

Supporting Information

Surface and Electronic Properties of Hydrogen Terminated Si [001] Nanowires

Yuki Matsuda[†], Jamil Tahir-Kheli[†], and William A. Goddard III^{†#}

[†]*Materials and Process Simulation Center, California Institute of Technology, California 91125*

[#]*Graduate School of EEWS (WCU), Korea Advanced Inst. Science Technology, Daejeon, Korea;*

Table S1. Diameter, H/Si ratio, Component, Dimer Si atoms and Dangling-Bonds of Optimized H–SiNW structures

diameter (nm)	Si	H	H/Si ratio ^a	E_h /Si atom ^b (kcal/mol)	dimer Si ^c	dangling bond ^d
1.0	21	20	1.00	2.36	0	0
	21	16	0.80	5.54	4	0
	21	12	0.60	11.02	4	4
1.3	37	28	1.00	2.17	0	0
	37	24	0.86	3.83	4	0
	37	20	0.71	5.70	8	0
	37	16	0.57	5.32	8	4
1.6	52	32	1.00	1.67	0	0
	52	24	0.75	1.89	8	0
	52	20	0.63	2.76	8	4
1.9	76	40	1.00	1.53	0	0
	76	32	0.80	3.19	0	4
	76	28	0.70	1.61	12	0
	76	24	0.60	1.95	12	4
	76	22	0.55	3.81	12	6
2.5	129	52	1.00	1.20	0	0
	129	44	0.85	1.14	8	0
	129	36	0.69	1.26	16	0
	129	32	0.62	0.86	16	4
	129	28	0.54	1.54	16	8
	129	24	0.46	2.30	16	12
3.1	196	64	1.00	1.00	0	0
	196	56	0.88	2.10	0	8
	196	44	0.69	1.01	20	0
	196	42	0.66	0.07	20	2
	196	40	0.63	0.11	22	3
	196	32	0.50	1.11	22	11

^a We rescale the H/Si ratio for each diameter so that the fully saturated case has H/Si = 1.

^b Heat of formation energy referred to the Si bulk and hydrogen molecule per Si atom.

^c Number of reconstructed Si atoms.

^d Number of dangling-bond defects.

