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Supplementary Information

Chemical Vapor Etching of Silicon Wafer for the Synthesis of Highly Dense and Aligned sub-5 nm Silicon Nanowires Array

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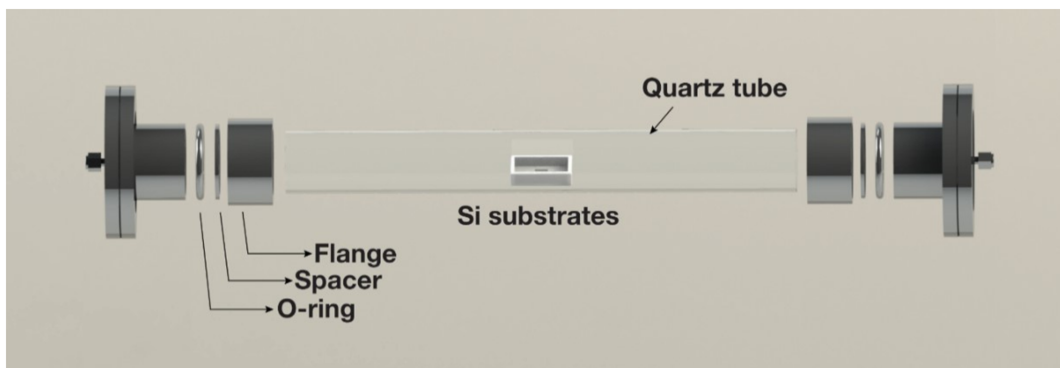


Fig. S1 Schematic illustration showing the setup of CVE reactor. Two spacers and Viton gaskets were used for sealing. When the new quartz tube was installed in the CVE system, the two Viton gasket were also replaced to new one.

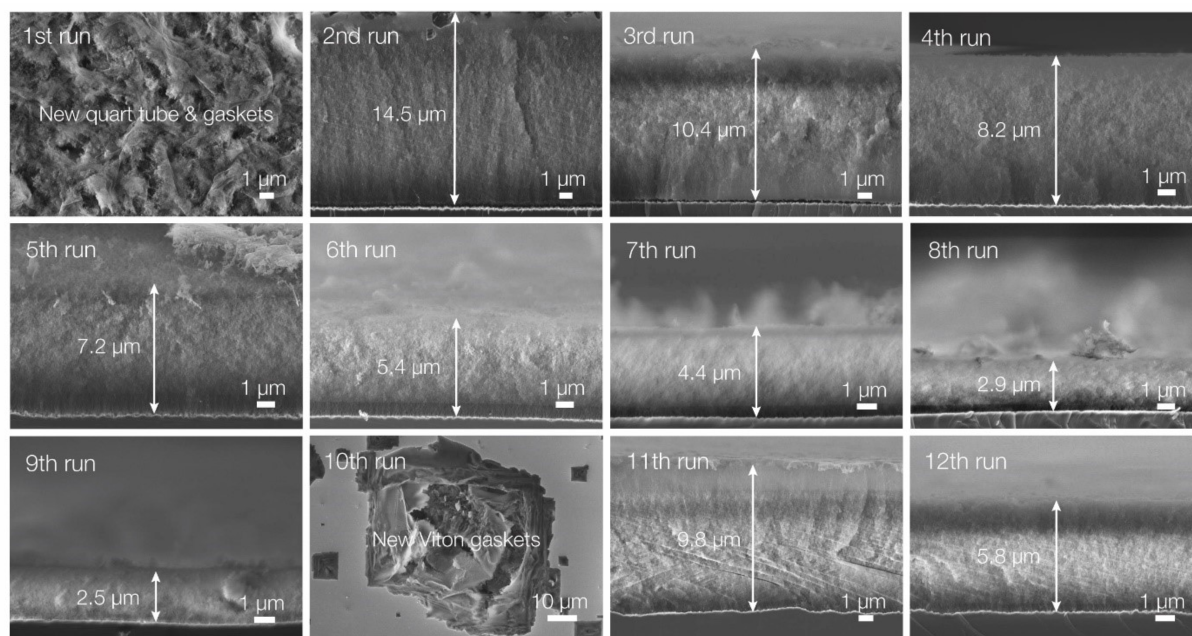


Fig. S2 Top-view and cross-sectional SEM images showing the changes in the morphologies and lengths of SiNW arrays under different CVE runs (1st-12th) after the installation of a new quartz tube and Viton gaskets. Except for the top-view SEM images after 1st and 10th run, all other images show the cross-sectional view of as-synthesized SiNWs.

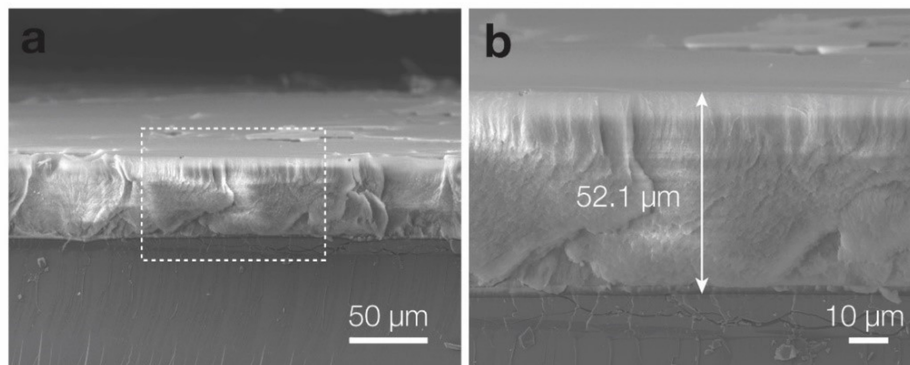


Fig. S3 (a) Cross-sectional SEM image of the SiNW arrays formed with the addition of 2 Viton O-rings. (b) Enlarged SEM image along the white dashed line in (a), showing the nanowire length of 52.1 μm.

