Ru – Si (Ruthenium – Silicon)

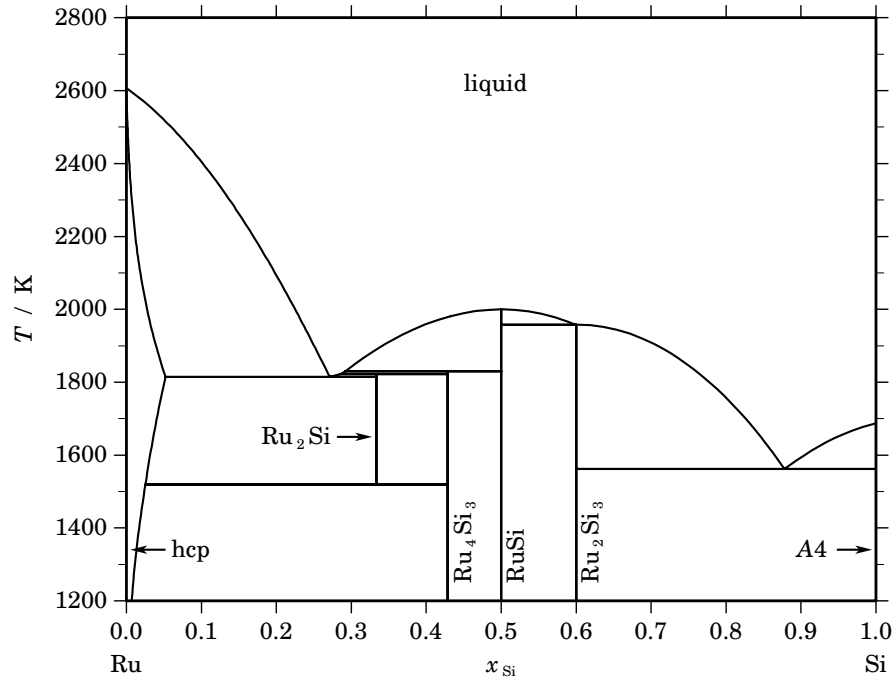

Fig. 1. Calculated phase diagram for the system Ru-Si.

Ruthenium silicides are of interest for manufacturing high-density integrated circuit devices since they have a very good lattice match with silicon and relatively low electrical resistance. Other potential applications are in light emitting diodes and thermoelectrical devices.

Assessed thermodynamic datasets for the Ru-Si system have been reported by [2001Du, 2001Liu] which are based on essentially the same experimental data from the literature. Here, the assessment of [2001Du] has been selected for presentation. The phase diagram data have been selected mainly from [1999Per] with additional information from [1965Obr]. The system contains seven stable phases: the liquid with a continuous miscibility range, the Ru-based hcp phase with limited solubility of Si, the terminal Si-phase with practically no solubility for Ru and 4 ruthenium silicides with narrow homogeneity ranges. The compound Ru_5Si_3 which has been reported in [1970Eng, 1988Wei] has not been confirmed in the redetermination of the phase diagram by [1999Per]. For the thermodynamic modelling of RuSi and Ru_2Si_3 heat capacity measurements have been available [1997Kun, 1998Per]. The specific heat of the remaining two compounds has been approximated according to the Neumann-Kopp rule. Enthalpies of formation have been determined experimentally for Ru_4Si_3 [1997Per], RuSi [1988Top, 1997Per, 1998Cic] and Ru_2Si_3 [1997Per, 1998Cic, 1998Mes]. Since the transformation temperatures of the polymorphic forms of both RuSi and Ru_2Si_3 are not known in both cases only a single compound is used in the modelling. No thermodynamic data have been reported for the liquid. More recently, a new compound, $RuSi_2$, has been observed by DTA to form peritectoidally at 1235 K [2002Iva].

