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Supporting Information

Exploration of stable stoichiometries, physical properties and hardness in the Rh-Si system: A first-principles study

Jing-Jing Wang,[a] Andreas Hermann,[b] Xiao-Yu Kuang,[a,*] Yuan-Yuan Jin,[a] Cheng Lu,[c,*] Chuan-Zhao Zhang,[a] Meng Ju,[a] Meng-Ting Si[c] and Toshiaki Iitaka[d,*]

[a]*Institute of Atomic and Molecular Physics, Sichuan University, Chengdu, 610065, China*

[b]*Centre for Science at Extreme Conditions and SUPA, School of Physics and Astronomy, The University of Edinburgh, Edinburgh EH9 3JZ, United Kingdom*

[c]*Department of Physics, Nanyang Normal University, Nanyang, 473061, China*

[d]*Computational Astrophysics Laboratory, RIKEN (The Institute of Physical and Chemical Research) 2-1 Hirosawa, Wako, Saitama 351-0198, Japan*

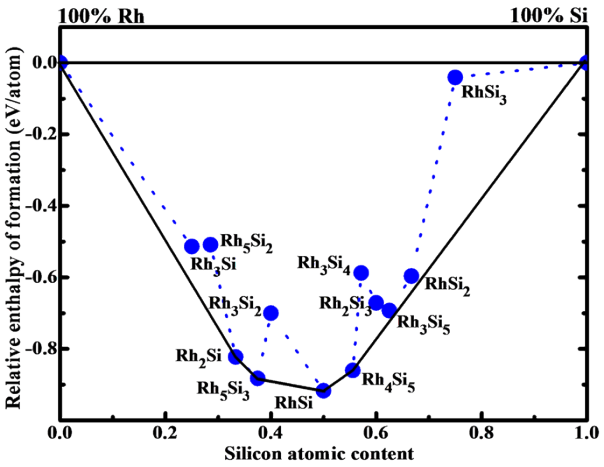

Fig. S1. Relative enthalpies of formation for rhodium silicides. The solid line denotes the ground state convex hull at LDA+U level.

* Correspondence author: scu_kuang@163.com, lucheng@calypso.cn, tiitaka@riken.jp.

