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

Sun, Changqing; Bo, Maolin; Wang, Yan; Huang, Yongli; Zhang, Xi; Zhang, Ting; Li, Can

2014

Bo, M., Wang, Y., Huang, Y., Zhang, X., Zhang, T., Li, C., et al. (2014). Coordination-resolved local bond contraction and electron binding-energy entrapment of Si atomic clusters and solid skins. *Journal of Applied Physics*, 115(14), 144309-.

<https://hdl.handle.net/10356/98231>

<https://doi.org/10.1063/1.4871399>

© 2014 AIP Publishing LLC. This paper was published in *Journal of Applied Physics* and is made available as an electronic reprint (preprint) with permission of AIP Publishing LLC. The paper can be found at the following official DOI: [<http://dx.doi.org/10.1063/1.4871399>]. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper is prohibited and is subject to penalties under law.

Downloaded on 26 Apr 2023 20:21:04 SGT

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

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

Citation: [Journal of Applied Physics](#) **115**, 144309 (2014); doi: 10.1063/1.4871399

View online: <http://dx.doi.org/10.1063/1.4871399>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jap/115/14?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Influence of the cluster dimensionality on the binding behavior of CO and O₂ on Au₁₃](#)

J. Chem. Phys. **136**, 024312 (2012); 10.1063/1.3676247

[Structures and relative stability of medium-sized silicon clusters. V. Low-lying endohedral fullerenelike clusters Si₃₁ – Si₄₀ and Si₄₅](#)

J. Chem. Phys. **124**, 164311 (2006); 10.1063/1.2191494

[Binding of propene on small gold clusters and on Au\(111\): Simple rules for binding sites and relative binding energies](#)

J. Chem. Phys. **121**, 3756 (2004); 10.1063/1.1769366

[Multiple Si = O bonds at the silicon cluster surface](#)

J. Appl. Phys. **94**, 2130 (2003); 10.1063/1.1586954

[Tight-binding studies of the tendency for boron to cluster in c-Si. I. Development of an improved boron–boron model](#)

J. Appl. Phys. **84**, 2471 (1998); 10.1063/1.368408

Re-register for Table of Content Alerts

Create a profile.

Sign up today!

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

Maolin Bo,¹ Yan Wang,^{1,2,a)} Yongli Huang,¹ Xi Zhang,³ Ting Zhang,¹ Can Li,⁴ and Chang Q. Sun^{1,3,4,a)}

¹Key Laboratory of Low-Dimensional Materials and Application Technologies, Xiangtan University, Hunan 411105, China

²School of Information and Electronic Engineering, Hunan University of Science and Technology, Hunan 411201, China

³School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore 639798

⁴Center for Coordination Bond Engineering, School of Materials Science and Engineering, China Jiliang University, Hangzhou 330018, China

(Received 6 January 2014; accepted 2 April 2014; published online 10 April 2014)

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. [<http://dx.doi.org/10.1063/1.4871399>]

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 of both the $2p$ and the valence bands on the inverse of particle size.^{15–18} XPS measurements also revealed that the spectral intensity of the high-energy (closing to Fermi level, E_F) component increases with the incident beam energy 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, physical origin of the energy shift^{19–22} 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 of^{26,27} further confirmed the entrapment of electronic binding energy (BE).

II. PRINCIPLES AND CALCULATION METHODS

A. Tight binding approximation

According to the band theory, the ν th energy level of an isolated atom, $E_\nu(0)$, is determined by the integral of the intra-atomic potential, $V_{\text{atom}}(r)$, and the eigenwave function of an atom at the specific i th 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 $E_\nu(z=0)$ to $E_\nu(z=12)$ by an amount of $E_\nu(12) - E_\nu(0)$ that is proportional to the cohesive energy per bond of an atom with 12 neighbors of standard²⁸

$$\begin{aligned}
 E_\nu(0) &= \langle v, i | V_{\text{atom}}(r) | v, i \rangle \\
 E_\nu(12) - E_\nu(0) &= \langle v, i | V_{\text{cry}}(r) | v, i \rangle + \sum_{j=1}^{j=z} \langle v, i | V_{\text{cry}}(r) | v, j \rangle \\
 &= \alpha \left(1 + \frac{z\beta}{\alpha} \right) \cong \alpha \propto E_b.
 \end{aligned} \quad (1)$$

