Applied Surface Science 255 (2009) 9348–9357

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Calculation of the surface energy of hcp-metals with the empirical electron theory

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ARTICLE INFO

Article history:
Received 27 June 2009
Received in revised form 11 July 2009
Accepted 12 July 2009
Available online 16 July 2009

Keywords:
Surface energy
Empirical electron theory
Valence electron structure
Dangling bond
Hcp-metals

ABSTRACT

A brief introduction of the surface model based on the empirical electron theory (EET) and the dangling bond analysis method (DBAM) is presented in this paper. The anisotropy of spatial distribution of covalent bonds of hexagonal close-packed (hcp) metals such as Be, Mg, Sc, Ti, Co, Zn, Y, Zr, Tc, Cd, Hf, and Re, has been analyzed. And under the first-order approximation, the calculated surface energy values for low index surfaces of these hcp-metals are in agreement with experimental and other theoretical values. Correlated analysis showed that the anisotropy of surface energy of hcp-metals was related with the ratio of lattice constants (*c*/*a*). The calculation method for the research of surface energy provides a good basis for models of surface science phenomena, and the model may be extended to the surface energy estimation of more metals, alloys, ceramics, and so on, since abundant information about the valence electronic structure (VES) is generated from EET.

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1. Introduction

Surface energy, one of the basic quantities in surface science, plays an important role in several physical and chemical processes such as fracture, catalysis, crystal growth, etc. However, surface energies are difficult to determine experimentally and just few data exist [1–4]. Some of these experiments are performed at high temperatures and contain uncertainties of unknown magnitude [1,2]. Some of the experimental surface energy data [3,4] stem from surface tension measurements in the liquid phase extrapolated to 0 K [5]. Recently, Bonzel and Edmundts [6,7] have shown that analyzing the equilibrium shape of crystallites at various temperatures by scanning tunneling microscopy can yield absolute values of the surface energies versus temperature, but this technique has not yet been widely applied. Therefore, to determine the surface energy theoretically is very important.

Early theoretical calculations were based on perturbation theory [8] or non-perturbative variational method [9]. In the last few years, there have been several methods to calculate the surface energy of metals using either the first-principles calculations [5,10–21], or semi-empirical methods [22–34]. However, most first-principles methods are computationally demanding and have typically been used only for particular cases, focusing on a few elements or on a special application for a given metal surface. And most semi-empirical methods are based on some existent experiment results, and do much more approach, and usually use fitted parameters, focusing on a few systems which have some needed parameters and functions.

The starting point of our surface model is the valence electron structure (VES) calculated by the empirical electron theory in solid and molecule (EET) [35–38] established by Yu. And a brief introduction of EET is given in Appendix A.

2. Summary of the EET surface model

The main objective in the present study will be the first evaluation of the surface energy of hexagonal close-packed (hcp) metals from their VES by utilizing the number and the type of the dangling bonds on particular crystal surface based on the dangling bond analysis method (DBAM). And the VES, which refers to the bond names, the bond lengths, the covalent electron numbers (valence electron distribution), and so on, can be deduced by the bond length difference (BLD) [37,38]. And in the latter section the VES of hcp-metals can be calculated.

Surface energy is one of the most important static physical quantities characterizing metal surface. And the surface energy is defined as the additional value of the free energy per unit area of particular crystal surface, therefore, the surface energy of particular crystal surface is given by the below expression

$$\gamma = \frac{\Delta E}{\Delta S} \tag{1}$$

where ΔE represents the additional value of the free energy with the forming of new surface; ΔS is the added area of the crystal surface.

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doi:10.1016/j.apsusc.2009.07.034

When all bonds between two nearest crystal planes were broken, the two nearest crystal planes form two new crystal surfaces. Therefore the energy requirement for the procedure is just the additional free energy.

$$\Delta E = \sum_{\alpha} I_{\alpha}^{d} E_{\alpha} \tag{2}$$

where α represents bond name; E_α represents the bond energy of α bond; and I_α^d is the equivalent dangling bond number of α bond on particular crystal plane, whose value is determined with DBAM.

In EET, according to the bond energy formula [38,39], the bond energy E_α can be calculated from the VES of hcp-metals. Therefore, the key of this surface energy model is calculation of VES and the DBAM.

3. Calculation of VES and bond energy of the hcp-metals

The hcp-metals, the conventional crystal cell is showed in Fig. 1 and the solid lines indicate the primitive crystal cell, and the lattice constants (a and c) are shown in Table 1, belong to the A3 type crystal structure. And the atom coordinates are $(0, 0, 0)$ and $(1/3, 2/3, 1/2)$. So the experiment bond lengths which cannot be neglected can be obtained: $D_A = a$, $D_B = \sqrt{a^2/3 + c^2/4}$, $D_C = \sqrt{4a^2/3 + c^2/4}$, $D_D = c$, $D_E = \sqrt{7a^2/3 + c^2/4}$, $D_F = \sqrt{3}a$, $D_G = \sqrt{a^2 + c^2}$.

