Supplementary Material: Resolving the Metastable Si-XIII Structure through Convergent Theory and Experiment

Fabrizio Rovaris[a,1], Corrado Bongiorno[b,1], Anna Marzegalli[a], Mouad Bikerouin[a], Davide Spirito[c,f], Gerald J. K. Schaffar[d], Mohamed Zaghloul[b], Agnieszka Anna Corley-Wiciak[c], Francesco Montalenti[a], Verena Maier-Kiener[d], Giovanni Capellini[c,e], Antonio M. Mio[b], Emilio Scalise[a,*]

[a] *Department of Materials Science. University of Milano Bicocca, Via R. Cozzi 55, 20125, Milano, Italy*
[b] *Institute for Microelectronics and Microsystems (IMM). Consiglio Nazionale delle Ricerche (CNR), Strada VIII 5, 95121, Catania, Italy*
[c] *IHP-Leibniz-Institut für innovative Mikroelektronik, Im Technologiepark 25, 15236, Frankfurt(Oder), Germany*
[d] *Department of Materials Science. Montanuniversität Leoben, Roseggerstrasse 12, 8700, Leoben, Austria*
[e] *Department of Science. Università Roma Tre, V.le G. Marconi 446, 00146, Rome, Italy*
[f] *BCMaterials. Basque Center for Materials, Applications and Nanostructures, UPV/EHU Science Park, 48940, Leioa, Spain*

Atom	Wyckoff	x	y	z
Si_1	$2i$	0.014	0.492	0.689
Si_2	$2i$	0.986	0.508	0.311
Si_3	$2i$	0.170	0.943	0.974
Si_4	$2i$	0.830	0.057	0.026
Si_5	$2i$	0.653	0.685	0.163
Si_6	$2i$	0.347	0.315	0.837
Si_7	$2i$	0.380	0.826	0.318
Si_8	$2i$	0.620	0.174	0.682

Table S1: Crystal structure of Si-XIII. Space group $P\bar{1}$ (No. 2), triclinic system, point group $\bar{1}$. All 8 atomic positions (fractional coordinates) of the primitive unit cell are listed; atoms are grouped in pairs related by the inversion center of the $2i$ Wyckoff site.

*Corresponding author
[1] This authors equally contributed

Phase (Space group)	Approx.	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]	V [Å^3/atom]	ΔE [meV/atom]
	LDA	3.805	3.805	3.805	60.0	60.0	60.0	19.48	0
	PBEsol	3.842	3.842	3.842	60.0	60.0	60.0	20.05	0
dc ($Fd\bar{3}m$)	PBE	3.861	3.861	3.861	60.0	60.0	60.0	20.35	0
	SCAN	3.839	3.839	3.839	60.0	60.0	60.0	20.01	0
	GAP	3.861	3.861	3.861	60.0	60.0	60.0	20.36	0
	Lit. [1]	3.840	3.840	3.840	60.0	60.0	60.0	20.03	–
	LDA	5.671	5.671	5.671	109.9	109.9	109.9	17.29	112
	PBEsol	5.720	5.720	5.720	109.9	109.9	109.9	17.73	116
R8 ($R\bar{3}$)	PBE	5.759	5.759	5.759	109.8	109.8	109.8	18.12	158
	SCAN	5.749	5.749	5.749	109.8	109.8	109.8	18.04	205
	GAP	5.749	5.749	5.745	109.6	109.6	109.6	18.16	175
	Exp.	5.620	5.620	5.620	109.8	109.8	109.8	16.87	–
	Lit [2] (at 8.2 Gpa)	5.620	5.620	5.620	110.1	110.1	110.1	16.69	–
	LDA	5.670	5.670	5.670	109.5	109.5	109.5	17.54	124
	PBEsol	5.720	5.720	5.720	109.5	109.5	109.5	18.00	119
BC8 ($Ia\bar{3}$)	PBE	5.758	5.758	5.758	109.5	109.5	109.5	18.37	157
	SCAN	5.747	5.747	5.747	109.5	109.5	109.5	18.26	186
	GAP	5.754	5.754	5.754	109.5	109.5	109.5	18.33	165
	Lit. [2]	5.748	5.748	5.748	109.5	109.5	109.5	18.28	–
	LDA	5.150	5.745	6.204	109.1	100.0	107.1	19.78	98
	PBEsol	5.200	5.797	6.263	109.1	100.0	107.0	20.35	94
Si-XIII ($P\bar{1}$)	PBE	5.225	5.828	6.297	109.0	100.0	107.0	20.70	98
	SCAN	5.191	5.807	6.266	109.1	100.0	107.0	20.38	116
	GAP	5.186	5.796	6.385	109.0	100.8	106.3	20.72	128
	Exp.	5.20	5.74	6.21	109	100	107	20.00	-

Table S2: Equilibrium lattice parameters of the proposed Si-XIII structure obtained from DFT relaxations with different exchange-correlation functionals and the GAP interatomic potential, compared to the metastable R8 and BC8 phases and the reference *dc*-Si. The atomic volume and cohesive energy are also reported, showing that the Si-XIII phase lies closer to the stable *dc*-Si, both in terms of atomic volume and, more notably, in cohesive energy. For the *dc*, R8, and BC8 phases values reported in the literature are reported together with the references they were taken from. For the Si-XIII and R8 phases, cell parameters estimated on the basis of the experimental SAED patterns are also reported. Note that the current estimated values for the R8 phase suggest a possible deformation of the R8 structure due to residual strain, in agreement with previous observations of the R8 phase obtained by nanoindentation [3].

