VOLUME 88, NUMBER 15 PHYSICAL REVIEW LETTERS 15 APRIL 2002

Work Functions at Facet Edges

C. J. Fall,[1,2,*] N. Binggeli,[2] and A. Baldereschi[1,2]

[1] *Institut Romand de Recherche Numérique en Physique des Matériaux, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*

[2] *Institut de Physique Appliquée, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland*

(Received 14 September 2001; published 1 April 2002)

We perform *ab initio* pseudopotential calculations for metal crystals with finite facets of different crystallographic orientation to investigate the work function profile near crystal edges. We examine local edge effects, and address the problem of the coexistence of different face-dependent local work functions at crystal edges. By modeling the electronic dipoles at the metal surface, we show how nonvanishing surface charges spontaneously appear on metals with inequivalent facets. Our studies of Al crystal nanowires with (100) and (111) facets are extended to derive the dependence of the work function on the crystal morphology in the macroscopic limit.

DOI: 10.1103/PhysRevLett.88.156802 PACS numbers: 73.30.+y, 71.15.Dx, 73.20.At, 79.60.Bm

The work functions of elemental metals depend on the crystallographic orientation of the surface [1]. The resulting work-function difference between two surfaces of the same metal with different orientation can be as high as 1 eV [2]. Since the Fermi energy is uniform within a crystal and the electrostatic potential outside a smooth metal surface is essentially constant beyond about 1 nm, different surface work functions around a single crystal must correspond to changes in the vacuum potential which are eminently *local.* On the other hand, at sufficiently large distances from a finite crystal, the crystalline anisotropy is no longer significant, and the electrostatic potential must be *isotropic* and *constant.* This macroscopic limit at infinite distance, however, should still depend, in general, on both the orientation of the facets and on the *global* crystal morphology. Experimentally, local changes in the work function and the associated electric fields have been observed recently with atomic to nanometer scale resolution near metal surfaces by scanning-tunneling, electrostatic-force, and field-emission microscopy [3–7]. Sharp metallic edges can be fabricated, for example, by buildup of low-index surfaces through atomic surface diffusion in an electric field [8]. Theoretically, however, the mechanism which allows for different local work functions to exist simultaneously near a crystal edge has not been examined yet on a microscopic scale. Also, the relation between the apparent work function at an infinite distance and the orientation-dependent local work functions close to the facets has been explored only for a few, very specific geometries [9,10]. In this Letter, we address both of these fundamental issues through *ab initio* calculations for aluminum crystals with (100) and (111) facets.

Previous theoretical investigations of the influence of crystal edges on the local work function have been limited to studies of the electrostatic potential around a 90° jellium edge [11]. On the other hand, for selected metal surface geometries including no edges, i.e., infinite planes, cylinders, and spheres, macroscopic patch-field approaches have been developed to evaluate the electrostatic potential outside surface areas having a different potential than that of the surrounding surface (patch work functions) [5,9]. A general rule that has been established for these systems is that, for any periodic arrangement of the local work functions, the apparent work function is equal to the surface-area weighted average of the individual work functions [9]. We will show here, however, that crystals including finite faces and edges give rise, in general, to a different macroscopic limit.

Facet edges are studied in Al crystal nanowires with (100) and (111) lateral faces. The wires extend to infinity along the wire axis. We thus simulate infinitely long edges between smooth facets. The lateral dimension of each facet is chosen sufficiently large to describe single-surface properties at its center. The *ab initio* computations are performed within the local density approximation (LDA) to density functional theory, using the Ceperley-Alder exchange-correlation functional [12]. We use a Troullier-Martins pseudopotential in the Kleinman-Bylander form [13]. The valence charge density is determined by expanding the electronic wave functions on a plane-wave basis (16-Ry cutoff), using the supercell technique. The periodic boundary conditions on the supercell introduce periodic replicas of the wire, which are separated by vacuum regions equivalent to five and four Al layers for the (100) and (111) faces, respectively. For the Brillouin-zone integrations, we use a set of Monkhorst-Pack special k-points (8 and 7 for the wires in Figs. 1 and 2, respectively), together with a 0.01-Ry Gaussian level broadening to position the Fermi energy [14].