In perfect crystals $(c/a = 2\sqrt{2}/\sqrt{3} \approx 1.633)$, $D_A = D_B$, and $D_E = D_F$. For those hcp-metals with the parameters a and c not corresponding to idealization, if $c/a > 1.633$, then $D_A < D_B$, and $D_E > D_F$. If $c/a < 1.633$, then $D_A > D_B$, and $D_E < D_F$. And the bond length calculation results are shown in Table 2. The equivalent bond number of the bonds can be calculated with the formula [35–38,40].

$$I_\alpha = I_M I_S I_K \tag{3}$$

where I_M represents the reference atom number in the structure or the molecule; I_S represents the equivalent bond number for a reference atom to form α bond; I_K is a parameter, which equals 1 when the two atoms that form the bond are of the same kind or 2 when the two atoms are of different kinds. Therefore, the equivalent bond numbers of α bond are: $I_A = 2 \times 6 \times 1 = 12$, $I_B = 2 \times 6 \times 1 = 12$, $I_C = 2 \times 6 \times 1 = 12$, $I_D = 2 \times 2 \times 1 = 4$, $I_E = 2 \times 12 \times 1 = 24$, $I_F = 2 \times 6 \times 1 = 12$, $I_G = 2 \times 12 \times 1 = 24$.

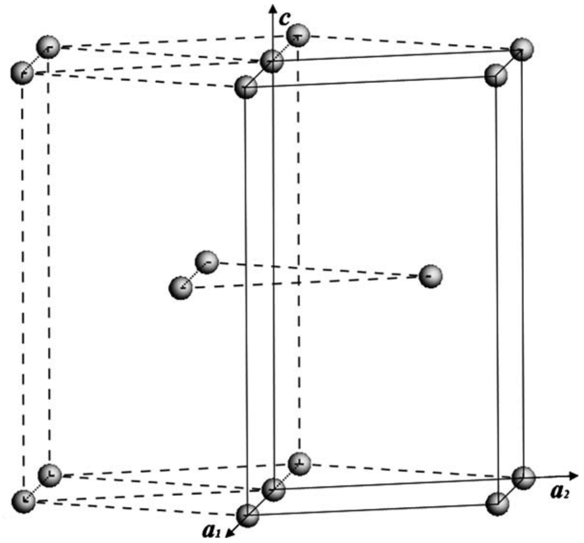

Fig. 1. Crystal cell of hcp-metals.

According to the Pauling bond length formula in EET [35–38]:

$$D_\alpha = 2R(1) - \beta \lg n_a \tag{4}$$

where D_α $(\alpha = A, B, \ldots, G)$ represents the bond length; $R(1)$ represents the single bond radius of the atom which form the bond; n_α represents the number of covalent electron pairs on the bond; and β is a factor whose value is determined with formula (A8) in Appendix A. Therefore, the following $r_{\alpha'}$ $(\alpha' = B, C\ldots)$ equation can be obtained:

$$\lg r_{\alpha'} = \lg(n_{\alpha'}/n_A) = (D_A - D_{\alpha'})/\beta$$

Therefore,

$$\sum Ir = I_A + \sum_{\alpha'=B}^{\alpha'=G} I_{\alpha'} r_{\alpha'}$$

Table 1
The lattice constants of hcp-metals.

hcp-metal	$a_1 = a_2 = a$/nm	c/nm	c/a	hcp-metal	$a_1 = a_2 = a$/nm	c/nm	c/a
Be	0.22856	0.35832	1.568	Y	0.36451	0.57305	1.572
Mg	0.32094	0.52105	1.624	Zr	0.32312	0.51477	1.593
Sc	0.3308	0.52653	1.592	Tc	0.27350	0.4388	1.604
Ti	0.29506	0.46788	1.586	Cd	0.29788	0.56167	1.886
Co	0.25070	0.40690	1.623	Hf	0.31946	0.50511	1.581
Zn	0.26649	0.49468	1.856	Re	0.27600	0.44580	1.615

Table 2
The bond length calculation results of hcp-metals.

hcp-metal/nm	D_A	D_B	D_C	D_D	D_E	D_F	D_G
Be	0.22856	0.222512	0.318985	0.35832	0.392417	0.395878	0.425009
Mg	0.32094	0.319699	0.453001	0.52105	0.555169	0.555884	0.61196
Sc	0.3308	0.325246	0.463911	0.52653	0.569774	0.572962	0.621822
Ti	0.29506	0.289393	0.41329	0.46788	0.507808	0.511059	0.553147
Co	0.2507	0.249684	0.353826	0.4069	0.433639	0.434225	0.477931
Zn	0.26649	0.291289	0.394799	0.49468	0.476323	0.461574	0.561894
Y	0.36451	0.355508	0.509169	0.57305	0.626196	0.63135	0.679157
Zr	0.32312	0.317882	0.453272	0.51477	0.556653	0.55966	0.607778
Tc	0.2735	0.270315	0.384542	0.4388	0.471884	0.473716	0.517057
Cd	0.29788	0.329311	0.444048	0.56167	0.534706	0.515943	0.635772
Hf	0.31946	0.312734	0.447054	0.50511	0.549465	0.553321	0.597654
Re	0.276	0.274001	0.388912	0.4458	0.476895	0.478046	0.524322

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