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Maolin Bo, Yan Wang, Yongli Huang, Xi Zhang, Ting Zhang, Can Li, and Chang Q. Sun

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Coordination-resolved local bond contraction and electron binding-energy entrapment of Si atomic clusters and solid skins

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Consistency between x-ray photoelectron spectroscopy measurements and density-function theory calculations confirms our bond order-length-strength notation-incorporated tight-binding theory predictions on the quantum entrapment of Si solid skin and atomic clusters. It has been revealed that bond-order deficiency shortens and strengthens the Si-Si bond, which results in the local densification and quantum entrapment of the core and valence electrons. Unifying Si clusters and Si(001) and (111) skins, this mechanism has led to quantification of the 2p binding energy of 96.089 eV for an isolated Si atom, and their bulk shifts of 2.461 eV. Findings evidence the significance of atomic undercoordination that is of great importance to device performance. © 2014 AIP Publishing LLC.

I. INTRODUCTION

Si atoms associated with defects, surface skins, and nanoclusters of various shapes demonstrate many fascinating properties, which make them essential elements in concurrent technologies.¹–⁶ It has been recognized that these unusual properties arise from the interaction between undercoordinated atoms,⁷,⁸ but a systematic characterization and consistent understanding of the energetic behavior of the core and the valence electrons are still lacking though the energy shift of the valence band and the 2p core-level induced by atomic undercoordination at the (100) and the (111) surfaces and in the atomic clusters of Si have been intensively investigated.⁹–¹⁴ Recent investigations using a free-electron laser vacuum ultraviolet and x-ray photoelectron spectroscopy (XPS) of size-selected clusters revealed a linear dependence of the energy shifts on the valence component increases with the incident angle or with decreasing the angle between the incident beam and the surface normal, which indicates that this peak corresponds to the bulk (B) contribution. However, the physical origin of the energy shift¹⁹–²² and assignment of the energy components in the XPS profiles are yet uncertain. The underlying mechanism for the surface and size effect remains unclear, though it is often referred to the variation of surface-to-volume ratio²³ and the “initial-final states” relaxation in the process of ionization and excitation.²⁴

We report here with our findings in analyzing the XPS of Si surfaces and clusters based on the framework of BOLS (bond order-length-strength) correlation notation²⁵ and tight-binding (TB) theory. Reconciliation of the energy shifts of the 2p and the valence band of Si upon bulk, defect, surface, and nanocrystal leads to a consistent understanding of the energy shifts as a result of local bond strain of undercoordinated atoms. DFT (density function theory) calculations using the package of²⁶,²⁷ further confirmed the entrapment of electronic binding energy (BE).

II. PRINCIPLES AND CALCULATION METHODS

A. Tight binding approximation

According to the band theory, the νth energy level of an isolated atom, $E_i(0)$, is determined by the integral of the intraatomic potential, $V_{\text{atom}}(r)$, and the eigenvalue function of an atom at the specific ith atomic site, $|v, i\rangle$. Upon the involvement of the inter-atomic potential $V_{\text{cry}}(r)$, the core-level BE will shift from the origin $E_i(z = 0)$ to $E_i(z = 12)$ by an amount of $E_i(12) - E_i(0)$ that is proportional to the cohesive energy per bond of an atom with 12 neighbors of standard²⁸

$$E_i(0) = \langle v, i | V_{\text{atom}}(r) | v, i \rangle$$

$$E_i(12) - E_i(0) = \langle v, i | V_{\text{cry}}(r) | v, i \rangle + \sum_{j=1}^{12} \langle v, i | V_{\text{cry}}(r) | v, j \rangle$$

$$= z \left(1 + \frac{z\delta_i}{z}ight) \approx z \propto E_{\text{b}}. \quad (1)$$

The coordination number $z = 0$ and 12 represents an isolated atom and an atom in the bulk, respectively. The sum is over all $z$ neighbors of the specific ith atom. Because $\langle v, i | v, j \rangle = \delta_{ij}$ with $\delta_{ij}$ being the Kronig function (if $i = j$, $\delta_{ij} = 1$,

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otherwise, \( \delta_{ij} = 0 \), the term \( \beta \approx z \ll 1 \). Any perturbation to the bond energy \( E_b \) will shift the core level accordingly.