The local work function in vacuum, where the electronic charge vanishes, includes two contributions: (i) the difference between the local electrostatic potential and the Fermi energy of the metal, and (ii) the image potential. It is well known that the LDA incorrectly describes the asymptotic form of (ii). The LDA exchange-correlation potential falls off exponentially, whereas the actual nonelectrostatic potential contribution to the local work function should follow the classical image potential beyond a few atomic units

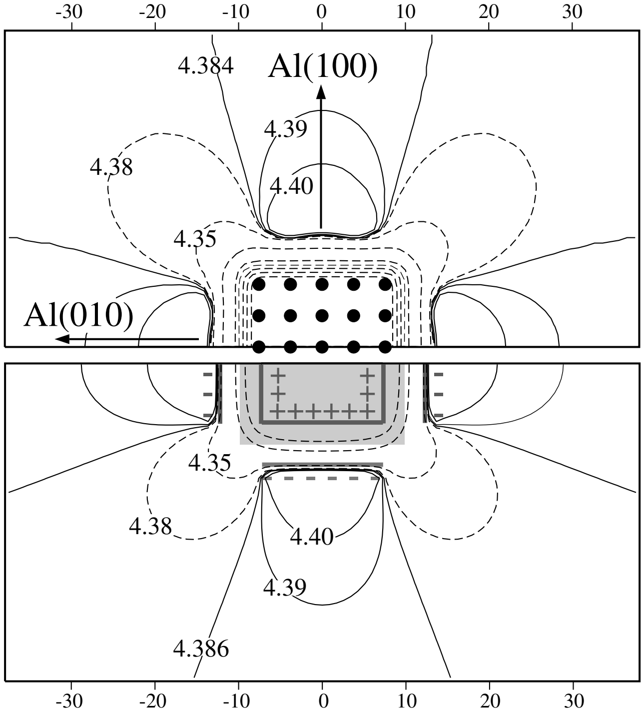

FIG. 1. Upper panel: Contour plot of the electrostatic component W_E, in eV, of the local work function near edges between Al(100) facets, without surface relaxation. Lower panel: Electrostatic potential created by a model distribution of the surface charge consisting of two uniformly charged parallel plates forming a finite capacitor. In both panels, continuous (dashed) lines indicate regions above (respectively below) the value at infinity. The axes are graduated in atomic units.

from the surfaces [15]. The latter contribution, however, known analytically for metallic edges of arbitrary angles [16], plays no role in the two main issues we are addressing here—coexistence and apparent work function. As the image potential becomes negligible at sufficient distances (~100 nm) from a given sample, the apparent work function is entirely determined by (i). The same is true for the work-function values of the infinitely extended surfaces. Furthermore, as the image potential exhibits a completely monotonic behavior around facet edges [17], any local *variation* in the work function around edges should also derive from the electrostatic contribution. In what follows, we will therefore focus on the electrostatic component, W_E, of the local work function.

To evaluate W_E precisely, we use a two-dimensional (2D) macroscopic averaging procedure. We average the self-consistent electrostatic potential $v(x, y, z)$ along the wire axis z. The xy atomic-scale oscillations of the resulting potential $\overline{v}(x, y)$—and corresponding charge density $\overline{\rho}(x, y)$—are then properly filtered out by a macroscopic average [18] over the 2D lattice unit cell of the crystal, to obtain a macroscopic potential $\overline{\overline{v}}(x, y)$. Relaxation is included for the surface layers of atoms only, retaining the crystalline periodicity in the central part of the wires and allowing the macroscopic average to be performed. W_E is determined by subtracting the Fermi level, E_F, from the macroscopic potential: $W_E(x, y) = \overline{\overline{v}}(x, y) - E_F$. To obtain from our supercell data the potential at large distances from an isolated nanowire, a special treatment is necessary to get rid of overlap terms. Outside a circle surrounding a single wire section, the electrostatic potential is obtained by modeling the macroscopic charge $\overline{\overline{\rho}}(x, y)$ with a 2D multipole expansion [19]. The Fermi energy E_F is obtained from a separate bulk calculation to avoid quantum-size effects [18]. The estimated uncertainty on the absolute value of W_E due to the LDA is of the order of 0.1 eV. However, as usual within the LDA, and consistent with gradient-correction calculations [20], for the relative values of the work functions we expect a better accuracy of the order of the numerical convergence of our