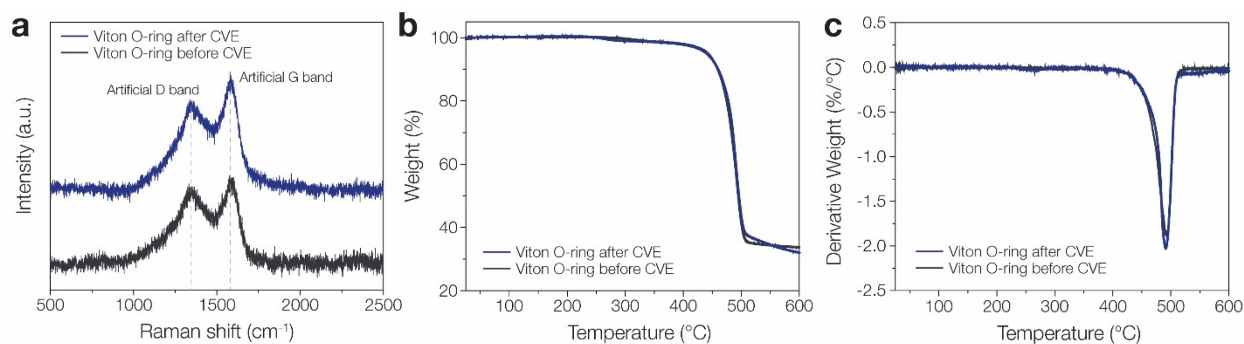


Fig. S4 (a) Raman spectra, (b) TGA profiles, and (c) derivative thermogravimetric analysis (DTG) curves of Viton O-ring before and after the chemical vapor etching of silicon, showing no obvious peak change after reaction.[1]

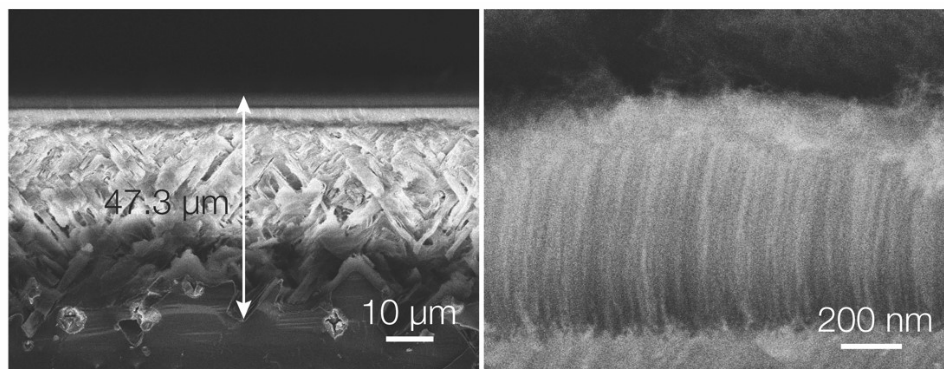


Fig. S5 Cross-sectional SEM images of the SiNWs grown with the addition of 1/8 fluorine-free silicone O-ring.

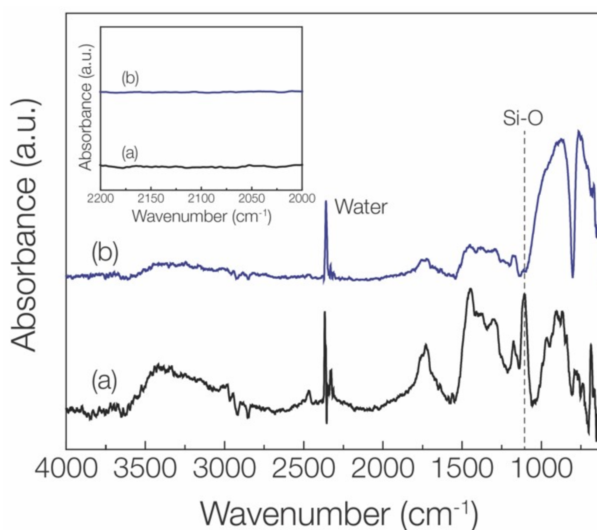


Fig. S6 FTIR spectra of (a) bare Si substrate and (b) heated Si substrate at 1150 °C for 1 h under the hydrogen flow without $SiCl_4$ supply. The inset shows the expanded Si–H stretch region ranging from 2000 cm^{-1} to 2200 cm^{-1}. No Si-H groups were observed at wavenumber around 2100 cm^{-1}.[2-5] The Si-O peak at around 1100 cm^{-1} was found to decrease after 1 h heating, which indicated the thermal decomposition of silicon suboxide layer without Si surface hydrogenation.[6,7]

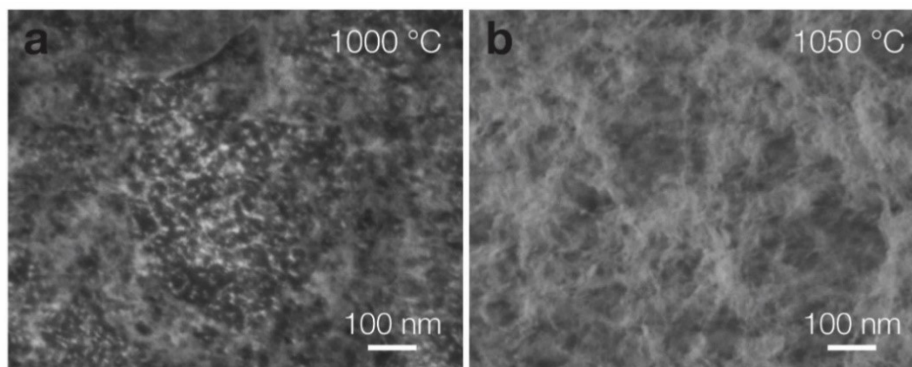


Fig. S7 Planar view of the SiNWs formed at the temperature of (a) 1000 ˚C and (b) 1050 ˚C without the addition of the O-ring.

