

Ab Initio Surface Properties of Ag-Sn alloys: Implications for Lead-Free Soldering

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Electronic Supplementary Information (ESI)

Table S1 Surface energies for Ag₃Sn. The values obtained with the FM method (see Section 2 of the main text) are reported in parenthesis.

hkl	Excess Sn ^a	Es min ^b [eV/Å ²]	Es max ^b [eV/Å ²]	average ^b [eV/Å ²]
001	0	0.0344(0.0330)	0.0344(0.0330)	0.0344(0.0330)
	0	0.0360	0.0360	0.0360
010	+1	0.0396	0.0377	0.0386
	-1	0.0459	0.0478	0.0469
011	+2	0.0349(0.0352)	0.0325(0.0327)	0.0336(0.0337)
	0	0.0429	0.0429	0.0429
	-3	0.0641	0.0679	0.0660
	-2	0.0498	0.0522	0.0510
	+3	0.0390(0.0373)	0.0353(0.0336)	0.0371(0.0354)
021	0	0.0361(0.0366)	0.0361(0.0366)	0.0361(0.0366)
023	0	0.0425 (0.0416)	0.0425 (0.0416)	0.0425 (0.0416)
100	0	0.0365 (0.0369)	0.0365(0.0369)	0.0365(0.0369)
110	1	0.0423	0.0411	0.0417
	-1	0.0516	0.0528	0.0522
	-3	0.0633	0.0669	0.0651
	3	0.0381(0.0362)	0.0346(0.0327)	0.0363(0.0345)
111	1	0.0426	0.0416	0.0421
	-1	0.0486	0.0495	0.0490
	0	0.0446	0.0446	0.0446
	-2	0.0527	0.0546	0.0537
	2	0.0410	0.0391	0.0400
	1	0.0431	0.0422	0.0427
121	0	0.0404	0.0404	0.0404
223	0	0.0445	0.0445	0.0445
221	0	0.0453	0.0453	0.0453
	0	0.0436	0.0436	0.0436
101	2	0.0367	0.0345	0.0356
	2	0.0373	0.0351	0.0362
	0	0.0446	0.0446	0.0446
	-2	0.0533	0.0555	0.0544
	0	0.0435	0.0435	0.0435
102	1	0.0407	0.0400	0.0403
120	0	0.0451	0.0451	0.0451

^a number of Sn atoms on each surface in excess with respect to the compound stoichiometry

^b max, min and average refer to the Sn chemical potential, see eq. 2 of the main text

Table S2 Surface energies for AgSn₂. The values obtained with the FM method (see Section 2 of the maintext) are reported in parenthesis.

hkl	Excess Sn ^a	Es min ^b [eV/Å ²]	Es max ^b [eV/Å ²]	average ^b [eV/Å ²]
001	-2	0.0402	0.0414	0.0408
	2	0.0259 (0.0226)	0.0247 (0.0214)	0.0253 (0.0220)
100	-2	0.0385	0.0399	0.0392
	0	0.0295	0.0295	0.0295
	2	0.0239 (0.0245)	0.0224 (0.0230)	0.0232 (0.0237)
101	-1	0.0355	0.0364	0.0360
	1	0.0260 (0.0252)	0.0251 (0.0242)	0.0255 (0.0247)
	0	0.0293	0.0293	0.0293
110	-1	0.0307	0.0317	0.0312
	-2	0.0460	0.0481	0.0470
	1	0.0247 (0.0208)	0.0236 (0.0197)	0.0242 (0.0202)
	2	0.0308 (0.0268)	0.0287 (0.0247)	0.0297 (0.0258)
111	-1	0.0291	0.0299	0.0295
	1	0.0278	0.0270	0.0274
	2	0.0272 (0.0241)	0.0256 (0.0233)	0.0264 (0.0237)
	-2	0.0325	0.0341	0.0333
121		0.0266 (0.0251)	0.0266 (0.0251)	0.0266 (0.0251)
	1	0.0312	0.0300	0.0306

^a number of Sn atoms on each surface in excess with respect to the compound stoichiometry

^b max, min and average refer to the Sn chemical potential, see eq. 2 of the main text

Table S3 Surface energies for the most stable surfaces of β-Sn (most stable terminations). The values obtained with the FM method (see Section 2 of the main text) are reported in parenthesis.

hkl	Es [eV/Å ²]
100	0.0225(0.0250)
101	0.0229(0.0224)
201	0.0243
112	0.0222(0.0261)
122	0.0230

