PHYSICAL REVIEW B VOLUME 46, NUMBER 11 15 SEPTEMBER 1992-I

Calculation of the electronic structure of stepped metal surfaces

H. Ishida
Institute for Solid State Physics, University of Tokyo, Roppongi, Minato-ku, Tokyo 106, Japan

A. Liebsch
Institut für Festkörperforschung, Forschungszentrum Jülich, D-5170 Jülich, Germany
(Received 1 May 1992)

We perform systematic electronic-structure calculations for regularly stepped (vicinal) jellium surfaces with varying step densities, step heights, and electron densities within the local-density-functional theory. The results reproduce the experimentally observed linear dependence of the work function on the step density up to a very high step density. The induced change in the electrostatic potential and in the density of states in the neighborhood of the step site suggest higher chemical reactivity near steps than at low-index flat surfaces.

Steps on metal surfaces have been studied during the last two decades as a prototype of surface defects inherent in any surface in nature.[1,2] Experimentally, a stepped surface with the well-defined step density and orientation can be prepared with use of vicinal surfaces, i.e., crystal surfaces whose surface normal is close to those of low-index planes. A number of experiments demonstrated that stepped surfaces show markedly different electronic properties than flat low-index surfaces. Among them are the work-function reduction, the larger sticking probability for adsorbates, and the promotion of catalytic reactions. Also, Janz *et al.*[3] found recently that the optical second-harmonic efficiency of the Al surface is strongly influenced by the presence of monatomic steps. Steps also play a crucial role in the crystal growth and surface structure transitions.[4]

In contrast to the above-mentioned recent progress in experiments, theoretical efforts towards understanding the electronic structure of steps were limited to rather simplified model analyses based on the tight-binding Hamiltonian,[5,6] small cluster calculations,[7,8] and the jellium model combined with approximate model electron densities.[9,10] Very recently, Nelson and Feibelman[11] made a detailed study of the structure relaxation of the Al(331) stepped surface using the Car-Parrinello[12] approach in a repeating-slab geometry. Nevertheless, the detailed knowledge of how the interaction between steps changes the subtle charge rearrangements at the step site as a function of step density is still lacking. Instead of focusing on a particular surface, in the present study we present results of systematic self-consistent density-functional calculations of the electronic structure of regularly stepped (vicinal) jellium surfaces with varying step densities, step heights, and positive background densities. The various electronic contributions to the interaction between steps are fully included in our approach. Although the jellium model cannot take into account localized *d* states of transition metals, it is a realistic model for simple metals such as Al and Na. It should also be useful for the elucidation of various general properties of stepped metal surfaces in the same way as the work of Lang and Kohn[13] for flat jellium surfaces played an important role in the study of low-index metal surfaces. Our calculations reproduce the experimentally observed linear dependence of the work-function change on the step density even at very high step densities, which means that the charge redistribution due to the presence of steps is highly localized in the immediate vicinity of steps. We also study the electrostatic potential and the density of states in the neighborhood of the step that are closely related to the chemical properties of the step site.

In order to simulate vicinal surfaces, we utilize the semi-infinite jellium whose positive-charge profile has a periodic modulation corresponding to the step structure at the surface. One period consists of a terrace of width x_w and a ledge of height x_h whose surface is oriented perpendicularly to the two neighboring terrace surfaces (90° step). The calculation is performed within the local-density approximation in the density-functional theory. In contrast to previous model approaches, the electron density is calculated exactly from the solution of the Kohn-Sham equation.[14] The semi-infinite problem is handled with use of the complex embedding potential invented by Inglesfield.[15] The calculational scheme is essentially the same as that used in the study of the electronic structure of atomic overlayers on semi-infinite jellium[16] except that the numerical problem is reduced to a two-dimensional one in the present case because of translational invariance in the edge direction. We use the higher-dimensional Anderson method reformulated by Blügel for the iteration procedure toward self-consistency.[17] Convergence is assumed when the difference between the input and output dipole layers becomes less than 0.0003 eV. In the present paper, we show results for the jellium surfaces with $r_s = 2$ and 4, which approximately correspond to the free-electron densities of Al and Na, respectively. x_w and x_h are chosen as $m \cdot a_0$ and $n \cdot a_0$, where a_0 is the lattice spacing for the (001) plane, i.e., $a_0 = 3.83$ a.u. for Al and 3.99 a.u. for Na. This configuration corresponds to the $[m(001) \times n(100)]$ structure in the nomenclature of Lang *et al.*[18]