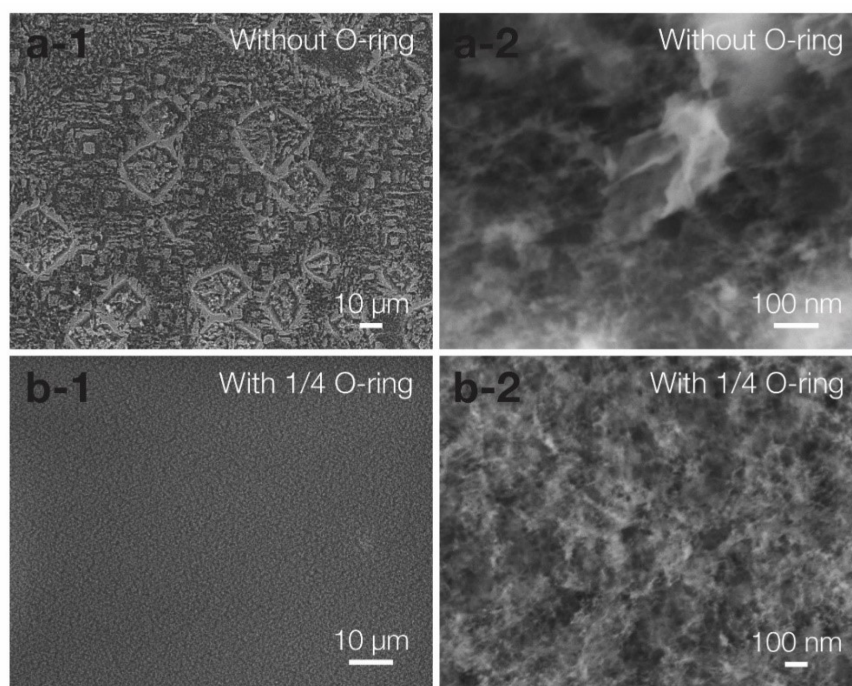


Fig. S8 Top-view SEM images of (100) Si substrate etched in ultra-high purity Ar gas atmosphere (a) without and (b) with 1/4 O-ring addition.

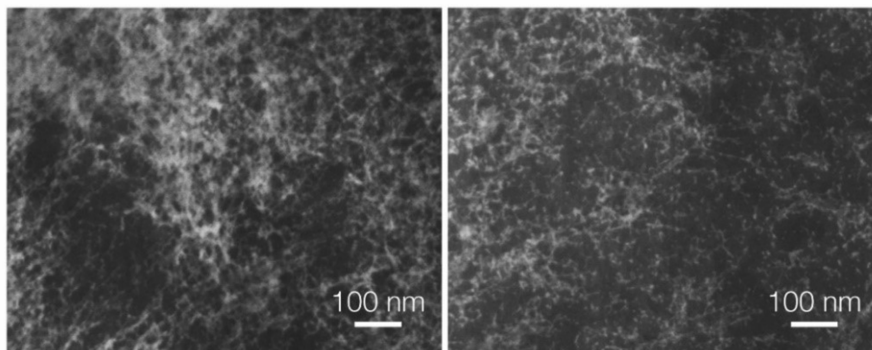


Fig. S9 Planar view of (100) Si substrate etched with 20% H_2/Ar gas.

Table S1 Comparison of the equilibrium composition before and after mixing 10% H_2/Ar gas with $SiCl_4$ through bubbling at 25 °C.

	H_2 (g)	**Ar (g)**	**O_2 (g)**	**$SiCl_4$ (g)**	**SiO_2 (s)**
Before bubbling	9.00	1.00	1.00E-4	7.00	0.00
After bubbling	9.00	1.00	3.56E-22	7.00	1.00E-4

*We conducted the thermodynamic analysis on the equilibrium composition before and after mixing 10% H_2/Ar gas with $SiCl_4$ by bubbling. We assumed that the concentration oxygen concentration is 10 ppm in 10% H_2/Ar gas at 25 °C before bubbling, considering the amount of oxidant gases in 10% H_2 balanced Ar gas (99.995%, $O_2 < 4$ ppm, $H_2O < 3$ ppm, Airgas USA, LLC) is less than 7 ppm. As shown in Table S1, 10 ppm O_2 in the H_2-Ar mixture reacts with $SiCl_4$ to form SiO_2 of 1.00E-4 mol by bubbling, leaving 3.56E-22 mol O_2 in the mixture gas. This implies that the $SiCl_4$-H_2-Ar gas mixture contains negligible amounts of oxidant gases after bubbling. Thus, we assume that the primary source of the oxidant gases is the residual air, adsorbed inside the reaction system after creating a vacuum at around 50–60 mTorr.

Table S2 Summary of the calculated surface areas and the corresponding concentration of oxidant gas for different amounts of O-ring.

	Amount of O-ring							
	$^{1}/_{32}$	**$^{1}/_{16}$**	**$^{1}/_{8}$**	**$^{1}/_{4}$**	**$^{1}/_{2}$**	**$^{3}/_{4}$**	**1**	**2**
Surface area (cm^2)	2.9	4.0	6.2	10.5	19.3	27.2	36.8	73.7
Oxidant gas concentration (ppm)	0.14	0.19	0.29	0.49	0.91	1.28	1.78	3.46

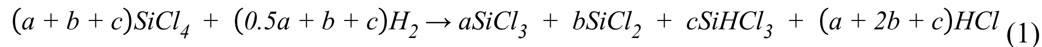
*The steady-state outgassing rate of Viton O-ring after multiple runs is calculated to be 2×10^{-8} Torr·liter·$cm^{-1}\cdot s^{-1}$ (i.e., 1.6×10^{-6} sccm) at operating temperature (180 ˚C), and the concentration of oxidant gases from outgassing is estimated to be 0.047 ppm. By multiplying it by the surface area of different amounts of O-ring, corresponding oxidant gas concentration is evaluated.

Table S3 Summary of the calculated interplanar distance of {111} plane, lattice parameter, and lattice contraction of the silicon nanowires formed with the different amounts of O-ring.