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 i th atom. Because $\langle v, i | v, j \rangle = \delta_{ij}$ with δ_{ij} being the Kronecker function (if $i=j$, $\delta_{ij}=1$,

^{a)}Electronic addresses: ywang8@hnust.edu.cn and ecqsun@ntu.edu.sg

otherwise, $\delta_{ij}=0$), the term $z\beta/\alpha \ll 1$. 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 Δ_H to the local Hamiltonian and hence results in a CLS (core level shift). The bond relaxation in length and energy follows:

$$\begin{aligned} C_z &= d_z/d_b = 2/\{1 + \exp[(12-z)/8z]\} \\ C_z^{-m} &= E_z/E_b. \end{aligned} \quad (2)$$

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

$$\Delta_H = \begin{cases} C_z^{-m} - 1 & (Surface) \\ \tau K^{-1} \sum_{\leq 3} C_z(C_z^{-m} - 1) & (Clusters), \end{cases} \quad (3)$$

τ 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 $\Delta E_v(12)$, the under-coordination induced CLS, $\Delta E_v(z)$, follows:

$$\frac{\Delta E_v(z)}{\Delta E_v(12)} = \frac{E_v(z) - E_v(0)}{E_v(12) - E_v(0)} = \frac{E_z}{E_b} C_z^{-m} = 1 + \Delta_H. \quad (4)$$

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 $E_v(0)$, the bulk shift, $\Delta E_v(12)$, and the z dependent shift

$$\begin{aligned} \frac{E_v(z) - E_v(0)}{E_v(z') - E_v(0)} &= \frac{C_z^{-m}}{C_{z'}^{-m}} (z' \neq z) \text{ or} \\ E_v(0) &= \frac{C_{z'}^m E_v(z') - C_z^m E_v(z)}{C_{z'}^m - C_z^m} (z' \neq z) \\ E_v(z) - E_v(0) &= [E_v(12) - E_v(0)] \times C_z^{-m}. \end{aligned} \quad (5)$$

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 v th energy level $E_v(0)$ and its bulk shift $\Delta E_v(12)$

$$E_v(K) = E_v(12) + [E_v(12) - E_v(0)] \times \Delta_H. \quad (6)$$

Generally, the size-induced shifts of the BE for nanoparticles exhibit an inverse linear size relationship in a form of: $E_v(K) = A + BK^{-1}$, where A and B are constants that

correspond to the intercept and the gradient of the $E_v(K^{-1})$ line, respectively. Comparing the experimental scaling relationship with the theoretical expression in Eq. (6) yields

$$\begin{cases} A = E_v(12) \\ B = [E_v(12) - E_v(0)] \times \tau \sum_{i \leq 3} C_z(C_z^{-m} - 1). \end{cases} \quad (7)$$

With the derived $E_v(12)$, $E_v(0)$, 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 $a=5.431 \text{ \AA}$, $b=10.861 \text{ \AA}$, $c=16.073 \text{ \AA}$ ($\alpha=\beta=\gamma=90.0^\circ$) and $a=5.431 \text{ \AA}$, $b=13.302 \text{ \AA}$, $c=18.679 \text{ \AA}$ ($\alpha=\beta=90.0^\circ$ and $\gamma=114.1^\circ$), respectively. The geometrical optimization and electronic structures were obtained based on LDA(CA-PZ) functional.²⁶ In each case, the subsequent slabs have been separated by a vacuum region of $12 \text{ \AA}$ 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-Plank scheme, gives a BZ sampling interval smaller than $0.05 \text{ \AA}^{-1}$.

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_i) 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 (S_1), and the second (S_2) atomic layers of the surface. Including the common B component ($z=12$), there are a total of $l=5$ components for these

FIG. 1. Decomposition of the Si 2*p* spectra for (a) Si(100)³⁴ and (b) Si(111)³⁵ surfaces with four Gaussian components representing the bulk B, S₂, and S₁ states from higher(smaller absolute value) to lower BE. These components follow the constraints of Eq. (5). Derived information is given in Table I.

two surfaces. There will be a combination of $N = 10 = C_1^2 = 1!/[1!(1-2)!]$ values of $E_\nu(0)$. Using the least-root-mean-square approach, we can find the average of $\langle E_\nu(0) \rangle = \sum_N \langle E_{\nu i}(0) \rangle / N$ and the standard deviation. A fine tuning of the CN values of the components will minimize the σ 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 2*p* 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 $z_{ib} = z/12$ is the reduced CN and $z = 12$ is the bulk value.