In Fig. 1(a), we show the contour map of the electron density for Al ($r_s = 2$) with $(m,n) = (10,1)$ on the vertically cut plane perpendicular to the ledge direction. The dotted lines show the profile of the positive background charge. This figure demonstrates how the electron charge, which cannot completely follow the profile of the positive charge at the ledge, redistributes itself in the vicinity of the step in order to lower the overall kinetic energy. Essentially, charge flows form the top region of the step towards the lower corner (Smoluchowski effect).[19] As we will discuss below, this redistribution is the origin of the lowering of the work function observed for stepped metal surfaces. Scattering of the one-electron wave functions at the surface leads to a superposition of Friedel oscillations in two directions: orthogonal to the terrace and to the ledge, as shown by the closed density contours that form a two-dimensional pattern in the interior of the jellium. Apart from these Friedel oscillations, the electron density near the surface is seen to distribute itself almost perfectly in one-dimensional fashion along most of the terrace. This means that effects on the electronic structure of the terrace caused by the step are confined to a small region of the order of the screening length. Actually, we found that, in the vicinity of the step, the charge-contour maps of stepped surfaces with smaller terrace widths (smaller m) look very similar to those in Fig. 1(a). This is also true for the surface with a two-atom height [$(m,n) = (10,2)$ and $r_s = 2$] shown in Fig. 1(b). For this step height, the contour lines start to display plateaus running parallel to the jellium profile not only along the terrace but also along the ledge. Figure 1(c) shows the electron-density map for Na ($r_s = 4$) with $(m,n) = (10,1)$. The charge distribution at the terrace is disturbed in a slightly larger range around the step as compared with Fig. 1(a) because of the larger screening length of Na.

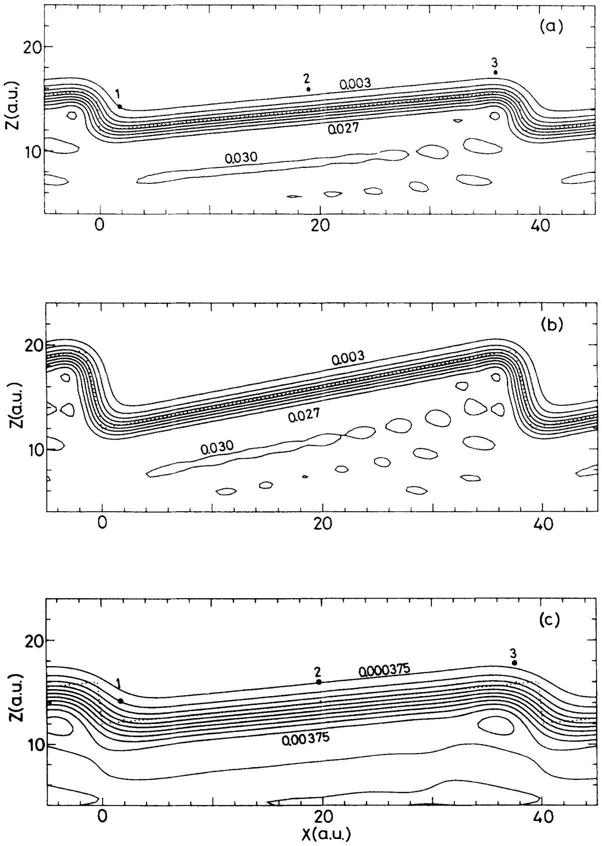

FIG. 1. Contour maps of the electron charge density of regularly stepped jellium surfaces on vertically cut planes perpendicular to the ledge direction. (a) Al ($r_s = 2$) single step, (b) Al ($r_s = 2$) double step, and (c) Na ($r_s = 4$) single step. Contour spacings are 3.0×10^{-3} and 3.75×10^{-4} a.u. for $r_s = 2$ and 4, respectively. The dotted lines indicate the profile of the background positive charge of jellium.