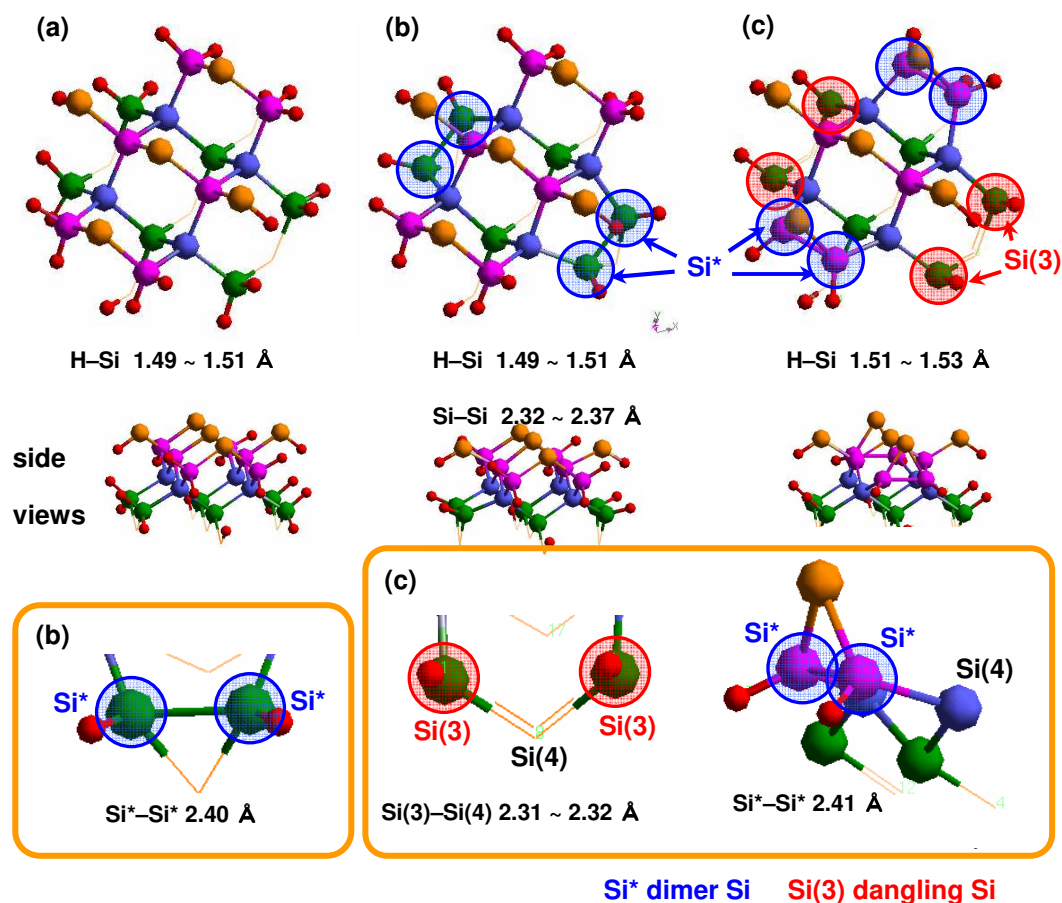


Figure S1. Detailed geometries of the optimized H-SiNW structures with $d = 1.0$ nm.

(a) $H/Si = 1.00$, $Si_{21}H_{20}$, fully saturated. No reconstructed Si atoms. All Si atoms are 4-coordinate.

(b) $H/Si = 0.80$, $Si_{21}H_{16}$. Four reconstructed Si atoms per unit cell. No dangling bonds.

(c) $H/Si = 0.60$, $Si_{21}H_{12}$. Four reconstructed Si atoms and four dangling bonds per unit cell. Geometry is highly distorted (Si-Si distance has large variation).

Heats of formation are (a) 49.5 kcal/mol, (b) 116.4 kcal/mol, and (c) 231.5 kcal/mol as referred to Si crystal and H_2 .

