IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Reply to comment on 'Modelling of surface energies of elemental crystals'

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2009 J. Phys.: Condens. Matter 21 198002

(http://iopscience.iop.org/0953-8984/21/19/198002)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 129.252.86.83
The article was downloaded on 29/05/2010 at 19:36

Please note that terms and conditions apply.

IOP PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **21** (2009) 198002 (3pp) doi:10.1088/0953-8984/21/19/198002

REPLY

Reply to comment on 'Modelling of surface energies of elemental crystals'

D Liu[1,2], H M Lu[3,4] and Q Jiang[1,2,5]

[1] Key Laboratory of Automobile Materials (Jilin University), Ministry of Education, Changchun 130022, People's Republic of China
[2] Department of Materials Science and Engineering, Jilin University, Changchun 130022, People's Republic of China
[3] National Laboratory of Solid State Microstructures, Department of Materials Science and Engineering, Nanjing University, Nanjing 210093, People's Republic of China
[4] Department of Physics, Nanjing University, Nanjing 210093, People's Republic of China

E-mail: Jiangq@jlu.edu.cn

Received 4 March 2009
Published 22 April 2009
Online at stacks.iop.org/JPhysCM/21/198002

Abstract
In reply to the comment by Luo *et al*, our theoretical model for the surface energy of elemental crystals is further developed to improve the prediction accuracy of the surface energy of the high-Miller-index facets. It is considered that the previous predicted unit surface area could not denote the actual one since the facets now are uneven. With the modification, the accuracy for the prediction of surface energy in units of J m^{-2} is improved.

In this comment [1], Luo *et al* have improved our previous model [2] for predicting surface energies (γ) of elemental crystals of the high-Miller-index (HI) facets. They suggested that for HI facets, such as (110) of A1, (100) and (111) of A2 and $(10\bar{1}0)$ of A3 structures, the coordination number (CN) imperfection at the subsurface layer, and even the second subsurface layer, should be considered separately. In our previous work [2], the surface bond deficit Z_S is calculated by $Z_S = Z_B - Z_{(hkl)}$, where Z_B is the bulk CN of the nearest neighbours of an atom and $Z_{(hkl)}$ is the total broken bonds of unit area at the (hkl) facet [3, 4] where different cases of distinct layers are not specially considered, which is significant for calculating γ values at the facets [2]. Adding this effect, our model established in [2] has been revised by Luo *et al* [1]:

$$\gamma = E\sum_i\{[2 - Z_{Si}/Z_B - (Z_{Si}/Z_B)^{1/2}] + \beta[2 - Z'_{Si}/Z'_B - (Z'_{Si}/Z'_B)^{1/2}]\}/[(2+2\beta)A_S], \quad (1)$$

where Z_{Si} and Z'_{Si}, Z_B and Z'_B denote surface and bulk CN of the nearest neighbours and next-nearest neighbours on the ith surface layer, E is the bulk cohesive energy and A_S is the surface area per atom. β is a structural coefficient, $\beta = 0$ for A1 and A3, $\beta = 1/2$ for A2 and simple cubic (SC), and $\beta = 3/10$ for A4 structures. In equation (1), the unique improvement is that the bond deficit of subsurface layers is separately calculated while other values remain from our original definition. Luo *et al* indeed give better accuracy for γ values of HI facets than our original model [1].

Following the idea of Luo *et al* [1], we find that calculations on γ values of HI facets could be further improved. In equation (1), to compare the determined γ values with experimental results, γ values in units of eV/atom should be transferred to units of J m^{-2} by dividing by A_S [2]. However, HI facets are no longer planes in an atomic level. Accordingly, A_S of HI facets cannot be obtained simply from the ratio of the surface area and the number of atoms on a facet and should be re-examined. Figure 1 shows several actual morphologies of HI facets. For example, the Ag(110) facet, from an A1 structure, is uneven and the first-layer atoms (surface atoms) form ridges, which are separated by the lower second-layer atoms (subsurface-layer atoms). In our previous calculation [2], $A_S = \sqrt{2}a^2/2$, where a is the lattice constant. However, if the first- and second-layer atoms are respectively considered, in light of figure 1, we found that the Ag(110) facet consists of two Ag(111) facets and the corresponding A_S is

[5] Author to whom any correspondence should be addressed.