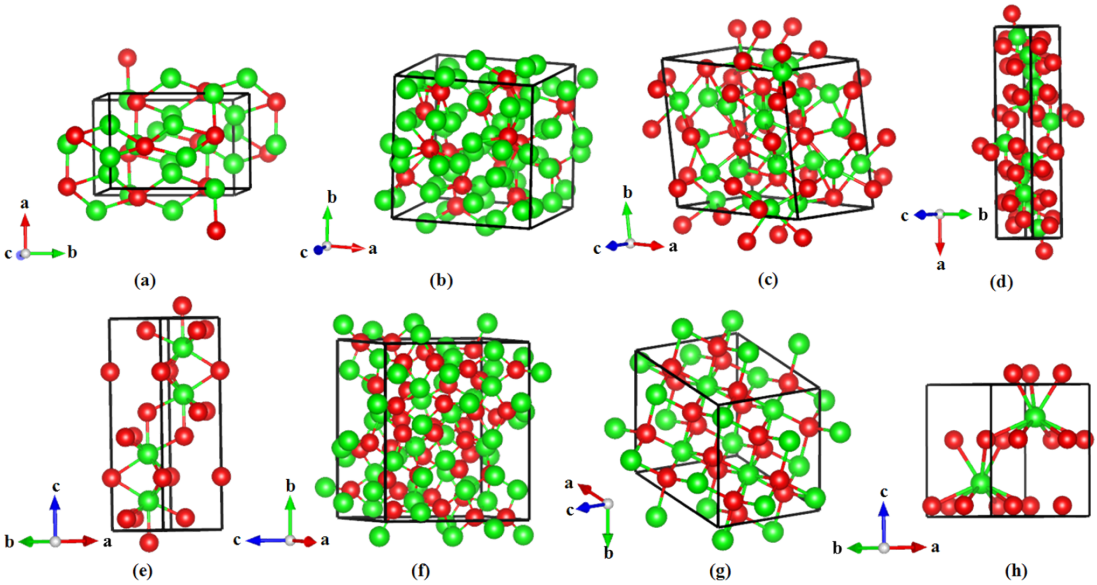

Fig. S2. Optimized structures of rhodium silicides: (a) Rh_3Si (*Pnma*), (b) Rh_5Si_2 ($P4_12_12$), (c) Rh_3Si_2 ($Cmc2_1$), (d) Rh_3Si_4 (*Pnma*), (e) Rh_2Si_3 ($P6_3/mmc$), (f) Rh_3Si_5 ($P2_1/c$), (g) $RhSi_2$ (*Cmce*), (h) $RhSi_3$ ($P6_3mc$). The green and red spheres represent rhodium and silicon atoms, respectively.

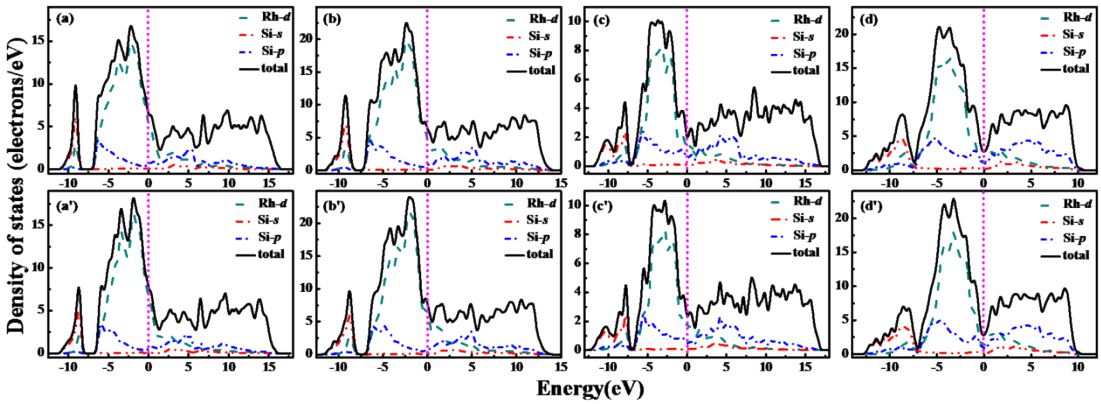

Fig. S3. Calculated total and partial DOSs of (a) Rh_2Si (*Pnma*), (b) Rh_5Si_3 (*Pbam*), (c) RhSi (*Pnma*), and (d) Rh_4Si_5 ($P2_1/m$) using LDA+U functional, and (a') Rh_2Si (*Pnma*), (b') Rh_5Si_3 (*Pbam*), (c') RhSi (*Pnma*), and (d') Rh_4Si_5 ($P2_1/m$) using GGA-PBE functional, respectively. The Ferm level is at 0 eV.

