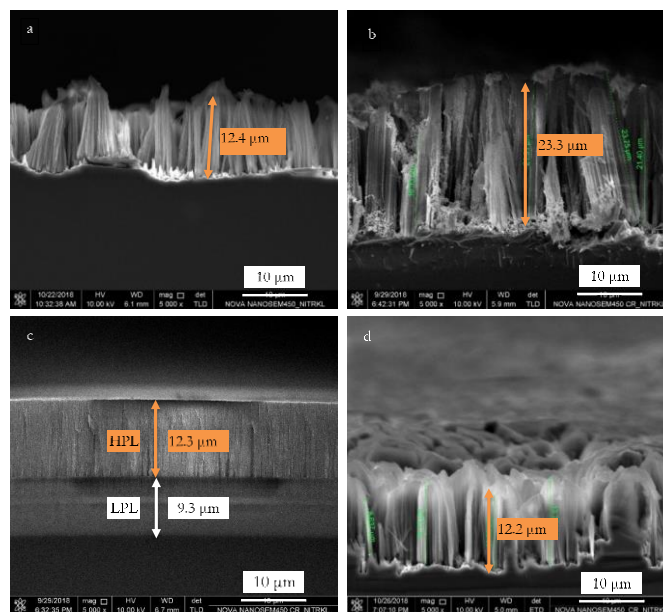


Figure 4. Cross-sectional FESEM images of etched-Si using (a) Si+M_I, (b) Si+M_{II}, (c) PSi+M_I and (d) PSi+M_{II}.

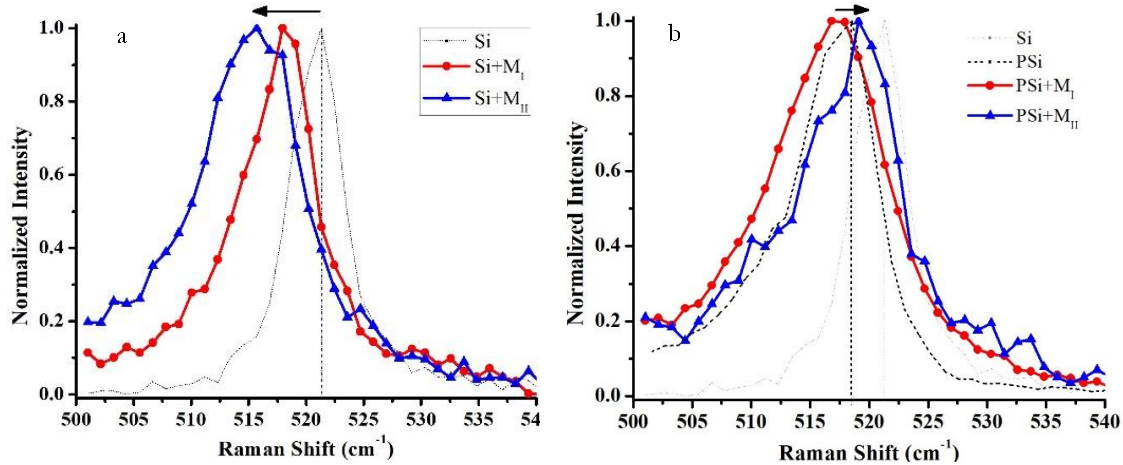


Figure 5. Raman peak shift of etched-Si fabricated by M_I and M_{II} using (a) Si and (b) PSi substrate.

Table 1 summarizes the crystallinity of the Si-, PSi-substrate, and etched-Si. The MACE produces SiNWs having higher crystallinity using Si substrate compared to that of the PSi substrate because the PSi consists of a larger surface area leading to the formation of an amorphous SiO_x layer. Therefore, the SiNWs fabricated using Si substrate finds suitable applications in the solar cell. The HRTEM and Raman characterization show the fabricated SiNWs, using the PSi substrate, consists of crystalline and amorphous phases. Controlling the amorphous phase of the SiNWs, using the PSi substrate, is a low-cost and highly efficient technique for LIB.

Table 1. Observed length, tensile strain (ξ), and crystallinity (ρ_c) of etched-Si fabricated from M_I and M_{II} using Si- and PSi-substrate.