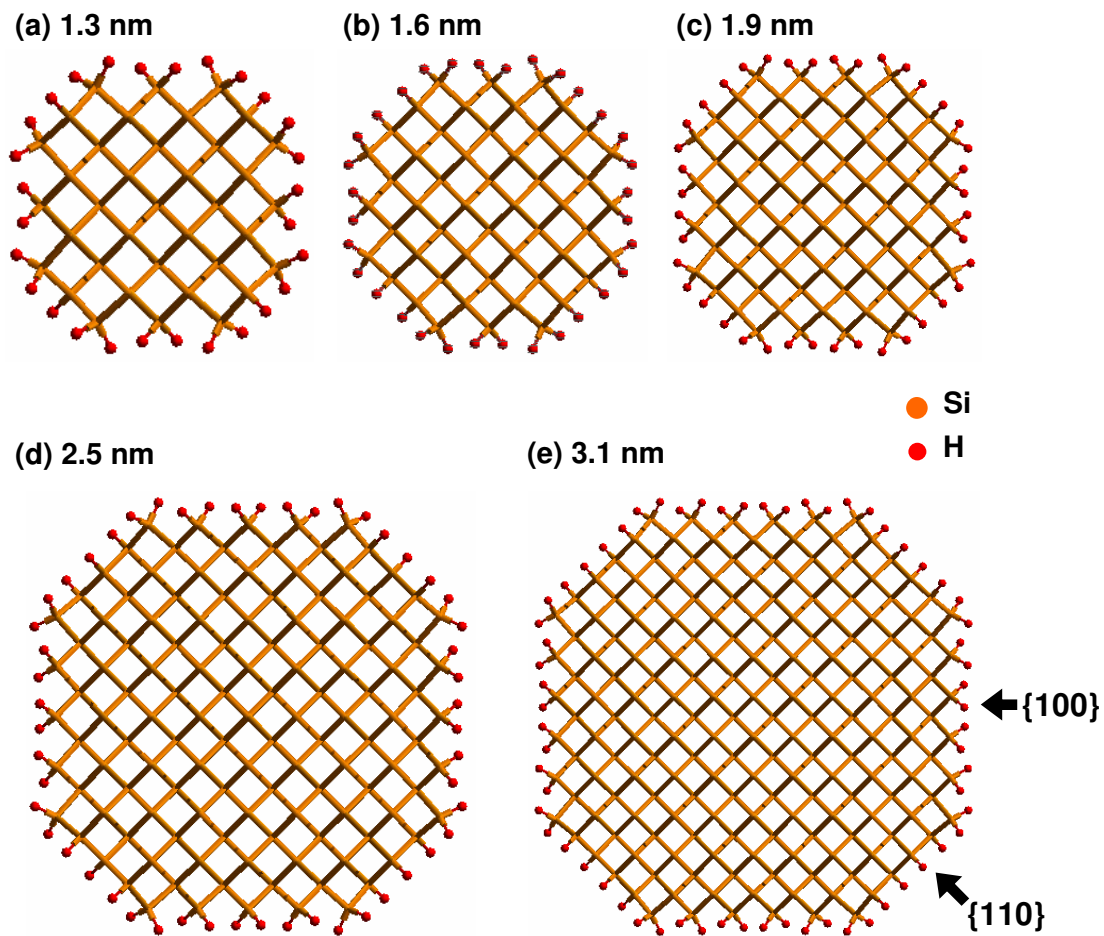


Figure S2. Cross section views of the saturated H-SiNWs ($H/Si = 1$) with diameters of (a) 1.3 nm ($Si_{37}H_{28}$), (b) 1.6 nm ($Si_{52}H_{32}$), (c) 1.9 nm ($Si_{76}H_{40}$), (d) 2.5 nm ($Si_{129}H_{52}$), and (e) 3.1 nm ($Si_{196}H_{64}$).