 © 2009 IOP Publishing Ltd Printed in the UK

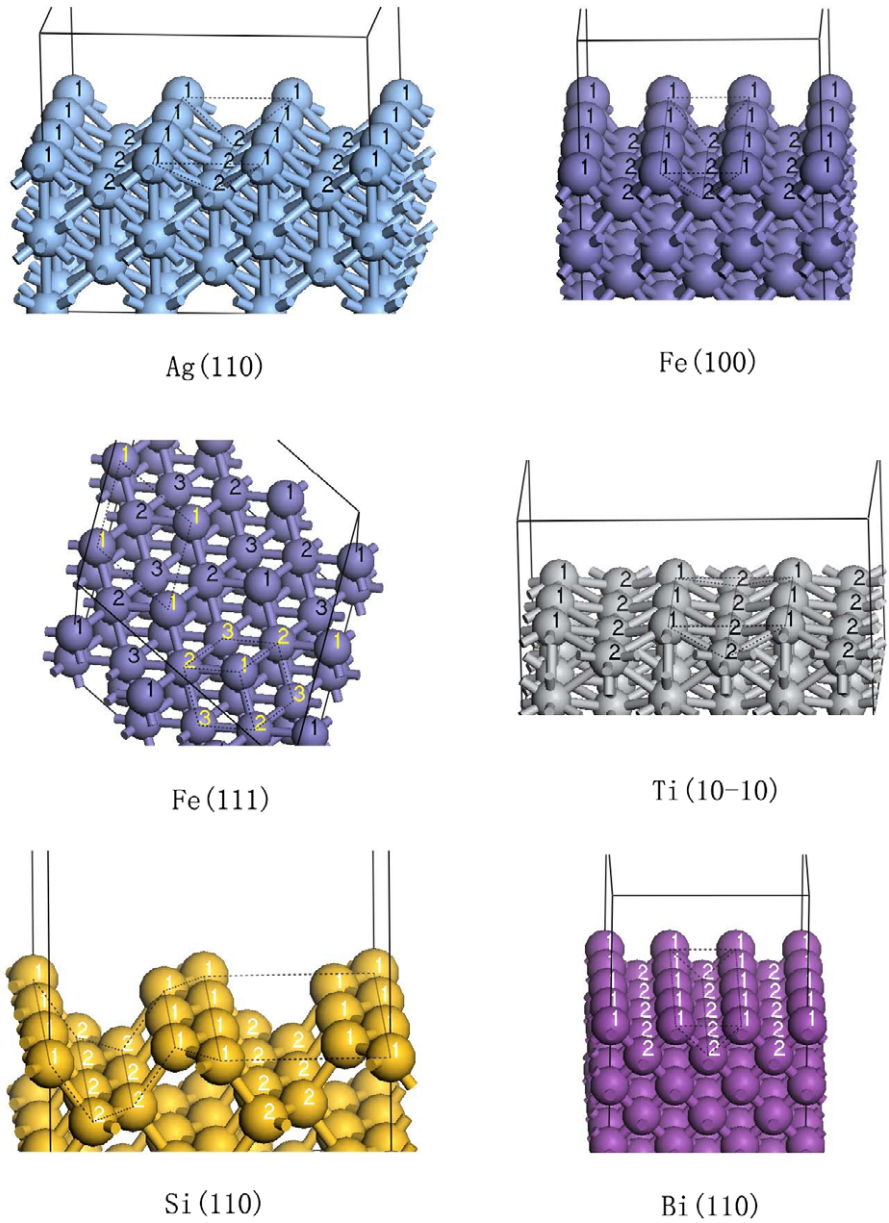

Figure 1. The morphology of the HI facets of several elements, which denotes different structures. (This figure is in colour only in the electronic version)

Table 1. The original and revised A_S for the HI facets of different structures.

	A_S (m^2/atom)					
Facet	A1(110)	A2(100)	A2(111)	A3(10$\bar{1}$0)	A4(110)	SC(110)
Original [2]	$\sqrt{2}a^2/2$	a^2	$\sqrt{3}a^2$	$\sqrt{8/3}a^2$	$\sqrt{2}a^2/4$	$\sqrt{2}a^2$
Revised	$\sqrt{3}a^2/2$	$\sqrt{2}a^2$	$3\sqrt{2}a^2/2$	$\sqrt{3}a^2$	$(\sqrt{6}+\sqrt{2})a^2/8$	$2a^2$