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					LIQUID	$(Ru,Si)_1$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$(Ru,Si)_1$
Ru_2Si	$C23$	Co_2Si	$oP12$	$Pnma$	RU2SI	Ru_2Si_1
Ru_4Si_3	···	···	$oP28$	$Pnma$	RU4SI3	Ru_4Si_3
αRuSi	$B20$	FeSi	$cP8$	$P2_13$	RUSI	Ru_1Si_1
βRuSi	$B2$	CsCl	$cP2$	$Pm\overline{3}m$	RUSI	Ru_1Si_1
αRu_2Si_3	···	···	$oP40$	$Pbcn$	RU2SI3	Ru_2Si_3
βRu_2Si_3	···	···	$tI80$	$P\overline{4}c2$	RU2SI3	Ru_2Si_3
$A4$	$A4$	C(diamond)	$cF8$	$Fd\overline{3}m$	DIAMOND_A4	$(Ru,Si)_1$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{Si}			$\Delta_r H$ / (J/mol)
liquid $\rightleftharpoons$ RuSi	congruent	1999.8	0.500	0.500		−72028
liquid $\rightleftharpoons$ Ru_2Si_3	congruent	1957.9	0.600	0.600		−63893
liquid $\rightleftharpoons$ RuSi + Ru_2Si_3	eutectic	1957.9	0.599	0.500	0.600	−63939
liquid + RuSi $\rightleftharpoons$ Ru_4Si_3	peritectic	1830.0	0.292	0.500	0.429	−17095
liquid + Ru_4Si_3 $\rightleftharpoons$ Ru_2Si	peritectic	1822.4	0.286	0.429	0.333	−30723
liquid $\rightleftharpoons$ hcp + Ru_2Si	eutectic	1814.5	0.271	0.052	0.333	−45476
liquid $\rightleftharpoons$ Ru_2Si_3 + $A4$	eutectic	1561.7	0.878	0.600	1.000	−50965
Ru_2Si $\rightleftharpoons$ hcp + Ru_4Si_3	eutectoid	1519.7	0.333	0.025	0.429	−1559

Table IIIa. Integral quantities for the liquid phase at 2700 K.

x_{Si}	ΔG_m [J/mol]	ΔH_m [J/mol]	ΔS_m [J/(mol·K)]	G_m^E [J/mol]	S_m^E [J/(mol·K)]	ΔC_P [J/(mol·K)]
0.000	0	0	0.000	0	0.000	0.000
0.100	−17380	−8782	3.185	−10082	0.482	0.000
0.200	−29461	−15915	5.017	−18227	0.856	0.000
0.300	−38035	−21287	6.203	−24322	1.124	0.000
0.400	−43360	−24783	6.880	−28251	1.285	0.000
0.500	−45463	−26290	7.101	−29902	1.338	0.000
0.600	−44270	−25693	6.880	−29162	1.285	0.000
0.700	−39628	−22880	6.203	−25915	1.124	0.000
0.800	−31282	−17736	5.017	−20048	0.856	0.000
0.900	−18745	−10147	3.185	−11448	0.482	0.000
1.000	0	0	0.000	0	0.000	0.000

Reference states: Ru(liquid), Si(liquid)

Table IIIb. Partial quantities for Ru in the liquid phase at 2700 K.

x_{Ru}	ΔG_{Ru} [J/mol]	ΔH_{Ru} [J/mol]	ΔS_{Ru} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Ru}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Ru}}$ [J/(mol·K)]	a_{Ru}	γ_{Ru}
1.000	0	0	0.000	0	0.000	1.000	1.000
0.900	−3315	−805	0.930	−950	0.054	0.863	0.959
0.800	−8959	−3372	2.069	−3950	0.214	0.671	0.839
0.700	−17236	−7928	3.447	−9229	0.482	0.464	0.663
0.600	−28481	−14701	5.104	−17014	0.856	0.281	0.469
0.500	−43093	−23919	7.101	−27532	1.338	0.147	0.293
0.400	−61581	−35809	9.545	−41011	1.927	0.064	0.161
0.300	−84708	−50599	12.633	−57680	2.623	0.023	0.077
0.200	−113895	−68516	16.807	−77764	3.425	0.006	0.031
0.100	−153183	−89787	23.480	−101492	4.335	0.001	0.011
0.000	−∞	−114641	∞	−129092	5.352	0.000	0.003

Reference state: Ru(liquid)

Table IIIc. Partial quantities for Si in the liquid phase at 2700 K.

x_{Si}	ΔG_{Si} [J/mol]	ΔH_{Si} [J/mol]	ΔS_{Si} [J/(mol·K)]	$G^{\mathrm{E}}_{\mathrm{Si}}$ [J/mol]	$S^{\mathrm{E}}_{\mathrm{Si}}$ [J/(mol·K)]	a_{Si}	γ_{Si}
0.000	−∞	−95677	∞	−110128	5.352	0.000	0.007
0.100	−143967	−80570	23.480	−92276	4.335	0.002	0.016
0.200	−111467	−66088	16.807	−75337	3.425	0.007	0.035
0.300	−86566	−52457	12.633	−59538	2.623	0.021	0.071
0.400	−65678	−39905	9.545	−45108	1.927	0.054	0.134
0.500	−47834	−28660	7.101	−32273	1.338	0.119	0.237
0.600	−32729	−18950	5.104	−21262	0.856	0.233	0.388
0.700	−20308	−11000	3.447	−12301	0.482	0.405	0.578
0.800	−10628	−5041	2.069	−5619	0.214	0.623	0.779
0.900	−3808	−1298	0.930	−1443	0.054	0.844	0.938
1.000	0	0	0.000	0	0.000	1.000	1.000

