Supplementary Information

Title: Skin-resolved bond contraction, core electron entrapment, and valence charge polarization of Ag and Cu atomic clusters

Authors: Shideh Ahmadi, Xi Zhang, Yinyan Gong, Chin-Hua Chia, Chang Q. Sun

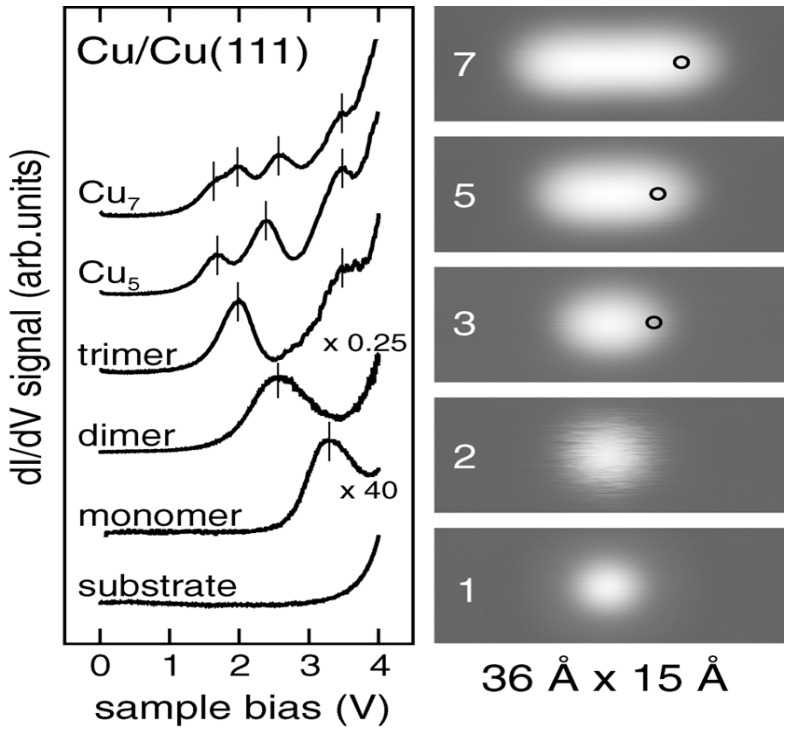
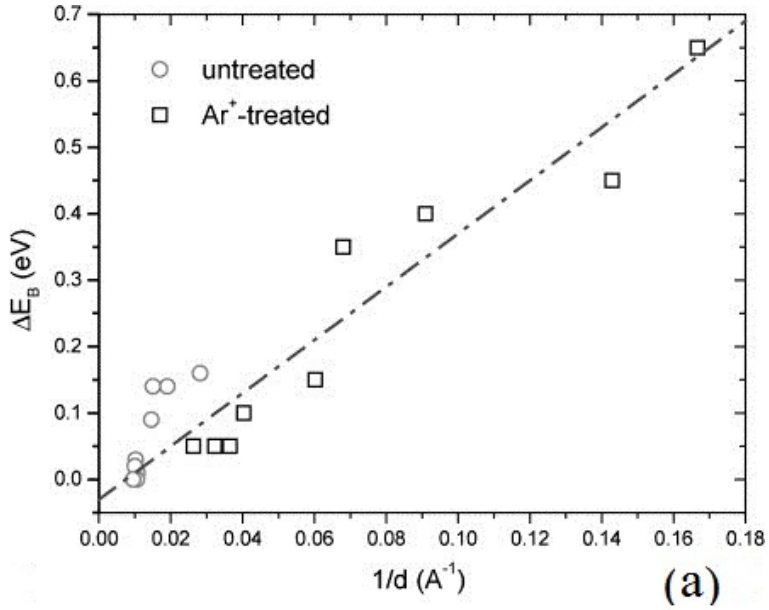
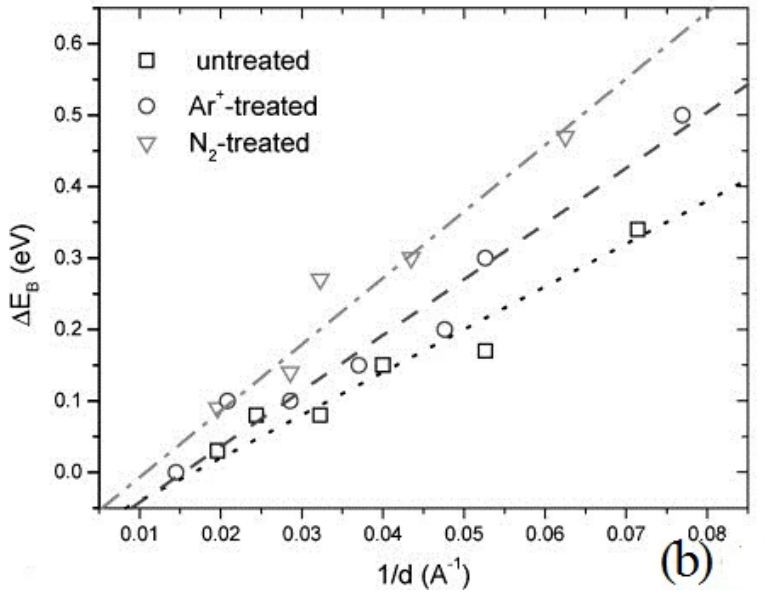