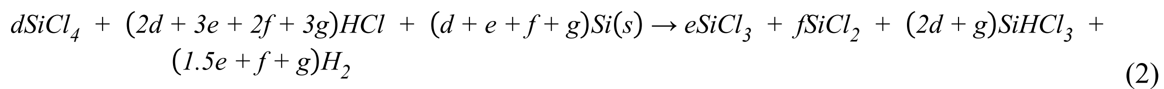
Amount of O-ring	d_{111} spacing (Å)	Lattice parameter (Å)	Lattice contraction (%)	Average contraction (%)
¼ O-ring	2.54	4.40	19.04	18.35
	2.56	4.44	18.32	
	2.59	4.48	17.47	
	2.54	4.40	18.94	
	2.57	4.45	18.00	
½ O-ring	2.59	4.48	17.47	17.75
	2.57	4.46	17.89	
	2.57	4.46	17.89	
	2.59	4.48	17.47	
	2.57	4.45	18.00	
1 O-ring	2.57	4.45	18.00	18.01
	2.58	4.47	17.68	
	2.59	4.48	17.47	
	2.53	4.37	19.45	
	2.59	4.48	17.47	

Thermodynamical analysis

We performed the thermodynamic analysis on the equilibrium composition before and after the CVE etching using FactSage thermochemical software. The equilibrium calculations were conducted as a function of the input ratios for the following components: $SiCl_4$, $SiCl_3$, $SiCl_2$, SiCl, SiH, SiH_4, Si_2H_6, $SiHCl_3$, SiH_2Cl_2, SiH_3Cl, Cl_2, Cl, H_2, H, HCl, Si_3, Si_2, and Si for the $SiCl_4$-H_2 system, and Table S4 tabulates the thermodynamical data for 16 basic reactions involved in the equilibrium at 1150 ˚C.[8,9] The system is estimated with the following conditions: (1) the total pressure in the system remains to be 1 atm, (2) the ratio $SiCl_4/H_2$ is determined by the input ratio $SiCl_4/H_2$, which is 7:1. The initial amounts of substance (in mole) for $SiCl_4$, H_2, Ar and Si (s) are set to be 7, 1, 9, and 2 under 10% H_2/Ar gas atmosphere. The number for H_2 varies from 0 to 5 based on the H_2 concentration (0%, 0.1%, 1%, 2%, 5%, 10%, 20%, and 50%). The equilibrium partial pressure before and after Si etching is calculated at different reaction temperatures (1000 ˚C, 1050 ˚C, 1100 ˚C, and 1150 ˚C) with different hydrogen input ratios (0%, 0.1%, 1%, 2%, 5%, 10%, 20%, and 50%), and the detailed values are summarized in Tables S5-15. Table 1 tabulates the equilibrium partial pressure of primary reactants and products at 1150 ˚C. It shows that the supplied $SiCl_4$ and H_2 gases react with each other and form compounds, such as HCl, $SiCl_3$, $SiCl_2$, and $SiHCl_3$, before reaching the surface of the Si substrate. Upon encountering the Si substrate, the chemical etching reaction occurs concomitantly with the re-establishment of thermodynamic equilibrium. The partial pressure of $SiCl_4$ and HCl have decreased (or have been consumed), while the partial pressure of $SiCl_3$, $SiCl_2$, $SiHCl_3$, and H_2 have increased (or have been generated) during the Si etching reaction. Based on these results, the dominating Si etching reaction can be expressed as follows[10]:



$$(a+b+c)SiCl_4 + (0.5a+b+c)H_2 \rightarrow aSiCl_3 + bSiCl_2 + cSiHCl_3 + (a+2b+c)HCl \quad (1)$$



$$dSiCl_4 + (2d+3e+2f+3g)HCl + (d+e+f+g)Si(s) \rightarrow eSiCl_3 + fSiCl_2 + (2d+g)SiHCl_3 + (1.5e+f+g)H_2 \quad (2)$$

, where a-g are the coefficients for the dominating reactants and products. Here, we identify the major reactant and reaction products in the Si etching process as follows: $SiCl_4$ and HCl are the major etchants; $SiCl_3$, $SiCl_2$, $SiHCl_3$, and H_2 are the major products. In the presence of H_2 gas, another important etchant, HCl, is generated by the reaction of $SiCl_4$ with H_2 in the first place.

Table S4 The logarithm of the equilibrium constants of the Si-H-Cl system at different temperatures (1000 °C, 1050 °C, 1100 °C, and 1150 °C).

