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# Atomistic origin, temperature dependence, and responsibilities of surface energetics: An extended broken-bond rule

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There has long been confusion regarding the origin and temperature dependence of surface energetics and its responsibility for the processes and phenomena at a surface. From the perspective of bonds broken and its consequences on the remaining bonds of the undercoordinated surface atoms, we suggested herewith two essential concepts supplementing to the existing definition of surface energy for clarification purposes. One is the energy-density-gain per unit volume in surface skin and the other is the remaining cohesive-energy per discrete atom upon bond order loss once the surface is formed. The former governs the strength and elasticity while the latter dominates the thermal and structural stability of the surface. The shortened and strengthened bonds between the undercoordinated atoms dictate surface energetics and the effects of thermal expansion and vibration dominate their temperature dependence. Reproduction of the measured size and temperature dependency has led to information about the bond energy, which may go beyond traditional approaches and evidence the validity of the approaches.

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## I. INTRODUCTION

The surface energetics play the key and central roles in surface and nanosolid sciences because the surface energetics links the microscopic bonding configuration at an interfacial region with its macroscopic properties, such as strength, elasticity, wettability, reactivity, diffusivity, stability, etc.[1–5] During the past decades, increasing efforts have been focused on processes that are strongly influenced by surface energetic effects such as reconstruction, relaxation, interfacial mixing, segregation, self-organization, and melting at solid surfaces. However, detailed knowledge about the processes of surface energetic identities is yet lacking,[1,2,6,7] in particular, the atomistic origin, temperature dependence, and their responsibilities for surface phenomena and processes are yet far from clear.

Traditionally, the surface energy ($\gamma_s$), or surface free energy for a solid, or the surface tension for a liquid, is defined as the energy needed to cut a given crystal into two halves, or energy consumed (loss) upon surface formation.[8] Usually, unrelaxed structures at zero temperature are considered in the discussion of surface energies. The values obtained are then corrected for relaxations of the surface atoms, without mentioning reconstructions of the surface. In some cases, these corrections are thought very small, so a simplified model can be made without including relaxations. The temperature dependence involves the phonons and their modification on the surface; the vibrational effects sometimes have to be taken into account when the temperature dependence is studied. The elegantly accepted approaches for the defined surface energy are the broken-bond rules,[2,9–11] which are comparatively summarized as follows:

$$\gamma_s = \begin{cases} \dfrac{W_S - W_B}{20} n_d(n_d - 10) & \text{(Galanakis)} \\ (1 - z_s/z_b)E_B & \text{(Haiss)} \\ (1 - \sqrt{z_s/z_b})E_B & \text{(Desjonqueres)} \\ \dfrac{[2 - z_s/z_b - (z_s/z_b)^{1/2}] + \lambda[2 - z'_s/z'_b - (z'_s/z'_b)^{1/2}]}{2 + 2\lambda} E_B & \text{(Jiang)}. \end{cases} \tag{1}$$

(1) Galanakis *et al.*[9] correlated the surface energy of some $d$ metals to the broken bond in the tight-binding approximation. The $n_d$ is the number of $d$ electrons. $W_S$ and $W_B$ are the bandwidths for the surface and bulk density of states, which are assumed rectangular forms.

(2) Haiss *et al.*[2] related the surface energy directly to the multiplication of the broken bond number with the cohesive energy per bond $E_b = E_B/z_b$ at 0 K. The $\gamma_s$ values are estimated by determining the broken-bond number $z_{(hkl)} = z_b - z_s$, (where $z_s$ is the coordination number of a surface atom and $z_b$

the corresponding bulk one), for creating a surface area by cutting a crystal along a certain crystallographic (*hkl*) plane.

(3) A second-moment tight-binding approximation conducted by Desjonquères *et al.*,[10] suggested that the surface energy gain is proportional to $\sqrt{z_S}$, instead of $z_s$, due to the lowering of the occupied states. According to this approximation, the rearrangement of the electronic charge does not practically change the nature of the remaining bonds when one bond is broken. Thus, the energy needed to break a bond is independent of the surface orientation, so that the $\gamma_s$ value is proportional to the square root of the number of the nearest-neighboring broken bonds.

(4) To obtain a more general expression, Jiang *et al.*[11] suggested that an average of the approximations of Haiss and Desjonquères and an extension to counting the contribution from the second nearest neighbors could be more comprehensive, where the prime denotes the next-nearest neighbors of the surface atoms and λ is the total bond strength ratio between the next-nearest and the nearest neighbors.

Besides the thermodynamic considerations, the kinetic processes of lattice vibration play significant roles in the anisotropy of surface properties.[12] The amplitudes and frequencies of atomic vibrations,[13] as well as the bond lengths and strengths at a surface are different from their corresponding bulk values because of the effect of bond broken.[14] During growth the adatoms and atomic vacancies also contribute to the surface energy. With these contributing factors, the surface energetics becomes even more complicated.

