Supporting information:

Dangling bond defects on Si surfaces and their consequences on energy band diagrams

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Figure SI1: UP(HeII) spectra of flashed (sample index i_a and i_b) and flash-annealed (ii_a) Si 100 surface (left) and LEED pattern after flash-annealing at 125 eV beam energy (right) indicating a 2x1 surface reconstruction. Flashed samples do not reveal any LEED pattern.

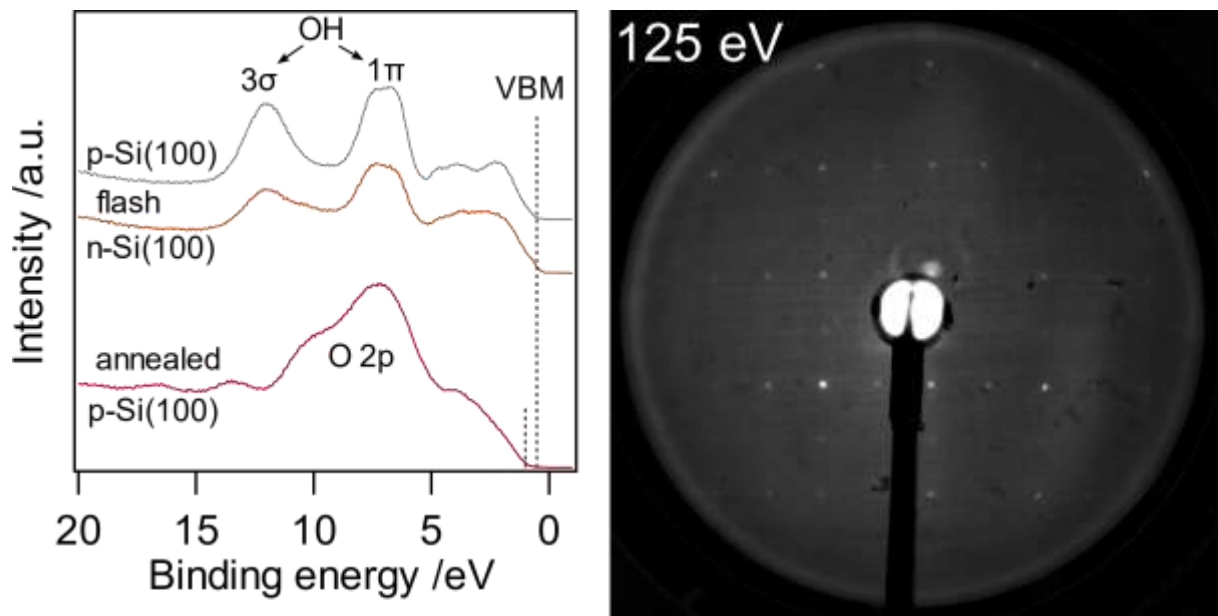

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Table 2: Oxide thickness calculations according to Seah and Spencer [1].

Sample	p-100: I_{SiO2}/I_{Si}	n-100: I_{SiO2}/I_{Si}	Average ratio	Thickness /nm
Native oxide	0.19	0.22	0.21	0.81
Thermal oxide	0.29	0.27	0.28	1.05

Oxide stoichiometry O/Si-ratio determined with:

$$c_O/c_{Si} = \frac{A_O}{A_{Si}}$$

with

$$A_O = \frac{I_{O1s}}{ASF(BE) \cdot T_{spec}(BE) \cdot d(BE)}$$

$$A_{Si} = \frac{I_{Si2p\ ox}}{ASF(BE) \cdot T_{spec}(BE) \cdot d(BE)}$$

with raw area of O 1s I_{O1s} and oxide-related Si 2p $I_{Si2p\ ox}$, Scofield atomic sensitivity factors ASF [2], spectrometer transmission function $T_{spec}(BE)$ and thin film related escape depth correction $d(BE)$ as