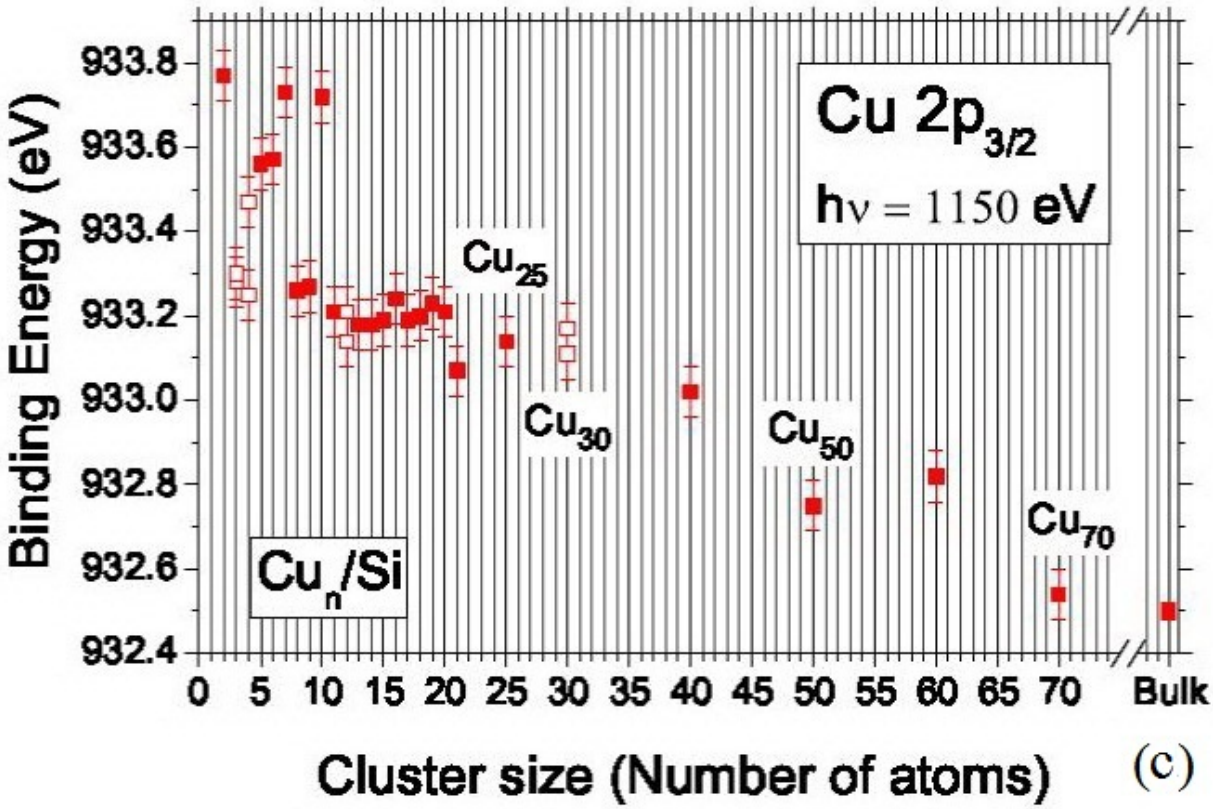
Fig. SI STS spectroscopy and STM imaging of Cu_N clusters[1] revealed the size-induced polarization with the LDOS of Cu_1 (monomer) at 3.2 eV, Cu_2 (dimer) at 2.6 eV, and Cu_3 (trimer) at 2.0 eV. (Reprinted with permission from S. Fölsch, P. Hyldgaard, R. Koch, and K. H. Ploog, "Quantum confinement in monatomic Cu chains on Cu (111)", Phys. Rev. Lett. **92**, 056803-056806 (2004). Copyright (2013) by the American Physical Society.)