The $E_\nu(0)$ and $E_\nu(12)$ 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 2*p* core-level shift for Si

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

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

$$N = 4\pi K^3/3$$

$$K^{-1} = (3N/4\pi)^{-1/3} = 1.29N^{-1/3}. \quad (8)$$

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

$$E_\nu(N) = E_\nu(12) + [E_\nu(12) - E_\nu(0)] \times \left[1.29\tau N^{-1/3} \sum_{i \leq 3} C_z (C_z^{-m} - 1) \right]. \quad (9)$$

As in the BOLS convention, we choosing $z_1 = 4(1-0.75/K) = 3.16$ ($K^{-1} = 0.281$) 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.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 ($\epsilon_z = C_z - 1$ (%)), relative BE shift ($\delta E_z = \Delta E(z)/\Delta E(12) - 1 = (C_z^{-4.88} - 1)(\%)$), relative atomic cohesive energy ($E_C = E_C(z)/E_C(12) - 1 = (z_{ib} C_z^{-4.88} - 1)(\%)$), and the relative BE density ($E_D = E_D(z)/E_D(12) = (C_z^{-7.88} - 1)(\%)$) in various registries of Si^{34,35} skins ($m = 4.88$).

		Si 2p	Si 2p				
	z	(Si ⁺ _N)	(skins)	$-\epsilon_z(\%)$	δE_z	δE_D	$-\delta E_C$
$E_\nu(0)$	0	100.38	96.089	...	...	...	...
$E_\nu(12)$	B 12	102.84	98.550	0	0	0	0
$\Delta E_\nu(12)$	...	2.46	2.461	...	...	...	...
Si(100)	S ₂	6.76	99.224	4.84	27.39	47.85	28.23
	S ₁	5.10	99.871	8.44	53.74	100.26	34.66
Si(111)	S ₂	7.08	99.143	4.34	24.18	41.86	26.73
	S ₁	5.32	99.751	7.83	48.88	90.15	34.00

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

$$E_{si+2p}(12) = E_{si2p}(12) + \Phi = 102.84 \text{ eV},$$

$$E_{2p}(K) = E_{si+2p}(12) + [E_{si+2p}(12) - E_{si+2p}(0)]$$

$$\times \left[1.29\tau N^{-1/3} \sum_{i \leq 3} C_z(C_z^{-m} - 1) \right]$$

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

Likewise, $E_{vb}(N) = 4.46 + 14.04 N^{-1/3} \text{ eV}$ and $E_{si2p}(12) = 98.55 \text{ eV}$ are the bulk values derived from the surface XPS spectra.^{37–39} $\Phi = 4.29 \text{ eV}$ is the photoionization energy.^{15,40} With the value of $\Delta E_{2p}(12) = E_{si+2p}(12) - E_{si+2p}(0) = 2.46 \text{ eV}$ derived from surface analysis,⁴¹ we can then determine the shape factor $\tau = 2.50$ and $E_{si+2p}(0) = 100.38 \text{ eV}$ in the size dependent spectra.⁴²

Figure 3 shows that the direct $2p$ photoionization threshold of $106\text{--}111 \text{ eV}$ increases linearly with $N^{-1/3}$, as does the valence band photoionization threshold in the range of $8\text{--}13 \text{ eV}$. 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

FIG. 3. The $2p$ core band and valence band change of Si_N^+ cluster ions, $N = 5\text{--}92$, are plotted versus $N^{-1/3}$.

FIG. 4. (a) Geometric structures of stepped Si(210) surface show the distances between atom E and its neighbors denoted 1, 2, 3 are $2.577 \text{ \AA}$, $3.572 \text{ \AA}$, $3.394 \text{ \AA}$ and with respect to the bulk standard of $3.840 \text{ \AA}$, $4.503 \text{ \AA}$, $3.840 \text{ \AA}$, respectively. (b) The s-orbit local DOS of the Si(210) surface shift more than that of the Si(100) surface toward E_F .