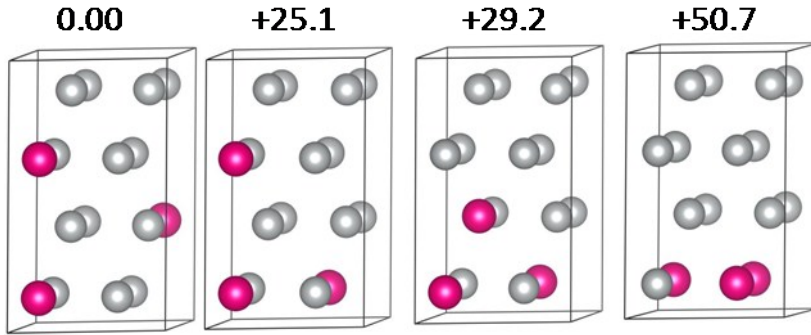


Figure S1 Various configurations of $\text{Ag}_{13}\text{Sn}_3$ ($2 \times 2 \times 2$ hcp-Ag supercell). The leftmost one is the most stable; for the other structures the energy (meV/atom) with respect to the most stable configuration is reported

Table S4 energy of $\text{Ag}_{35}\text{Sn}_9$ slabs, with various positions of Sn atoms

structure ^a	Energy ^b (meV/ slab-atom)
1-0-1-1-1-1-1-1-1-0-1 (Fig. 2e, main text)	0.00
2-0-1-1-0-1-0-1-1-0-2 (Fig. 2f, main text)	0.44
1-1-1-1-1-0-1-1-1-1-1	1.60
2-1-0-1-0-1-0-1-0-1-2	2.69
1-1-0-1-1-1-1-1-0-1-1	2.75
2-1-1-0-0-1-0-0-1-1-2	4.10
0-1-1-1-1-1-1-1-1-1-0	27.94
4-0-0-0-0-1-0-0-0-0-4	71.94
0-4-0-0-0-1-0-0-0-0-4-0	112.20

^a the nomenclature consists of a number for each of the 11 layers composing the slab. That number represents the number of Sn atoms in the corresponding slabs (*cf* first two entries with Fig. 2e-f of the main text)

^b energy given with respect to the most stable structure

Table S5 Comparison between calculated (PBE/plane waves) and predicted (“surface mixing rule”, see Section 3.3 and ref. 31 of the main text) oxygen adsorption energies. The 5th column ($E_{O}^{ads-mix}$) reports the adsorption energy predicted by the surface mixing rule, and the 6th column reports the difference with respect to the DFT energy (ϵ). The same goes for 7th and 8th columns ($E_{O}^{ads-mix'}$ and ϵ'), with the difference that the surface mixing rule value is calculated by substituting the adsorption energy of pure Ag with that of the Ag3 site in the considered alloy. We mention that a linear fitting of $E_{O}^{ads-DFT}$ vs $E_{O}^{ads-mix'}$ (excluding $Ag_4Sn^{(50)}$, for the reasons discussed in the main text) results in a linear coefficient much closer to the ideal value of 1.0 and higher R^2 with respect to $E_{O}^{ads-DFT}$ vs $E_{O}^{ads-mix}$ (linear coefficient: 0.998 vs 1.133 ; R^2 : 0.824 vs 0.744).

system	surface	site ^a	$E_{O}^{ads-DFT}$ (eV)	$E_{O}^{ads-mix}$ (eV)	ϵ	$E_{O}^{ads-mix'}$ (eV)	ϵ'
Ag ₃ Sn	001	Ag2Sn	1.80	2.05	0.25	1.75	-0.05
Ag ₃ Sn	011	AgSn2	2.81	3.05	0.24	2.90	0.09
Ag ₃ Sn	011	Ag2Sn	2.14	2.05	-0.08	1.75	-0.38
Ag ₄ Sn ⁽²⁵⁾	001	Ag2Sn	1.61	2.05	0.44	1.47	-0.14
Ag ₄ Sn ⁽⁵⁰⁾	001	Ag2Sn	2.14	2.05	-0.09	1.47	-0.67
Ag ₄ Sn ⁽⁵⁰⁾	001	AgSn2	2.45	3.05	0.43	2.76	0.14

a)the 3 atoms forming the hollow sites are indicated

Table S6 Oxygen adsorption energies E_{O}^{ads} on supercells (lower coverage) for selected surfaces of Ag-Sn alloys

system	surface	site ^a	E_{O}^{ads} (eV), single cell ^c	E_{O}^{ads} (eV), supercell
Sn	100	Sn3 ^b	4.05 ^c	4.25 ^d
Ag ₃ Sn	001	Ag2Sn ^b	1.80	1.94 ^e
Ag ₃ Sn	001	Ag3	0.60	0.66 ^e
Ag ₃ Sn	011	AgSn2 ^b	2.81	2.82 ^f
Ag ₄ Sn ⁽²⁵⁾	001	Ag2Sn ^b	1.61 ^c	1.70 ^e