Measurements at temperatures above the Debye temperature indicate that the surface energy (tension), surface stress, and the Young's modulus of a specimen vary linearly with temperature of testing[15–19]

$$\gamma_s(T) = \gamma_s(T_m) + \alpha_t(T_m - T) = \gamma_s(0) - \alpha_t T \quad (\mathrm{J/m^2}), \quad (2)$$

where $\gamma_s(T_m)$ corresponds to the $\gamma_s$ value at melting; $\alpha_t$ is the slope of variation, and $T_m$ the melting point of the bulk specimen.

It is noted that the dimensions of most definitions in Eq. (1) are in eV/atom wise, which reflects the energy loss per discrete atom. However, the dimension of Eq. (2) is in $\mathrm{J/m^2}$, which represents the remaining energy density per unit area. The inconsistency in the dimension wises has caused long confusion about the surface energetics. On the other hand, the atomistic origin, temperature dependence, and the responsibility of the surface energy either in terms of eV/atom or $\mathrm{J/nm^2}$ are yet far from clear. The objective of this work is to show that the recently developed bond-order-length-strength (BOLS) correlation[14] mechanism could allow us to clarify the confusion by proposing two additional terms with functional dependence on the bonding identities and their temperature dependence.

## II. THEORY

### A. Atomistic definition of surface energetics

In fact, the performance of a surface is governed by the remaining energies in the surface skin or by the remaining bond energy of the discrete surface atoms instead of the energy loss upon surface formation. Therefore, two complementary terms are necessary for a better understanding of the surface energetics and its responsibility. The suggested terms are: (i) the energy-density gain in the surface skin and (ii) the bond-energy-remain per discrete atom upon surface formation. On the other hand, energy per unit volume in the surface skin of a certain thickness could be more appropriate than the energy per unit area without considering the skin thickness, as energy is always a volume-related quantity.

The key idea of the BOLS correlation is that the termination of lattice periodicity, or bond broken, causes the remaining bonds of the undercoordinated atoms to contract (from $d$ to $d_i$ by $d_i = c_i d$) spontaneously associated with bond strength gain (from $E_b$ to $E_i$ by $E_i = c_i^{-m} E_b$), and hence, localization and densification of charge, energy, and mass occur to the surface skin,[13] where $c_i$ is the coefficient of bond contraction and $m$ the index for bond nature. The subscript $i$ represents the specific $i$th undercoordinated atom of concern. The excessive energy stored in the surface skin not only takes the responsibility for the mechanical properties but also perturbs the Hamiltonian and related properties such as the band gap expansion, core level shift, and the electroaffinity (separation between the vacuum level and the conduction band edge) enhancement. On the other hand, the resultant effects of bond number reduction and bond strength gain vary the atomic cohesive energy (the product of bond energy and bond number) from the bulk value, which determines surface chemistry such as wettability, diffusivity, reactivity, and thermal and structural stability such as melting, evaporation, and self-assembly growth. The BOLS correlation mechanism can be applied to liquid surface of which the spacing between the first and the second atomic layers of liquid Sn contracts by 10% relative to that of subsequent layers.[20] Energy and electron densification and localization surrounding the undercoordinated atoms have been widely observed as defect states,[21] end states,[22,23] edge states,[24,25] and surface states.[26–28] The adatoms or vacancies during growth should produce the localized states that contribute to the surface energy. Therefore, the shortened and strengthened bonds between the undercoordinated surface atoms should take the full responsibility of the surface energetics and the unusual properties in the surface region.[12] We can hence establish the functional dependence of the surface energetics on the bonding identities and their temperature dependence without other parameters being involved. The definitions, analytical expressions, and the responsibilities of the surface energetics are summarized in Table I.

### B. Temperature dependence

Extending the BOLS to temperature domain leads to a $T$-dependent BOLS ($T$-BOLS) relation. At a given temperature $T$, the magnitude of the cohesive energy per bond is the difference between the binding energy at 0 K and the thermal energy of vibration;[29] the bond length is also subject to expansion

$$E_i(T) = E_i(0) - \int_0^T \eta_{1i}(t)\,dt \underset{T \gg \theta_D}{\cong} E_i(0) - \eta_{1i} T,$$

TABLE I. Definition of surface energy-density gain, surface atomic coherency and their origins and functionalities.