Sample	Length of etched-Si (μm)	ξ (%)	ρ_c (%)
c-Si substrate	-	0	99.999
Si+ M_I	12.4 ± 0.2	0.17	70.92
Si+ M_{II}	23.3 ± 0.3	1.00	84.91
PSi substrate	$13.5 \pm 0.3^*$	0.43	74.66
PSi+ M_I	$21.6 \pm 0.1^{**}$	1.12	82.46
PSi+ M_{II}	12.2 ± 0.2	0.32	64.21

*Thickness to PSi; **Total thickness (HPL + LPL = $12.3 + 9.3$) of etched Si

A sessile water drop contact-angle technique measures the contact angle of etched-Si using the Cassie model [43], as shown in Fig. 6. After the fabrication of SiNWs by MACE, Ag nanoparticles stay in between the NWs, which should be removed by HNO_3 ; however, surface tension disallows the HNO_3 to penetrate the holes between the NWs to

clean the Ag nanoparticles [44]. The remaining Ag nanoparticles may act as functionalization of the surface, i.e., exhibiting low surface energy and chemical affinity that increases the wetting and adhesion property of SiNWs surface [45, 46]. The surface becomes superhydrophobic, i.e., contact angle $> 150^\circ$, after the formation of SiNWs/etched-Si because the water droplet sits on the tip of the SiNWs/etched Si. Lai et al. [47] reported that a higher length of the SiNWs exhibits a higher contact angle. Though the length and crystallinity of the SiNWs fabricated using Si+ M_I combination is lower. However, the lower strain on the SiNWs decreases the surface energy, which helps to achieve the highest contact angle (169.1°). The amorphous phase of the SiNWs fabricated using the PSi substrate may affect the surface energy as well as hydrophobicity due to which PSi+ M_{II} combination exhibits the lowest contact angle (157.2°). However, superhydrophobicity remains in the fabricated SiNWs.

The top of the etched-Si (i.e., front surface) and the back surface of the Si substrate are covered with 10 nm thick thermally evaporated aluminum (Al) contact, as shown in Fig. 7, to perform I-V measurement. The I-V measurement was carried out in a dark room at room temperature. Current flows through the etched-Si structure when subjected to an external supply voltage (V) ranging from -5 V to 5 V with a step size of 0.1 V.

The I-V characteristics of etched-Si fabricated using the four combinations of the applied bias are described, in across mode (i.e., V_{across}), as shown in Fig. 8 and surficial mode (i.e., V_{surface}), as shown in Fig. 9. All the I-V curves correspond to NWs, or



etched-Si show a diode-like behavior with rectifying nature. The I-V curve shows the exact result for any particular sample while taking several observations on different areas of the metal contacts, which explains the uniformity of the junctions. Reproducibility on electrical results is advantageous while fabricating other devices. Therefore, one advantage of using MACE is to get uniformity and reproducibility.

Reports [48, 49] suggest that the I-V curve of SiNWs is non-linear (i.e., diode-like behavior), indicating non-ohmic contact, which is due to two Schottky barriers connected back to back at the metal contacts [50], as shown in Fig. 7 (a). However, other reports [51–53] describes that the Al/SiNWs junction controls the non-linear I-V behavior and the rectifying nature since the Si/Al junction is ohmic. One reason for the rectifying behavior is due to the depletion region formed in the Al/SiNWs junction when electron flows from Al to SiNWs, leading to negative type SiNWs concerning Si. Another possible reason for the rectifying behavior is because of the QCE that increases the bandgap in the SiNWs side, causing potential barriers [53–55]. The shape of the nonlinearity depends on the Schottky barrier height. Biasing the SiNWs with low voltage, few electrons can overcome the barrier height resulting in low current. The I-V curve becomes linear after applying a higher bias voltage [56]. The I-V curves are linear for the etched-Si, fabricated from Si+M_{II} and PSi+M_I combinations, as shown in Fig. 8, and that from Si+M_I and PSi+M_I combinations, as shown in Fig. 9. The formation/dominant nature of the ohmic contacts is one of the reasons for the linear I-V curve at any bias level. A higher current flows through a larger diameter of SiNWs compared to that of a smaller