^a the 3 atoms forming the hollow sites are indicated

^b most stable adsorption site for the corresponding surface

^c Ag₄Sn (that is based on hcp-Ag lattice) and Sn have small cells, that would result in a very high oxygen coverage. Therefore, we evaluated E_{O}^{ads} starting from 2x2 and 1x2 supercells, respectively.

^d 2x2 supercell

^e supercell obtained by applying a $\begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}$ rotation matrix to the two-dimensional surface unit cell.

^f 2x1 supercell

Table S7 Sulphur adsorption energies E_S^{ads} on supercells (lower coverage) for selected surfaces of Ag-Sn alloys

system	surface	site ^a	E_S^{ads} (eV), single cell ^c	E_S^{ads} (eV), supercell
Sn	100	Sn3 ^b	1.30 ^c	2.02 ^d
Ag ₃ Sn	001	Ag2Sn ^b	0.52	0.69 ^e
Ag ₃ Sn	001	0.56	0.67 ^e	
Ag ₃ Sn	011	AgSn2 ^b	1.45	1.51 ^f
Ag ₄ Sn ⁽²⁵⁾	001	Ag2Sn ^b	0.48 ^c	1.70 ^e

^a the 3 atoms forming the hollow sites are indicated

^b most stable adsorption site for the corresponding surface

^c Ag₄Sn (that is based on hcp-Ag lattice) and Sn have small cells, that would result in a very high sulphur coverage. Therefore, we evaluated E_S^{ads} starting from 2x2 and 1x2 supercells, respectively.

^d 2x2 supercell

^e supercell obtained by applying a $\begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}$ rotation matrix to the two-dimensional surface unit cell.

^f 2x1 supercell

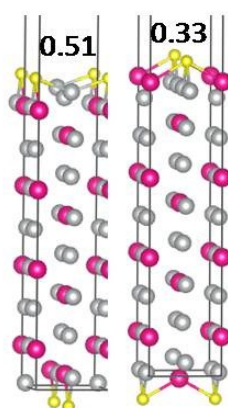


Figure S2 Additional sulphur adsorption positions on Ag₃Sn(001) surface. Adsorption energies (see eq. 3b of the main text) are reported on top of each structure

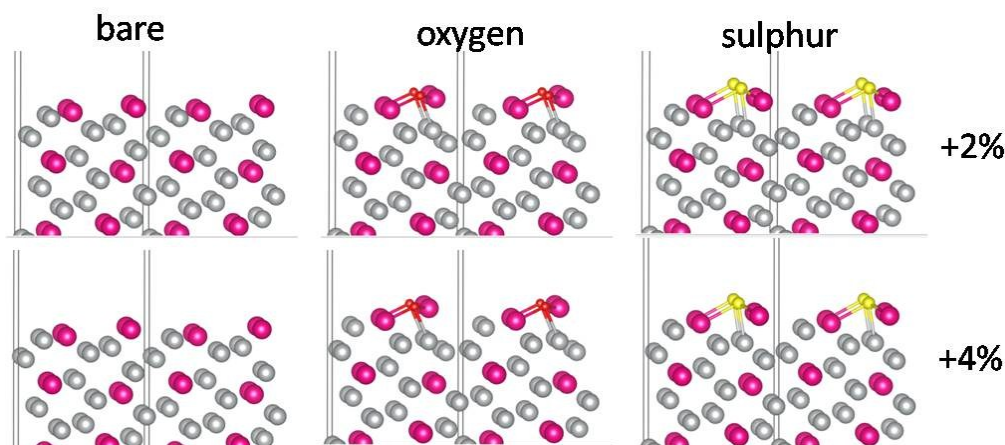


Figure S3 Ag₃Sn(011) surfaces upon lattice expansion (indicated on the right): bare (left), with oxygen adsorbed onto them (middle), and with adsorbed sulphur (right). The adsorption sites are AgSn2 for oxygen, and AgSn3 for sulphur (see also Fig. 7c of the main text).