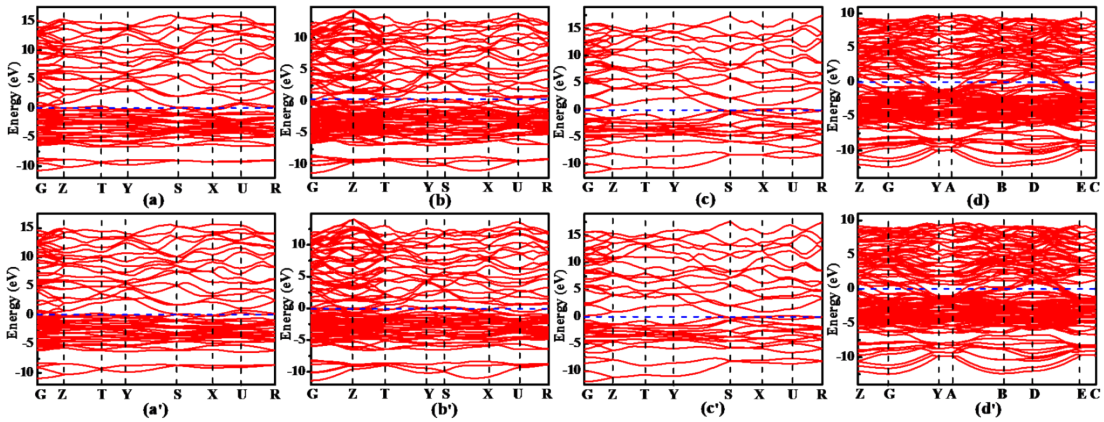

Fig. S4. Calculated band structures of (a) Rh_2Si (*Pnma*), (b) Rh_5Si_3 (*Pbam*), (c) RhSi (*Pnma*), and (d) Rh_4Si_5 ($P2_1/m$) using LDA+U functional, and (a') Rh_2Si (*Pnma*), (b') Rh_5Si_3 (*Pbam*), (c') RhSi (*Pnma*), and (d') Rh_4Si_5 ($P2_1/m$) using GGA-PBE functional, respectively. The Ferm level is at 0 eV.

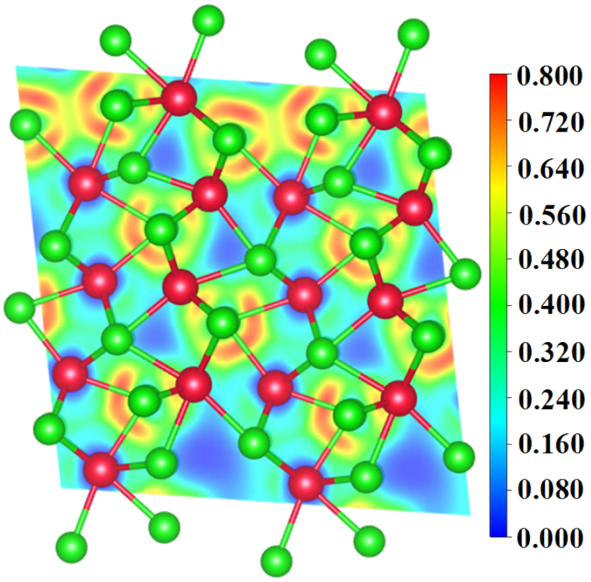

Fig. S5. Electron localization function (ELF) maps projected on to (010) plane of $P2_1/m$ phase Rh_4Si_5. The ELF isosurfaces value is 0.8.

Table S1. Calculated lattice parameters, *a*, *b*, and *c* (Å); volume (V in Å^3) per atom; density (g/cm^3), and relative total energy per chemical formula unit (Δ*H* in eV) of rhodium silicides with various stoichiometries, compared with experimental and other theoretical data.