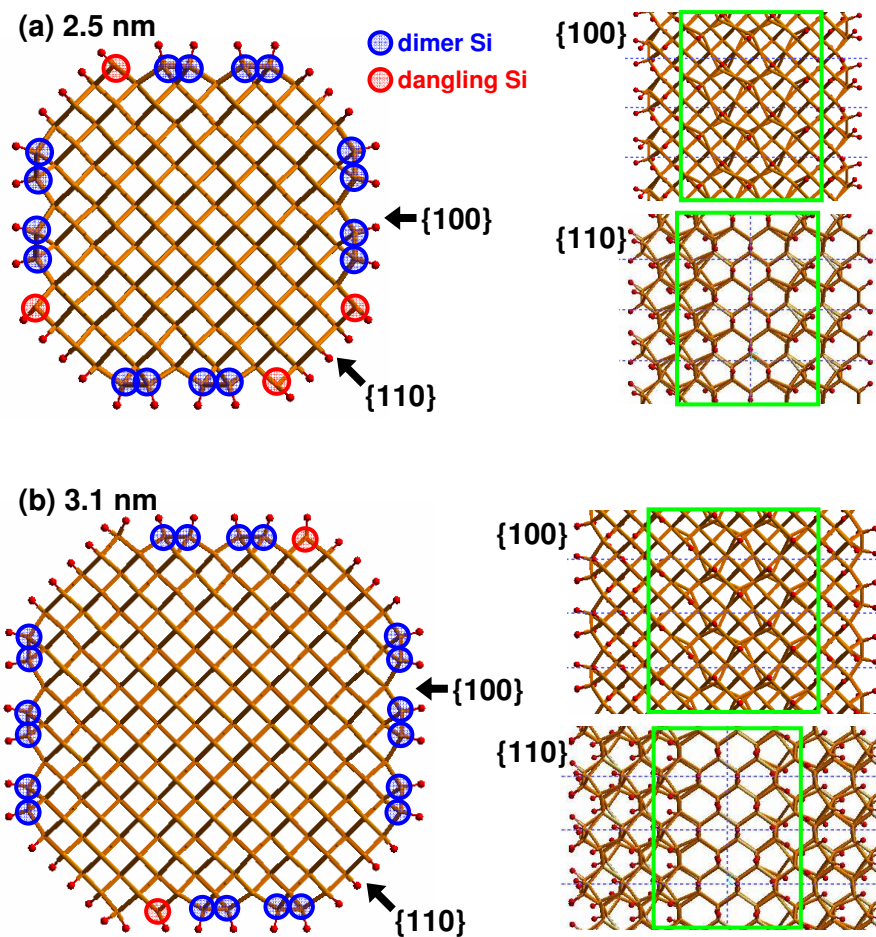


Figure S3. Cross section and side views ($\{100\}$ and $\{110\}$ surfaces) of the unsaturated H-SiNW models with diameters of (a) 2.5 nm ($H/Si = 0.62$, $Si_{129}H_{32}$), and (b) 3.1 nm ($H/Si = 0.66$, $Si_{196}H_{42}$), which equilibrium structures of the same diameter.

Dimer Si atoms are shown with blue circles and dangling Si atoms are shown with red circles on the $\{100\}$ surface. The four $\{110\}$ surfaces show saturated hydrogen coverage.

