First-Principles Study of Surface Work Function and Surface Energy of Hexagonal Metals: Postprint

Authors: Ji Depeng, Wang Shaoqing

Date: 2023-03-19T00:00:00+00:00

Abstract

First-principles calculations were performed for the work function and surface energy of different surfaces of four hexagonal pure metals: Be, Mg, Ti, and Zr. The results show that for these four metals, the work function and surface energy differ significantly among different surface orientations. The (0001) surface has the highest work function and the lowest surface energy, while the (0111) surface has the lowest work function and the highest surface energy. For the two metals in the same group, the variation pattern of the work function F for different surfaces is similar, showing: F(0001)>F(0221)>F(1010)>F(1231)>F(1230)>F(0111), whereas the variation pattern of the surface energy g is completely opposite, showing: g(0001)

Work function Surface energy First-principles

Classification:

Materials Science

>>

Materials Science (General)

Citation:

DOI:10.12074/202303.00627V1 CSTR:32003.36.ChinaXiv.202303.00627.V1

Recommended citation: Ji Depeng, Wang Shaoqing. First-principles study of surface work function and surface energy of hexagonal metals. Chinese Academy of Sciences Preprint Platform. [ChinaXiv:202303.00627V1] (Click to copy)

Full Text

First-Principles Study of Surface Work Function and Surface Energy of Hexagonal Metals

JI Depeng, WANG Shaoqing
Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016

Abstract

Surface energy and work function are crucial for understanding metal surface properties. While numerous studies have investigated body-centered cubic (bcc) and face-centered cubic (fcc) metals, hexagonal close-packed (hcp) metals remain relatively unexplored, particularly regarding high-index surfaces. This work presents first-principles calculations of work functions and surface energies for Be, Mg, Ti, and Zr, examining six distinct surface orientations: (0001), (0221), (1010), (1231), (1230), and (0111). The results reveal a strong correlation between these properties: work functions follow the sequence $\Phi(0001) > \Phi(0221) > \Phi(1010) > \Phi(1231) > \Phi(1230) > \Phi(0111)$, while surface energies exhibit the inverse trend $\gamma(0001) < \gamma(0221) < \gamma(1010) < \gamma(1231) < \gamma(1230) < \gamma(0111)$. Furthermore, for metals within the same group, those with smaller atomic numbers (Be and Ti) exhibit larger work functions and surface energies compared to their heavier counterparts (Mg and Zr). Notably, the (0001) surface displays the highest work function but lowest surface energy, consistent with experimental observations.

Keywords: work function, surface energy, first-principles

With advancing surface science, understanding the physical properties of material surfaces has become increasingly important. Surface energy (γ) and work function (Φ) represent fundamental parameters for characterizing surface properties, providing insights into surface stability, chemical reactivity, adsorption and reconstruction phenomena, and corrosion susceptibility. Skriver et al. [**?**] and Andersen et al. [**?**, **?**, **?**] systematically investigated these properties using the TB-LMTO (tight-binding linear muffin-tin orbital) method, though their studies focused primarily on low-index surfaces rather than systematically examining high-index surfaces of the same metal. Rohwerder and Turcu [**?**] attempted direct measurement of surface potentials using scanning Kelvin probe force microscopy (SKPFM), but methodological limitations prevented attainment of ideal surface conditions, yielding only composite results that incorporate various surface factors and making it extremely difficult to obtain accurate values for pristine surfaces.

Density functional theory (DFT) has been widely applied to calculate surface work functions and energies. This approach enables efficient computation of numerous surface types after reasonable model simplification, even for surfaces that are theoretically possible but experimentally challenging to observe. Kokko et al. [?] systematically studied the work functions and surface energies of Li(100), Li(110), and Li(111). Singh-Miller and Marzari [?] investigated several low-index surfaces (001), (110), (111), and (0001) of Al, Pd, Pt, Ti, and other metals. Skriver and Rosengaard [?] examined surface energies and work functions of close-packed planes in various pure metals, establishing relationships with atomic number and identifying trends for fcc metals: $\Phi(111) > \Phi(100) > \Phi(110)$ and $\gamma(110) > \gamma(100) > \gamma(111)$. However, these studies primarily addressed common surfaces of cubic systems and the (0001) surface of hexagonal systems. The significant difference between a, b-axis and c-axis lattice parameters in hexagonal unit cells complicates the ideal structure of high-index surfaces, substantially increasing research difficulty. Consequently, systematic investigations of high-index surfaces in hcp metals remain scarce, with most work focusing on the (0001) plane [?, ?, ?].