untreated
Ar+-treated
ΔEB (eV)
1/d (A-1)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18

(a)


untreated
Ar+-treated
N2-treated
ΔEB (eV)
1/d (A-1)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08

(b)


Cu 2p3/2
hν = 1150 eV
Cu25
Cu30
Cu50
Cu70
Cun/Si
Binding Energy (eV)
933.8
933.6
933.4
933.2
933.0
932.8
932.6
932.4
0 5 10 15 20 25 30 35 40 45 50 55 60 65 70 Bulk
Cluster size (Number of atoms)

(c)

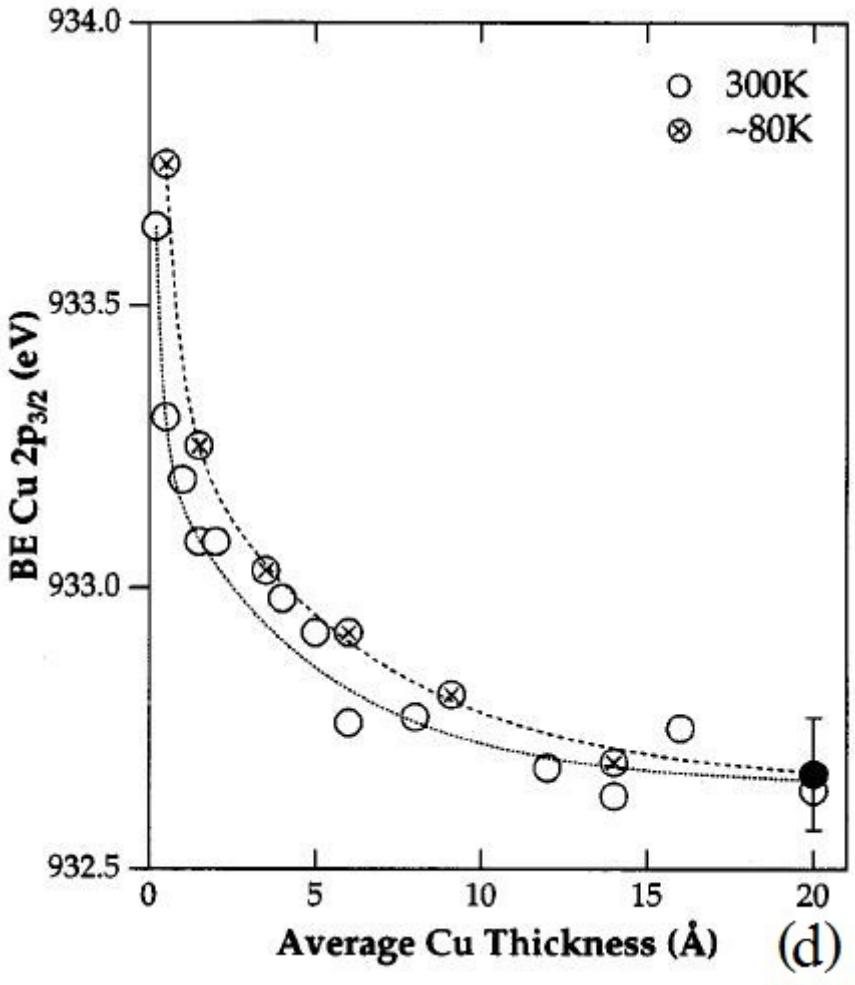


Fig. SII Measured of the core-level shift is versus the inverse of nanoparticles size of Cu on (a) highly ordered pyrolytic graphite (HOPG)/Ar^+ and (b) Dow Cyclotene 3022 (CYCL)/Ar^+ substrates, [2] (Reprinted permission from "Initial- and final-state effects on metal cluster/substrate interactions, as determined by XPS: copper clusters on Dow Cyclotene and highly oriented pyrolytic graphite", D. Q. Yang and E. Sacher, Appl. Surf. Sci. **195**, 