Next we discuss the work-function change that originates from the change in the electrostatic potential confining electrons. First, we note that the stepped surface should have the same dipole potential barrier as the flat surface if the terrace and ledge surfaces had the same dipole moment μ_0 (per unit area) as the flat surface oriented in each surface normal direction. [In this case, the terrace and the ledge each contribute $4\pi\mu_0 x_w^2/(x_w^2 + x_h^2)$ and $4\pi\mu_0 x_h^2/(x_w^2 + x_h^2)$, respectively, to the dipole potential barrier of the macroscopic surface. Thus, the sum is $4\pi\mu_0$, the flat surface value.] Hence, the work-function change in the presence of steps is a microscopic effect originating from the charge redistribution localized near the step. We denote the dipole moment associated with this charge redistribution per unit edge length by $d_\perp$ ($d_\parallel$) for the component perpendicular (parallel) to the terrace. The work-function change $\Delta\Phi$ is then written as

$$\Delta\Phi = 4\pi \frac{x_w d_\perp + x_h d_\parallel}{x_w^2 + x_h^2} . \tag{1}$$

For low step densities ($x_w \gg x_h$), we have

$$\Delta\Phi \sim 4\pi d_\perp / \sqrt{x_w^2 + x_h^2} ,$$

i.e., $\Delta\Phi$ is proportional to the step density.

In Fig. 2, we plot the calculated work-function change $\Delta\Phi$ as a function of $1/\sqrt{x_w^2 + x_h^2}$ ($\sim 1/x_w$ for low step densities). Each curve displays results for a series of stepped surfaces with the fixed step height and the jellium density corresponding to the three cases shown in Fig. 1, but with varying terrace widths ($2 \le m \le 10$). It is seen that $\Delta\Phi$ fits a linear curve up to a very high step density. For $m \le 3$ the work-function change becomes slower than linear, since now the redistributed charge densities on neighboring steps start to overlap and may be modified. The initial linearity of $\Delta\Phi$ implies (1) that $d_\parallel$ is considerably smaller than $d_\perp$, so that the second term in Eq. (1) can be outweighted by the first one even at the high step density ($m/n \sim 3$) and, more importantly, (2) that $d_\perp$ remains essentially constant up to a very high step density. The second aspect may be understood from Fig. 1, in which the disturbance in the electronic charge distribution is highly localized near the step, as stated previously. The dipole moment $d_\perp$ stems from the charge depletion near the upper edge of the step and the charge increase near the lower corner of the step. The double step for Al

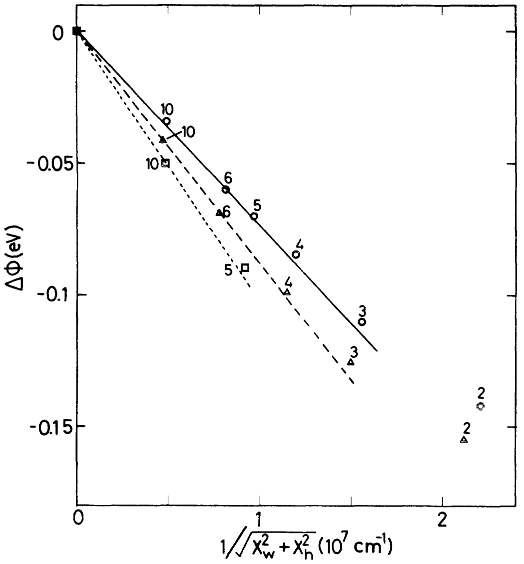

FIG. 2. Calculated work-function change $\Delta\Phi$ as a function of $1/\sqrt{x_w^2+x_h^2}$, where x_w is the terrace width and x_h the step height. Data on solid, dashed, and dotted lines correspond to the Al single step, Na single step, and Al double step, respectively. The small numbers indicate the parameter m for the terrace width. $x_w = ma_0$, where $a_0 = 3.83$ a.u. for Al and 3.99 a.u. for Na.

($r_s=2$, $n=2$) has a larger $d_\perp$ than the monatomic step because of the larger separation between these two regions. The larger $d_\perp$ for Na ($r_s=4$) as compared with that of Al may be attributed again to its larger screening length, i.e., the electron gas with a lower density can follow the abrupt change of the positive charge profile at the ledge less efficiently.

The linear dependence of the work function on the step density has been reported so far for W, Au, and Pt.[20–22] For W(110), Krahl-Urban[20] obtained $d_\perp \sim 0.065$ D (per unit length) for the step running parallel to [001]. This value is much larger than 0.015 D, which we obtained for the Al double step ($r_s=2$, $n=2$). It might be that the relocation of the d charge as suggested by Desjonqueres and Cyrot-Lackmann[5] within the tight-binding calculation has a large contribution to the dipole moment in the case of transition metals. An indirect support for this argument is the experimental result of Besocke, Krahl-Urban, and Wagner,[22] who showed that the dipole moment associated with the step for Au with its closed d shell is more than two times smaller than that of Pt. We hope that the work-function change due to steps will be measured for simple metals to verify our predictions and to clarify the large difference as compared to the changes observed for the transition metals.