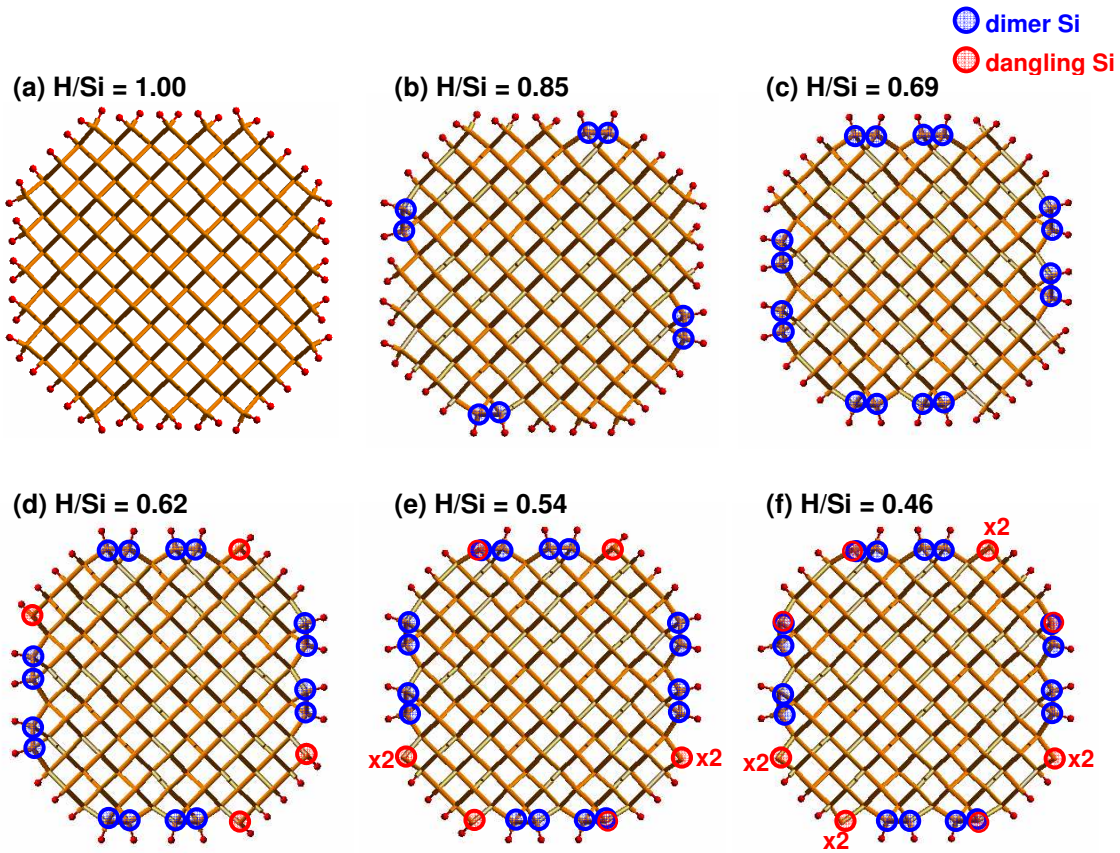


Figure S4. Cross section views of the H-SiNW models with $d = 2.5$ nm. H/Si ratio = (a) 1.00 (saturated), $\text{Si}_{129}\text{H}_{52}$, (b) 0.85, $\text{Si}_{129}\text{H}_{44}$, (c) 0.69, $\text{Si}_{129}\text{H}_{43}$, (d) 0.62, $\text{Si}_{129}\text{H}_{32}$, (e) 0.54, $\text{Si}_{129}\text{H}_{28}$, and (f) 0.46, $\text{Si}_{129}\text{H}_{24}$.

Dimer Si atoms are shown with blue circles and dangling Si atoms are shown with red circles on the $\{100\}$ surface. 'x2' expresses two dangling bonds per Si atom. The four $\{110\}$ surfaces show saturated hydrogen coverage.

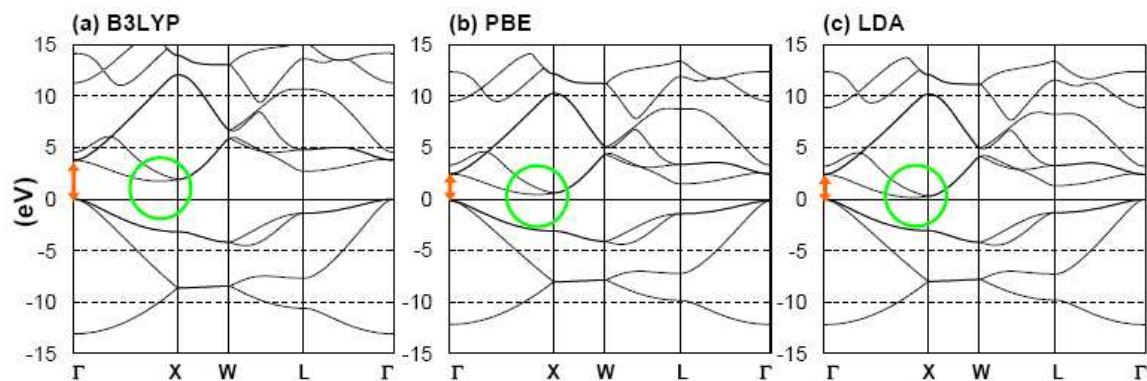


Figure S5. Band structures of Si crystal calculated using (a) B3LYP, (b) PBE, and (c) LDA. The VBM is set at 0 eV for comparison. The direct band gaps at Γ are shown with an orange arrow and the CBM is shown with a green circle. The position of the CBM is approximately 82 % for B3LYP and 85 % for PBE and LDA from Γ to X. The calculated band gaps are given in Table 1.

