

Interrelation of Work Function and Surface Stability: The Case of BaAl₄

M. A. Uijtewaal,^{*,†} G. A. de Wijs,[†] R. A. de Groot,^{†,‡} R. Coehoorn,[§]
V. van Elsbergen,^{||} and C. H. L. Weijtens^{||}

Radboud University, IMM, Post Office Box 9010, 6500 GL, Nijmegen, The Netherlands, University of Groningen, MSC, Chem. Phys. Lab., Nijenborgh 4, Groningen, NL-9747 AG, The Netherlands, Philips Research Laboratories, Prof. Holstlaan 4, 5656 AA, Eindhoven, The Netherlands, and Philips Research Laboratories, Weissshausstr 2, D-52066 Aachen, Germany

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The relationship between the work function (Φ) and the surface stability of compounds is, to our knowledge, unknown but very important for applications such as organic light-emitting diodes. This relation is studied using first-principles calculations on various surfaces of BaAl₄. The most stable surface [Ba-terminated (001)] has the lowest Φ (1.95 eV), which is lower than that of any elemental metal including Ba. Adding barium to this surface neither increases its stability nor lowers its work function. BaAl₄ is also strongly bound. These results run counter to the common perception that stability and a low Φ are incompatible. Furthermore, a large anisotropy and a stable low-work-function surface are predicted for intermetallic compounds with polar surfaces.

I. Introduction

The long-standing problem of the precise relationship between the work function (Φ) and the stability of metals has become pressing with the increased application of electron-emitting materials in technology. Two examples are vacuum electronic devices such as cathode-ray tubes (CRTs) and cathodes for organic light-emitting diodes (OLEDs). In CRTs, a thin layer of a low- Φ metal is often present on top of a cathode made from a structurally stable material to enhance its electron-emitting properties.¹ Electron injection into OLEDs strongly depends on the cathode work function,² while the lifetime of the device can be limited by the stability of the cathode material. OLEDs with an alloy interface between the cathode and the polymer have been found to be superior, in terms of lifetime and luminosity, to those with single-element cathodes.^{3,4} Thus the relationship between Φ and stability⁵ is crucial. However, it is poorly understood, especially for more complex metals.

The general rule for elements is that a low work function and high stability are incompatible: the element with the lowest work function, cesium ($\Phi = 2.14$ eV),⁶ is highly reactive and has a low melting temperature. Noble metals (silver/gold/platinum) on the other hand are hardest to oxidize, but their Φ is at least twice as large (4.25/5.1/5.65 eV).⁶ It is generally believed that this must always be the case, i.e., that a low Φ implies loosely bound electrons that easily mediate reactions. The work function surface anisotropy, however, can be quite large: for tungsten, it is of the order of 1 eV.⁷ The anisotropy was already theoretically addressed by Smoluchowski.⁸ According to his model, at a “more open”⁹ surface, relaxation of the electrons “smoothes” the surface charge. A dipole moment is built up that lowers Φ .¹⁰ This is schematically shown in Figure 1. Although the work function is lowered for a more-open surface, the surface energy increases and stable, low-work-function surfaces are forbidden by the model. Hardly any extensions to the model have been suggested since,¹¹ certainly not for more complex metals. Experimental results for transition-metal alloys suggest the so-called alloy effect,¹² which implies that the stability and Φ of alloys interpolate between those of the

* To whom correspondence should be addressed. E-mail: M.Uijtewaal@science.ru.nl.

[†] Radboud University.

[‡] University of Groningen.

[§] Philips Research Laboratories, The Netherlands.

^{||} Philips Research Laboratories, Germany.

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- (5) The stability of a state implies an energy difference with another (transition) state. Hence several types of stability exist: towards decomposition, roughening, chemical reactions, etc. The energy of the roughened surface, for example, contains contributions from surfaces of other indices. These will differ little for (elemental) cubic systems but not so for layered compounds. Lowering the energy of the state under consideration increases its stability indiscriminately. Therefore, no distinction is made in general. The type of stability is specified only when necessary.