The chemical behavior of surfaces is known to be strongly modified in the presence of steps. For example, for simple metals, Testoni and Stair[23] showed that the sticking probability of O on Al(111) is increased by a factor of 4 by introducing steps on the surface. Ibach[24] argued that the activation barrier for molecules in dissociating from a precursor state into atoms may be very sensitive to the electrostatic potential, which can be modified by steps. In a similar way, Lang, Holloway, and Norskov[25] explained promotion (poisoning) of catalytic reactions in the presence of electropositive (negative) adatoms based on the induced dipole field surrounding adatoms. In Fig. 3, we show a contour map of the calculated electrostatic potential (Hartree potential associated with the electron charge and the positive charge of jellium) for Na ($r_s=4$) with $(m,n)=(10,1)$. Corresponding to the charge map in Fig. 1(c), the potential behaves one dimensionally along most of the terrace. There appears a fairly deep potential minimum (~ -0.5 eV) in the interior of jellium near the ledge. As pointed out by Kesmodel and Falikov,[9] such a local field created inside the metal by s and p electrons may affect the level and occupation of localized d (or core) electrons of step atoms considerably. It is seen that the contour lines in outer regions protrude markedly towards the vacuum above the ledge as a result of the reduced electron density in this region. On the other hand, near the corner between the ledge and the lower terrace, these contour lines follow the profile of the positive background charge much better; towards the step they bend slightly inward reflecting the charge increase near the corner. We found a similar pattern also for Al ($r_s=2$).

Another quantity relevant to the chemical reactivity of surfaces is the density of states near the Fermi energy (E_F) as suggested by Feibelman and Hamman[26] in the study of catalytic promotion or poisoning induced by adatoms. They considered that a higher density of states at E_F owing to the charge transfer from adatoms may lead to higher chemical reactivity of the surface. In Fig. 4, we show the density of states for Al and Na with $(m,n)=(10,1)$ calculated in a small sphere of radius 2 a.u. centered at three sites along the terrace as marked in Figs. 1(a) and 1(c). The distance between the sphere center and the terrace surface is chosen as 2 a.u. for all of them. On sees a noticeable enhancement of the density of states at the corner site between the ledge and the terrace. This may be understood from the increased charge density near the corner shown in Fig. 1. Thus the corner site

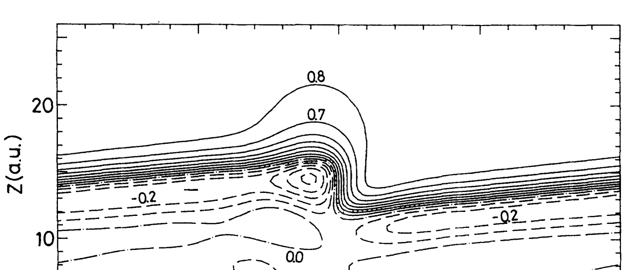

FIG. 3. Contour map of the electrostatic potential on the vertically cut plane perpendicular to the ledge direction for the Na ($r_s=4$) monoatomic step with $(m,n)=(10,1)$. The solid, dashed, and dash-dotted lines correspond to positive, negative, and zero values, respectively. The contour spacing is 0.1 eV.

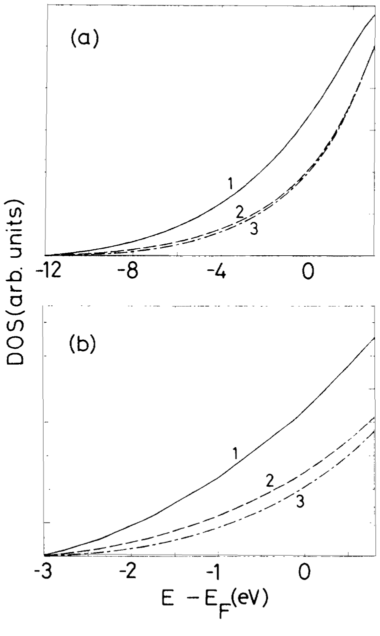

FIG. 4. Calculated density of states in a small sphere of radius 2 a.u. for three different sites on the (a) Al and (b) Na stepped surfaces with $(m,n)=(10,1)$. The small number on each curve indicates the location of the sites marked in Figs. 1(a) and 1(c).

