XPS quantification of the hetero-junction interface energy

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ABSTRACT

We present an approach for quantifying the heterogeneous interface bond energy using X-ray photoelectron spectroscopy (XPS). Firstly, from analyzing the XPS core-level shift of the elemental surfaces we obtained the energy levels of an isolated atom and their bulk shifts of the constituent elements for reference; then we measured the energy shifts of the specific energy levels upon interface alloy formation. Subtracting the referential spectrum from that collected from the alloy, we can distil the interface effect on the binding energy. Calibrated based on the energy levels and their bulk shifts derived from elemental surfaces, we can derive the bond energy, energy density, atomic cohesive energy, and free energy at the interface region. This approach has enabled us to clarify the dominance of quantum entrapment at CuPd interface and the dominance of polarization at AgPd and BeW interfaces, as the origin of interface energy change. Developed approach not only enhances the power of XPS but also enables the quantification of the interface energy at the atomic scale which has been an issue of long challenge.

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1. Introduction

Bonds and electrons associated with the hetero-coordinated atoms and their energetics determine the performance of impurities, interfaces, alloys, compounds and composites such as the mechanical strength, thermal stability [1], dielectric constant [2] and charge transport in p-n junctions which directly influence the application of hetero-coordinated materials in many fields of thermal barrier coatings [3], wear-resistance [4,5], optoelectronic devices [4] and MOS devices [6]. During the past decades, extensive investigations have been conducted to understand the role of interface and quantify the interface energetics [7–9]. However, detailed knowledge about the origin of interface energy and precision measurements remain high challenge.

Traditionally, the notions of interface energy (γ i), or interface free energy for an inhomogeneous solid are defined as the energy needed to form the interface from the respective bulk crystal phases [10]. Up to now, methods have been proposed to obtain the value of the interface energy [7,10–14]. For instances, the nearest-neighbor broken-bond (NNBB) approach [12,14] correlated the interfacial energy to the enthalpy ΔFsol of the solution solid, which can be calculated by accumulating all bond energies. A further modification of the NNBB model was conducted by Sonderegger et al. [11,13] who considered arbitrary bond lengths and then created a general broken-bond (GBB) model for more complex geometries such as multi-component system and interfaces of spherical precipitates. Nishizawa et al. [15] correlated the interfacial energies to the formation energy and the pair-wise interaction energies between component atoms. Jiang et al. [7] proposed analytical model for calculating the interface energies of solid–liquid, solid–solid, and solid–vapor and their size dependence based on classic thermodynamics. They related the interface energy to the Gibbs free energy for molecules of unit interface area.

Besides the theoretical progress in understanding the origin of interface energy, various experimental and computational techniques have been applied to measure the γ i such as the peel test [16], pressurized blister test [17], microscratch method [18], superlayer test [19], ab initio calculation using Peierls–Nabarro model [10], and molecular dynamics simulations [20]. Despite the extensive efforts in qualitative estimation of the interface energies, correlation between the interfacial energies and the bond identities of the interface and their responsibilities for interface phenomena remain to be established.

In this presentation, we demonstrate an approach for precise quantification of the interface bond energy, binding energy density, and atomic cohesive energy based on formulating and analyzing X-ray photoelectron spectroscopy (XPS) measurements and an
extension of the bond order-length-strength (BOLS) correlation theory [21–23]. It is clarified that energy entrapment or polarization induced by bond order distortion and bond nature alteration originates the hetero-coordinated interface energies.

2. Principles

2.1. Atomistic definition of interface energy

In fact, the performance of an interface is governed by the excessive energies in the interface region or by the bond energy of the discrete interface atoms instead of the energy cost upon interface formation. Therefore, two complementary notions are necessary [24] for a better understanding of the interface energetics and their responsibilities. One is the energy-density gain and the other the cohesive energy per discrete atom upon interface formation. On the other hand, energy per unit volume at the interface region could be more meaningful than the energy per unit area, as energy is always a volume-related quantity [23,24].