Phase	Space group	Δ*H*	*a*			*b*			*c*			*V*	*ρ*
				Expt.	Theor.		Expt.	Theor.		Expt.	Theor.		
Rh_3Si	*C*2/*m*	–0.55	8.06			7.47			5.49			14.06	9.94
	Pnma	–0.56	5.36			7.99			5.27			14.12	9.90
	*I*4/*mcm*	–0.55	5.50			5.50			5.50			14.10	9.92
	Pm-3*m*	–0.38	3.84			3.84			3.87			14.11	9.91
	Fm-3*m*	–0.25	6.12			6.12			6.12			14.30	9.77
Rh_5Si_2	$P4_12_12$	–0.51	9.53			9.53			8.80			14.25	9.50
	Pnma	–0.82	5.58	5.41[a]		3.99	3.93[a]		7.40	7.38[a]		13.72	9.44
	*I*4/*mmm*	–0.78	4.01			4.01			5.62			15.02	8.62
Rh_2Si	*P*-3*m*1	–0.65	4.19			4.19			4.19			13.81	9.37
	$P6_322$	–0.65	4.18			4.19			5.46			13.82	9.37
	P-62*m*	–0.11	7.66			7.66			2.81			15.87	8.16
	$P6_3/mmc$	–0.65	4.19			4.19			5.46			13.82	9.37
	Pbam	–0.86	5.45	5.32[a]		10.32	10.13[a]		3.90	3.90[a]		13.72	9.06
Rh_5Si_3	$P6_3/mcm$	–0.44	7.39			7.39			4.99			14.78	8.41
	Ia-3*d*	–0.44	8.40			8.40			8.40			14.24	8.73
Rh_3Si_2	$Cmc2_1$	–0.68	13.29			11.43			7.50			14.25	8.50
RhSi	$P2_1/c$	–0.88	4.63	4.59[b]		4.62	4.57[b]		5.64	5.53[b]		13.66	7.96
	Pnma	–0.91	5.60	5.56[b]	5.60[c]	3.11	3.70[b]	3.11[c]	6.45	6.38[b]	6.45[c]	14.05	7.74
	$P2_13$	–0.88	4.70	4.68[b]	4.73[c]	4.73	4.68[b]	4.73[c]	4.73	4.68[b]	4.73[c]	13.26	7.40
	Pm-3*m*	–0.63	2.90	2.96[d]		2.90	2.96[d]		2.99	2.96[d]		13.34	8.15
Rh_4Si_5	$P2_1/m$	–0.82	12.47			3.55			6.01			14.53	7.01
Rh_3Si_4	*Pnma*	–0.56	20.57			4.45			4.50			14.71	6.79
	Pbcn	–0.61	10.58			9.09			6.03			14.50	6.65
Rh_2Si_3	*P*-4*c*2	–0.56	5.69			5.69			8.99			14.58	6.61
	$P6_3/mmc$	–0.62	3.76			3.76			12.52			15.36	6.27
Rh_3Si_5	$P2_1/c$	–0.65	6.48			14.24			11.64			14.99	6.22
	Cmce	–0.55	6.98			6.98			8.09			15.46	5.70
$RhSi_2$	*P*4/*mmm*	–0.42	2.93			2.93			5.25			15.08	5.84
	Fm-3*m*	–0.55	5.71			5.71			5.71			15.49	5.68
$RhSi_3$	$P6_3mc$	–0.03	4.81			4.81			6.36			15.95	4.87
	$P6_3/mmc$	–0.02	4.36			4.36			7.44			15.30	5.08

[a] Ref. 1, [b] Ref. 2, [c] Ref. 3, [d] Ref. 4.

Table S2. Optimized Structural Parameters for the rhodium silicides.

	Structure	Lattice parameters	Atom	Positions(*x, y, z*)		
				x	*y*	*z*
Rh_3Si	*Pnma*	*a*=10.72, *b*= 7.99, *c*=5.27	Rh1(8d)	0.1818	0.0227	0.3143
			Rh2(4c)	0.0007	0.2500	0.9538
			Si1(4c)	0.9441	0.2500	0.4882
Rh_5Si_2	$P4_12_12$	*a*=9.53, *b*=9.53, *c*=8.80	Rh1(8b)	0.4421	0.1687	0.3593
			Rh2(8b)	0.1722	0.2211	0.1710
			Rh3(8b)	0.3886	0.4244	0.1814
			Rh4(8b)	0.3816	0.0292	0.0615
			Rh5(4a)	0.1622	0.1622	0.5000
			Rh6(4a)	0.4291	0.4291	0.5000
			Si1(8b)	0.5016	0.2504	0.0433
			Si2(8b)	0.3885	0.2057	0.6187
Rh_2Si	*Pnma*	*a*=5.58, *b*=3.99, *c*=7.40	Rh1(4c)	0.8433	0.2500	0.0713
			Rh2(4c)	0.9755	0.2500	0.6927
			Si1(4c)	0.2735	0.2500	0.1056
Rh_5Si_3	*Pbam*	*a*=5.45, *b*=10.32, *c*=3.90	Rh1(2c)	0.0000	0.5000	0.0000
			Rh2(4g)	0.1606	0.2120	0.0000
			Rh3(4h)	0.3330	0.3931	0.5000
			Si1(4h)	0.4082	0.1558	0.5000
			Si2(2a)	0.0000	0.0000	0.0000
Rh_3Si_2	$Cmc2_1$	*a*=8.16, *b*=8.16, *c*=6.92	Rh1(4)	0.2902	0.0562	0.5180
			Rh2(4)	0.2912	0.0534	0.9000
			Rh3(4)	0.4439	0.0495	0.2170
			Rh4(4)	0.6799	0.3151	0.2250
			Rh5(2)	0.0000	0.0000	0.0000
			Rh6(2)	0.2345	0.2345	0.0240
			Rh7(2)	0.2330	0.2330	0.4000
			Rh8(2)	0.3814	0.3814	0.7140
			Si1(4)	0.1790	0.0610	0.2140
			Si2(4)	0.4860	0.1820	0.5060
			Si3(4)	0.4940	0.1920	0.9200
			Si4(2)	0.1570	0.1570	0.7120
			Si5(2)	0.4090	0.4090	0.2180
RhSi	*Pnma*	*a*=5.60, *b*=3.11, *c*=6.45	Rh1(4c)	0.0029	0.2500	0.2032
			Si1(4c)	0.1849	0.2500	0.5561
Rh_4Si_5	$P2_1/m$	*a*=12.47, *b*=3.55, *c*=6.01	Rh1(2e)	0.0499	0.2500	0.2091
			Rh2(2e)	0.2731	0.2500	0.1070
			Rh3(2e)	0.5001	0.2500	0.2994
			Rh4(2e)	0.7308	0.2500	0.2866
			Si1(2e)	0.6350	0.2500	0.6385
			Si2(2e)	0.4221	0.2500	0.8933
			Si3(2e)	0.2237	0.2500	0.4649
			Si4(2e)	0.9229	0.2500	0.4876
			Si5(2e)	0.1395	0.7500	0.9790
Rh_3Si_4	*Pnma*	*a*=20.56, *b*=4.45, *c*=4.50	Rh1(4c)	0.0486	0.2500	0.5239
			Rh2(4c)	0.2136	0.2500	0.0464
			Rh3(4c)	0.3651	0.2500	0.2606
			Si1(4c)	0.1690	0.2500	0.5500
			Si2(4c)	0.4384	0.2500	0.2096
			Si3(4c)	0.4384	0.2500	0.2096