187-195 (2002) Copyright (2013) with permission from Elsevier.) (c) Binding energy of Cu-2$p_{3/2}$ measured by XPS spectra for Cu/Si substrate at various cluster sizes, which revealed Cu-band entrapment as the cluster size decreases,[3] (Reprinted permission from N. Ferretti, "X-ray photoelectron spectroscopy of size selected copper clusters on silicon", (2009) with permission from N. Ferretti by Berlin library), and (d) Measured bonding energy as a function of Cu coverage on Al_2O_3 substrate at 300K (open circle) and 80K (cross circle).[4] (Reprinted with permission from "Initial stages of Cu growth on ordered Al2O3 ultrathin films", Y. Wu, E. Garfunkel, and T. E. Madey, J. Vac. Sci. Technol., A **14**, 1662-1667 (1996). Copyright (2013) American Vacuum Society.)

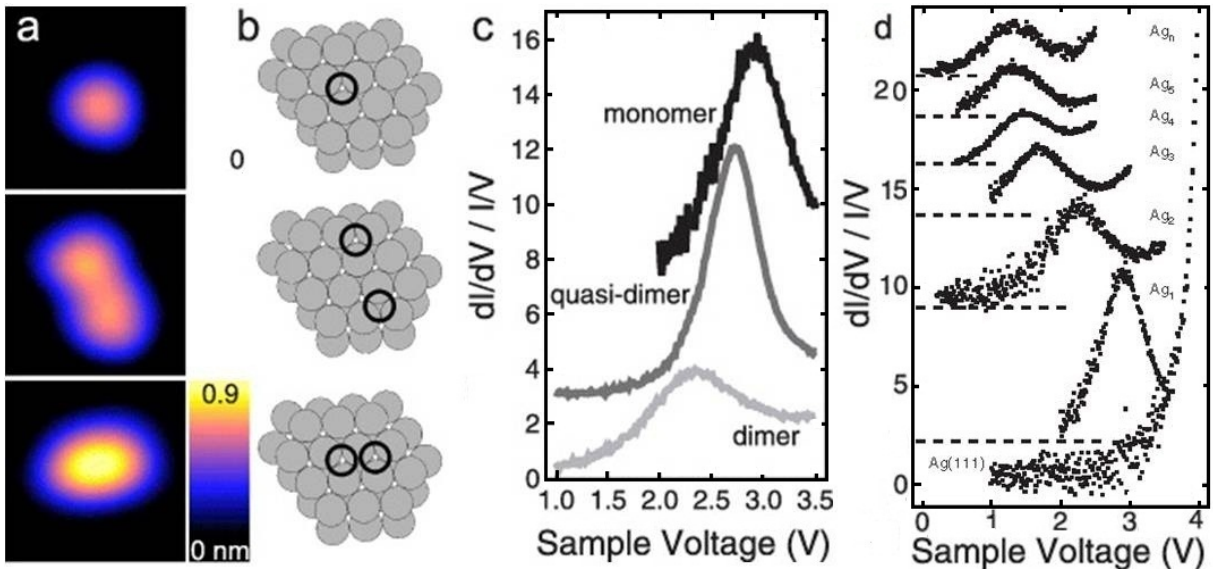
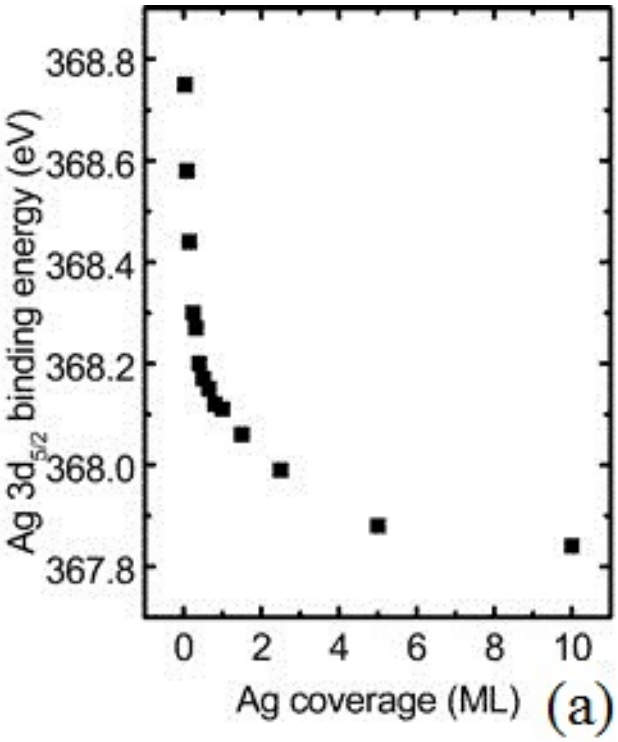
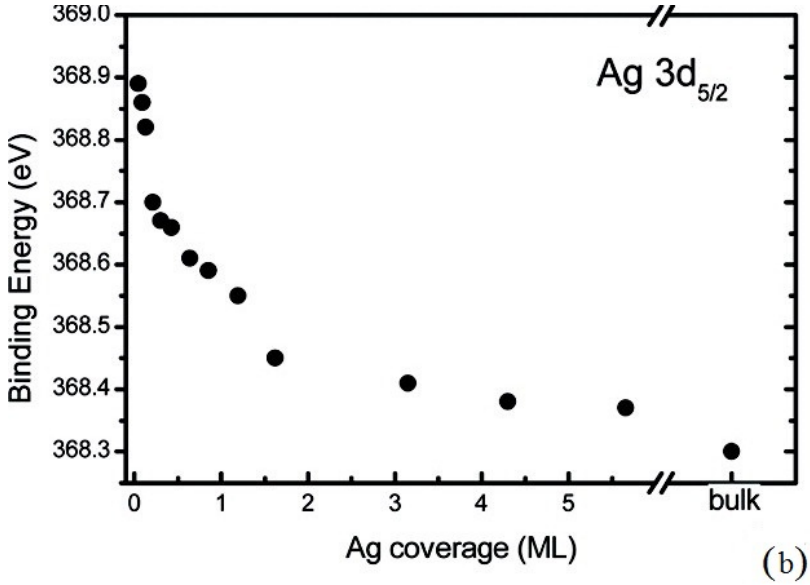