2.2. BOLS: under- and hetero-coordination perturbed Hamiltonian

The original BOLS correlation theory for undercoordinated system [21,25,26] indicates that bonds between undercoordinated atoms become shorter and stronger. Local densification and quantum entrapment happen to the bonding energy and the bonding and core electrons. The densely entrapped electron will in turn polarize the nonbonding electrons [27]. These entities provide perturbation to the Hamiltonian,

\[
C_i = 2 \left\{ 1 + \exp \left[ \frac{12 - z}{8\varepsilon_i} \right] \right\}^{-1} \quad \text{(bond-contraction-coefficient)}
\]

\[
C_{\text{ext}}^m - \frac{E_b}{E_b} = 1 + \Delta H \quad \text{(bond-strengthening-coefficient)}
\]

where \( z \) is the effective coordination number (CN) and \( m \) is the bond nature indicator.

The key idea of the extended BOLS theory [21–23] to a hetero-coordinated interface is that the mixing of two or more constituents makes the bonds between the hetero-coordinated atoms to relax spontaneously in both length and energy, and hence, localization, densification, entrapment or polarization of charge, energy, and mass occur to the interface region. The energy stored at the interface perturbs the Hamiltonian and related properties such as the core level shift. The influence on the core level shift provides us with an opportunity to measure quantitatively the interface energy.

In the interface region, the single-body Hamiltonian undergoes the perturbation due to the bond nature alteration with charge entrapment or polarization according to the tight-binding band theory [28,29], which is expressed as:

\[
H = - \frac{n^2\Psi^2}{2m} + V_{\text{atom}}(r) + V_{\text{cryst}}(r, l)
\]

\[
= - \frac{n^2\Psi^2}{2m} + V_{\text{atom}}(r) + V_{\text{cryst}}(r, B)(1 + \Delta H)
\]

where the intraatomic trapping potential, \( V_{\text{atom}}(r) \), determines the specific vth energy level of an isolated atom \( E_v(0) \), from which the binding energies (BE) starts to shift upon the crystal potential \( V_{\text{cryst}}(r) \) being involved. \( \Delta H \) is the perturbation due to bond nature alteration, entrapment or polarization. The parameters \( B \) and \( l \) represent the bulk and the interface, respectively. Only the \( V_{\text{cryst}}(r) \) can be perturbed because the intraatomic potential \( V_{\text{atom}}(r) \) is intrinsically unchanged. Extensive evidence has shown that bond energy changes indeed at the hetero-coordinated interface. For instance, a 3% Ti–N bond contraction at the TiN/Si3N4 interface [30] and an 8% bond contraction around the impurity As at the Te sublattice in CdTe have been observed using extended X-ray absorption fine structure and X-ray absorption near edge spectroscopy [31]. The higher energy density at the SiO2/Si (0 01) interface has been detected by a grazing incident X-ray reflectivity [32].

2.3. Binding energy shift of an isolated atom

In order to determine the interface energy, we need to find the BE of an isolated atom of the constituent elements first. In order to do so, we incorporate the BOLS correlation into the band theory by taking the surface-induced Hamiltonian perturbation into consideration. The BE shift of a specific vth energy level of an atom in the surface layer \( \Delta E_v(z) \) with respect to that of an isolated atom is:

\[
\Delta E_v(z) = E_v(z) - E_v(0) = \Delta E_v(B)(1 + \Delta H) = (\alpha + z\beta)(1 + \Delta H)
\]

where

\[
\Delta E_v(B) = E_v(B) - E_v(0) = (\alpha + z\beta) \propto E_b \quad \text{Bulk core level shift}
\]

\[
E_v(0) = -< v | V_{\text{atom}}(r) | v, l > \quad \text{Atomic core level}
\]