may be chemically more reactive than a site on the flat surface. On the other hand, the density of states on top of the ledge is slightly lower than in the middle of the terrace, i.e., the chemical reactivity will be reduced due to the depletion of charge (ballustrade effect). For Al, this effect is less pronounced than for Na because of the shorter screening length. Our results agree qualitatively with those of Thompson and Huntington,[10] who studied the adsorption energy of atoms at a stepped Na surface using a simplified version of the local-density-functional theory and an analytical variational jellium electron density. For stepped transition-metal surfaces, this effect might be more pronounced than for the simple metals, since the *d*-electron density of states of step atoms may change quite a lot by losing more nearest-neighbor atoms than the other surface atoms.

In summary, we used the density-functional approach to study the electronic structure of the regularly stepped (vicinal) jellium surfaces as a function of step height, terrace width, and bulk electron density. The results reproduce the observed linear dependence of the work function on the step density. The disturbance of the electronic structure due to the presence of steps was found to be highly localized in the immediate vicinity of the steps. The analysis of the electrostatic potential and of the local density of states suggests that the chemical behavior of the surface may be strongly modified near the step. In the future, we are planning to study the dynamical response properties of the stepped surfaces as well as the adsorption of atoms at the step using the present approach.

One of us (H.I.) would like to thank the Alexander von Humboldt Foundation for its support during his stay in Jülich.

---

[1] K. Wandelt, Surf. Sci. **251/252**, 387 (1991).
[2] H. Wagner, in *Solid Surface Physics,* edited by G. Höhler Springer Tracts of Modern Physics (Springer, Berlin, 1979).
[3] S. Janz, D. J. Bottomley, H. M. van Driel, and R. S. Timsit, Phys. Rev. Lett. **66**, 1201 (1990).
[4] E. Pehlke and J. Tersoff, Phys. Rev. Lett. **67**, 465 (1991); *ibid.* **68**, 816 (1992).
[5] M. C. Desjonqueres and F. Cyrot-Lackmann, Solid State Commun. **18**, 1127 (1976).
[6] V. T. Rajan and L. M. Falikov, J. Phys. C **9**, 2533 (1976).
[7] G. S. Painter, P. J. Jennings, and R. O. Jones, J. Phys. C **8**, L199 (1975).
[8] T. Yamaguchi and N. Fujima, Surf. Sci. **242**, 233 (1991).
[9] L. L. Kesmodel and L. M. Falikov, Solid State Commun. **16**, 1201 (1975).
[10] M. D. Thompson and H. B. Huntington, Surf. Sci. **116**, 522 (1982).
[11] J. S. Nelson and P. J. Feibelman, Phys. Rev. Lett. **68**, 2188 (1992).
[12] R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).
[13] N. D. Lang and W. Kohn, Phys. Rev. B **1**, 4555 (1970).
[14] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).
[15] J. E. Inglesfield, J. Phys. C **14**, 3795 (1981).
[16] H. Ishida, Phys. Rev. B **42**, 10 899 (1990); **41**, 12 288 (1990).
[17] S. Blügel (unpublished).
[18] B. Lang, R. W. Joyner, and G. A. Somorjai, Surf. Sci. **30**, 440 (1970).
[19] R. Smoluchowski, Phys. Rev. **60**, 661 (1941).
[20] B. Krahl-Urban, E. A. Niekisch, and H. Wagner, Surf. Sci. **64**, 52 (1977).
[21] K. Besocke and H. Wagner, Phys. Rev. B **8**, 4597 (1973).
[22] H. Besocke, B. Krahl-Urban, and H. Wagner, Surf. Sci. **68**, 39 (1977).
[23] A. L. Testoni and P. C. Stair, Surf. Sci. **171**, L491 (1986).
[24] H. Ibach, Surf. Sci. **53**, 444 (1975).
[25] N. D. Lang, S. Holloway, and J. K. Norskov, Surf. Sci. **150**, 24 (1985).
[26] P. J. Feibelman and D. R. Hamman, Phys. Rev. Lett. **52**, 61 (1984).