Fig.SIII (a) STM/S imagines for Ag_N clusters shows the unoccupied state polarization depend on the undercoordination, (b) Ag monomer, Ag quasi-dimer and Ag_2 dimer on Ag(111) substrate, (c) the unoccupied states for the monomer, quasi-dimer, and dimer are positioned at 3.0, 2.7, and 2.4 eV, respectively,[5] (Reprinted with permission from "Evolution of unoccupied resonance during the synthesis of a silver dimer on Ag(111)", New J. Phys. 11, 063020-063027 (2009). Copyright (2013), IOP Publishing & Deutsche Physikalische Gesellschaft. CC BY-NC-SA), and (d) normalized STS spectra obtained from clean Ag(111) surface and Ag_N (N=1-5, 10) clusters. The respective zero of the spectra shows with dashed lines.[6] (Reprinted with permission from A. Sperl, J. Kröger, N. Néel, H. Jensen, R. Berndt, A. Franke, and E. Pehlke, "Unoccupied states of individual silver clusters and chains on Ag (111)", Phys. Rev. B **77**, 085422-085428 (2008). Copyright (2013) by the American Physical Society.)


368.8
368.6
368.4
368.2
368.0
367.8
Ag 3d5/2 binding energy (eV)
0
2
4
6
8
10
Ag coverage (ML)

(a)


369.0
368.9
368.8
368.7
368.6
368.5
368.4
368.3
Binding Energy (eV)
Ag 3d5/2
0
1
2
3
4
5
bulk
Ag coverage (ML)

(b)