\[
\alpha = -< v | V_{\text{cryst}}(r, B)(1 + \Delta H) | v, i > \quad \text{Exchange integral}
\]

\[
\beta = -< v | V_{\text{cryst}}(r, B)(1 + \Delta H) | v, j > \quad \text{Overlap integral}
\]

\[
E_v(0) \quad \text{is the reference point, from which the core level shifts. The}
\]

\[
\Delta E_v(B) \quad \text{represents the shift of a particular vth level from the}
\]

\[
E_v(0), \quad |v, l> \quad \text{is the specifically localized Bloch wave function at a specific}
\]

\[
i \text{th atomic site. The parameter} \; z \; \text{is the effective coordination number.} \Delta H \; \text{is the perturbation due to the under-coordination induced quantum entrapment. The overlap integral} \; \beta \; \text{is in the} \; 10^{-12} eV \; \text{order that is much smaller than the exchange integral} \; \alpha \; \text{that is in the} \; 10^6 eV \text{level. Therefore, the interatomic bond (exchange) energy dominates the BE shift. Eq. (3) can be reorganized as:}
\]

\[
E_v(l) - E_v(0) = 1 + \Delta H = C_i
\]

The subscript \( i \) denotes an atom in the \( i \)th atomic layer, which may be counted up to three from the outermost atomic layer inward. The coordination number \( z \) is determined by the atomic layer location and crystal orientation. For instance, it has been determined that \( z = 4.0, 3.87, \) and 4.26 (\( i = 1 \)) for the outermost layer and \( z = 5.73, 5.40, \) and 6.31 (\( i = 2 \)) for the second of an fcc (1 0 0), (1 1 0) and (1 1 1) surface [33]. According to the zone-selective photoelectronic purification [34,35], we have the constraints for the relative shift of each surface component,

\[
E_v(z) - E_v(0) = \frac{C^m}{C^z}, (z \neq z')
\]

which yields,

\[
E_v(0) = \frac{C^m E_v(z) - C^m E_v(z')} {C^z - C^z'}
\]

\[
\Delta E_v(B) = \frac{E_v(z) - E_v(0)}{C^z}
\]

Using Eq. (5), we can readily determine the energy level of an isolated atom \( E_v(0) \) and its bulk shift \( \Delta E_v(B) \). These peak energies of the components may fluctuate slightly with varying experimental conditions such as temperature, crystal orientation, and incident radiation beam angle, but the \( \Delta E_v(B) \) and \( E_v(0) \) will not change for a given specimen.

A surface XPS spectrum can be decomposed into B, S2, S1, and S0 components corresponding to the bulk, second layer, first layer, and surface defects with lower atomic CNs \( z \), as shown in Fig. 1(a), which illustrates the BOLS-derived BE shift decomposition. The BE energy shift of less-coordinated components should be positive due to the BOLS mechanism. The lower the \( z \) value, the deeper
the energy shifts. The intensities of the components are subject to the fraction of the specifically z-coordinated atoms, which is constrained by the measured intensity of the spectrum. The reference $E_v(0)$ and the bulk change $\Delta E_v(B)$ for calibrating interface energy are thus obtained from formulating and analyzing the core level shift of the constituent elemental surfaces.

2.4. Interface core level shift

As shown in Eq. (3), the XPS BE shift is uniquely proportional to the crystal potential at equilibrium, i.e., cohesive energy per bond [34]. Any perturbation to the crystal potential by the quantum entrapment (QT) or polarization (P) at the interface will lead to the core level shift:

$$\Delta E_v(I) = \frac{V_{\text{cryst}}(r, l)}{V_{\text{cryst}}(r, B)} = 1 + \Delta H = y\gamma > 1 \quad \text{entrapment}$$

$$\Delta E_v(I) = \frac{V_{\text{cryst}}(r, l)}{V_{\text{cryst}}(r, B)} = 1 + \Delta H = y\gamma < 1 \quad \text{polarization}$$

(6)

where $\Delta E_v(I)$ represents the shift of a particular vth level from the $E_v(0)$; $\gamma$ is the bond energy reduced by that of the ideal bulk constituent. $\gamma > 1$ or $\gamma < 1$ means that the potential $V_{\text{cryst}}(r, l)$ becomes deeper or shallower than the otherwise $V_{\text{cryst}}(r, B)$ of the specific component.