**B. BOLS: Local quantum entrapment**

According to the BOLS notation, the shorter and stronger bonds between under-coordinated atoms cause local densification and quantum entrapment of the electronic BE at sites surrounding the under-coordinated atoms. This entrapment provides perturbation \( \Delta_{KL} \) to the local Hamiltonian and hence results in a CLS (core level shift). The bond relaxation in length and energy follows:

\[
C_z = d_z/d_b = 2/\left[1 + \exp\left((12 - z)/8z\right)\right]
\]

\[
C^{-m}_z = E_c/E_b.
\]  

(2)

The bond nature index \( m = 4.88 \) for silicon describes how the bond strength change with bond length. Incorporating the BOLS into the tight-binding approximation yields

\[
V_{cry}(\Delta_H) = V_{cry}(r)[1 + \Delta_H],
\]

where

\[
\Delta_H = \left\{\begin{array}{ll}
C^{-m}_z - 1 & \text{(Surface)} \\
\tau K^{-1} \sum_{z < 3} C_z (C^{-m}_z - 1) & \text{(Clusters)},
\end{array}\right.
\]  

(3)

\( \tau \) is the shape factor (\( \tau = 1, 2, \) and 3 corresponds to a thin plate, a cylindrical rod, and a sphere dot, respectively). \( K \) being the dimensionless form of size is the number of atoms lined along the radius of a nanoparticle.25

With respect to the bulk shift \( \Delta E_i(12) \), the under-coordination induced CLS, \( \Delta E_i(z) \), follows:

\[
\frac{\Delta E_i(z)}{\Delta E_i(12)} = \frac{E_i(z) - E_i(0)}{E_i(12) - E_i(0)} = \frac{E_c}{E_b} C^{-m}_z = 1 + \Delta_H.
\]  

(4)

With the given energies of the surface XPS spectral components related to \( z \) and \( z' \) coordination numbers and their correlation, we can determine the referential \( E_i(0) \), the bulk shift, \( \Delta E_i(12) \), and the \( z \) dependent shift

\[
\frac{E_i(z) - E_i(0)}{E_i(z') - E_i(0)} = \frac{C^{-m}_{z'} - 1}{C^{-m}_z} \text{ or }
\]

\[
E_i(0) = \frac{C^m_{z'} E_i(z') - C^m_z E_i(z)}{C^m_{z'} - C^m_z},
\]

\[
E_i(z) = E_i(0) \times C^{-m}_z.
\]  

(5)

Using the sum rule of the core–shell structure and taking the surface-to-volume ratio into effect, we can deduce the \( K \) dependence of \( \psi \)th energy level \( E_i(0) \) and its bulk shift \( \Delta E_i(12) \)

\[
E_i(K) = E_i(12) + [E_i(12) - E_i(0)] \times \Delta_H.
\]  

(6)

Generally, the size-induced shifts of the BE for nanoparticles exhibit an inverse linear size relationship in a form of: \( E_i(K) = A + BK^{-1} \), where \( A \) and \( B \) are constants that correspond to the intercept and the gradient of the \( E_i(K^{-1}) \) line, respectively. Comparing the experimental scaling relationship with the theoretical expression in Eq. (6) yields

\[
\begin{align*}
A &= E_i(12) \\
B &= [E_i(12) - E_i(0)] \times \sum_{z \leq 3} C_z (C^{-m}_z - 1).
\end{align*}
\]  

(7)

With the derived \( E_i(12) \), \( E_i(0) \), \( m \), and the given \( z \) values for the outermost three atomic layers, we are able to decompose the measured XPS spectra into the corresponding surface and bulk components.