diameter of SiNWs for the same value of externally applied bias voltage [57]. The I-V characteristics of the etched-Si formed using PSi+M_I clearly shows a deviation because of the HPL and LPL formation, as shown in Fig. 7 (b). The current may flow through the HPL, LPL, and PSi substrate, as marked in green color, when subjected to V_{across} ; however, current flows only through the HPL when V_{surface} is applied, as marked in red color in Fig. 7 (b). The pores in the HPL and LPL create a high resistive path due to which, at lower supply voltage, the current profile is nearly flat. The I-V characteristics of SiNWs fabricated using PSi+M_{II} combination shows a small amount of current flow (in pico-ampere range) for both types of the supplied voltage source (i.e., V_{across} , and V_{surface}), as shown in the inset of Fig. 8 (b) and Fig. 9 (b), because of poly c-Si (as described in Fig. 3 b), higher amorphous phase (i.e., a-Si, as described in Fig. 3 d), and SiO_x layer (as described in Fig. 3 g) that increases the resistivity further compared to PSi.

The SiNWs thus formed consist of nanocrystals of Si, especially Si QDs, on the surface, which finds a wide application in various fields, majorly in the solar cell. The use of SiNWs, along with QDs in the fabrication of solar cells, overcomes the measure problem of the static and indirect bandgap of Si. The Si QDs on the 1-D structure of SiNWs make the Si to be used as a direct bandgap semiconductor, which can also be used in optoelectronic devices. Engineering on the diameter of SiNWs or/and QDs size can tune the bandgap according to requirements; therefore, a vast area of research is still open to optimize the solar cell performance.

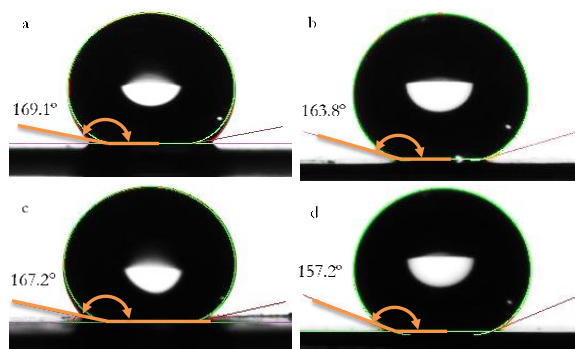


Figure 6. Contact angle measurement of etched-Si using (a) Si+M_I, (b) Si+M_{II}, (c) PSi+M_I, and (d) PSi+M_{II}.

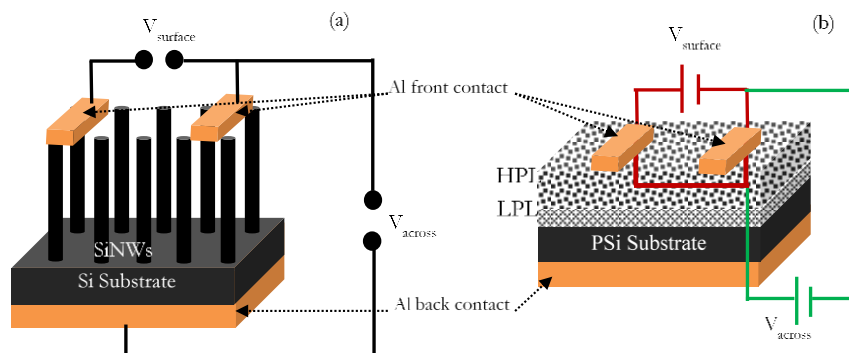


Figure 7. Schematic of I-V measurement of (a) SiNWs (b) HPL and LPL.