| Definitions | $T$-dependent expression | Atomistic origin | Functionality |
|---|---|---|---|
| Surface energy density ($\gamma_{ds}$) (eV/nm$^3$) | $\frac{\Sigma_{i\leqslant 2}E_i(T)/d_i^3(T)d_i(T)}{\Sigma_{i\leqslant 2}d_i(T)}$ | Energy gain per unit area due to bond broken induced strain and bond strength gain | Surface stress; elasticity; Hamiltonian; surface optics; dielectrics; surface trapping states; electron and photon transport dynamics; work function, etc |
| Surface atomic coherency ($\gamma_{fs}$) (eV/atom) | $\frac{\Sigma_{i\leqslant 2}z_iE_i(T)}{2}$ | Binding energy remain per discrete atom upon surface formation | Thermal stability; melting and evaporating ability; wettability; diffusivity; reactivity; acoustics; self-assembly; reconstruction. |
| Surface energy ($\gamma_s$) | $z_bE_b-\gamma_{fs}$ or equivalent to the expressions in Eq. (1) | Traditional definition of energy loss per atom upon surface formation | |

$$d_i(T) = d_i\left(1+\int_0^T \alpha_i(t)dt\right) \underset{T\gg\theta_D}{\cong} d_i(1+\alpha_i T), \tag{3}$$

where $\eta_{1i}(t)$ is the specific heat per bond, which follows Debye approximation. The internal energy $\int_0^T\eta_{1i}(t)dt \cong \omega^2x^2/2$ corresponds to the thermal vibration that contributes to the weakening of the bond strength. The $\omega$ and $x$ represent the frequency and amplitude of vibration, respectively. At $T\ll\theta_D$, the thermal expansion coefficient $\alpha_i$ is temperature dependent.[30,31] The $T\gg\theta_D$ approximation coincides with the experimentally derived form of temperature dependence, Eq. (2). According to Eq. (3), the proposed temperature dependence of surface energy density, $\gamma_{di}$, and the surface atomic coherency, $\gamma_{fi}$, can be expressed as

$$\gamma_{di}(T) \propto \frac{E_i(T)}{d_i^3(T)} = \frac{E_i(0)-\int_0^T \eta_{1i}(t)dt}{d_i^3\left(1+\int_0^T\alpha_i(t)dt\right)^3},$$

$$\gamma_{fi}(T) \propto z_iE_i(T) = z_i\left[E_i(0)-\int_0^T\eta_{1i}(t)dt\right].$$

Similarly, the stress and Young's modulus are in the same dimension as surface energy density

$$P_i(T) = -\left.\frac{\partial u(r)}{\partial V}\right|_{r=d_i} \propto Y_i(T) = -V\left.\frac{\partial^2 u(r)}{\partial V^2}\right|_{r=d_i} \propto \frac{E_i(T)}{d_i^3} = \gamma_{di}(T),$$

where $u(r)$ is the pairing potential and $V$ is the volume. This expression demonstrates the correspondence of surface energy density to the mechanical stress and elasticity. The proportional form is used thus because we are concerned about the relative change of these qualities to those of the bulk counterparts.

Because of the relations,[29] $E_i(0)=c_i^{-m}E_b(0)$, and $T_{mi}=z_{ib}c_i^{-m}T_m$, where $\Delta_i$ is the perturbation to atomic cohesive energy, we have, $\eta_{1i}(T_{mi})/\eta_1(T_m)=z_{bi}=z_b/z_i$ with $z_b$ being the bulk coordination number of 12 as standard. The relative changes of the surface energetics in the $i$th atomic layer to the bulk values at 0 K ($\gamma_d$ and $\gamma_f$) measured at $T$ can be derived as

$$\frac{\gamma_{di}(T)}{\gamma_d(0)} = \frac{d^3}{d_i^3\left(1+\int_0^T\alpha_i(t)dt\right)^3}\,\frac{E_i(0)-\int_0^T\eta_{1i}(t)dt}{E_b(0)} = \frac{c_i^{-(3+m)}}{\left(1+\int_0^T\alpha_i(t)dt\right)^3}\begin{cases}1-\dfrac{\int_0^T\eta_1(t)dt}{z_{ib}c_i^{-m}E_b(0)}, & (T\leqslant\theta_D)\\[2ex] 1-\dfrac{\eta_1T}{z_{ib}c_i^{-m}E_b(0)}, & (T>\theta_D)\end{cases},$$

$$\frac{\gamma_{fi}(T)}{\gamma_f(0)} \cong z_{ib}c_i^3\left(1+\int_0^T\alpha_i(t)dt\right)^3\frac{\gamma_{di}(T)}{\gamma_d(0)}. \tag{4}$$

## III. RESULTS AND DISCUSSION

### A. Flat surfaces: bond nature dependence

Generally,[14,29] for a flat surface, $z_1=4$, $z_2=6$, and $z_{i\geqslant 3}=12$, and correspondingly, the bond contraction coefficient

TABLE II. Predicted bond nature ($m$) dependence of ratios of energy density, $\langle\gamma_d\rangle$, and atomic cohesion (free energy), $\langle\gamma_f\rangle$, of a surface with respect to the bulk values. Subscript 1 and 2 refers to the top first and second layers. $\langle\gamma_{ss}/\gamma_{sb}\rangle$ is approximately equal to $1-\langle\gamma_{fs}/\gamma_{fb}\rangle$ according to the traditional definitions.