			Si4(4c)	0.4089	0.7500	0.5137
Rh_2Si_3	$P6_3/mmc$	a=3.76, b=3.76, c=12.52	Rh1(4f)	0.3333	0.6666	0.1391
			Si1(4f)	0.3333	0.6666	0.9423
			Si2(2b)	0.0000	0.0000	0.2500
Rh_3Si_5	$P2_1/c$	a =6.47, b=14.24, c=11.64	Rh1(4e)	6.4780	14.2392	11.635
			Rh2(4e)	0.5642	0.5944	0.3961
			Rh3(4e)	0.9517	0.7525	0.2446
			Rh4(4e)	0.0833	0.9553	0.2722
			Rh5(4e)	0.2297	0.6667	0.1321
			Rh6(4e)	0.2334	0.8345	0.9940
			Si1(4e)	0.9279	0.8433	0.0692
			Si2(4e)	0.7456	0.4890	0.5759
			Si3(4e)	0.8648	0.6104	0.3292
			Si4(4e)	0.3289	0.9433	0.1648
			Si5(4e)	0.8565	0.6123	0.1087
			Si6(4e)	0.3519	0.9355	0.5086
			Si7(4e)	0.9495	0.6481	0.9068
			Si8(4e)	0.2547	0.9879	0.7050
			Si9(4e)	0.3770	0.7504	0.8548
			Si10(4e)	0.5524	0.7777	0.1965
$RhSi_2$	$Cmce$	a =11.41, b=8.05, c=8.09	Rh1(8d)	0.2501	0.0000	0.5000
			Rh2(8f)	0.5000	-0.2464	0.2534
			Si1(16g)	0.1248	-0.2498	0.4977
			Si2(16g)	0.3745	0.0025	0.2499
$RhSi_3$	$P6_3mc$	a =4.81, b=4.81, c=6.36	Rh1(2b)	0.3333	0.6666	0.2522
			Si1(6c)	0.8333	0.1666	0.0822

Table S3. Calculated (at GGA and LDA levels) and experimental lattice parameters, *a*, *b*, and *c*; volume V per atom, density, and relative total energy per chemical formula unit Δ*H* of rhodium silicides with various stoichiometries.