Component	Formation Reaction	Equilibrium Constant	$\log_{10}K_n$			
			1000 °C	1050 °C	1100 °C	1150 °C
$SiCl_4$	$Si\ (s) + 2Cl_2 \rightleftharpoons SiCl_4$	$K_1 = p_{SiCl4}p^{-2}_{Cl2}$	18.507	18.270	18.032	17.796
$SiCl_3$	$Si\ (s) + 3/2Cl_2 \rightleftharpoons SiCl_3$	$K_2 = p_{SiCl3}p^{-3/2}_{Cl2}$	12.895	12.829	12.763	12.697
$SiCl_2$	$Si\ (s) + Cl_2 \rightleftharpoons SiCl_2$	$K_3 = p_{SiCl2}p^{-1}_{Cl2}$	8.026	8.086	8.146	8.205
$SiCl$	$Si\ (s) + 1/2Cl_2 \rightleftharpoons SiCl$	$K_4 = p_{SiCl}p^{-1/2}_{Cl2}$	-2.440	-2.254	-2.069	-1.885
SiH	$Si\ (s) + 1/2H_2 \rightleftharpoons SiH$	$K_5 = p_{SiH}p^{-1/2}_{H2}$	-8.869	-8.676	-8.484	-8.292
SiH_4	$Si\ (s) + 2H_2 \rightleftharpoons SiH_4$	$K_6 = p_{SiH4}p^{-2}_{H2}$	-5.562	-5.747	-5.931	-6.116
Si_2H_6	$2Si\ (s) + 3H_2 \rightleftharpoons Si_2H_6$	$K_7 = p_{Si2H6}p^{-3}_{H2}$	-11.304	-11.647	-11.990	-12.333
$SiHCl_3$	$Si\ (s) + 1/2H_2 + 3/2Cl_2 \rightleftharpoons SiHCl_3$	$K_8 = p_{SiHCl3}p^{-1/2}_{H2}p^{-3/2}_{Cl2}$	13.414	13.213	13.013	12.813
SiH_2Cl_2	$Si\ (s) + H_2 + Cl_2 \rightleftharpoons SiH_2Cl_2$	$K_9 = p_{SiH2Cl2}p^{-1}_{H2}p^{-1}_{Cl2}$	7.539	7.359	7.180	7.000
SiH_3Cl	$Si\ (s) + 3/2H_2 + 1/2Cl_2 \rightleftharpoons SiH_3Cl$	$K_{10} = p_{SiH3Cl}p^{-3/2}_{H2}p^{-1/2}_{Cl2}$	1.161	0.987	0.813	0.639
Cl	$1/2Cl_2 \rightleftharpoons Cl$	$K_{11} = p_{Cl}p^{-1/2}_{Cl2}$	-1.832	-1.721	-1.609	-1.497
H	$1/2H_2 \rightleftharpoons H$	$K_{12} = p_{H}p^{-1/2}_{H2}$	-5.591	-5.482	-5.373	-5.264
HCl	$1/2H_2 + 1/2Cl_2 \rightleftharpoons HCl$	$K_{13} = p_{HCl}p^{-1/2}_{H2}p^{-1/2}_{Cl2}$	3.823	3.834	3.845	3.856
$Si\ (g)$	$Si\ (s) \rightleftharpoons Si\ (g)$	$K_{14} = p_{Si(g)}$	-9.767	-9.496	-9.227	-8.958
$Si_2\ (g)$	$2Si\ (s) \rightleftharpoons Si_2\ (g)$	$K_{15} = p_{Si^2(g)}$	-9.277	-8.731	-8.182	-7.630
$Si_3\ (g)$	$3Si\ (s) \rightleftharpoons Si_3\ (g)$	$K_{16} = p_{Si^3(g)}$	-8.319	-7.639	-6.955	-6.266

Table S5 Equilibrium partial pressures of components in the $SiCl_4$-10% H_2-Si system at 1000 °C.

	Input	Before encountering Si		After encountering Si		
Gas Phase	**Mole**	**Mole**	**Partial pressure**	**Mole**	**Partial pressure**	**Change**
Ar	9	9.000	0.522	9.000	0.519	-
$SiCl_4$	7	6.398	0.371	5.881	0.339	↓
H_2	1	0.549	0.032	0.611	0.035	↑
HCl	0	0.698	0.040	0.325	0.019	↓
$SiCl_3$	0	0.304	0.018	0.636	0.037	↑
$SiCl_2$	0	0.095	0.006	0.451	0.026	↑
$SiHCl_3$	0	0.202	0.012	0.444	0.026	↑
SiH_2Cl_2	0	8.82E-04	5.12E-05	4.64E-03	2.67E-04	↑
Cl	0	2.36E-06	1.37E-07	1.04E-06	6.02E-08	↓
H	0	2.19E-06	1.27E-07	2.31E-06	1.33E-07	↑
SiH_3Cl	0	1.08E-06	6.24E-08	1.35E-05	7.79E-07	↑
SiCl	0	2.07E-08	1.20E-09	2.24E-07	1.29E-08	↑
Cl_2	0	3.46E-09	2.00E-10	6.73E-10	3.88E-11	↓
SiH_4	0	5.47E-10	3.17E-11	1.64E-08	9.47E-10	↑
SiH	0	2.22E-11	1.29E-12	5.74E-10	3.31E-11	↑
Si (g)	0	1.28E-11	7.44E-13	3.15E-10	1.82E-11	↑
Si_2 (g)	0	4.26E-16	2.47E-17	2.56E-13	1.47E-14	↑
Si_3 (g)	0	3.03E-18	1.75E-19	4.43E-14	2.55E-15	↑
Si_2H_6	0	3.46E-19	2.00E-20	2.80E-16	1.62E-17	↑
Total	17	17.247	1.000	17.353	1.000	-
Si (s)	2	2	-	1.583	-	-

Table S6 Equilibrium partial pressures of components in the $SiCl_4$-10% H_2-Si system at 1050 °C.

	Input	**Before encountering Si**		**After encountering Si**		
Gas Phase	**Mole**	**Mole**	**Partial pressure**	**Mole**	**Partial pressure**	**Change**
Ar	9	9.000	0.519	9.000	0.511	-
$SiCl_4$	7	6.270	0.361	5.544	0.315	↓
H_2	1	0.474	0.027	0.588	0.033	↑
HCl	0	0.877	0.051	0.404	0.023	↓
$SiCl_3$	0	0.410	0.024	0.882	0.050	↑
$SiCl_2$	0	0.147	0.008	0.767	0.044	↑
$SiHCl_3$	0	0.173	0.010	0.411	0.023	↑
SiH_2Cl_2	0	6.82E-04	3.93E-05	4.37E-03	2.48E-04	↑
Cl	0	7.02E-06	4.05E-07	2.93E-06	1.66E-07	↓
H	0	4.53E-06	2.61E-07	5.08E-06	2.89E-07	↑
SiH_3Cl	0	7.61E-07	4.39E-08	1.31E-05	7.45E-07	↑
SiCl	0	6.25E-08	3.60E-09	7.97E-07	4.53E-08	↑
Cl_2	0	1.24E-08	7.16E-10	2.13E-09	1.21E-10	↓
SiH_4	0	3.52E-10	2.03E-11	1.63E-08	9.26E-10	↑
SiH	0	6.18E-11	3.56E-12	2.12E-09	1.20E-10	↑
Si (g)	0	5.07E-11	2.92E-12	1.57E-09	8.93E-11	↑
Si_2 (g)	0	2.10E-15	1.21E-16	1.99E-12	1.13E-13	↑
Si_3 (g)	0	1.38E-17	7.94E-19	3.99E-13	2.27E-14	↑
Si_2H_6	0	1.79E-19	1.03E-20	3.11E-16	1.76E-17	↑
Total	17	17.351	1.000	17.600	1.000	-
Si (s)	2	2	-	1.392	-	-

Table S7 Equilibrium partial pressures of components in the $SiCl_4$-10% H_2-Si system at 1100 °C.