**C. DFT computation**

In order to verify the BOLS-TB predictions of the broken-bond-induced quantum entrapment, we conducted DFT calculations of the bond length, charge transfer, and valence charge distribution of Si(100) and (210) surfaces. The relativistic DFT calculations were conducted using the CASTEP code.29 The Ultrasoft pseudopotential was chosen as approximations for Si to deal with the core potentials including some degree of relativistic effects.30 Calculations of the Si(100) and (210) stepped surfaces have been performed using the symmetrical 4 atomic layers with the bottom being fixed as bulk and these upper three atomic layers are free as surface.31,32 The lattice parameters of the rebuilt supercell of the Si(100) and Si(210) are \( a = 5.431 \, \text{Å}, \ b = 10.861 \, \text{Å}, \ c = 16.073 \, \text{Å} \) (\( x = \beta = \gamma = 90.0\)°) and \( a = 5.431 \, \text{Å}, \ b = 13.302 \, \text{Å}, \ c = 18.679 \, \text{Å} \) (\( x = \beta = 90.0\)° and \( \gamma = 114.1\)°), respectively. The geometrical optimization and electronic structures were obtained based on LDA(CAPZ) functional.26 In each case, the subsequent slabs have been separated by a vacuum region of 12 Å thick. The plane wave cutoff was 240 eV, for thus refined structures final, accurate energy values were then computed with the same code using a precise cutoff energy of 280 eV in all cases.33 This latter feature allows us to carry out the calculations including only non-equivalent points in the \( k \)-space grid \( 16 \times 8 \times 2 \) used for sampling the Brillouin zone (BZ) of Si(100) and Si(210) surfaces; this grid, chosen according to a Monkhorst-Pack scheme, gives a BZ sampling interval smaller than 0.05 Å\(^{-1}\).

**III. RESULTS AND DISCUSSION**

**A. XPS: Skin-resolved quantum entrapment**

According to constraints on the energy separation between each component, Eq. (5), each XPS spectrum is decomposed into the bulk (B) and surface (S) components from higher (smaller value) to lower BE upon background correction. The number of components is taken with respect to the originally reported count,34–36 but the peak energies are subject to refinement to fit the overall peak intensity.

On the basis of the BOLS-TB approaches, we decomposed the XPS 2p spectra from clean Si(100)34 and Si(111)35 surfaces (see Fig. 1 and Table I). The spectra were decomposed into the B, the first (S1), and the second (S2) atomic layers of the surface. Including the common B component (\( z = 12 \)), there are a total of \( l = 5 \) components for these
two surfaces. There will be a combination of \( N = 10 \) = \( C_i^2 = \frac{1}{[(l - 2)!]2!} \) values of \( E_i(0) \). Using the least-root-mean-square approach, we can find the average of \( \langle E_i(0) \rangle = \sum \langle E_i(0) \rangle / N \) and the standard deviation. A fine tuning of the CN values of the components will minimize the \( \sigma \) and hence improve the accuracy of the effective CN for each sublayer, and hence to determine the local strain, the BE density, and the cohesive energy per discrete atom in differently oriented surface layers. With the derived \( z \) value and the 2p BE for each XPS component, one is able to predict the \( z \)-resolved local lattice strain, BE shift, atomic cohesive energy \( E_C \), and binding energy density \( E_D \) in the Si skins, as shown in Figure 2 and Table I, where \( z_{th} = z / 12 \) is the reduced CN and \( z = 12 \) is the bulk value.

The \( E_i(0) \) and \( E_i(12) \) are intrinsic constants, which are identical for all the surfaces and atomic clusters of a given material. Using the least-root-mean-square optimization, we obtain the \( z \)-resolved 2p core-level shift for Si

\[
E_i(z) = \langle E_i(0) \rangle \pm \sigma + \Delta E_i(12)C_z^{-m} = 96.089 \pm 0.008 + 2.461C_z^{-4.88}.
\]

FIG. 1. Decomposition of the Si 2p spectra for (a) Si(100)\textsuperscript{34} and (b) Si(111)\textsuperscript{35} surfaces with four Gaussian components representing the bulk B, \( S_2 \), and \( S_1 \) states from higher(smaller absolute value) to lower BE. These components follow the constraints of Eq. (5). Derived information is given in Table I.