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, and 3 by 32.89%, 21.68%, and 11.61%, respectively. In fact, the highly coordinated atoms prefer larger first-neighbor distances than atoms and the otherwise. Therefore, inner atoms represent the ideal distance of the bulk, while skin atoms show bond contraction. Results obtained here agree with the reported bond contraction observed in Ag, Au, Cu, Ni, Pd, Pt, and Fe atomic chains^{43,44} with clarification of the quantum entrapment and polarization in this contribution.

According to the principal of least energy, any spontaneous process proceeds toward the direction of energy reduction. Therefore, the spontaneous process of 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.

ACKNOWLEDGMENTS

Financial supports from NSF (Nos. 11242005 and 11172254) and Scientific Research Fund of Hunan Provincial Education Department (Grant No. 12C0132).

- ¹C. Q. Sun, *Relaxation of the Chemical Bond* (Springer Press, Berlin, 2014).
- ²R. Q. Zhang, Y. L. Zhao, and B. K. Teo, *Phys. Rev. B* **69**(12), 125319 (2004).
- ³V. Petkov, C. M. Hessel, J. Ovtchinnikov, A. Guillaussier, B. A. Korgel, X. Liu, and C. Giordano, *Chem. Mater.* **25**(11), 2365 (2013).
- ⁴L. Pan, S. Xu, X. Liu, W. Qin, Z. Sun, W. Zheng, and C. Q. Sun, *Surf. Sci. Rep.* **68**(3–4), 418 (2013).
- ⁵J. Wang, G. Wang, F. Ding, H. Lee, W. Shen, and J. Zhao, *Chem. Phys. Lett.* **341**(5–6), 529 (2001).
- ⁶U. K. Bhaskar, T. Pardo, V. Passi, and J.-P. Raskin, *J. Appl. Phys.* **113**(13), 134502 (2013).
- ⁷V. Zamudio-Bayer, L. Leppert, K. Hirsch, A. Langenberg, J. Rittmann, M. Kossick, M. Vogel, R. Richter, A. Terasaki, T. Möller, B. V. Issendorff, S. Kümmel, and J. T. Lau, *Phys. Rev. B* **88**(11), 115425 (2013).
- ⁸J. S. Pan, A. T. S. Wee, C. H. A. Huan, H. S. Tan, and K. L. Tan, *J. Appl. Phys.* **79**(6), 2934 (1996).
- ⁹C. J. Karlsson, E. Landemark, Y. C. Chao, and R. I. G. Uhrberg, *Phys. Rev. B* **50**(8), 5767 (1994).
- ¹⁰F. Jolly, F. Rochet, G. Dufour, C. Grupp, and A. Taleb-Ibrahimi, *J. Non-Cryst. Solids* **280**(1–3), 150 (2001).
- ¹¹C. J. Karlsson, F. Owman, E. Landemark, Y. C. Chao, P. Mårtensson, and R. I. G. Uhrberg, *Phys. Rev. Lett.* **72**(26), 4145 (1994).
- ¹²E. Landemark, C. Karlsson, Y. C. Chao, and R. Uhrberg, *Phys. Rev. Lett.* **69**(10), 1588 (1992).
- ¹³T. Bekkay, E. Sacher, and A. Yelon, *Surf. Sci.* **217**(1–2), L377 (1989).
- ¹⁴T. Nagatomi, T. Kawano, and R. Shimizu, *J. Appl. Phys.* **83**(12), 8016 (1998).
- ¹⁵M. Vogel, C. Kasigkeit, K. Hirsch, A. Langenberg, J. Rittmann, V. Zamudio-Bayer, A. Kulesza, R. Mitrić, T. Möller, B. V. Issendorff, and J. Lau, *Phys. Rev. B* **85**(19), 195454 (2012).