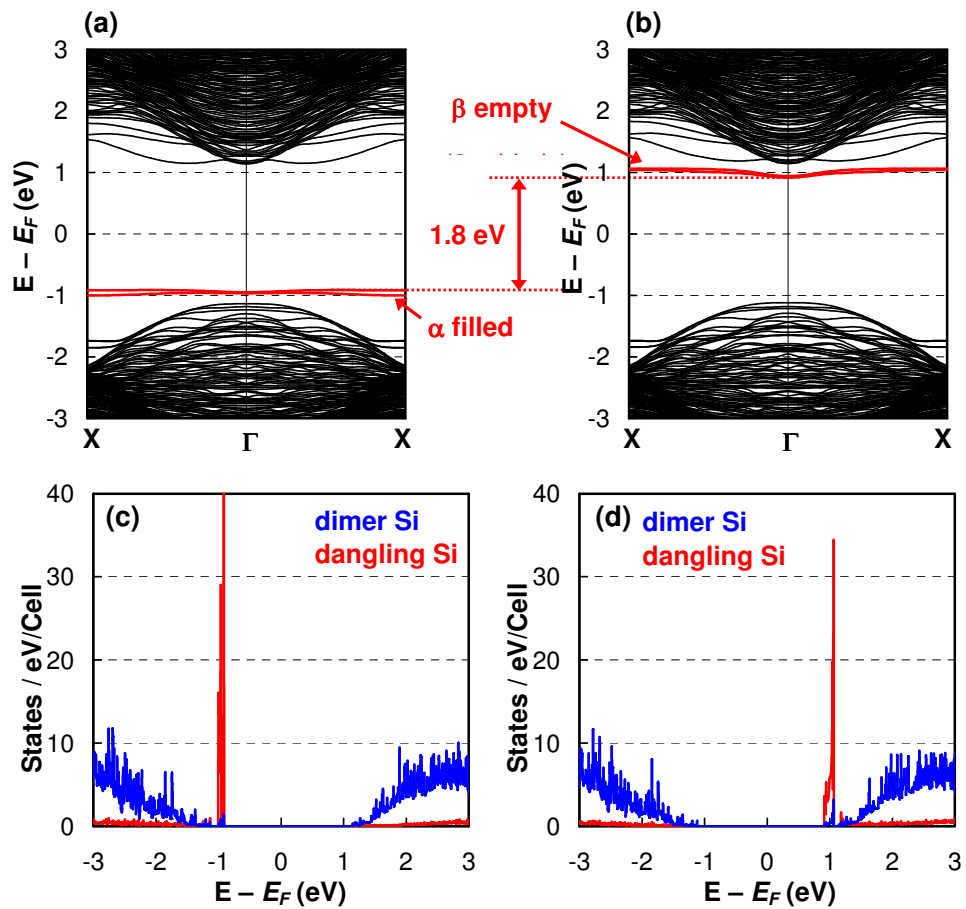


Figure S6. Band structures of unsaturated H-SiNW with $d = 2.5$ nm ($\text{Si}_{129}\text{H}_{32}$) using UB3LYP. (a) α electrons and (b) β electrons. Partial density of states of Si atoms (per unit cell) of (c) α and (d) β electrons (blue; dimer Si atoms, red; dangling Si atoms). We find that the four dangling bond Si atoms lead to new LUMO and HOMO states in the band gap.

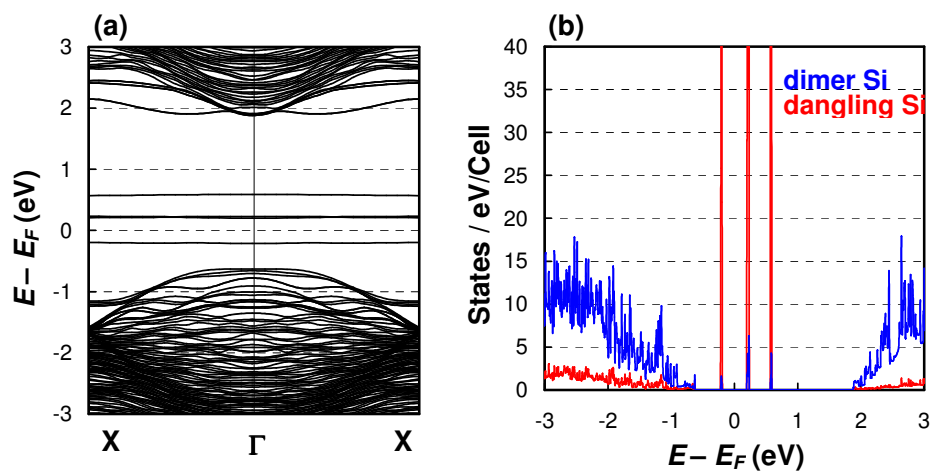


Figure S7. (a) Band structures of unsaturated H-SiNW with $d = 2.5$ nm ($\text{Si}_{129}\text{H}_{32}$) using RB3LYP. (b) Partial density of states of the Si atoms (per unit cell) of (blue; dimer Si atoms, red; dangling Si atoms).

Note that the band gap is 0.39 eV, which is 1.3 eV smaller than the UB3LYP calculation shown in Figure S5. The total energetic from the single point energy calculation by RB3LYP shows 1.5 eV higher than that of UB3LYP (Figure S6).