Si-XIII ($P\bar{1}$)				R8			
hkl	simulated	measured	deviation	*hkl*	simulated	measured	deviation
(001)	5.606	5.62	0.014 (0.2%)	(-110)	4.598	4.54	-0.058 (-1.3%)
(-110)	4.365	4.35	-0.015 (-0.3%)	(0-11)	4.598	4.59	-0.008 (-0.2%)
(1-11)	3.573	3.54	-0.033 (-0.9%)	(-101)	4.598	4.59	-0.008 (-0.2%)
(-111)	3.328	3.33	0.002 (0.1%)	(-12-1)	2.655	2.64	-0.015 (-0.6%)
(101)	3.186	3.18	-0.006 (-0.2%)	(-211)	2.655	2.64	-0.015 (-0.6%)
(011)	3.168	3.16	-0.008 (-0.3%)	(-1-12)	2.655	2.66	0.005 (0.2%)
(1-12)	2.441	2.42	-0.021 (-0.9%)	(0-12)	2.655	2.66	0.005 (0.2%)
(-112)	2.284	2.3	0.016 (0.7%)	(-102)	2.655	2.66	0.005 (0.2%)
(2-11)	2.223	2.22	-0.003 (-0.1%)	(-221)	2.051	2.03	-0.021 (-1%)
(-121)	2.205	2.2	-0.005 (-0.2%)	(1-22)	2.051	2.03	-0.021 (-1%)
(102)	2.15	2.16	0.01 (0.5%)	(-1-13)	1.867	1.88	0.013 (0.7%)
(012)	2.116	2.14	0.024 (1.1%)	(0-23)	1.735	1.75	0.015 (0.9%)
(2-21)	2.086	2.06	-0.026 (-1.2%)	(-203)	1.735	1.75	0.015 (0.9%)
(021)	2.014	2.03	0.016 (0.8%)	(1-33)	1.452	1.45	-0.002 (-0.1%)
(-221)	1.985	1.97	-0.015 (-0.8%)	(-313)	1.452	1.45	-0.002 (-0.1%)
(201)	1.984	1.98	-0.004 (-0.2%)				
(2-12)	1.784	1.75	-0.034 (-1.9%)				
(1-13)	1.765	1.72	-0.045 (-2.5%)				
(-122)	1.726	1.75	0.024 (1.4%)				
(-131)	1.581	1.59	0.009 (0.6%)				
(3-11)	1.552	1.54	-0.012 (-0.8%)				

Table S3: Measured and simulated d-spacings for each (hkl) observed reflection of Si-XIII and R8. Simulated values are obtained using the experimental lattice parameters reported in Table S2. For each reflection, the deviation between measured and simulated d-spacings is reported both as a value and as a percentage.

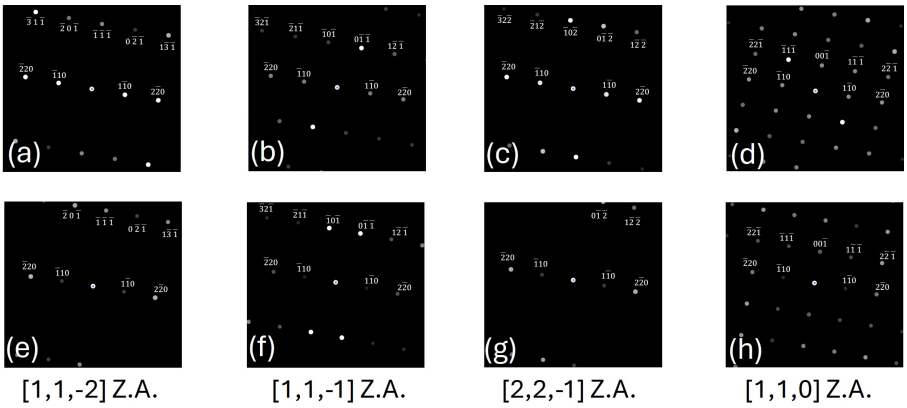

Figure S1: (a-d) Simulated SAED of the Si-XIII phase across multiple zone axes, as reported in Fig. 1(h-k). For comparison, the corresponding simulated SAED of the R8 phase is shown in panels (e-h). Indexing of the R8 phase is presented in the rhombohedral basis, as defined in Table S2

References

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