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- (9) An open surface is understood as one with a relatively small number of atoms per unit area.
- (10) The energy of a surface dipole is the work it costs to move an electron through this dipole. Natural as it may seem, the charge-smoothing dipole moment cannot be used to split the work function into a bulk and a surface part, as is often done in the literature. Within the bulk, the potential is periodic (no dipole) and outside it there is no charge. It follows that the reference for this dipole is the average (electrostatic) potential on the outer surface of the bulk unit cells, which means that it is surface dependent. It is discussed in this paper.
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Figure 1. Schematic illustration of Smoluchowski smoothing of the electron charge density (striped area) at an open surface. The gray area is formed by bulk Wigner–Seitz cells. Signs indicate the net charge. The dipole thus formed lowers the work function.

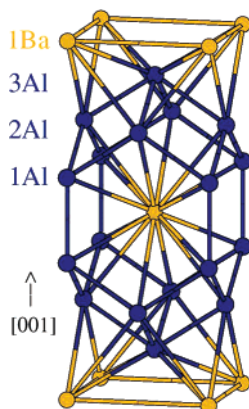


Figure 2. Body-centered tetragonal unit cell of BaAl_4 containing two formula units. The labels refer to the layer and atom type. 1Al and 3Al atoms are equivalent in the bulk.

constituting elements. As a consequence, it is believed that stable, low-work-function surfaces are not possible for more complex metals either.

Nevertheless, the work function and stability of compounds mainly constitute a terra incognita. In this paper, the relationship between Φ and stability of compounds is studied for the first time by calculating ab initio the structural relaxation, work function, and surface energy of various surfaces of BaAl_4 . The motivation to study the BaAl_4 system was the successful use of Ba–Al alloy cathodes in OLEDs and the high melting point of this compound ($>1000^\circ\text{C}$). In the Ba–Al phase diagram,¹³ the melting point of BaAl_4 is the highest, much higher than those of the constituents, which indicates a strongly bound structure. Moreover, we show that the work function for one of the crystal surfaces is very low.

II. Ab Initio Calculations

The BaAl_4 crystal structure¹⁴ is depicted in Figure 2. It is body-centered tetragonal, with alternately three aluminum layers (1Al, 2Al, and 3Al) and one barium layer (1Ba) in the [001] direction. Both Al and Ba atoms are located approximately according to their elemental crystal structures (body-centered cubic (bcc) and face-centered cubic (fcc), respectively). The (100) surface is stoichiometric, and there are four (001) surfaces. They are constructed by cutting the bulk *above* the accordingly labeled layers in Figure 2. Two other (001) surfaces are also considered: “2Ba” (one bcc barium layer added to 1Ba) and “ $1/2\text{Ba}$ ” (half a barium layer removed from 1Ba).

From bulk calculations we find that $a = 4.56 \text{ \AA}$, that $c = 11.39 \text{ \AA}$, and that the remaining free parameter in the structure, the height of the third aluminum layer, is $0.381c$. These values compare very well (deviations $\approx 1\%$) with those obtained experimentally.¹⁴ The bulk density of states (DOS) shows a quasigap just below the Fermi level, in accordance with the previously calculated DOS of BaAl_4 and other isoelectronic compounds with the same structure.¹⁴ The valence electrons are mainly located on Al atoms. The binding energy (E_{bind}) is $1.42 \text{ eV/formula unit (FU)}$ with respect to the elemental bulk metals. Together with the quasigap, it hints at BaAl_4 's stability.