Reference state: Si(liquid)

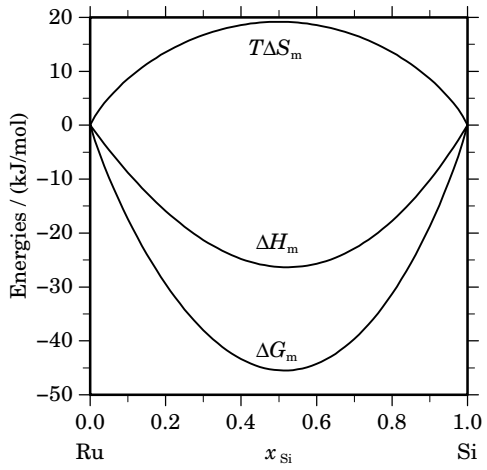

Fig. 2. Integral quantities of the liquid phase at T=2700 K.

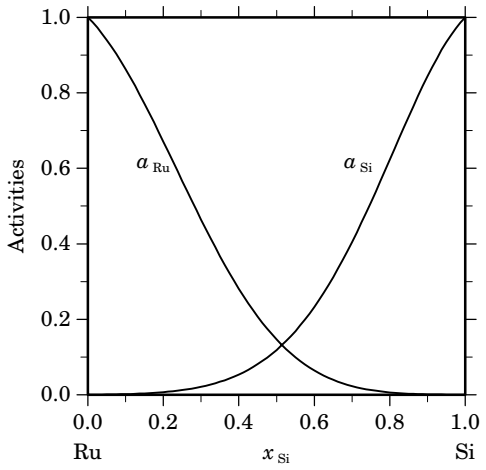

Fig. 3. Activities in the liquid phase at T=2700 K.

Table IV. Standard reaction quantities at 298.15 K for the compounds per mole of atoms.

Compound	x_{Si}	$\Delta_{\mathrm{f}}G^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}H^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}S^{\circ}$ / (J/(mol·K))	$\Delta_{\mathrm{f}}C_P^{\circ}$ / (J/(mol·K))
Ru_2Si_1	0.333	−34167	−35195	−3.446	0.000
Ru_4Si_3	0.429	−45949	−47788	−6.169	0.000
Ru_1Si_1	0.500	−51627	−52988	−4.562	−0.315
Ru_2Si_3	0.600	−47019	−47723	−2.360	−0.149

References

[1965Obr] W. Obrowski: Metallwiss. Tech. (Berlin) **19** (1965) 741–742.

[1970Eng] I. Engstrom: Acta Chem. Scand. **24** (1970) 1466–1468.

[1988Top] L. Topor, O.J. Kleppa: Z. Metallkd. **79** (1988) 623–628.

[1988Wei] F. Weitzer, P. Rogl, J.C. Schuster: Z. Metallkd. **79** (1988) 154–156.

[1997Kun] J.J. Kuntz, L. Perring, P. Feschotte, J.C. Gachon: J. Solid State Chem. **133** (1997) 439–444.

[1997Per] L. Perring, P. Feschotte, J.C. Gachon: Thermochim. Acta **293** (1997) 101–108.

[1998Cic] A. Ciccioli, G. Balducci, G. Gigli, L. Perring, J.J. Kuntz, J.C. Gachon: Ber. Bunsenges. Phys. Chem. **102** (1998) 1275–1278.

[1998Per] L. Perring, F. Bussy, J.J. Kuntz, J.C. Gachon: Ber. Bunsenges. Phys. Chem. **102** (1998) 1211–1216.

[1998Mes] S.V. Meschel, O.J. Kleppa: J. Alloys Comp. **274** (1998) 193–200.

[1999Per] L. Perring, F. Bussy, J.C. Gachon, P. Feschotte: J. Alloys Comp. **284** (1999) 198–205.

[2001Du] Y. Du, K.H. Chen, J.C. Schuster, L. Perring, B.Y. Huang, Z.H. Yua, J.C. Gachon: Z. Metallkd. **92** (2001) 323–327.

[2001Liu] Y.Q. Liu, G. Shao, K.P. Homewood: J. Alloys Comp. **320** (2001) 72–79.

[2002Iva] L. Ivanenko, G. Behr, C.R. Spinella, V.E. Borisenko: J. Cryst. Growth **236** (2002) 572–576.