| $m$ | $\gamma_{d1}/\gamma_{db}$ | $\gamma_{d2}/\gamma_{db}$ | $\langle\gamma_{ds}/\gamma_{db}\rangle$ | $\gamma_{f1}/\gamma_{fb}$ | $\gamma_{f2}/\gamma_{fb}$ | $\langle\gamma_{fs}/\gamma_{fb}\rangle$ |
|---|---|---|---|---|---|---|
| 1 (Metal) | 1.668 | 1.281 | 1.468 | 0.379 | 0.532 | 0.455 |
| 2 | 1.895 | 1.363 | 1.62 | 0.43 | 0.566 | 0.498 |
| 3 | 2.153 | 1.45 | 1.79 | 0.489 | 0.602 | 0.546 |
| 4 | 2.447 | 1.542 | 1.98 | 0.556 | 0.64 | 0.598 |
| 5 | 2.781 | 1.641 | 2.192 | 0.632 | 0.681 | 0.656 |
| 2.56 (Carbon) | 2.036 | 1.411 | 1.713 | 0.462 | 0.586 | 0.524 |
| 4.88 (Silicon) | 2.738 | 1.628 | 2.165 | 0.622 | 0.676 | 0.649 |

$c_i(z_i)=2/\{1+\exp[(12-z_i)/(8z_i)]\}$ leads to $c_1=0.88$, $c_2=0.94$, and $c_{i\geqslant 3}=1$. For metals such as Au, Ag, and Cu, $m=1$; for carbon, $m=2.56$; for Si, $m=4.88$. For other alloys and compounds, the $m$ approaches four. Averaging the sum over the top two atomic layers, we can obtain the mean energy-density-gain per unit area within the two atomic layers, $\langle\gamma_{ds}\rangle=(\Sigma_{i=2}\gamma_{di}d_i)/(\Sigma_{i=2}d_i)$ and the mean energy remain per discrete atom in the top two atomic layers, $\langle\gamma_{fs}\rangle=[\Sigma_{i=2}\gamma_{fi}]/2$, at $T\sim 0$ K, as tabulated in Table II. Results show that at $T=0$, the surface-energy density (in eV/nm$^3$ unit) is always higher and the surface atomic coherency (in eV/atom unit) is lower than the corresponding bulk values. Therefore, it is not surprising that measurements show inconsistence values of previously defined surface energy because of the difference in dimensionality definitions.

### B. Curved surfaces: curvature and bond nature dependence

Considering the outermost two atomic layers of a spherical dot, it is ready to derive the $T$ independent $\langle\gamma_{ds}/\gamma_{db}\rangle$ and $\langle\gamma_{fs}/\gamma_{fb}\rangle$ as a function of the bond nature and the curvature by using, $z_1=4\times(1\text{-}0.75/K_j)$ and $z_2=z_1+2$.[14] $K_j$ is the dimensionless form of size ($K_j=R/d_0$, where $R$ is the radius of a spherical dot, and $d_0$ is the bond length of bulk material).