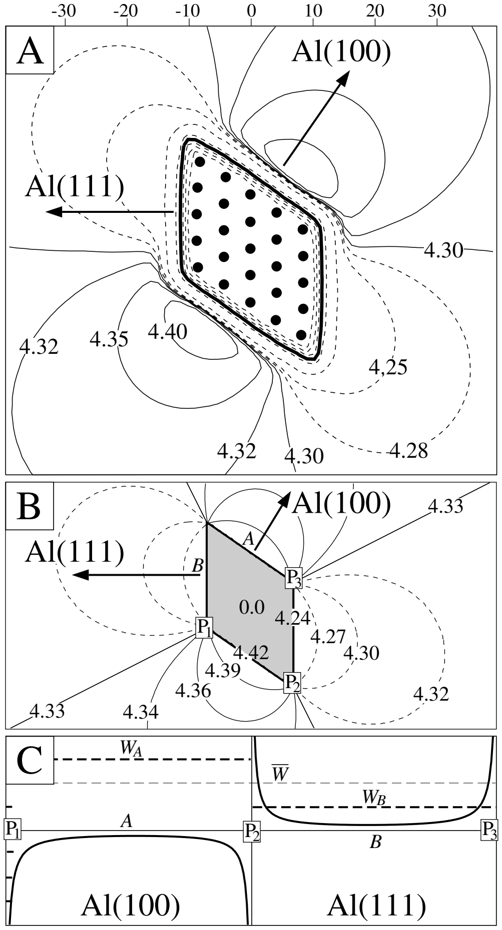

FIG. 2. Panel (A): Contour plot of the electrostatic component W_E, in eV, of the local work function around relaxed edges between Al(100) and Al(111) facets. The disks indicate the atomic columns. The axes are graduated in atomic units. Panel (B): Model of the local work function outside a larger Al crystal with apparent (100) and (111) facets of identical length, drawn at an arbitrary scale. Continuous (dashed) lines in panels (A) and (B) indicate regions above (respectively below) the value at infinity. Panel (C): Potential just outside the model crystal surfaces (W_A and W_B, dashed lines) and corresponding surface charge density along the facets (thick solid lines). The apparent work function is $\overline{W} = W_A + W_B$.

results with the computational parameters reported above, i.e., 0.03 eV.

Before discussing inequivalent facet edges, we first consider the simpler case of a 90° edge between two equivalent Al(100) facets. The local work function $W_E(x, y)$ around an Al(100)-Al(010) facet edge is shown in Fig. 1. Outside the center of each facet, we practically recover the work function value we find from a separate computation for the infinitely extended Al (100) surface, i.e., 4.42 eV [18]. Toward the edges, the local work function dips noticeably, and the contour lines extend further into the vacuum. We note that the electrostatic potential calculated here *ab initio* is strikingly different from that previously obtained for a 90° jellium edge in the Thomas-Fermi approximation [11], where a nearly monotonic behavior of the potential around the edge was obtained.

We can understand qualitatively the work-function reduction near facet edges by calculating the electrostatic potential produced by a model distribution of the surface dipoles. In the lower panel of Fig. 1, we propose a model charge density consisting of oppositely charged parallel plates, forming a finite capacitor, arranged on the facets of the crystal. The uniform charge sheets are separated by a distance $d_m = 2.65$ Å, on the order of the Thomas-Fermi screening length, and the charge density on each capacitor is a fitted quantity, to allow for a fraction of the wire work function to be taken as a rigid isotropic contribution. The electrostatic potential created by this model shows a distribution analogous to that calculated *ab initio.* In particular, near the edges, the characteristic leaking of the contour lines into the vacuum, due to the reduced charge density, is well reproduced [21].

This model of the surface dipoles can be used to scale up our results, and predict the spatial behavior of the work function of larger samples. The model demonstrates that more extended regions at the work function of an infinite surface will exist outside the facets of larger crystals; the modifications of the work function near edges, instead, will remain essentially unchanged [22]. We believe that analogous reductions in potential should occur near crystal corners, where three crystal facets meet. The influence of edges (and all the more of corners) in determining the apparent work function is reduced thus with increasing crystal dimensions. If all the facets present on the crystal surface are equivalent, the apparent work function of a large enough sample is then independent of its global morphology.