	Input	Before encountering Si		After encountering Si		
Gas Phase	**Mole**	**Mole**	**Partial pressure**	**Mole**	**Partial pressure**	**Change**
Ar	9	9.000	0.515	9.000	0.502	-
$SiCl_4$	7	6.129	0.351	5.100	0.284	↓
H_2	1	0.390	0.022	0.564	0.031	↑
HCl	0	1.079	0.062	0.490	0.027	↓
$SiCl_3$	0	0.524	0.030	1.169	0.065	↑
$SiCl_2$	0	0.207	0.012	1.239	0.069	↑
$SiHCl_3$	0	0.141	0.008	0.373	0.021	↑
SiH_2Cl_2	0	4.78E-04	2.73E-05	4.03E-03	2.25E-04	↑
Cl	0	1.98E-05	1.13E-06	7.59E-06	4.23E-07	↓
H	0	8.66E-06	4.96E-07	1.06E-05	5.89E-07	↑
SiH_3Cl	0	4.64E-07	2.66E-08	1.25E-05	6.96E-07	↑
SiCl	0	1.60E-07	9.17E-09	2.57E-06	1.44E-07	↑
Cl_2	0	4.29E-08	2.46E-09	6.12E-09	3.41E-10	↓
SiH_4	0	1.85E-10	1.06E-11	1.59E-08	8.86E-10	↑
SiH	0	1.39E-10	7.95E-12	7.11E-09	3.96E-10	↑
Si (g)	0	1.62E-10	9.30E-12	7.01E-09	3.91E-10	↑
Si_2 (g)	0	7.42E-15	4.25E-16	1.34E-11	7.49E-13	↑
Si_3 (g)	0	4.04E-17	2.31E-18	3.08E-12	1.71E-13	↑
Si_2H_6	0	6.54E-20	3.74E-21	3.32E-16	1.85E-17	↑
Total	17	17.469	1.000	17.939	1.000	-
Si (s)	2	2	-	1.116	-	-

Table S8 Equilibrium partial pressures of components in the $SiCl_4$-10% H_2-Si system at 1150 °C.

	Input	Before encountering Si		After encountering Si		
Gas Phase	**Mole**	**Mole**	**Partial pressure**	**Mole**	**Partial pressure**	**Change**
Ar	9	9.000	0.512	9.000	0.490	-
$SiCl_4$	7	5.981	0.340	4.546	0.247	↓
H_2	1	0.301	0.017	0.541	0.029	↑
HCl	0	1.289	0.073	0.581	0.032	↓
$SiCl_3$	0	0.639	0.036	1.478	0.080	↑
$SiCl_2$	0	0.270	0.015	1.903	0.104	↑
$SiHCl_3$	0	0.109	0.006	0.330	0.018	↑
SiH_2Cl_2	0	3.02E-04	1.71E-05	0.004	1.99E-04	↑
Cl	0	5.34E-05	3.03E-06	1.83E-05	9.97E-07	↓
H	0	1.52E-05	8.65E-07	2.09E-05	1.14E-06	↑
SiH_3Cl	0	2.42E-07	1.37E-08	1.17E-05	6.36E-07	↑
SiCl	0	3.55E-07	2.02E-08	7.61E-06	4.14E-07	↑
Cl_2	0	1.43E-07	8.11E-09	1.61E-08	8.76E-10	↓
SiH_4	0	7.93E-11	4.51E-12	1.53E-08	8.33E-10	↑
SiH	0	2.56E-10	1.46E-11	2.19E-08	1.19E-09	↑
Si (g)	0	4.34E-10	2.47E-11	2.83E-08	1.54E-09	↑
Si_2 (g)	0	1.96E-14	1.11E-15	7.95E-11	4.33E-12	↑
Si_3 (g)	0	8.12E-17	4.62E-18	2.06E-11	1.12E-12	↑
Si_2H_6	0	1.66E-20	9.44E-22	3.44E-16	1.87E-17	↑
Total	17	17.590	1.000	18.382	1.000	-
Si (s)	2	2	-	0.740	-	-

Table S9 Equilibrium partial pressures of components in the $SiCl_4$-0% H_2-Si system at 1150 °C.

	Input	Before encountering Si		After encountering Si		
Gas Phase	**Mole**	**Mole**	**Partial pressure**	**Mole**	**Partial pressure**	**Change**
Ar	10	10.000	0.588	10.000	0.544	-
$SiCl_4$	7	6.992	0.411	4.853	0.264	↓
$SiCl_3$	0	7.63E-03	4.49E-04	1.553	0.085	↑
$SiCl_2$	0	3.30E-05	1.94E-06	1.965	0.107	↑
Cl	0	5.05E-03	2.97E-04	1.86E-05	1.01E-06	↓
SiCl	0	4.43E-13	2.60E-14	7.74E-06	4.21E-07	↑
Cl_2	0	1.32E-03	7.78E-05	1.66E-08	9.05E-10	↓
Si (g)	0	5.52E-18	3.25E-19	2.83E-08	1.54E-09	↑
Si_2 (g)	0	3.27E-30	1.92E-31	7.95E-11	4.33E-12	↑
Si_3 (g)	0	1.79E-40	1.05E-41	2.06E-11	1.12E-12	↑
Total	17	17.006	1.000	18.371	1.000	-
Si (s)	2	2	-	0.629	-	-

Table S10 Equilibrium partial pressures of components in the $SiCl_4$-0.1% H_2-Si system at 1150 °C.