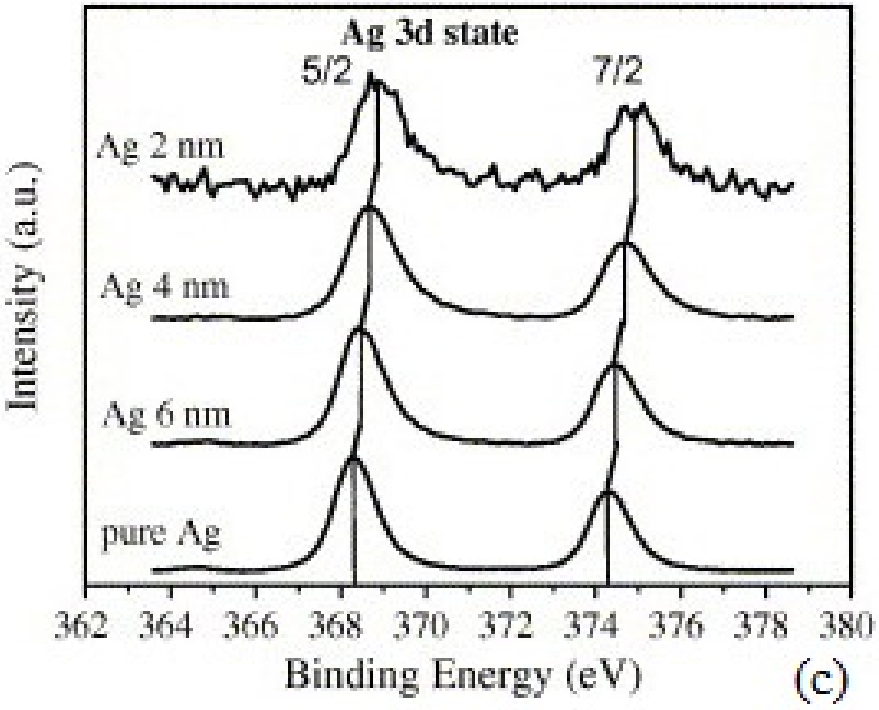


Fig. SIV XPS Ag-3d core level binding energy depended on the particle size for (a) Ag/Al_2O_3,[7] (Reprinted with permission from "The Growth of Silver on an Ordered Alumina Surface", K. Luo, X. Lai, C. W. Yi, K. A. Davis, K. K. Gath, and D. W. Goodman, J. Phys. Chem. B **109**, 4064-4068 (2005). Copyright (2013) American Chemical Society.) (b) Ag/CeO_2,[8] (Reprinted with permission from "Growth, Structure, and Stability of Ag on CeO_2(111): Synchrotron Radiation Photoemission Studies", D. Kong, G. Wang, Y. Pan, S. Hu, J. Hou, H. Pan, C. T. Campbell, and J. Zhu , J. Phys. Chem. B **109**, 6715-6725 (2005). Copyright (2013) American Chemical Society.) and (c) Ag/HOPG substrates.[9] (Reprinted with permission from I. Lopez-Salido, D. C. Lim, and Y. D. Kim, "Ag nanoparticles on highly ordered pyrolytic graphite (HOPG) surfaces studied using STM and XPS", Surface Science, 588, 6-18 (2005). Copyright (2013) with permission from Elsevier.)

References

1 S. Fölsch, P. Hyldgaard, R. Koch, and K. H. Ploog, Physical Review Letters **92**, 056803 (2004).

2 D. Q. Yang and E. Sacher, Applied Surface Science **195**, 187 (2002).

3 N. Ferretti, Technische Universtität Berlin, 2008.

[4] Y. Wu, E. Garfunkel, and T. E. Madey, Journal of Vacuum Science and Technology A **14**, 1662 (1996).
[5] A. Sperl, J. Kröger, R. Berndt, A. Franke, and E. Pehlke, New J. Phys. **11**, 063020 (2009).
[6] A. Sperl, J. Kröger, N. Néel, H. Jensen, R. Berndt, A. Franke, and E. Pehlke, Physical Review B **77**, 085422 (2008).
[7] K. Luo, X. Lai, C. W. Yi, K. A. Davis, K. K. Gath, and D. W. Goodman, The Journal of Physical Chemistry B **109**, 4064 (2005).
[8] D. Kong, G. Wang, Y. Pan, S. Hu, J. Hou, H. Pan, C. T. Campbell, and J. Zhu, The Journal of Physical Chemistry C **115**, 6715 (2011).
[9] I. Lopez-Salido, D. C. Lim, and Y. D. Kim, Surface Science **588**, 6 (2005).