The first-principles calculations were carried out using density functional theory (DFT) in the local density approximation (LDA)^{15,16} with generalized gradient corrections (GGA).¹⁷ We used the total energy and molecular dynamics program called VASP (Vienna Ab initio Simulation Package),^{18,19} which has the projector-augmented-wave method (PAW)^{20,21} implemented. Nonlinear core corrections²² were applied for both barium and aluminum. A semi-core of Ba 5s and 5p electrons was included. The Kohn–Sham orbitals were expanded in plane waves with cutoffs of 18 Ry. The Brillouin zones for the (100) and (001) surface calculations were sampled with $1 \times 16 \times 8$ and $12 \times 12 \times 1$ Monkhorst–Pack²³ k -point grids, respectively, resulting in 8 and 21 k points, respectively, in their irreducible parts. The (periodically repeated) unit cell for the (100) surface calculation contained a slab with a thickness of seven bulk unit cells and 16-\AA vacuum. The supercells for the (001) surface calculations contained slabs with thicknesses of 6 FU and 20-\AA vacuum.

III. Work Function

The work function is defined as the amount of energy it takes to extract electrons from a metal, i.e., bring them from the Fermi level to the vacuum. At locations that are microscopically far from the material but macroscopically near it, Φ is surface dependent. The work function at large distance is then an average over the various surfaces.²⁵ The work function of a surface is calculated by constructing a supercell with a slab of material, with only this surface and vacuum. Figure 3 illustrates this using the (001) Ba–

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(24) Although it is impossible to sharply define a surface dipole moment (a bulk reference must be chosen) still it would be useful to introduce a bulk Φ . Figure 3 shows three bulk reference potentials: E_F , $\langle V \rangle_{\text{bulk}}$, and the highest potential in the bulk (V_{max}). If we choose E_F , it follows that there is no bulk work function at all. If we use $\langle V \rangle_{\text{bulk}}$, Φ_{bulk} even becomes negative, which suggests that the bulk material does not bind electrons. $\Phi_{\text{bulk}} = V_{\text{max}}$ remains. It can be located at a precise position, namely, as far as possible from the nuclei, i.e., in a corner of a Wigner–Seitz cell, it is always positive (2.79 eV for BaAl_4), and the surface dipole can have either sign, as can be read from Figure 4.

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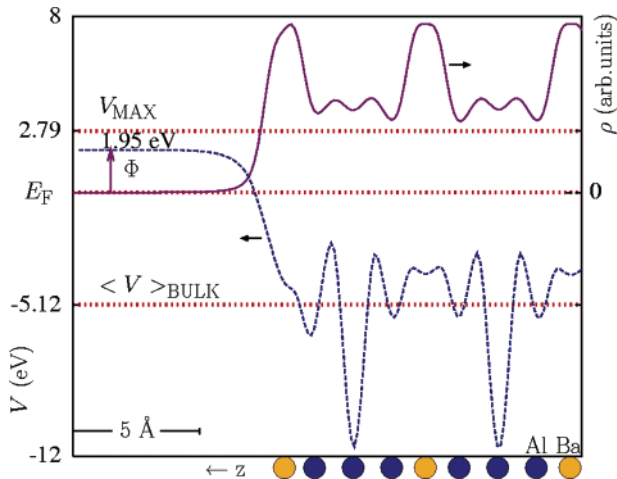


Figure 3. The BaAl₄ (001) 1Ba surface. Laterally averaged charge density (ρ solid line, arbitrary units) and (electrostatic) potential (V dashed line, eV relative to E_F) as function of position perpendicular to the surface (z). The position of the Ba and Al layers is indicated with light and dark spheres, respectively. At -5.12 eV is the average bulk potential, and at 2.79 eV is the highest potential in the bulk.²⁴ The work function is 1.95 eV.

terminated surface. About 10 \AA of empty space suffices for the electrostatic potential²⁶ to converge to its vacuum value (V_{vac}). A thick slab, however, is required for the Fermi level (E_F) to be accurate. A more efficient method is to link the surface calculation to a bulk one where E_F is very accurate. The average potential in the bulk ($\langle V \rangle_{\text{bulk}}$) is set equal to the average potential in the middle of the slab. Accuracies of a few hundredths of an eV can thus be achieved with only six to eight bulk unit cells, depending on direction.²⁷ The work function of the 1Ba surface is 1.95 eV.