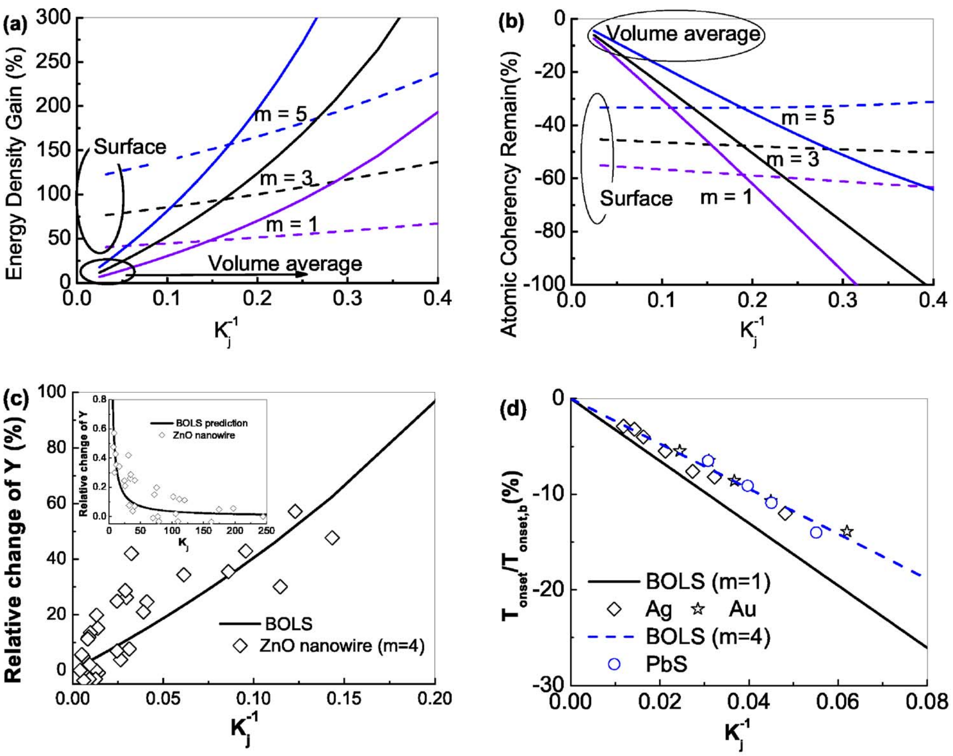

FIG. 1. (Color online) Prediction of curvature—induced (a) energy-density-gain per unit volume (%) and (b) cohesive-energy-remain per discrete atom averaged over the surface skins (surface) of two atomic layers and averaged over the entire spherical solid (volume average). The former increases whereas the latter drops with the decrease of solid size. The volume average of (a) determines the size dependence of strength and elasticity and the volume average of (b) dictates the thermal stability as intensively addressed in Ref. 13. Panels (c) and (d) compare the predictions to the measured size dependent relative change of Young's modulus of ZnO nanowires (Ref. 32) and the cohesive energy (evaporation temperature) for PbS, Ag and Au nanosolids (Ref. 33). Insert in (c) is the same set of data expressed in $Y$-$K_j$ wise.

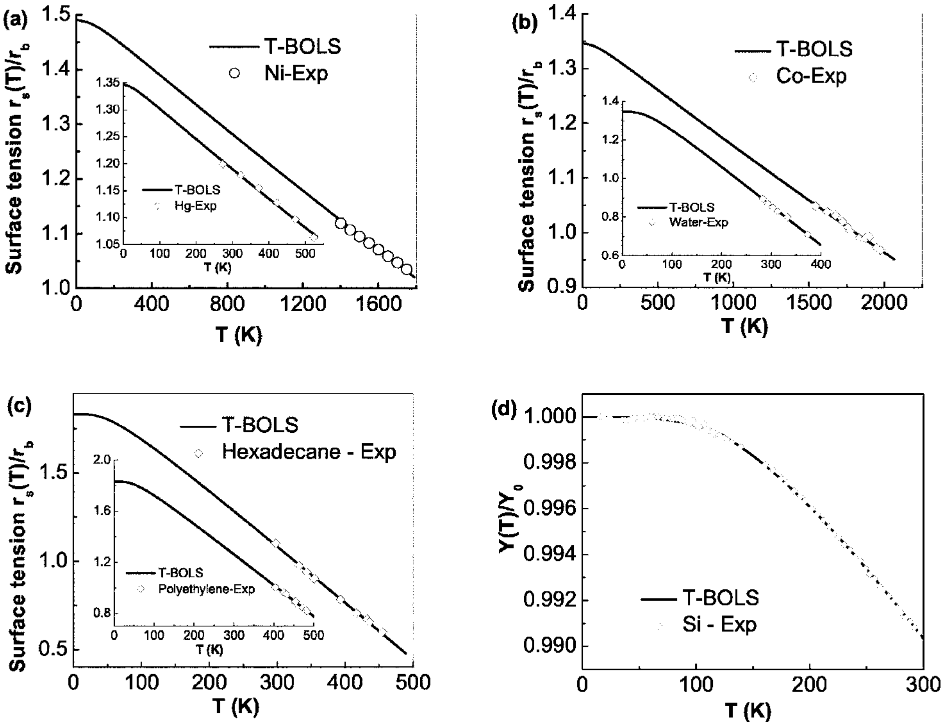

FIG. 2. Estimation of $E_b(0)$ by reproducing the measured temperature dependence of surface tension for (a) Hg (Ref. 18) and Ni (Ref. 17) liquid, (b) Co (Ref. 37) and $H_2O$ (Ref. 38) liquid, and (c) hexadecane and polyethylene (Ref. 39), and the temperature dependence of (d) Young's modulus of Si (Ref. 40). The input and output are summarized in Table III.

According to the core-shell structure, the size dependent relative change of a measurable quantity $Q$ follows the relation:[14]

$$\frac{\Delta Q(K_j)}{Q(\infty)} = \sum_{i\leqslant 3}\gamma_{ij}\frac{\Delta q_i}{q_0},$$

$$q_i = \begin{cases}\gamma_{di} = E_i/d_i^3 \propto Y_i\\ \gamma_{fi} = z_iE_i \propto T_{Ci}\end{cases},$$