We now turn to the more complex case of inequivalent facets. The work function near acute and obtuse edges between two Al(100) and Al(111) facets is shown in Fig. 2 (panel A), where we observe an anisotropy of the electrostatic potential in the vacuum. The local work function outside each facet reproduces well the work function value we find from separate calculations for the infinite surface, i.e., 4.42 and 4.23 eV for the (100) and (111) surfaces, respectively [18] (which, in turn, agree well with experiment and previous calculations [23]). We note that a macroscopically flat potential, characteristic of a bulk metallic behavior, is obtained within a sizable section of the wire. The spatial behavior of the potential in vacuum is qualitatively different from that observed for equivalent facet edges. The potential rises continuously perpendicularly to the low-work-function Al(111) facets, while it goes through a maximum perpendicularly to the high-work-function Al(100) facets. At infinity, the apparent work function is intermediate between the two face-dependent work functions. Local edge effects clearly do not play a major role in determining the general behavior of the work function here. The potential gradients, i.e., the macroscopic electric fields, that develop around edges, from the (100) to the (111) facet, indicate that this behavior is dominated by a different mechanism, namely, charge transfer between facets.

This charge transfer can be understood by modeling the *ab initio* dipole density in the 2D section of our nanowires. As edge effects play a relatively minor role, we neglect them in the model, and take the limit $d_m \rightarrow 0$. This will allow us also to predict the local work function around large (macroscopic) samples, where d_m is much smaller than the typical facet dimensions. We thus impose two face-dependent uniform distributions of point dipoles on the crystal facets. If the dipole distributions (or, equivalently, the work function) differ from one facet to another, the surface dipoles create inside the metal a variation of electrostatic potential. Surface charges have thus to develop on the crystal facets to allow a macroscopically constant potential in the metal to coexist with face-dependent surface dipoles. We include thus a second ingredient in the model, i.e., a surface charge distribution. We determine this distribution by requiring that the electrostatic potential is constant inside the metal and that the crystal remains globally neutral. The charge distribution is obtained numerically using a technique similar to the charge simulation method [24]. The potential and surface charge predicted by the model are displayed in Fig. 2 (panels B and C, respectively) for a macroscopic Al wire with (100) and (111) facets.

This model reproduces well the general behavior of the local work function obtained from the *ab initio* calculations. The surface dipoles and surface charges combine to create a macroscopically flat potential in the bulk of the metal, as is physically required, and the observed variation of electrostatic potential outside the crystal. The surface charge density is negative (positive) on the high (respectively low) work-function surface, and has a highly inhomogeneous behavior on the facet. While small at the center of each facet, the magnitude of the charge distribution increases strongly near the edges (and here tends to infinity at the edge as a result of the assumption that the surface dipole is infinitely thin [5]).

With this model, we can also examine in general the dependence of the apparent work function $\overline{W}$ of the wire on

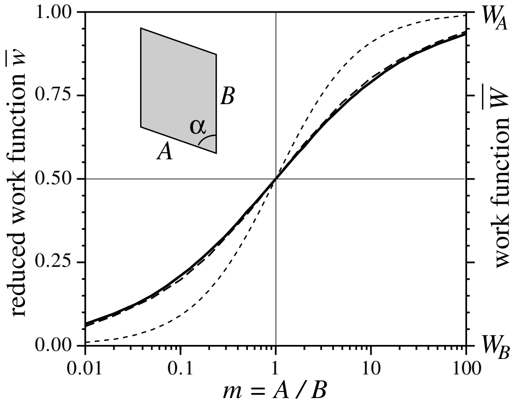

FIG. 3. Reduced apparent work function $\overline{w}$ of an infinitely long wire, with facets of lateral dimensions A and B separated by an angle α (see inset), and of work functions W_A and W_B, respectively, as a function of the aspect ratio $m = A/B$, for $\alpha = 90°$ (thick solid line) and $\alpha = 10°$ (thick dashed line). The thin dashed line gives the reduced work function according to the surface-weighted average rule.

its facet dimensions A and B, angle α, and surface work functions W_A and W_B (see inset of Fig. 3). We note that by linearity it is possible to define a reduced apparent work function $\overline{w}$ such that $\overline{W} = W_B + (W_A - W_B)\overline{w}$, where $\overline{w}$ is independent of W_A and W_B. Furthermore, from scaling properties of the 2D Poisson equation, one can show that $\overline{w}$ depends only on the crystal geometry, i.e., on the aspect ratio $m = A/B$ and the angle α [25]. In Fig. 3, we display the calculated reduced work function $\overline{w}$ of wires with a rectangular ($\alpha = 90°$) or highly slanted parallelogram section ($\alpha = 10°$), as a function of their aspect ratio. Our results show that $\overline{W}$ is very weakly sensitive on the angle α; i.e., we predict a near-universal dependence of the apparent work function on a single parameter, namely, the aspect ratio m of the crystal. This dependence, however, differs significantly from the result of the commonly used surface-weighted average rule, which we expect thus to apply only in the limit of a high density of inequivalent facets.