$\sqrt{3}a^2/2$. Figure 1 also presents the morphology of Fe(100), Ti(10$\bar{1}$0) and Bi(110) facets, which are separately on behalf of A2, A3 and SC structures. They have the similar case to Ag(110). For the Fe(111) facet, both the subsurface-layer and the second subsurface-layer atoms have broken bonds. For the Fe(111) morphology in figure 1, the rhombic area in the upper left corner denotes A_S of the first layer while the corrected A_S shown in the lower right corner is composed of three inclined rhombuses sharing a first-layer vertex atom. For the Si(110) facet of the A4 structure, A_S is composed of two inclined rectangular areas between the rows of first- and second-layer atoms, one rectangular area between two rows of first-layer atoms and one rectangular area between two rows of second-layer atoms. According to the above rule, the calculated A_S

Table 2. γ values of the A1(110) facet in terms of equation (1). The corresponding previous theoretical, simulation and experimental values are also shown.

(110) facet	E (eV/atom)	a (Å)	γ (J m^{-2}) [2]	[1]	This work	[5]	[6, 7]
Cu	3.49	3.66	2.33	2.29	1.87	2.24	1.79, 1.83
Ag	2.95	4.18	1.51	1.48	1.21	1.24	1.25, 1.25
Au	3.82	4.20	1.95	1.91	1.56	1.7	1.51, 1.5
Ni	4.44	3.58	3.11	3.05	2.49	2.37	2.38, 2.45
Pd	3.90	3.85	2.36	2.31	1.89	2.23	2, 2.05
Pt	5.86	4.02	3.26	3.2	2.61	2.82	2.49, 2.48
Rh	5.75	3.87	3.44	3.38	2.76	2.9	2.66, 2.7
Ir	6.96	3.91	4.08	4	3.27	3.61	3.05, 3
Pb	2.03	5.11	0.7	0.69	0.56	0.45	0.59, 0.6
Al	3.39	4.05	1.86	1.82	1.49	1.27	1.14, 1.16
Ca	1.85	5.62	0.52	0.51	0.42	0.58	0.5, 0.49
Sr	1.72	6.17	0.40	0.39	0.32	0.43	0.42, 0.41
Ac	4.26	5.79	1.14	1.11	0.91	0.68	1.54, 1.6
Th	6.21	5.19	2.07	2.03	1.66	1.45	1.5

Table 3. γ values of A2(100) and (111) facets, SC(110) and A4(110) facets in terms of equation (1). The corresponding previous theoretical, simulation and experimental values are also shown.

	E (eV/atom)	a (Å)	Facets	γ (J m^{-2}) [2]	[1]	This work	[5]	[6, 7]
Li	1.64	3.51	(100)	0.75	0.75	0.53	0.52	0.52, 0.53
			(111)	0.91	0.79	0.65	0.59	
Na	1.11	4.2	(100)	0.36	0.35	0.25	0.26	0.26, 0.26
			(111)	0.44	0.38	0.31	0.29	
K	0.94	5.3	(100)	0.18	0.18	0.13	0.14	0.13, 0.15
			(111)	0.22	0.20	0.16	0.15	
Rb	0.85	5.71	(100)	0.14	0.14	0.1	0.11	0.12, 0.11
			(111)	0.18	0.16	0.13	0.12	
Cs	0.81	6.14	(100)	0.12	0.12	0.08	0.09	0.1, 0.1
			(111)	0.15	0.13	0.1	0.09	
Ba	1.90	5.03	(100)	0.43	0.42	0.3	0.35	0.38, 0.37
			(111)	0.52	0.45	0.37	0.40	
Ra	1.66	5.15	(100)	0.36	0.35	0.25	0.29	
			(111)	0.43	0.37	0.3	0.32	
Eu	1.86	4.58	(100)	0.50	0.49	0.35	0.46	0.45, 0.45
			(111)	0.6	0.53	0.43	0.52	
V	5.32	3.02	(100)	3.27	3.25	2.3	3.03	2.62, 2.56
			(111)	4.02	3.5	2.86	3.54	
Cr	4.1	2.85	(100)	2.83	2.81	1.99	3.98	2.35, 2.30
			(111)	3.47	3.03	2.47	3.89	
Fe	4.29	2.86	(100)	2.94	2.93	2.07	2.22	2.42, 2.48
			(111)	3.61	3.15	2.57	2.73	
Nb	7.58	3.3	(100)	3.91	3.89	2.75	2.86	2.66, 2.70
			(111)	4.8	4.18	3.41	3.05	
Mo	6.83	3.17	(100)	3.81	3.79	2.68	3.84	2.91, 3
			(111)	4.68	4.08	3.33	3.74	
Ta	8.12	3.35	(100)	4.07	4.04	2.86	3.1	2.9, 3.15
			(111)	4.97	4.34	3.54	3.46	
W	8.92	3.17	(100)	4.99	4.96	3.51	4.64	3.27, 3.68
			(111)	6.11	5.33	4.35	4.45	
Sb(SC)	2.75	3.36	(110)	0.77	0.83	0.59	0.66	0.60, 0.54
Bi(SC)	2.18	3.26	(110)	0.66	0.71	0.5	0.54	0.49, 0.49
Po(SC)	1.50	3.34	(110)	0.42	0.45	0.32	0.37	
Si(A4)	4.63	5.43	(110)	1.7	1.59	1.16		1.14
Ge(A4)	3.86	5.66	(110)	1.3	1.22	0.89		0.88