$$\gamma_{ij} = N_i/N_j = V_i/V_j = \tau c_i K_j^{-1}, \qquad (5)$$

where $q_i$ is the density of $Q$ and $\gamma_{ij}$ is the portion of the undercoordinated atoms of the entire solid. $\tau=1$, 2, and 3 is the dimensionality of a plate, rod, or spherical dot, correspondingly. Based on Eq. (5) we can predict the trend of bond nature and curvature dependence of the surface energetics, as shown in Figs. 1(a) and 1(b). It can be seen that the surface energetics changes slightly with the curvature. The volume average of the energy-density gain agrees with the observed size (diameter$=2K_jd_0$) dependence of the Young's modulus of $ZnO_2$ nanowires.[32] The size dependence of cohesive-energy remain is consistent with the measured trends of critical temperature for evaporation $T_C$ ($T_{\mathrm{onset}}$) of Ag, Au, and PbS nanostructures.[33] Ideally, the $T_C$ for Au and Ag nanosolid should follow the $m=1$ curve and that of PbS follow the $m=4$ curve. However, contamination during heating should alter the surface bond nature and energy. Therefore, it is not surprising why the measurement of Au and Ag does not follow the $m=1$ curve. Measurement under ultrahigh vacuum may rectify the deviation. The predicted size dependence of cohesive-energy remain also agrees with the measured size effect on the binding energy per atom of Ag particles,[34] and the structural phase transition temperature for Pb nanoislands on Si substrate.[35] Intensive investigation of the size-induced solid liquid, magnetic, ferroelectric, and superconductive phase transitions of nanostructures has formed the subject of Ref. 36.

### C. Temperature dependence: Atomic cohesive energy

For the temperature dependence, the nomalized bond energy, $E_i$, the $\langle\gamma_{ds}\rangle$, and the $\langle\gamma_{fs}\rangle$ can be expressed as

$$\frac{E_i(T)}{E_b(0)} = c_i^{-m}\left(1 - \frac{\int_0^T \eta_1(t)dt}{z_{ib}c_i^{-m}E_b(0)}\right),$$

$$\left\langle\frac{\gamma_{ds}(T)}{\gamma_{db}(0)}\right\rangle = \frac{\sum_{i\leqslant 2} c_i^{-2}(T)\frac{E_i(T)}{E_b(0)}}{\sum_{i\leqslant 2} c_i(T)},.$$

$$\left\langle\frac{\gamma_{fs}(T)}{\gamma_{fb}(0)}\right\rangle = \sum_{i\leqslant 2} z_{ib}\frac{E_i(T)}{E_b(0)}. \qquad (6)$$

Based on this relation we can reproduce the measured temperature dependence of surface energy, surface tension, and Young's modulus with derivatives of $E_b(0)$. To be inline

TABLE III. (a) Information about $E_b(0)$ derived from reproduction of the measured $T$-dependent surface tension of Ni, Hg, $H_2O$, and Co liquids. The bond energy $E_b(0)$ for elemental specimen is available by dividing the atomic coherency $E_B(0)$ with bulk atomic coordination. The $E_b(0)$ for Si is derived from the precise fitting of the Young's modulus (energy density). The thermal expansion coefficient and the Debye temperature are input parameters. (b) for polymers. Thermal expansion coefficients are not available and therefore not used in the practices on polymers. Experimental data are sourced from Ref. 39.

(a)

| | $\gamma_s(T_m)$ (mJ/m$^2$) | $\alpha_t$ (mJ/(m$^2$ K) | $\alpha_i$ ($10^{-5}$ K$^{-1}$) | $\theta_D$ (K) | $T_m$ (K) | $E_B(0)$ (eV) |
|---|---|---|---|---|---|---|
| Ni | 1823 | 0.46 | 1.6 | 375 | 1728 | 3.645 |
| Hg | 493 | 0.22 | 6.04 | 100 | 234.32 | 1.79 |
| Co[37] | 1930 | 0.33 | 13.0 | 385 | 1768 | 4.80 |
| $H_2O$ | 75.4 | 0.162 | — | 192 | 273 | 0.38 |
| Si | — | — | Ref. 31 | 647 | 1687 | 4.18 |

(b)

| | $\gamma_s(T_m)$ (mJ/m$^2$) | $\alpha_t$ (mJ/(m$^2$ K) | $\Delta T$ (°C) | $T_m$ (K) | $E_B(0)$ (eV) |
|---|---|---|---|---|---|
| hexadecane (C16) | 49.5 | 0.094 | 298–373 | 291 | 0.30 |
| PE (C2000) | 26.89 | 0.065 | 403–493 | 407 | 0.41 |
| PEO | 41.9 | 0.08 | 343–463 | 333 | 0.40 |
| PCAP | 40.32 | 0.068 | 373–398 | 333 | 0.43 |
| PEKK | 39.4 | 0.08 | 571–618 | 578 | 0.60 |
| PBT, poly (butylene terephthalate) | 41.46 | 0.08 | 493–523 | 496 | 0.54 |
| Poly (trimethylene terephthalate) | 38.86 | 0.067 | 538–562 | 496 | 0.56 |
| PET | 37.73 | 0.0646 | 513–593 | 528 | 0.59 |
| Poly (amide ester) copolymer | 47.6 | 0.08 | 433–463 | 433 | 0.52 |
| nylon 66 | 34.1 | 0.115 | 543–563 | 533 | 0.47 |
| Polyamide MPMD-12 | 39.16 | 0.081 | 463–623 | 463 | 0.49 |

with the current definition of energy density, we may assume a thickness $D$ to revise the surface tension to energy density, $\gamma_s(T)/D$, and therefore

$$\frac{\gamma_s(T)}{\gamma_b(0)} = \frac{\gamma_s(T_m)}{\gamma_b(0)} + \frac{\alpha_t T_m}{\gamma_b(0)}\left(1 - \frac{T}{T_m}\right) = \frac{\gamma_s(0)}{\gamma_b(0)} - \frac{\alpha_t T}{\gamma_b(0)}. \qquad (7)$$