It is a pleasure to thank A. Franciosi for discussions. One of us (C. J. F.) acknowledges support from the Swiss NSF under Grant No. 20-55811.98. The calculations were performed at EPFL and at the CSCS in Manno.

---

*Present address: School of Physics, University of Exeter, Exeter EX4 4QL, United Kingdom.

[1] J. Hölzl and F. K. Schulte, in *Springer Tracts in Modern Physics: Solid Surface Physics,* edited by G. Höhler and E. A. Niekisch (Springer-Verlag, Berlin, 1979), Vol. 85, Chap. 1, pp. 1–150.

[2] Y. Yamamoto and T. Miyokawa, J. Vac. Sci. Technol. B **16**, 2871 (1998).

[3] D. Gekhtman *et al.,* Phys. Rev. Lett. **82**, 3887 (1999).

[4] R. M. Nyffenegger, R. M. Penner, and R. Schierle, Appl. Phys. Lett. **71**, 1878 (1997).

[5] N. A. Burnham, R. J. Colton, and H. M. Pollock, Phys. Rev. Lett. **69**, 144 (1992); **70**, 247 (1993); J. E. Inglesfield, *ibid.* **70**, 246 (1993).

[6] G. R. Condon and J. A. Panitz, J. Vac. Sci. Technol. B **16**, 23 (1998).

[7] J. F. Jia *et al.,* Phys. Rev. B **58**, 1193 (1998).

[8] V. T. Binh and J. Marien, Surf. Sci. **202**, L539 (1988).

[9] C. Herring and M. H. Nichols, Rev. Mod. Phys. **21**, 185 (1949).

[10] V. Sahni, J. P. Perdew, and J. Gruenebaum, Phys. Rev. B **23**, 6512 (1981).

[11] G. Schreckenbach, R. Kaschner, and P. Ziesche, Phys. Rev. B **46**, 7864 (1992).

[12] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[13] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991); L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1425 (1982).

[14] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976); C.-L. Fu and K.-M. Ho, *ibid.* **28**, 5480 (1983).

[15] M. Heinrichsmeier, A. Fleszar, W. Hanke, and A. G. Eguiluz, Phys. Rev. B **57**, 14 974 (1998); I. D. White, R. W. Godby, M. M. Rieger, and R. J. Needs, Phys. Rev. Lett. **80**, 4265 (1998).

[16] K. I. Nikoskinen and I. V. Lindell, IEEE Trans. Antennas Propag. **45**, 179 (1995).

[17] C. J. Fall, Ph.D. thesis, EPFL, 1999.

[18] C. J. Fall, N. Binggeli, and A. Baldereschi, Phys. Rev. B **58**, R7544 (1998).

[19] C. R. Anderson, SIAM J. Sci. Stat. Comput. **13**, 923 (1992).

[20] We have repeated our computations for one of the wires, and also for Al surfaces, using the generalized gradient approximation (Perdew-Burke-Ernzerhof functional). The gradient correction rigidly shifts the LDA work functions of the (100) and (111) surfaces downwards by 0.17 eV, and lowers by about the same amount (0.15–0.17 eV) the local work functions around the wire in Fig. 1.

[21] This anisotropic feature, due to the rearrangement of the electrons away from the (energetically unfavorable) edge region, is much less pronounced in [11] probably because of the use of a non-self-consistent field approach.

[22] Both features are consistent with *ab initio* calculations that we performed also for a larger (seven-atom thick) wire.

[23] See, e.g., W. Hummel and H. Bross, Phys. Rev. B **58**, 1620 (1998), and references therein.

[24] N. H. Malik, IEEE Trans. Electr. Insul. **24**, 2 (1989).

[25] The local work-function distribution in the vacuum [as seen in panel (B) of Fig. 2] scales with the overall crystal dimension; the corresponding surface charge density on each facet is inversely proportional to the crystal dimension (explaining the near-vanishing charge densities on the facets of macroscopic crystals).