Recent studies by Wang et al. [?] on bcc and fcc metals revealed systematic trends: for bcc metals (Nb, Mo, Ta, W), work functions follow $\Phi(110) > \Phi(133) > \Phi(120) > \Phi(111) > \Phi(311) > \Phi(100)$, while for fcc metals, $\Phi(111) > \Phi(100) > \Phi(211) > \Phi(123) > \Phi(310) > \Phi(110)$. Tang et al. [?] calculated surface energies for several Mg surfaces using first-principles methods, but comprehensive studies on other hcp metals and additional high-index surfaces remain lacking. This work investigates six surfaces of four hcp metals—Be, Mg, Ti, and Zr—to elucidate the relationship between work function and surface energy across different orientations.

1. Theoretical Background

1.1 Surface Energy

Surface energy effectively reflects surface stability. Numerous computational approaches exist for calculating this property, all fundamentally based on the energy difference between a surface model and its bulk counterpart. For models with identical upper and lower surfaces, the surface energy is calculated as:

$$\gamma = \frac{E_{\text{slab}} - N \cdot E_{\text{bulk}}}{2S}$$

where E_{slab} is the total energy of the surface model, N is the number of atoms in the model, E_{bulk} is the energy per atom in the bulk material, and S is the surface area. Model construction must ensure identical surface states for both upper and lower surfaces.

1.2 Work Function

The work function is defined as the minimum energy required to remove an electron from inside a material to a point just outside its surface, representing the work an electron must do to escape the metal’ s binding potential:

$$\Phi = E_{\text{vacuum}} - E_{\text{Fermi}}$$

where E_{vacuum} corresponds to the vacuum energy level and E_{Fermi} to the Fermi energy. In first-principles calculations, absolute values of E_{vacuum} and E_{Fermi} are difficult to obtain individually, but their relative difference can be calculated directly, yielding work function values equivalent to experimental results:

$$\Phi = E'_{\text{vacuum}} - E'_{\text{Fermi}}$$

where E'_{Fermi} is the calculated Fermi level and E'_{vacuum} is the calculated vacuum energy level for the specific surface model. Although these values vary with calculation conditions, their difference remains constant. [Figure 1: see original paper] illustrates the calculation model and corresponding potential distribution curve. The work function is obtained by computing this energy difference.

2. Computational Methods

2.1 Calculation Model

This study investigates four hcp metals—Be, Mg, Ti, and Zr—calculating surface energies and work functions for six surface configurations: (0001), (0111), (0221), (1010), (1230), and (1231). Periodic boundary conditions were employed to construct supercell models for each surface orientation, with lateral dimensions of 1 × 1 and varying numbers of metal layers along the longitudinal direction. The slab thickness was selected based on surface complexity while ensuring identical symmetry for upper and lower surfaces to represent the same surface orientation. [Figure 2: see original paper] shows the six surface configurations for Mg; the other three metals exhibit similar structures.

2.2 Calculation Details

Calculations were performed using the VASP (Vienna Ab initio Simulation Package) software [**?**] with the PAW (Projector-Augmented Wave) method and PBE (Perdew-Burke-Ernzerhof) generalized gradient approximation [**?**, **?**]. A plane-wave cutoff energy of 400 eV was adopted, with a uniform vacuum layer thickness of 1.6 nm. K-point meshes were selected based on surface model thickness, with a single k-point along the vacuum direction due to its large thickness, while maintaining a total of at least 40 k-points in the model. Convergence criteria were set to an energy precision of less than 1×10^{-6} eV and forces on each atom below 0.002 eV/(nm · atom).

Prior to surface calculations, lattice constants for the four metals were optimized and compared with experimental values [?], as shown in . The calculated a- and c-axis lattice parameters and c/a ratios differ from experimental values by less than 1%, which is within acceptable error margins.