Introducing $D$ does not vary the normalized form of surface tension. Equilibrating Eq. (7) to

$$\left\langle \frac{\gamma_{ds}(T)}{\gamma_{db}(0)} \right\rangle \underset{T \gg \theta_D}{\cong} \frac{c_1^{-(m+2)} + c_2^{-(m+2)}}{(c_1 + c_2) \times (1 + \alpha T)^3} - \frac{z_{b1} c_1^{-2} + z_{b2} c_2^{-2}}{(c_1 + c_2) \times (1 + \alpha T)^3} \frac{\eta_1 T}{E_b(0)},$$

leads to

$$\begin{cases} \gamma_b(0)/D & \underset{\alpha T \ll 1}{\cong} \dfrac{\gamma_s(0)/D}{\dfrac{c_1^{-(m+2)} + c_2^{-(m+2)}}{c_1 + c_2}} = A_1(m)\gamma_s(0)/D \\ E_b(0) & \underset{\alpha T \ll 1}{\cong} \dfrac{z_{b1} c_1^{-2} + z_{b2} c_2^{-2}}{c_1 + c_2} \dfrac{\eta_1 \gamma_b(0)}{\alpha_t} = A_2 \dfrac{\gamma_b(0)}{\alpha_t} \end{cases}.$$

Figure 2 shows the reproduction of the measured temperature dependence of surface tension of (a) liquid Hg and Ni, (b) Co and $H_2O$, (c) hexadecane and polyethylene, and (d) the Young's modulus for Si. In the calculations, the Debye temperature and the thermal expansion coefficient for the corresponding specimens are the input parameters; the $E_b(0)$ is the derived information, as summarized in Table III. No other parameters are involved. Table III also shows results obtained from the fitting of the temperature dependence of organic samples. Therefore, the temperature dependence of surface tension and the Young's modulus has given us an opportunity to derive information regarding atomic cohesive energy in the bulk. The accuracy of the determination is strictly subject to the measurement. Artifacts such as surface contamination and sample purity may lead to errors to the derived $E_b(0)$.

## IV. CONCLUSION

In conclusion, correlation between the surface energetics and the interatomic bonding has been established from the perspective of BOLS correlation. Major conclusions are drawn as follows:

(1) The concepts of energy-density-gain per unit volume and cohesive-energy remain are suggested essential to classify the surface energetics and their responsibilities.

(2) Functional dependence of the surface energetics on the bonding identities has been established to represent the fact that the variation of surface energetics from the bulk values arises from the shortened and strengthened bonds between the undercoordinated atoms.

(3) The thermal weakening of surface energetics is dominated by thermal expansion and vibration, through the internal energy following the integration of Debye' specific heat.

(4) Predicted volume average of the energy density and cohesive energy agrees with the measured size dependence of Young's modulus and critical temperatures for evaporation, melting, and phase transition.

(5) This approach allows us to estimate the bond energy by reproducing the measured temperature dependence of surface tension and Young's modulus, which is beyond the scope of existing models.

It is noted that the adatoms or atomic vacancies during growth will affect the surface energy in a dynamic way by introducing additional traps nearby because of the bond order loss, which is within the BOLS expectation. As we focus here on a surface in static states, the dynamic behavior of adatoms and vacancies is not immediate concern in the present case. However, the dynamic process of adatom growth or defect/impurity formation and its influence on the surface energy would be a challenging topic for further studies. The present approach derives information of bond energy limiting only to elemental specimens. For compounds or alloys, we can obtain the mean value of atomic coherency. 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 $E_b(0)$ values. Discriminating the contribution of defect concentration, surface chemical contamination, or artifacts due to experimental techniques from the intrinsically true contribution to the derived $E_b(0)$ would be even more interesting. Nevertheless, results given here and progress made insofar may demonstrate that our approach could represent the true situation of observations with the seemingly simple approaches.

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[1] H. Ibach, Surf. Sci. Rep. **29**, 193 (1997).

[2] W. Haiss, Rep. Prog. Phys. **64**, 591 (2001).

[3] H. M. Lu and Q. Jiang, Phys. Rev. Lett. **92**, 179601 (2004).

[4] A. Rytkönen, S. Valkealahti, and M. Manninen, J. Chem. Phys. **106**, 1888 (1997).

[5] W. (Kelvin) Thomson, Philos. Mag. **42**, 448 (1871).

[6] M. N. Magomedov, Russ. J. Phys. Chem. **79**, 711 (2005).

[7] S. B. Zhang and S.-H. Wei, Phys. Rev. Lett. **92**, 086102 (2004).