The work functions of the other BaAl₄ surfaces are calculated analogously. That of the (100) surface is reduced by structural relaxation from 3.54 to 3.43 eV. The work functions of the (001) 1Al, 2Al, and 3Al surfaces are 4.38 , 4.48 , and 3.98 eV, respectively. Relaxation has negligible effect. The work functions of the various surfaces are summarized in Figure 4. As plotted there, covering the Al surface with half a monolayer of barium (thus forming the $\frac{1}{2}\text{Ba}$ surface) already greatly reduces the work function (2.29 eV). The 1Ba work function is reduced even more to a surprisingly low value of 1.95 eV. This is below the Φ value of any element.⁶ An additional layer of barium (thus forming the 2Ba surface) increases Φ (2.13 eV) again. Experimental bulk values for Al (4.2 eV) and Ba (2.32 eV) are plotted for reference.⁶ These compare favorably with calculated work functions of bcc barium (2.36 eV (100) and 2.27 eV (111)) and fcc aluminum (4.34 eV (100) and 4.17 eV (111)).

The huge (>2 eV) variation in the (001) surface work function can be (qualitatively) explained from the difference in the atomic electronegativities. Ba is less electronegative (0.9)²⁸ than Al (1.5),²⁸ effecting charge transfer from barium to aluminum. The resulting surface dipole moment decreases

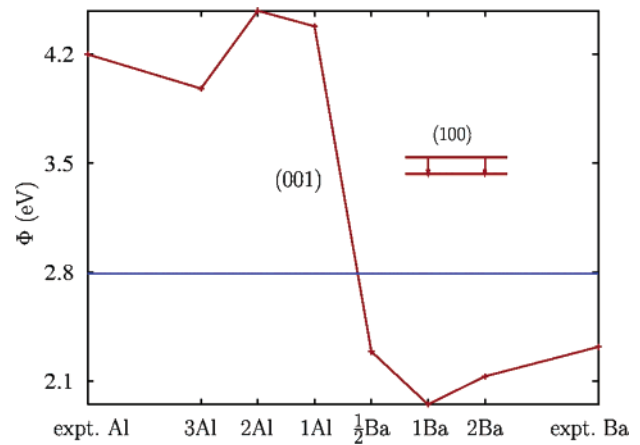


Figure 4. Work functions (eV) of the BaAl₄ (001) surfaces. Experimental bulk values for barium and aluminum are indicated at the borders. Lines connect the data points. The Φ value for the (100) surface before and after relaxation is inserted. (The dotted line is V_{max}).²⁴

the work function of the Ba surface to even under the elemental barium bulk value and increases Φ of the Al surfaces considerably. The dependence of Φ on Al coverage of the 1Ba surface can be understood if one realizes that the 1Al and 3Al surfaces are more open than the 2Al surface. According to the Smoluchowski model, Φ must then be lowered. The decrease in Φ during relaxation of the (100) surface can also be understood by combining charge transfer with Smoluchowski smoothing. The barium atoms at the surface move out ($\sim 0.1 \text{ \AA}$), as they favor an environment with a lower charge density, while the aluminum atoms at the surface tend to get closer together, as they favor an environment of a high charge density. We conclude that a monolayer coverage yields an extreme work function.

IV. Surface Energy

The (relative) stability of a surface is determined by the difference in surface energy (γ) between two surfaces.⁵ The surface energy is calculated as the energy of a slab with only this surface minus the energy of the bulk equivalent (formed by merging the (periodically repeated) slabs together), divided by two times the surface area, because a slab has two sides. This method was used for the (100) and (001) $\frac{1}{2}\text{Ba}$ surfaces. Slabs for the other (001) surfaces are nonstoichiometric, and so there is no equivalent bulk. Calculating γ now requires reservoirs of Ba and Al. By assumption of thermodynamic equilibrium, the chemical potential of the aluminum (μ_{Al}) and that of the barium (μ_{Ba}) reservoir are linked to the total energy per FU of BaAl₄ (E_{bulk})