- ¹⁶A. Fissel, J. Dąbrowski, and H. J. Osten, *J. Appl. Phys.* **91**(11), 8986 (2002).
- ¹⁷S. Kim, M. C. Kim, S.-H. Choi, K. J. Kim, H. N. Hwang, and C. C. Hwang, *Appl. Phys. Lett.* **91**(10), 103113 (2007).
- ¹⁸K. Kooser, D. T. Ha, E. Itäluu, J. Laksman, S. Urpelainen, and E. Kukk, *J. Chem. Phys.* **137**(4), 044304 (2012).
- ¹⁹Y. Wu, E. Garfunkel, and T. E. Madey, *J. Vac. Sci. Technol. A* **14**(3), 1662 (1996).
- ²⁰K. Luo, X. Lai, C. W. Yi, K. A. Davis, K. K. Gath, and D. W. Goodman, *J. Phys. Chem. B* **109**(9), 4064 (2005).
- ²¹E. G. Barbagiovanni, D. J. Lockwood, P. J. Simpson, and L. V. Goncharova, *J. Appl. Phys.* **111**(3), 034307 (2012).
- ²²Z. H. Lu and D. Grozea, *Appl. Phys. Lett.* **80**(2), 255 (2002).
- ²³J. Stapelfeldt, J. Wörmer, and T. Möller, *Phys. Rev. Lett.* **62**(1), 98 (1989).
- ²⁴G. Moretti, *J. Electron Spectrosc. Relat. Phenom.* **95**(2–3), 95 (1998).
- ²⁵C. Q. Sun, *Phys. Rev. B* **69**(4), 045105 (2004).
- ²⁶J. P. Perdew, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B* **46**(11), 6671 (1992).
- ²⁷L. Sham and M. Schlüter, *Phys. Rev. Lett.* **51**(20), 1888 (1983).
- ²⁸M. A. Omar, *Elementary Solid State Physics: Principles and Applications* (Addison-Wesley, New York, 1993).
- ²⁹P. J. D. Lindan, M. D. Segall, M. J. Probert, and C. J. Pickard, *J. Phys.: Condens. Matter* **14**, 2714 (2002).
- ³⁰B. Delley, *Phys. Rev. B* **66**(15), 155125 (2002).
- ³¹J. Carrasco, N. Lopez, F. Illas, and H. J. Freund, *J. Chem. Phys.* **125**(7), 074711 (2006).
- ³²Z. Yang, T. K. Woo, M. Baudin, and K. Hermansson, *J. Chem. Phys.* **120**(16), 7741 (2004).
- ³³J. C. Conesa, *J. Phys. Chem. B* **106**(13), 3402 (2002).
- ³⁴F. Himpsel, P. Heimann, T. Chiang, and D. Eastman, *Phys. Rev. Lett.* **45**(13), 1112 (1980).
- ³⁵F. Himpsel, G. Hollinger, and R. Pollak, *Phys. Rev. B* **28**(12), 7014 (1983).
- ³⁶Y. Sun, Y. Wang, J. S. Pan, L.-L. Wang, and C. Q. Sun, *J. Phys. Chem. C* **113**(33), 14696 (2009).
- ³⁷K. G. J. M. Jeske, J. W. Schultze, M. Thönissen, and H. Munder, *Surf. Interface Anal.* **22**(1–12), 363 (1994).
- ³⁸H. Sun, X. Qin, and F. Zaera, *J. Phys. Chem. Lett.* **2**(20), 2525 (2011).
- ³⁹W. M. Lau and X. W. Wu, *Surf. Sci.* **245**(3), 345 (1991).
- ⁴⁰C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., 1996).
- ⁴¹C. Q. Sun, L. K. Pan, Y. Q. Fu, B. K. Tay, and S. Li, *J. Phys. Chem. B* **107**(22), 5113 (2003).
- ⁴²T. P. Chen, Y. Liu, C. Q. Sun, M. S. Tse, J. H. Hsieh, Y. Q. Fu, Y. C. Liu, and S. Fung, *J. Phys. Chem. B* **108**(43), 16609 (2004).
- ⁴³A. Kara and T. S. Rahman, *Phys. Rev. Lett.* **81**(7), 1453 (1998).
- ⁴⁴F. Baletto, R. Ferrando, A. Fortunelli, F. Montalenti, and C. Mottet, *J. Chem. Phys.* **116**(9), 3856 (2002).