	Input	Before encountering Si		After encountering Si		
Gas Phase	**Mole**	**Mole**	**Partial pressure**	**Mole**	**Partial pressure**	**Change**
Ar	9.99	9.990	0.587	9.990	0.544	-
$SiCl_4$	7	6.978	0.410	4.846	0.264	↓
H_2	0.01	0.000	0.000	0.000	0.000	↑
HCl	0	0.020	0.001	0.012	0.001	↓
$SiCl_3$	0	0.022	0.001	1.551	0.084	↑
$SiCl_2$	0	0.000	0.000	1.964	0.107	↑
$SiHCl_3$	0	0.000	0.000	0.007	0.000	↑
SiH_2Cl_2	0	6.35E-14	3.73E-15	1.64E-06	8.93E-08	↑
Cl	0	1.78E-03	1.05E-04	1.86E-05	1.01E-06	↓
H	0	6.83E-09	4.02E-10	4.35E-07	2.37E-08	↑
SiH_3Cl	0	6.83E-22	4.01E-23	1.08E-10	5.86E-12	↑
SiCl	0	1.00E-11	5.91E-13	7.73E-06	4.21E-07	↑
Cl_2	0	1.65E-04	9.69E-06	1.66E-08	9.05E-10	↓
SiH_4	0	3.01E-30	1.77E-31	2.90E-15	1.58E-16	↑
SiH	0	9.73E-20	5.72E-21	4.57E-10	2.49E-11	↑
Si (g)	0	3.55E-16	2.09E-17	2.83E-08	1.54E-09	↑
Si_2 (g)	0	1.35E-26	7.96E-28	7.95E-11	4.33E-12	↑
Si_3 (g)	0	4.75E-35	2.79E-36	2.06E-11	1.12E-12	↑
Si_2H_6	0	1.15E-52	6.75E-54	2.84E-26	1.54E-27	↑
Total	17	17.012	1.000	18.371	1.000	-
Si (s)	2	2	-	0.632	-	-

Table S11 Equilibrium partial pressures of components in the $SiCl_4$-1% H_2-Si system at 1150 °C.

	Input	Before encountering Si		After encountering Si		
Gas Phase	**Mole**	**Mole**	**Partial pressure**	**Mole**	**Partial pressure**	**Change**
Ar	9.9	9.900	0.579	9.900	0.539	-
$SiCl_4$	7	6.818	0.399	4.797	0.261	↓
H_2	0.1	0.000	0.000	0.017	0.001	↑
HCl	0	0.198	0.012	0.105	0.006	↓
$SiCl_3$	0	0.166	0.010	1.539	0.084	↑
$SiCl_2$	0	0.016	0.001	1.954	0.106	↑
$SiHCl_3$	0	0.001	0.000	0.061	0.003	↑
SiH_2Cl_2	0	2.30E-08	1.34E-09	1.18E-04	6.45E-06	↑
Cl	0	2.28E-04	1.34E-05	1.86E-05	1.01E-06	↓
H	0	5.32E-07	3.11E-08	3.71E-06	2.02E-07	↑
SiH_3Cl	0	1.50E-13	8.79E-15	6.64E-08	3.62E-09	↑
SiCl	0	4.76E-09	2.78E-10	7.71E-06	4.20E-07	↑
Cl_2	0	2.69E-06	1.57E-07	1.65E-08	9.00E-10	↓
SiH_4	0	4.03E-19	2.36E-20	1.53E-11	8.31E-13	↑
SiH	0	2.80E-14	1.64E-15	3.89E-09	2.12E-10	↑
Si (g)	0	1.32E-12	7.72E-14	2.83E-08	1.54E-09	↑
Si_2 (g)	0	1.86E-19	1.09E-20	7.95E-11	4.33E-12	↑
Si_3 (g)	0	2.42E-24	1.42E-25	2.06E-11	1.12E-12	↑
Si_2H_6	0	3.42E-34	2.00E-35	1.08E-20	5.90E-22	↑
Total	17	17.099	1.000	18.373	1.000	-
Si (s)	2	2	-	0.649	-	-

Table S12 Equilibrium partial pressures of components in the $SiCl_4$-2% H_2-Si system at 1150 °C.

	Input	**Before encountering Si**		**After encountering Si**		
Gas Phase	**Mole**	**Mole**	**Partial pressure**	**Mole**	**Partial pressure**	**Change**
Ar	9.8	9.800	0.570	9.800	0.533	-
$SiCl_4$	7	6.662	0.388	4.754	0.259	↓
H_2	0.2	0.004	0.000	0.054	0.003	↑
HCl	0	0.385	0.022	0.185	0.010	↓
$SiCl_3$	0	0.284	0.017	1.529	0.083	↑
$SiCl_2$	0	0.048	0.003	1.945	0.106	↑
$SiHCl_3$	0	0.006	0.000	0.107	0.006	↑
SiH_2Cl_2	0	7.94E-07	4.62E-08	3.70E-04	2.01E-05	↑
Cl	0	1.31E-04	7.61E-06	1.85E-05	1.01E-06	↓
H	0	1.81E-06	1.06E-07	6.56E-06	3.57E-07	↑
SiH_3Cl	0	3.09E-11	1.80E-12	3.68E-07	2.00E-08	↑
SiCl	0	2.51E-08	1.46E-09	7.70E-06	4.19E-07	↑
Cl_2	0	8.77E-07	5.10E-08	1.65E-08	8.96E-10	↓
SiH_4	0	4.93E-16	2.87E-17	1.50E-10	8.17E-12	↑
SiH	0	8.79E-13	5.12E-14	6.89E-09	3.75E-10	↑
Si (g)	0	1.22E-11	7.10E-13	2.83E-08	1.54E-09	↑
Si_2 (g)	0	1.59E-17	9.22E-19	7.95E-11	4.33E-12	↑
Si_3 (g)	0	1.90E-21	1.10E-22	2.06E-11	1.12E-12	↑
Si_2H_6	0	4.43E-29	2.58E-30	3.34E-19	1.82E-20	↑
Total	17	17.190	1.000	18.374	1.000	-
Si (s)	2	2	-	0.664	-	-

Table S13 Equilibrium partial pressures of components in the $SiCl_4$-5% H_2-Si system at 1150 °C.