![Graph](image1.png)

FIG. 2. Coordination number (\( z \)) resolved local bond strain, BE shift (entrapment), atomic cohesive energy \( E_C \), and binding energy density \( E_D \).

This information is of great importance in understanding the surface behavior of these under-coordinated atoms.

**B. Size-resolved quantum entrapment**

If a cluster is approximately spherical, the number of atoms \( N \) is related to its radius \( K \) by

\[
N = 4\pi K^3 / 3
\]

\[
K^{-1} = (3N/4\pi)^{-1/3} = 1.29N^{-1/3}.
\]

Eq. (6) yields the \( N \)-dependence of the core level BE

\[
E_i(N) = E_i(12) + [E_i(12) - E_i(0)] \times \left[ \frac{1.29N^{-1/3}}{N} \sum_{i=1}^{3} C_i(C_i^{-m} - 1) \right].
\]

As in the BOLS convention, we choose \( z_1 = 4(1-0.75/K) = 3.16 \) (\( K^{-1} = 0.281 \)) from experiment date of the smallest cluster for the Si\(_n\) cluster outermost layer as the standard reference. The \( z_2 = z_1 + 2 \) and \( z_3 = 12 \) were taken to be 5.16 and 12, respectively.\textsuperscript{37} From the relation of \( C(z_i) \) in Eq. (2), \( C_1, C_2, \) and \( C_3 \) were calculated to be 0.8269, 0.9173, and unity, respectively, from which \( \Delta_{1,2,3} \approx 1.26, 0.48, \) and 0. The sum

**TABLE I.** The effective CN(z), lattice strain (\( \varepsilon \)), relative BE shift (\( \delta E_i = \delta E(z)/\delta E(12) - 1 = (C_i^{-m} - 1) \)), relative atomic cohesive energy \( E_C = E_C(z)/E_C(12) = (C_i^{-m} - 1) \), and the relative BE density \( E_D = E_D(z)/E_D(12) = (C_i^{-m} - 1) \) in various registries of Si\(_{10}^{34,38}\) skins (\( m = 4.88 \)).


<table>
<thead>
<tr>
<th>( z )</th>
<th>Si 2p (Si(_n))</th>
<th>Si 2p (skins)</th>
<th>( -\varepsilon_1(%) )</th>
<th>( \delta E_i )</th>
<th>( \delta E_D )</th>
<th>( -\delta E_C )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_i(0) )</td>
<td>0</td>
<td>100.38</td>
<td>96.089</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>( E_i(12) )</td>
<td>B</td>
<td>12</td>
<td>102.84</td>
<td>98.550</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( \Delta E_i(12) )</td>
<td>...</td>
<td>2.46</td>
<td>2.461</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>Si(100)</td>
<td>( S_2 )</td>
<td>6.76</td>
<td>...</td>
<td>99.224</td>
<td>4.84</td>
<td>27.39</td>
</tr>
<tr>
<td>Si(111)</td>
<td>( S_1 )</td>
<td>5.10</td>
<td>...</td>
<td>99.871</td>
<td>8.44</td>
<td>53.74</td>
</tr>
<tr>
<td>( S_1 )</td>
<td>7.08</td>
<td>...</td>
<td>99.143</td>
<td>4.34</td>
<td>24.18</td>
<td>41.86</td>
</tr>
<tr>
<td>( S_1 )</td>
<td>5.32</td>
<td>...</td>
<td>99.751</td>
<td>7.83</td>
<td>48.88</td>
<td>90.15</td>
</tr>
</tbody>
</table>
of $\Delta_H = \Delta_1 + \Delta_2 + \Delta_3 = 1.74$ determines the $\Delta E_{2p}(K)$. Therefore, we can calculate the BE change without needing any other assumptions