3. Results and Discussion

Calculated results for the (0001) surfaces of Be, Mg, Ti, and Zr were compared with literature data and experimental values [?, ?, ?, ?, ?, ?, ?, ?, ?] in . While few reports exist for other surfaces, the excellent agreement between our calculations and previous computational results, as well as the small differences with experimental data, confirms the reliability of our approach for subsequent analysis.

3.1 Results for Be and Mg

Convergence tests for Be and Mg surfaces were performed using slab thicknesses ranging from 12 to 36 atomic layers, exceeding the typical ~13 layers employed in most literature [?, ?, ?, ?]. The increased thickness was necessary for complex surface configurations with small interlayer spacings to ensure a metal thickness of approximately 1.0 nm. All calculations reached convergence before data analysis, as demonstrated in [Figure 3: see original paper]. Different surface orientations required varying numbers of layers, but all achieved convergence with surface energy fluctuations below 0.03 J/m^2 and work function variations less than 0.05 eV. Due to the large number of layers employed, each configuration yielded stable results, and final values were averaged over several converged thicknesses.

[Figure 4: see original paper] presents the calculated work functions and surface energies for Be and Mg surfaces, revealing substantial orientation-dependent differences. For Mg, work functions range from 3.48 eV for the (0111) surface to 3.71 eV for (0001)—a difference of 0.23 eV—while surface energies vary from 0.56 J/m^2 for (0001) to 0.84 J/m^2 for (0111), a difference of 0.28 J/m^2. Be exhibits similar trends but with larger variations: work functions span from 4.22 eV for (0111) to 5.23 eV for (0001) (a 1.01 eV difference), and surface energies range from 1.76 J/m^2 for (0001) to 2.83 J/m^2 for (0111) (a 1.07 J/m^2 difference).

Both metals display identical ordering: work functions decrease as $\Phi(0001) > \Phi(0221) > \Phi(1010) > \Phi(1231) > \Phi(1230) > \Phi(0111)$, while surface energies increase in the inverse order $\gamma(0001) < \gamma(0221) < \gamma(1010) < \gamma(1231) < \gamma(1230) < \gamma(0111)$. The work function reflects the ease of electron exchange at the surface; the (0001) surface, with the highest work function and lowest surface energy, is most stable and least prone to electron loss. Conversely, the (0111) surface, with the lowest work function and highest surface energy, exhibits poor stability and is unlikely to exist cleanly in practice. Since the surface orientation exposed during cutting or deformation is difficult to control, these substantial differences in work function and surface energy significantly influence material performance.

Surface energy directly relates to surface stability and reconstruction propensity. The calculated variations are considerable, and the inverse relationship with work function is evident. For corrosion prevention, surfaces with high energy and low work function should be minimized, and metals exhibiting low work functions for specific orientations require protective measures.

Additionally, Be shows higher work functions and surface energies than Mg for equivalent orientations. As these elements belong to the same group, metals with smaller atomic numbers exhibit larger work functions and surface energies, consistent with findings by Skriver et al. [?] and Wang et al. [?]. Within a group, larger atomic number correlates with higher atomic reactivity and lower work function, but also lower surface energy. This occurs because work function reflects the ability to retain electrons; smaller atomic number means smaller atomic radius and stronger nuclear control over valence electrons, making electron escape more difficult and increasing the work function. Meanwhile, surface energy depends on surface atomic coordination; smaller atomic number leads to smaller unit cell parameters and stronger interactions among surface atoms, raising surface energy.

3.2 Results for Ti and Zr

Similar calculations were performed for Ti and Zr, with results shown in [Figure 5: see original paper]. Ti exhibits work functions ranging from 3.22 eV for (0111) to 4.25 eV for (0001) (a 1.03 eV span), and surface energies from 1.96 J/m^2 for (0001) to 2.51 J/m^2 for (0111) (a 0.55 J/m^2 difference). For Zr, work functions vary from 3.20 eV for (0111) to 4.17 eV for (0001) (0.97 eV difference), and surface energies range from 1.60 J/m^2 for (0001) to 2.09 J/m^2 for (0111) (0.49 J/m^2 difference).