Incorporating the BOLS correlation [21] into the interface Hamiltonian, the energy shift of a specific vth energy level of an interface with respect to that of an isolated atom, as indicated in Fig. 1(b), is

$$\Delta E_v(I) = E_v(I) - E_v(0) = \Delta E_v(B)(1 + \Delta H) = y\alpha + z\beta$$

(7)

Any perturbation to the interatomic potential will lead to bond energy alteration and core level shift. Therefore, the chemical bond, potential well, and core level shift can be correlated.

Fig. 1(b) illustrates the XPS profiles of a particular energy level, for Cu 2p$_{3/2}$ example, deposited on a Pd substrate, evolved from pure Cu to alloy. Initially, the peak is centered at $E_{2p_{3/2}}(B)$ for Cu surface. Upon alloy formation by heating to a certain temperature, the $E_{2p_{3/2}}(B)$ evolves into $E_{2p_{3/2}}(I)$ with a peak in deeper energy, or called positive shift, $\gamma > 1$. A subtraction of the $E_{2p_{3/2}}(B)$ from the $E_{2p_{3/2}}(I)$ results in the residual spectrum that is purely the interface effect-quantum entrapment dominance, which means that the interface Cu−Cu bond is stronger than those in the Cu bulk and surface. Otherwise, a new peak presents above the main peak of pure Cu upon Cu/Pd alloy formation, then Cu−Pd interface polarization occurs. The interface polarization will screen in turn the interface crystal potential and weaken the Cu−Cu bond, instead. The quantum trapping for the Cu/Pd interface agrees with the finding of Popovic and Satpathy in calculating superlattices and microstructures, who found the essentiality to introduce a classical wedge-shaped potential well for the interface monolayer structure.

2.5. Quantitative interface energetics

According to the BOLS correlation and the band theory, the energy value of $V_{\text{cryst}}(r)$ at equilibrium is proportional to the mean cohesive energy per bond, $(E_v)$. That is, the interface BE shift is proportional to the local bond energy $(E_v)$. Using Eq. (6), we can determine the bond energy of a constituent element at the interface as follows:

$$\frac{(E_v)_I}{(E_v)_B} = \frac{\Delta E_v(I)}{\Delta E_v(B)} = y$$

(8)

where $(E_v)$ and $(E_B)$ represent the mean bond energy of the particular element at the interface and in the bulk. This allows us to obtain the value of $(E_v)$ with high precision. Note that the value of $\Delta E_v(B)$ can be determined by proper decomposition of the surface BE spectrum [33,36–38] and $(E_B)$ is a given constant for a specific element in bulk [39].

The interface bond energy $(E_{IS})$ and bond length $(d_{IS})$ consist of three parts: A–A, B–B and A–B interactions. The $(E_{IS})$ can be obtained in accordance with the approach [40,41], expressed as:

$$\langle E_{IS} \rangle = x\langle E_{IA} \rangle + (1 - x)\langle E_{IB} \rangle$$

(9)

The last term denotes the exchange interaction between atoms A and B. The interface lattice constant $(l_{IS})$ can be obtained using the Vegard’s modeling approach [42–44], shown as follows:

$$\langle l_{IS} \rangle = x\langle l_A \rangle + (1 - x)\langle l_B \rangle$$

(10)

With the derived $(l_{IS})$ and $(E_{IS})$, we are able to determine the binding energy density and atomic cohesive energy, and interface free energy:

$$E_C = z_I(E_{IS})$$

$$E_B = \frac{E_{\text{sum-cell}}}{\text{Vcell}} = \frac{N \cdot z_I \cdot (E_{IS})}{2l_{IS}}$$

$$y_I = \frac{E_{\text{sum-cell}}}{A_{\text{sectional}}} = \frac{N \cdot z_I \cdot (E_{IS})}{2l_{IS}^2}$$

(11)

where $z_I$ is the interface atomic coordination number; $N$ is the number of atom in a unit cell in the interface region.