Phase	Space	method	Δ*H* (eV)	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	*ρ* (g/cm^3)
Rh_2Si	*Pnma*	GGA	−0.82	5.58	3.99	7.40	13.72	9.44
		LDA+U	−0.82	5.63	3.97	7.32	13.62	9.50
		Expt.		5.41[a]	7.38[a]	7.38[a]		
Rh_5Si_3	*Pbam*	GGA	−0.86	5.45	10.32	3.90	13.72	9.06
		LDA+U	−0.88	5.47	10.26	3.88	13.61	9.13
		Expt.		5.32[a]	10.13[a]	3.90[a]		
RhSi	*Pnma*	GGA	−0.91	5.60	3.11	6.45	14.05	7.74
		LDA+U	−0.91	5.62	3.12	6.49	14.22	7.65
		Expt.		5.56[b]	3.70[b]	6.38[b]		
Rh_4Si_5	$P2_1/m$	GGA	−0.82	12.47	3.55	6.01	14.53	7.01
		LDA+U	−0.86	12.45	3.55	5.98	14.44	7.05

[a] Ref. 1, [b] Ref. 2,

Table S4. Calculated bond length d^{μ}, Mulliken overlap population P^{μ}, f_m, bond volume, and Vickers hardness H_v (GPa) for rhodium silicides with different structures.

Structure	Band	d^{μ}(Å)	P^{μ}	f_m	v_b^{μ}(Å^3)	H_v^{μ}	H_v
Rh_2Si	Si-Rh	2.415	0.130	0.321	3.812	7.026	11.9
(*Pnma*)		2.423	0.370	0.113	3.851	25.676	
		2.471	0.415	0.100	4.086	26.458	
		2.480	0.300	0.139	4.127	18.002	
		2.520	0.340	0.123	4.331	19.186	
		2.851	0.110	0.379	6.271	2.370	
Rh_5Si_3	Si-Rh	2.357	0.150	0.099	3.241	14.090	12.0
(*Pbam*)		2.369	0.130	0.114	3.292	11.697	
		2.420	0.425	0.035	3.508	37.476	
		2.443	0.370	0.040	3.608	30.962	
		2.483	0.340	0.044	3.792	26.096	
		2.577	0.360	0.041	4.239	23.003	
		2.725	0.040	0.371	5.009	1.269	
		2.750	0.105	0.141	5.150	4.344	
RhSi	Si-Rh	2.437	0.310	0.003	4.270	20.346	14.7, 14.8[a]
(*Pnma*)		2.444	0.350	0.003	4.306	22.655	
		2.526	0.225	0.005	4.756	12.323	
	Si-Si	2.691	0.260	0.004	5.749	10.387	
Rh_4Si_5	Si-Rh	2.324	0.435	0.002	3.943	32.657	20.1
($P2_1$/m)		2.338	0.010	0.071	3.943	0.698	
		2.400	0.410	0.002	3.943	30.777	
		2.411	0.420	0.002	3.943	31.529	
		2.428	0.220	0.003	3.943	16.490	
		2.437	0.330	0.002	3.943	24.761	
		2.438	0.350	0.002	3.943	26.265	
		2.462	0.435	0.002	3.943	32.657	
		2.463	0.095	0.007	3.943	7.090	
		2.485	0.365	0.002	3.943	27.393	
		2.486	0.260	0.003	3.943	19.498	
		2.499	0.040	0.018	3.943	2.954	
		2.520	0.395	0.002	3.943	29.649	
		2.526	0.275	0.003	3.943	20.625	
		2.612	0.385	0.002	3.943	28.897	
		2.687	0.370	0.002	3.943	27.769	
	Si-Si	2.774	0.235	0.003	3.943	17.618	
		2.779	0.250	0.003	3.943	18.746	
		2.596	0.360	0.002	3.943	27.017	
		2.601	0.400	0.002	3.943	30.025	
		2.651	0.295	0.002	3.943	22.129	
Si (*Fd*-3*m*)	Si-Si	2.374	0.730	0.001	10.297	11.074	11.1

[a] Ref.3

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