The same systematic ordering emerges: $\Phi(0001) > \Phi(0221) > \Phi(1010) > \Phi(1231) > \Phi(1230) > \Phi(0111)$ for work functions, and $\gamma(0001) < \gamma(0221) < \gamma(1010) < \gamma(1230) < \gamma(1231) < \gamma(0111)$ for surface energies, with only the (1230) and (1231) positions swapped compared to Be and Mg. As with Be and Mg, Ti exhibits higher work functions and surface energies than Zr for corresponding surfaces.

3.3 Discussion

First-principles calculations provide an efficient means to systematically investigate complex metal surfaces. Our results agree well with experimental values within acceptable error margins, and for simple orientations, the agreement is even closer, demonstrating the method' s utility for exploring surface physicochemical properties and guiding practical applications.

The calculations reveal consistent trends across all four hcp metals: work functions follow $\Phi(0001) > \Phi(0221) > \Phi(1010) > \Phi(1231) > \Phi(1230) > \Phi(0111)$, while surface energies follow $\gamma(0001) < \gamma(0221) < \gamma(1010) < \gamma(1231) < \gamma(1230) < \gamma(0111)$. The (0001) and (0221) surfaces exhibit high work functions but low surface energies, whereas (1230) and (0111) show the opposite behavior. Differences of approximately 1.0 eV in work function and 1.0 J/m^2 in surface energy significantly affect material stability. These established trends enable prediction of which orientations are unfavorable and more susceptible to reconstruction or decomposition under complex conditions, improving our understanding of material surfaces.

Furthermore, Be exhibits higher work functions and surface energies than Mg, and Ti exceeds Zr in these properties, reinforcing periodic table trends. Not only do simple physicochemical properties follow periodic patterns, but even work functions and surface energies of uncommon crystallographic orientations adhere to these relationships.

References

[1] Skriver H L, Rosengaard N M. Phys Rev, 1992; 45B: 9410
[2] Andersen O K, Jepsen O. Phys Rev Lett, 1984; 53: 2571
[3] Andersen O K, Pawlowska Z, Jepsen O. Phys Rev, 1986; 34B: 5253
[4] Lambrecht W, Andersen O K. Surf Sci, 1986; 178: 256
[5] Rohwerder M, Turcu F. Electrochim Acta, 2007; 53: 290
[6] Kokko K, Salo P T, Laihia R, Mansikka K. Surf Sci, 1996; 348: 168
[7] Singh-Miller N E, Marzari N. Phys Rev, 2009; 80B: 235407
[8] Skriver H L, Rosengaard N M. Phys Rev, 1992; 46B: 7157
[9] Wang J, Wang S Q. Surf Sci, 2014; 630: 216
[10] Tang J J, Yang X B, OuYang L Z, Zhu M, Zhao Y J. J Phys, 2014; 47D: 115305
[11] Boettger J C. Phys Rev, 1994; 49B: 16798
[12] Fiorentini V, Methfessel M. J Phys: Condens Matter, 1996; 8: 6525
[13] Kresse G, Hanfner J. Phys Rev, 1993; 47B: 558
[14] Kohn W, Sham L J. Phys Rev, 1965; 140A: 1133
[15] Blöchl P E. Phys Rev, 1994; 50B: 17953
[16] Gao S L, Yang Q, Li J L. Chemical Element Periodic Table. 3rd Ed., Beijing: Science Press, 2012: 30
[17] Vitos L, Ruban A V, Skriver H L, Kollar J. Surf Sci, 1998; 411: 186
[18] Feibelman P J. Phys Rev, 1992; 46B: 2532
[19] Tyson W R, Miller W A. Surf Sci, 1977; 62: 267
[20] De Boer F R, Boom R, Mattens W C M, Miedema A R, Niessen A K. Cohesion in Metals. Amsterdam: North-Holland Publishing Company, 1988: 1
[21] Michaelson H B. J Appl Phys, 1997; 48: 4729
[22] Wright A F, Feibelman P J, Atlas S R. Surf Sci, 1994; 302: 215
[23] Aghemenloh E, Idiodi J O A, Azi S O. Comput Mater Sci, 2009; 10: 1016

[24] Wang D D, Zhang J M, Xu K W. Surf Sci, 2006; 600: 2990
[25] Feibelman P J. Phys Rev, 1996; 53B: 13740

Note: Figure translations are in progress. See original paper for figures.

Source: ChinaXiv —Machine translation. Verify with original.