Hence, from the analysis of an XPS measurement, we are able to gain quantitative information of interface energetics.
3. Results and discussion

3.1. Core level shift of the elemental surface

In order to quantify the interface bond energy from the XPS measurements, we need to find the respective $\Delta E_v(B)$ and $E_v(0)$ values for each constituent element for calibration purposes. In terms of the tight binding and the BOLS theory, the interface binding energy, bulk binding energy, interface component binding energy, bulk shift, interface energy shift, and the ratio of $\Delta E_v(I)/\Delta E_v(B) = \gamma$ can be obtained as summarized in Table 2. The $\gamma$ values for Be and W in the BeW are ~0.87 and ~0.81, respectively. Similarly, the $\gamma$ values for Cu and Pd in the CuPd are 1.93 and 1.39. Ag and Pd in the AgPd are 0.69 and 0.75, respectively. $\gamma > 1$ means the interface potential $E_{\text{cryst}}(r, I)$ becomes deeper and $\gamma < 1$ shallower than the referential $E_{\text{cryst}}(r, B)$ of the specific constituent. The residual spectra of alloy BeW, CuPd, and AgPd are compared in Fig. 3, showing clearly the following:

1. The BeW interface alloy formation shifts both the Be 1s and the W 4f up as indicated by arrows in Fig. 3(a) and (b). The upward shift indicates the interface polarization and hence the interface is mechanically weaker than either Be or W as they stand alone.
2. In contrast, CuPd alloy formation causes interface strengthening, as shown in Fig. 3(c) and (d). Both the Cu 3d and Pd 3d core bands shift positively, indicating that quantum entrapment is dominant at the CuPd interface.
3. However, both the Ag 3d and Pd 3d at the AgPd interface shift negatively and the core bands shift higher binding energy, being the same to that of BeW.

3.2. Quantification of the interface bond energy

Generally, an alteration of the coordination environment and bond nature of the interface provides the perturbation to the Hamiltonian. That is, $E_{\text{cryst}}(r, I) = \gamma E_{\text{cryst}}(r, B)$. We can obtain the ratio, $\gamma = \Delta E_v(I)/\Delta E_v(B)$. From Eq. (8), we can determine the A–A and

---

**Fig. 2.** Decomposition of the Ag 3d$_{5/2}$ spectra for (a) Ag (1 1 1) and (b) Ag (1 0 0) surfaces with four Gaussian components each representing the bulk B, surfaces S$_2$ and S$_1$, and defects D states from higher (smaller absolute value) to lower BE. These components follow the constraints of Eq. (4) with derived parameters given in Table 1.

**Table 1** Summary of BOLS elucidated information regarding the crystal-orientation resolved effective CN($z$) and binding energy derived from the measured XPS profiles of Ag (1 1 1) [45] and Ag (1 0 0) [46] surfaces.