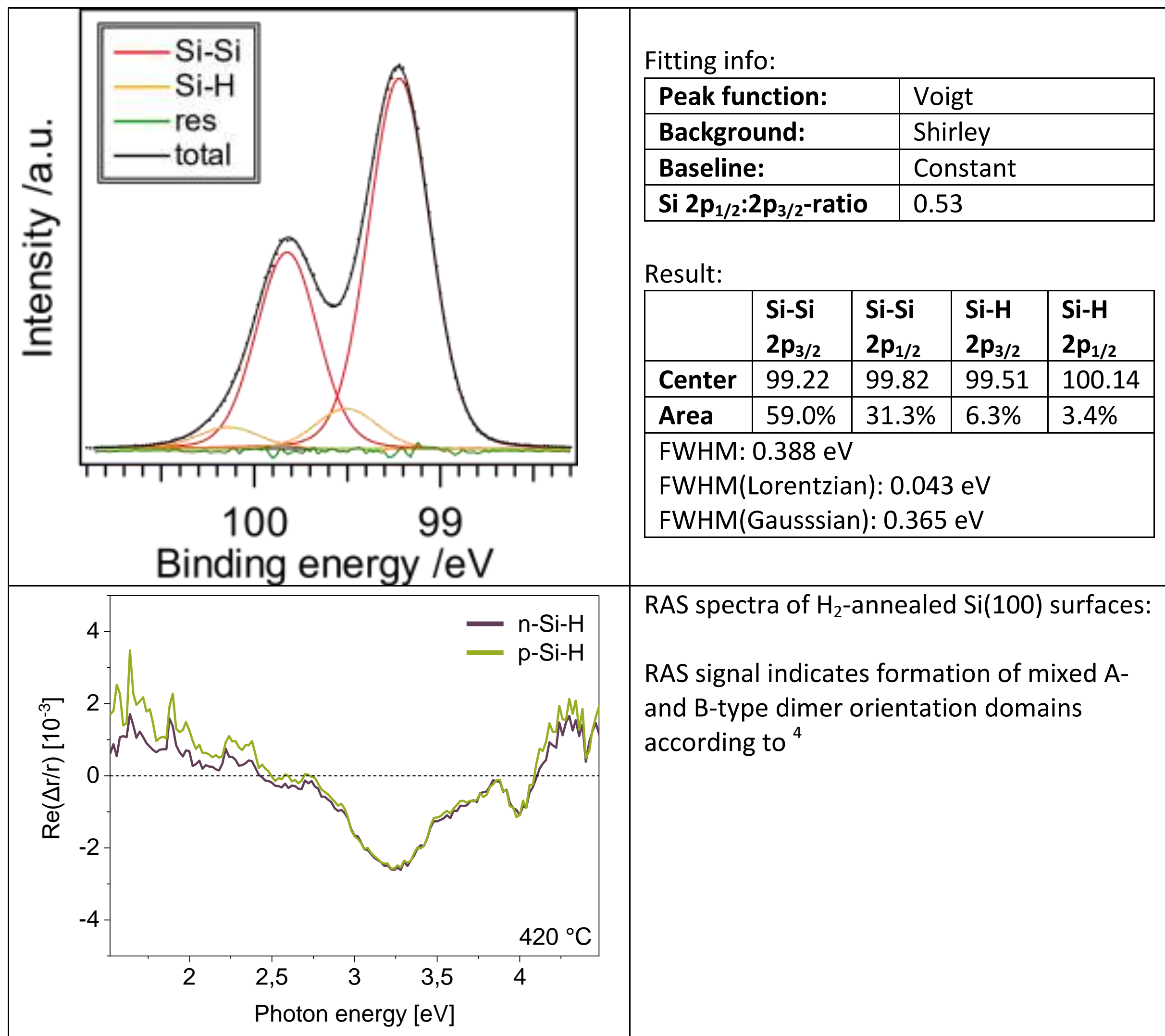
$$d(BE) = \int_0^t e^{-x/\lambda_{SiO2}(BE)} dx = \lambda_{SiO2}(BE) - \lambda_{SiO2}(BE)\, e^{-t/\lambda_{SiO2}(BE)}$$
$$= (1 - e^{-t/\lambda_{SiO2}(BE)})\lambda_{SiO2}(BE)$$

with oxide thickness t from Table 2 and inelastic mean free patch of photoelectrons in SiO_2 $\lambda_{SiO2}(BE)$, with $\lambda_{SiO2}\big(kinetic\ energy\ O\ 1s \approx 900\ eV\big) = 2.7$ nm and $\lambda_{SiO2}\big(kinetic\ energy\ Si\ 2p \approx 1400\ eV\big) = 3.8$ nm according to Tanuma, Powell and Penn [3].

Table 3: Oxide stoichiometry calculations with thin film related escape depth corrections.

Sample	A_{Si}	A_O	c_{Si}	c_O
p-Si (therm. oxide)	2155.72	4391.02	67.1%	33.9%
n-Si (therm. oxide)	1433.29	2743.03	65.7%	34.3%
p-Si (nat. oxide)	1519.53	2980.78	66.2%	33.8%
n-Si (nat. oxide)	2885.85	5483.23	65.5%	34.5%

Figure SI4: Si 2p fit of H_2-annealed p-Si(100):H (sample dry-H) and RAS signal of p- and n- prepared Si(100):H.