	Input	Before encountering Si		After encountering Si		
Gas Phase	**Mole**	**Mole**	**Partial pressure**	**Mole**	**Partial pressure**	**Change**
Ar	9.5	9.500	0.546	9.500	0.517	-
$SiCl_4$	7	6.321	0.363	4.658	0.253	↓
H_2	0.5	0.066	0.004	0.211	0.011	↑
HCl	0	0.829	0.048	0.365	0.020	↓
$SiCl_3$	0	0.490	0.028	1.506	0.082	↑
$SiCl_2$	0	0.150	0.009	1.926	0.105	↑
$SiHCl_3$	0	0.039	0.002	0.210	0.011	↑
SiH_2Cl_2	0	3.71E-05	2.13E-06	1.44E-03	7.85E-05	↑
Cl	0	7.28E-05	4.19E-06	1.84E-05	1.00E-06	↓
H	0	7.09E-06	4.08E-07	1.30E-05	7.09E-07	↑
SiH_3Cl	0	1.02E-08	5.84E-10	2.87E-06	1.56E-07	↑
SiCl	0	1.43E-07	8.22E-09	7.66E-06	4.17E-07	↑
Cl_2	0	2.69E-07	1.55E-08	1.63E-08	8.87E-10	↓
SiH_4	0	1.14E-12	6.54E-14	2.33E-09	1.27E-10	↑
SiH	0	3.52E-11	2.02E-12	1.37E-08	7.45E-10	↑
Si (g)	0	1.26E-10	7.27E-12	2.83E-08	1.54E-09	↑
Si_2 (g)	0	1.68E-15	9.65E-17	7.95E-11	4.33E-12	↑
Si_3 (g)	0	2.05E-18	1.18E-19	2.06E-11	1.12E-12	↑
Si_2H_6	0	1.56E-23	8.95E-25	2.05E-17	1.11E-18	↑
Total	17	17.395	1.000	18.377	1.000	-
Si (s)	2	2	-	0.699	-	-

Table S14 Equilibrium partial pressures of components in the $SiCl_4$-20% H_2-Si system at 1150 °C.

	Input	**Before encountering Si**		**After encountering Si**		
Gas Phase	**Mole**	**Mole**	**Partial pressure**	**Mole**	**Partial pressure**	**Change**
Ar	8	8.000	0.450	8.000	0.435	-
$SiCl_4$	7	5.591	0.314	4.386	0.239	↓
H_2	2	0.971	0.055	1.297	0.071	↑
HCl	0	1.823	0.102	0.891	0.048	↓
$SiCl_3$	0	0.763	0.043	1.439	0.078	↑
$SiCl_2$	0	0.413	0.023	1.869	0.102	↑
$SiHCl_3$	0	0.232	0.013	0.497	0.027	↑
SiH_2Cl_2	0	1.47E-03	8.25E-05	8.60E-03	4.68E-04	↑
Cl	0	4.23E-05	2.37E-06	1.82E-05	9.88E-07	↓
H	0	2.75E-05	1.55E-06	3.23E-05	1.76E-06	↑
SiH_3Cl	0	2.69E-06	1.51E-07	4.30E-05	2.34E-06	↑
SiCl	0	6.93E-07	3.90E-08	7.55E-06	4.10E-07	↑
Cl_2	0	8.84E-08	4.97E-09	1.58E-08	8.60E-10	↓
SiH_4	0	2.01E-09	1.13E-10	8.80E-08	4.78E-09	↑
SiH	0	1.14E-09	6.41E-11	3.39E-08	1.85E-09	↑
Si (g)	0	1.08E-09	6.08E-11	2.83E-08	1.54E-09	↑
Si_2 (g)	0	1.20E-13	6.75E-15	7.96E-11	4.33E-12	↑
Si_3 (g)	0	1.23E-15	6.90E-17	2.06E-11	1.12E-12	↑
Si_2H_6	0	3.31E-18	1.86E-19	4.74E-15	2.58E-16	↑
Total	17	17.794	1.000	18.389	1.000	-
Si (s)	2	2	-	0.800	-	-

Table S15 Equilibrium partial pressures of components in the $SiCl_4$-50% H_2-Si system at 1150 °C.

	Input	**Before encountering Si**		**After encountering Si**		
Gas Phase	**Mole**	**Mole**	**Partial pressure**	**Mole**	**Partial pressure**	**Change**
Ar	5	5.000	0.277	5.000	0.272	-
$SiCl_4$	7	4.983	0.276	4.081	0.222	↓
H_2	5	3.418	0.189	3.820	0.208	↑
HCl	0	2.648	0.147	1.503	0.082	↓
$SiCl_3$	0	0.886	0.049	1.364	0.074	↑
$SiCl_2$	0	0.623	0.034	1.804	0.098	↑
$SiHCl_3$	0	0.501	0.028	0.808	0.044	↑
SiH_2Cl_2	0	7.69E-03	4.26E-04	2.44E-02	1.33E-03	↑
Cl	0	3.30E-05	1.82E-06	1.79E-05	9.70E-07	↓
H	0	5.20E-05	2.88E-06	5.55E-05	3.01E-06	↑
SiH_3Cl	0	3.41E-05	1.89E-06	2.13E-04	1.16E-05	↑
SiCl	0	1.36E-06	7.54E-08	7.42E-06	4.03E-07	↑
Cl_2	0	5.30E-08	2.93E-09	1.53E-08	8.30E-10	↓
SiH_4	0	6.19E-08	3.43E-09	7.62E-07	4.14E-08	↑
SiH	0	5.43E-09	3.01E-10	5.83E-08	3.17E-09	↑
Si (g)	0	2.77E-09	1.53E-10	2.83E-08	1.54E-09	↑
Si_2 (g)	0	7.74E-13	4.29E-14	7.96E-11	4.33E-12	↑
Si_3 (g)	0	1.99E-14	1.10E-15	2.06E-11	1.12E-12	↑
Si_2H_6	0	8.91E-16	4.93E-17	1.21E-13	6.57E-15	↑
Total	17	18.066	1.000	18.404	1.000	-
Si (s)	2	2	-	0.918	-	-

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