<table>
<thead>
<tr>
<th>Ag</th>
<th>i</th>
<th>z</th>
<th>$E_{\text{ref}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom</td>
<td>0</td>
<td>363.02</td>
<td></td>
</tr>
<tr>
<td>Bulk</td>
<td>B</td>
<td>12</td>
<td>367.65</td>
</tr>
<tr>
<td></td>
<td>S$_2$</td>
<td>6.31</td>
<td>367.93</td>
</tr>
<tr>
<td>(1 1 1)</td>
<td>S$_1$</td>
<td>4.26</td>
<td>368.24</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>3.14</td>
<td>368.63</td>
</tr>
<tr>
<td>(1 0 0)</td>
<td>S$_2$</td>
<td>5.73</td>
<td>367.99</td>
</tr>
<tr>
<td></td>
<td>S$_1$</td>
<td>4.00</td>
<td>368.31</td>
</tr>
</tbody>
</table>
Table 2
Summary of the isolated binding energy (E_i(0)), bulk binding energy (E_i(B)), interface component binding energy (E_i(I)), bulk shift (∆E_i(B)), interface energy shift (∆E_i(I)) and the ratio of ∆E_i(I)/∆E_i(B) (γ) for the Cu 2p1/2, Pd 3d5/2, Be 1s, and W 4f7/2 core levels in the BeW, CuPd, and AgPd alloy interfaces (in eV unit).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>E-Level</th>
<th>E_i(0)</th>
<th>E_i(B)</th>
<th>E_i(I)</th>
<th>∆E_i(B)</th>
<th>∆E_i(I)</th>
<th>γ</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeW</td>
<td>Be 1s</td>
<td>106.42</td>
<td>111.11</td>
<td>110.48</td>
<td>4.69</td>
<td>4.06</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>W 4f7/2</td>
<td>28.91</td>
<td>31.08</td>
<td>30.66</td>
<td>2.17</td>
<td>1.75</td>
<td>0.81</td>
</tr>
<tr>
<td>CuPd</td>
<td>Cu 2p3/2</td>
<td>331.00</td>
<td>332.70</td>
<td>334.28</td>
<td>1.70</td>
<td>1.75</td>
<td>1.03</td>
</tr>
<tr>
<td></td>
<td>Pd 3d5/2</td>
<td>330.34</td>
<td>334.32</td>
<td>335.87</td>
<td>3.98</td>
<td>5.53</td>
<td>1.39</td>
</tr>
<tr>
<td>AgPd</td>
<td>Ag 3d5/2</td>
<td>363.02</td>
<td>367.65</td>
<td>366.47</td>
<td>4.63</td>
<td>3.45</td>
<td>0.75</td>
</tr>
</tbody>
</table>

B–B bond energy of the constituents in the interface. For instance, the bond energy of Be and W in the BeW alloy are 0.24 and 0.60 eV, respectively.

The bond energy of one element in different interfaces diverges. For example, in CuPd, the Pd–Pd bond energy is 0.45 eV but it is 0.22 eV in AgPd. As discussed, the mean bond energy is also influenced by the interaction between two different kinds of atoms in the interface. Then, using Eqs. (9) and (10), we can estimate the mean bond length, bond energy and lattice constant in the interface of the three alloys, which are listed in Table 3.

Fig. 3. The thermally-driven spectra and residual core level spectra of (a) Be 1s and (b) W 4f7/2 BE in the BeW interface upon annealing at 300 and 970K, (c) Cu 2p3/2 and (d) Pd 3d5/2 BE in the CuPd interface upon annealing at 540 and 940K, and (e) Ag 3d5/2 and (f) Pd 3d5/2 BE in the AgPd interface upon annealing at 300 and 573K show the direction of core level charge migration upon high-temperature alloying effect, indicated by arrows. The directions of charge migration may distinguish the style of interface potential, such as interface potential barrier and polarization (P) occurring in (a)–(b), (e)–(f) and interface potential well depression (QT) occurring in (c)–(d).
analyzing the core level shift of alloy, which is beyond the scope of existing approaches.

The accuracy of estimation is strictly subject to the measurement. Other factors such as materials purity, defect concentration, and testing techniques may lead to the accuracy of the derived $E_I(0)$ and $E_I(l)$ values. The developed approach could enhance the power of XPS for extracting more quantitative information regarding the interface properties. The concepts of quantum entrapment and polarization are essential for understanding the bonding and electronic behavior of hetero-coordinated atoms at the interface region.

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