Fitting info:

Peak function:	Voigt
Background:	Shirley
Baseline:	Constant
Si $2p_{1/2}$:$2p_{3/2}$-ratio	0.53

Result:

	Si-Si $2p_{3/2}$	**Si-Si $2p_{1/2}$**	**Si-H $2p_{3/2}$**	**Si-H $2p_{1/2}$**
Center	99.22	99.82	99.51	100.14
Area	59.0%	31.3%	6.3%	3.4%

FWHM: 0.388 eV
FWHM(Lorentzian): 0.043 eV
FWHM(Gausssian): 0.365 eV

RAS spectra of H_2-annealed Si(100) surfaces:

RAS signal indicates formation of mixed A- and B-type dimer orientation domains according to [4]

Figure SI5: LEED of H2-annealed n-Si(100):H (dry-H) at 52 eV shows (2x1)/(1x2) pattern with stronger intensities of the half order spots in the [011] direction confirming a strong prevalence of 1×2 domain. The 2×1 pattern corresponds to Si-Si dimers rotated by 90 °[4,5] (2×1 domain) from residual terraces with single-atomic layer steps

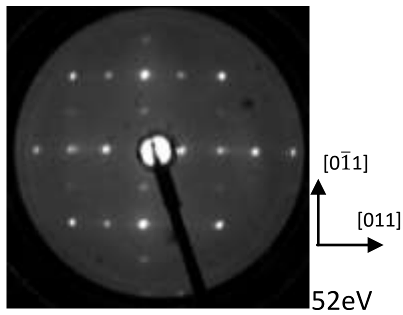
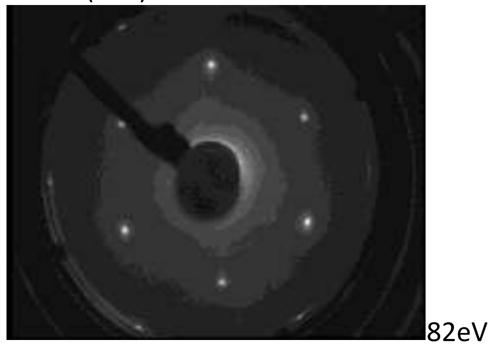


Figure SI6: Wet-chemical H-terminated Si (111-H) and (100-H) revealing both 1x1 LEED pattern, indicating fully hydrided Si surfaces[6].

n-Si-H (111)



n-Si-H (100)

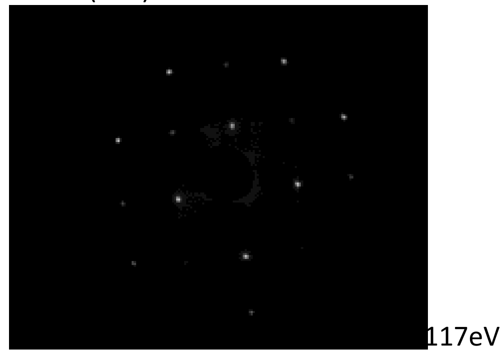
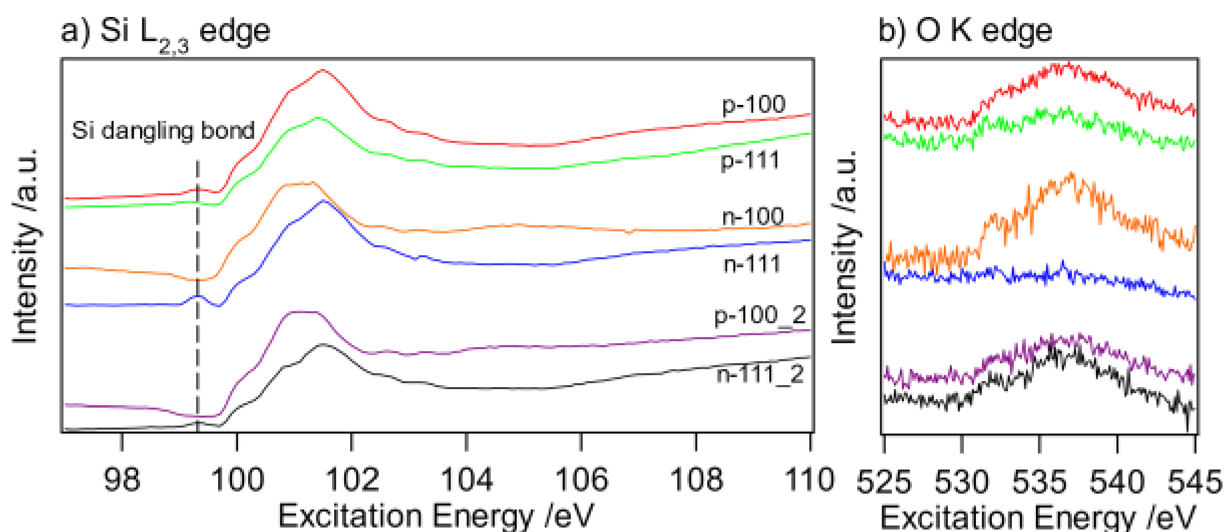


Figure SI7: XA spectra of wet-chemically prepared H-termination of Si with Si $L_{2,3}$ (a) and O K edges (b). The pre-edge feature in Si L-edge is assigned to the unoccupied dangling bond band of non-oxidized surfaces. The pre-edge feature vanishes with oxidation, shifting all acceptor states into the conduction band.



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