$$E_{st+2p}(12) = E_{st2p}(12) + \Phi = 102.84 \text{ eV},$$

$$E_{2p}(K) = E_{st+2p}(12) + \left[ E_{st2p}(12) - E_{st+2p}(0) \right]$$

$$\times \left[ 1.292N^{-1/3} \sum_{i=3}^\infty C_i(C_i^{-1} - 1) \right]$$

$$= 102.84 + 13.82N^{-1/3} \text{ eV}.$$  

Likewise, $E_{1p}(N) = 4.46 + 14.04N^{-1/3} \text{ eV}$ and $E_{st2p}(12) = 98.55 \text{ eV}$ are the bulk values derived from the surface XPS spectra.  

$\Phi = 4.29 \text{ eV}$ is the photoionization energy.  

With the value of $\Delta E_{2p}(12) = E_{st+2p}(12) - E_{st+2p}(0) = 2.46 \text{ eV}$ derived from surface analysis, we can then determine the shape factor $\tau = 2.50$ and $E_{st+2p}(0) = 100.38 \text{ eV}$ in the size dependent spectra.  

Figure 3 shows that the direct 2p photoionization threshold of 106–111 eV increases linearly with $N^{-1/3}$, as does the valence band photoionization threshold in the range of 8–13 eV. The results are in accordance with the BOLS expectation on the size-induced energy shifts of both the 2p and the valence bands for Si$_N$ atomic clusters. The size trend of the energy shift is in consistence with the surface positive shift. Therefore, both the size- and the surface-induced energy shifts of Si are dominated by the broken-bond-induced local strain and the skin-depth quantum entrapment. Note that the Si size-selected clusters have been reported by Vogel et al. using the first free-electron laser vacuum ultraviolet and soft x-ray photoelectron spectra and the confined cluster ions are irradiated by a monochromatic soft x-ray beam at BESSY II undulator beamline U125/2-SGM. These product ions are detected by a reflect on time-of-flight mass spectrometer as the photon energy is scanned across the silicon 2p core level binding energy with a step size.

C. DFT derivatives

In consistent with the BOLS predictions, the current DFT calculations confirm the spontaneous bond contraction of Si$_N^+$ and Si$_N^-$ at the stepped Si(210) surfaces. Figure 4(a) shows that Si(210) stepped surfaces Si bond contraction shortens the distances between atom E and its neighbors denoted 1, 2, 3 are 2.577 Å, 3.572 Å, 3.941 Å and with respect to the bulk standard of 3.840 Å, 4.503 Å, 3.840 Å, respectively. (b) The s-orbit local DOS of the Si(210) surface shift more than that of the Si(100) surface toward $E_F$.

According to the principal of least energy, any spontaneous process proceeds toward the direction of energy reduction. Therefore, the spontaneous bond contraction is associated with the inter-atomic trapping potential well depression or the single bond energy gain. Figure 4 compares the DFT results for the stepped Si(210) surface and the flat (100) surface. It can be seen from Figure 4(b) that the s-orbit local DOS of the Si(210) surface shift more than that of the (100) surface toward $E_F$. Si(210) step induced entrapment of the LDOS of s-orbit with respect to that of Si(100) surface. Trend consistency between calculations and XPS observations confirmed the BOLS predictions.

IV. CONCLUSION

Incorporating the BOLS-TB correlation with the DFT calculations and XPS measurements has led to a consistent...
insight into the physical origin of the generation of the localized edge states of Si surfaces and atomic clusters. Analyzing the XPS spectra for the Si(100) and (111) surfaces and Si clusters has resulted in the 2p BE of for an isolated Si atom as 96.089 ± 0.008 eV with a bulk shift of 2.461 eV, respectively. It is clarified that the surface- and size-induced BE shift arises from the broken-bond-induced local strain and skin-depth quantum entrapment. DFT calculations confirmed the BOLS expected trend consistency between calculations and XPS observations.

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