[8] R. Dingreville, J. M. Qu, and M. Cherkaoui, J. Mech. Phys. Solids **53**, 1827 (2005).

[9] I. Galanakis, N. Papanikolaou, and P. H. Dederichs, Surf. Sci. **511**, 1 (2002).

[10] M. C. Desjonquères and D Spanjaard, *Concepts in Surface Physics. Springer Series in Surface* (Springer-Verlag, Berlin, 1993), Vol. 30.

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

[12] O. L. Alerhand, J. D. Joannopoulos, and E. J. Mele, Phys. Rev. B **39**, 12622 (1989).

[13] C. Q. Sun, L. K. Pan, C. M. Li, and S. Li, Phys. Rev. B **72**, 134301 (2005).

[14] C. Q. Sun, Prog. Solid State Chem. **35**, 1 (2007).

[15] H. Fujii, T. Matsumoto, S. Izutani, S. Kiguchi, and K. Nogi, Acta Mater. **54**, 1221 (2006).

[16] Q. Zhao, Y. Lim, and E. W. Abel, J. Colloid Interface Sci. **280**, 174 (2004).

[17] F. Xiao, R. Yang, and C. Zhang, Mater. Sci. Eng., B **132**, 183 (2006).

[18] S. Halas and T. Durakiewicz, J. Phys.: Condens. Matter **14**, L735 (2002).

[19] H. Nakanishi, K. Nakazato, and K. Terashima, Jpn. J. Appl. Phys., Part 1 **39**(12A), 6487 (2000).

[20] O. G. Shpyrko, A. Y. Grigoriev, C. Steimer, P. S. Pershan, B. Lin, M. Meron, T. Graber, J. Gerbhardt, B. Ocko, and M. Deutsch. Phys. Rev. B **70**, 224206 (2004).

[21] Y. Niimi, T. Matsui, H. Kambara, and Hiroshi Fukuyama, Physica E (Amsterdam) **34**, 100 (2006).

[22] V. S. Stepanyuk, A. N. Klavsyuk, L. Niebergall, and P. Bruno, Phys. Rev. B **72**, 153407 (2005).

[23] J. N. Crain and D. T. Pierce, Science **307**, 703 (2005).

[24] Y. Kobayashi, K. Kusakabe, K. Fukui, and T. Enoki, Physica E (Amsterdam) **34**, 678 (2006).

[25] K. Nakada, M. Fujita, G. Dresselhaus, and M. S. Dresselhaus,

Phys. Rev. B **54**, 17954 (1996).

[26] T. Eguchi, A. Kamoshida, M. Ono, M. Hamada, R. Shoda, T. Nishio, A. Harasawa, T. Okuda, T. Kinoshita, and Y. Hasegawa, Phys. Rev. B **74**, 073403 (2006).

[27] J. Ciston, L. D. Marks, R. Feidenhans'l, O. Bunk, G. Falkenberg, and E. M. Lauridsen, Phys. Rev. B **74**, 085401 (2006).

[28] Th. Fauster, Ch. Reuß, I. L. Shumay, and M. Weinelt, F. Theilmann, and A. Goldmann, Phys. Rev. B **61**, 16168 (2000).

[29] C. Q. Sun, C. M. Li, S. Li, and B. K. Tay, Phys. Rev. B **69**, 245402 (2004).

[30] L. Li, Y. Zhang, Y. Yang, X. Huang, and G. Li, Appl. Phys. Lett. **87**, 031912 (2005).

[31] Y. Okada and Y. Tokumaru, J. Appl. Phys. **56**, 314 (1984).

[32] C. Q. Chen, Y. Shi, Y. S. Zhang, J. Zhu, and Y. J. Yan, Phys. Rev. Lett. **96**, 075505 (2006).

[33] K. K. Nanda, Appl. Phys. Lett. **87**, 021909 (2005).

[34] Y. P. Chiu, L. W. Huang, C. M. Wei, C. S. Chang, and T. T. Tsong, Phys. Rev. Lett. **97**, 165504 (2006).

[35] I. S. Hwang, S. H. Chang, C. K. Fang, L. J. Chen, and T. T. Tsong, Phys. Rev. Lett. **93**, 106101 (2004).

[36] C. Q. Sun, Y. Shi, C. M. Li, S. Li, and T. C. Au Yeung, Phys. Rev. B **73**, 075408 (2006).

[37] W. J. Yao, X. J. Han, M. Chen, B. Wei, and Z. Y. Guo, J. Phys.: Condens. Matter **14**, 7479 (2002).

[38] http://hyperphysics.phy-astr.gsu.edu/hbase/surten.html#c3M

[39] B. B. Sauer and G. T. Dee, Macromolecules **35**, 7024 (2002).

[40] U. Gysin, S. Rast, P. Ruff, E. Meyer, D. W. Lee, P. Vettiger, and C. Gerber, Phys. Rev. B **69**, 045403 (2004).