$$E_{\text{bulk}} = 4\mu_{\text{Al}} + \mu_{\text{Ba}} \quad (1)$$

The energy of, for example, the 1Ba surface, as a function of mBa, follows from the total energy of a slab with these surfaces exclusively ($E_{1\text{Ba}}$)²⁹

$$\gamma^{1\text{Ba}}(\mu_{\text{Ba}}) = [E_{1\text{Ba}} - \#FUE_{\text{bulk}} - \mu_{\text{Ba}}]/2A_S \quad (2)$$

where A_S is the surface area.

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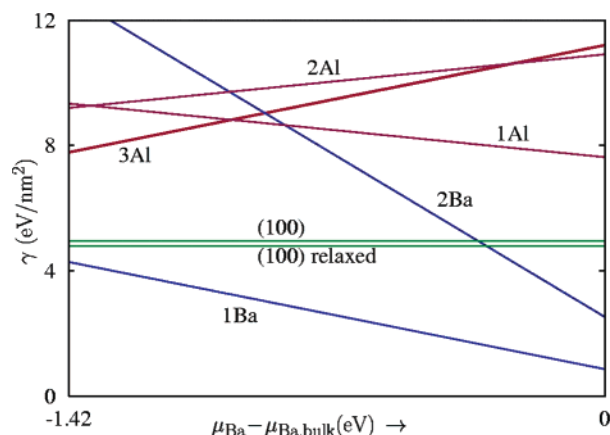


Figure 5. Surface energies (eV/nm^2) for the BaAl_4 surfaces as function of the barium chemical potential (eV). The potential ranges from the value for Al bulk to that of Ba bulk. The difference is the binding energy of BaAl_4 (eq 1 has been used). For the (100) surface, the effect of relaxation is indicated. The (001) 1Ba surface is the most stable.

The surface energies are drawn in Figure 5. Structural relaxation of the (100) surface lowers its energy from 4.96 to 4.82 eV/nm^2 . The energy of the (001) $\frac{1}{2}\text{Ba}$ surface equals 13.3 eV/nm^2 and is outside the range of the plot. For the other (001) surface, γ depends on the barium chemical potential. In the figure, μ_{Ba} varies over the thermodynamically allowed range between the Ba and Al bulk chemical potentials³⁰ as phase separation occurs outside this range. The single barium surface is the most stable one in the entire region and so other (001) surfaces cannot be formed.

The unusual stability of the low- Φ surface is explained in the same way as the relaxation of the (100) surface. Since barium is the less electronegative element, it favors a low electron density and makes the most stable surface. Additional barium layers at the surface decrease this stability,

as Ba–Ba bonds are less strong than Al–Ba bonds, especially when the barium in contact with aluminum is (partially) ionized.

V. Conclusions

As both the low Φ value of the 1Ba surface and its stability followed from Ba's lower electronegativity, we come to a remarkable prediction: For an intermetallic compound with polar surfaces, like BaAl_4 , the most stable surface has the lowest work function and relaxation can only decrease it further.

To summarize, we used first-principles calculations on various surfaces of BaAl_4 to study the interrelation of work function and stability. The bulk work function of BaAl_4 is 2.79 eV,²⁴ its anisotropy (1.5 eV) is huge, and the most stable surface (Ba terminated 001) has the lowest Φ value (1.95 eV), which is even lower than that of pure Ba. Adding barium to this surface neither increases its stability nor lowers its work function. The binding energy of 1.42 eV/FU, the quasigap in the DOS, and its melting temperature of over 1000 °C indicate BaAl_4 's stability. These results contradict the common perception that stability and a low Φ value are incompatible. They also run counter to the effect that alloy work functions are between those of the constituting elements. Its stable, very-low- Φ surface and the stable structure probably make BaAl_4 a good electron-emitting material. Furthermore, a stable low-work-function surface promises to be general for intermetallic compounds with polar surfaces.

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