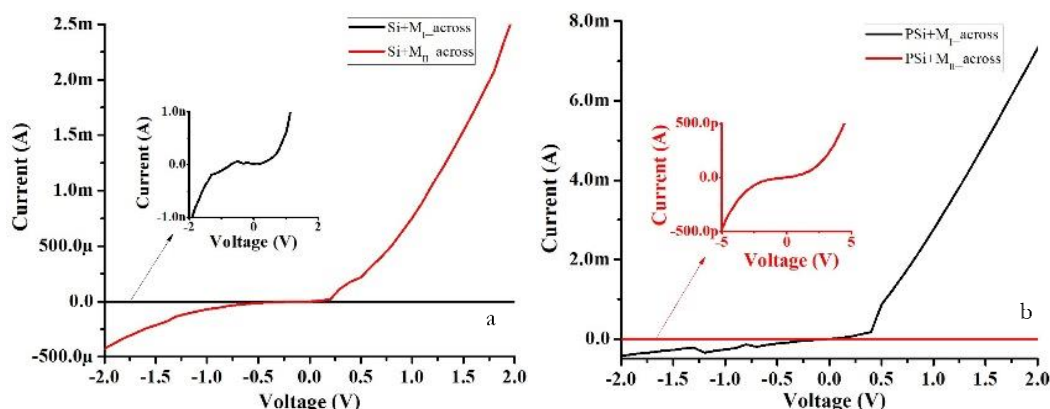


Figure 8. I-V measurement of etched-Si for biasing the sample by V_{across} in (a) Si and (b) PSi substrate.

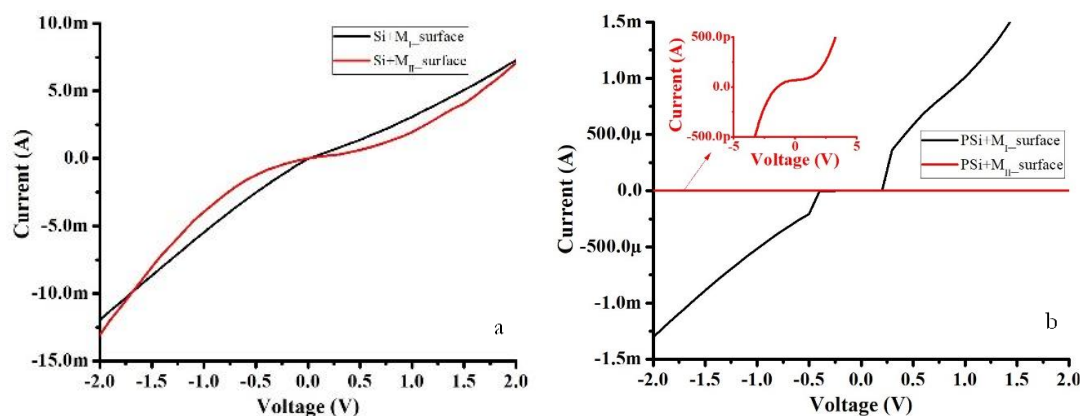


Figure 9. I-V measurement of etched-Si for biasing the sample by $V_{surface}$ in (a) Si and (b) PSi substrate.

4. Conclusions

The FESEM images confirm the fabrication of the SiNWs using various combinations of substrates and methods, i.e., Si+M_I, Si+M_{II}, and PSi+M_{II}; whereas PSi+M_I produces etched-Si of HPL and LPL. The MACE produces the highest length of the SiNWs (23.3 μm) using Si substrate in the 'Si+M_{II}' combination, which is suitable in solar

cell application. The Raman peak shift and line broadening are due to quantum confinement effect (i.e., QDs), strain (~ 0.17 - 1.12%), and amorphous phase (~ 15 - 35%) in SiNWs. The PSi substrate in PSi+M_{II} combination gives rise to the highest amorphous phase in the SiNWs, which finds suitable application in LIB due to porous SiNWs core and a-Si shell structure.



The amorphous oxide layer should be avoided by carrying the etching process in an inert environment. The contact angle measurement confirms the superhydrophobic surface of the etched-Si. The I-V characteristic of SiNWs is non-linear (i.e., diode-like behavior) due to the

Schottky barrier contacts at the metal-Si junctions. In the core-shell structure of porous SiNWs fabricated using P_{Si}+M_{II} combination, the formation of poly c-Si core, a-Si shell, and outer oxide layer allows lower current (in pico-ampere range) to pass through the NWs.

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Conflicts of Interest

The authors declare no conflict of interest.

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