Table 4. γ values of the A3 $(10\bar{1}0)$ facet in terms of equation (1). The corresponding previous theoretical, simulation and experimental values are also shown.

$(10\bar{1}0)$	E (eV/atom)	a (Å)	γ (J m^{-2}) [2]	[1]	This work	[5]	[6, 7]
Be	3.32	2.22	2.93	2.54	2.39	2.13	1.63, 2.70
Mg	1.51	3.20	0.64	0.55	0.52	0.78	0.79, 0.76
Zn	1.35	2.68	0.82	0.71	0.67		0.99, 0.99
Cd	1.16	3.06	0.54	0.47	0.44		0.76, 0.74
Tl	1.89	3.71	0.60	0.52	0.49	0.35	0.6, 0.58
Sc	3.90	3.30	1.55	1.35	1.27	1.53	1.28
Ti	4.86	2.95	2.44	2.11	1.99	2.52	1.9, 2.1
Co	4.4	2.53	2.99	2.59	2.44	3.04	2.52, 2.55
Y	4.38	3.55	1.52	1.32	1.24	1.24	1.13
Zr	6.26	3.25	2.58	2.24	2.11	2.11	1.91, 2
Tc	6.86	2.74	3.98	3.45	3.25	3.9	3.15
Ru	6.75	2.72	3.97	3.44	3.24	4.24	3.04, 3.05
La	4.47	3.87	1.3	1.12	1.06	0.92	1.02
Lu	4.44	3.51	1.57	1.36	1.28	1.42	1.23
Hf	6.44	3.20	2.74	2.38	2.24	2.31	2.19, 2.15
Re	8.05	2.76	4.6	3.99	3.76	4.63	3.63, 3.60
Os	8.18	2.75	4.71	4.08	3.85	5.02	3.44, 3.45

for the HI facets is shown in table 1 where the present A_S is always larger than our original A_S for all HI facets. Since Luo *et al* have used our original A_S values [1], all results from both our original work [2] and Luo *et al* [1] underestimate the actual surface area per atom and thus the obtained γ values should be larger than the real ones.

Based on the above consideration for A_S, γ values for some HI facets are re-determined and listed in tables 2–4. The previous theoretical works [1, 2], simulation [5] and experimental [6, 7] results are also shown in the tables. As shown in the tables, this work gives better prediction accuracy than those made by Luo *et al* [1], which implies that our revision of A_S is necessary and reasonable.

In conclusion, when subsurface layers are considered to determine the surface energy of HI facets, not only bond deficit, but also the surface area per atom, should be specially calculated.

References

[1] Luo X G, Li J P, Zhang X H and Han J C 2009 *J. Phys.: Condens. Matter* **21** 198001

[2] Jiang Q, Lu H M and Zhao M 2004 *J. Phys.: Condens. Matter* **16** 521

[3] Mackenzie J K, Moore A J W and Nicholas J F 1962 *J. Phys. Chem. Solids* **23** 185

[4] Mackenzie J K and Nicholas J F 1962 *J. Phys. Chem. Solids* **23** 197

[5] Vitos L, Ruban A V, Striver H L and Kollár J 1998 *Surf. Sci.* **411** 186

[6] Tyson W R and Miller W A 1977 *Surf. Sci.* **62** 267

[7] de Boer F R, Boom R, Mattens W C M, Miedema A R and Niessen A K 1998 *Cohesion in Metals* vol 1 (Amsterdam: North-Holland)