Resolution of an Ancient Surface Science Anomaly: Work Function Change Induced by N Adsorption on W{100}

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For many decades it has been assumed that an adsorbate centered above a metal surface and with a net negative charge should increase the work function of the surface. However, despite their electronegativity, N adatoms on W{100} cause a significant work function *decrease*. Here we present a resolution of this anomaly. Using density functional theory, we demonstrate that while the N atom carries a negative charge, of overriding importance is a reduction in the surface overspill electron density into the vacuum, when that charge is engaged in bonding to the adatom. This novel interpretation is fundamentally important in the general understanding of work function changes induced by atomic adsorbates.

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The work function Φ is one of the most fundamental properties of a metallic surface. As such it is of interest to a wide range of surface phenomena [1,2]. In particular, the measurement of Φ or, more precisely, work function changes $\Delta\Phi$, are routinely used in the study of adsorption processes on metal surfaces. Adsorbates generally alter Φ through modification of the surface dipole and thus measurement of $\Delta\Phi$ generally yields critical information on the degree of electronic charge reorganization upon adsorption [3]. Traditionally $\Delta\Phi$ is used to estimate the direction and extent of adsorbate-substrate electronic charge transfer [4,5]. A Φ increase implies substrate to adsorbate charge transfer and a Φ decrease implies adsorbate to substrate charge transfer. This simple model has been successfully employed to interpret a wide range of adsorption systems. However, the reliability of this approach is questioned by the existence of a long-standing anomaly relating to the work function change upon N adsorption on W{100}.

The dissociative adsorption of a diatomic molecule such as N_2 or O_2 on metal surfaces tends to lead to substrate to adsorbate electronic charge transfer with a concomitant increase in the Φ of the metal. For N adsorption on the {111}, {311}, {611}, {210}, and {310} planes of W this is true [6–8]. On W{100}, on the other hand, adsorption of N causes a 0.3–0.9 eV Φ *decrease* [6,7,9]. Models have been proposed to account for this anomalous Φ decrease [6,7]. However, these relied on N being positively charged. Given the greater electronegativity of N over W this assumption is counterintuitive.

Room temperature exposure of 0.5 of a monolayer (ML) N to W{100} leads to the formation of a sharp $(\sqrt{2} \times \sqrt{2})R45°$ low-energy-electron diffraction (LEED) pattern [7,9]. In a quantitative LEED structural analysis Bessent *et al.* [10] have shown that this consists of an overlayer of N atoms adsorbed at fourfold hollow sites, 0.4 Å above the top layer of W. Here we apply density functional theory (DFT) to this system, which until now has represented an important breach in our understanding of work function changes induced by atomic adsorbates. We show that N does indeed induce a Φ decrease. Of the utmost significance, however, we find that while the N atom does carry a negative charge, the overriding effect is a reduction in the extent of the electron density overspill into the vacuum when that charge is engaged in bonding to the adatom. This novel interpretation sheds new light on our basic understanding of work function changes induced by atomic adsorbates.

First-principle total energy calculations within the DFT framework were performed with the CASTEP code [11]. Norm-conserving Troullier-Martins pseudopotentials were employed. The Kohn-Sham orbitals were expanded in a plane wave basis with a cutoff of 800 eV. Exchange and correlation effects were described using the Perdew-Wang 1991 generalized gradient approximation [12]. W{100} was modeled by a periodic array of symmetric seven layer thick W slabs in $(\sqrt{2} \times \sqrt{2})R45°$ unit cells. The vacuum region between adjacent slabs was equivalent to 12 layers of W (> 17 Å). Nitrogen adsorption was investigated by placing a single N atom on both sides of the W slab, corresponding to a surface coverage on each side of 0.5 ML. During structure optimizations all atoms, except the central W layer, were allowed to relax. A Monkhorst-Pack mesh with $6 \times 6 \times 1$ **k**-point sampling within the surface Brillouin zone was employed.

The optimized structure of the $(\sqrt{2} \times \sqrt{2})R45°$ N overlayer on W{100}, along with certain structural parameters, is displayed in Fig. 1. Also shown in parentheses are the values determined from LEED [10]. It is clear that there is good agreement between the experimentally and theoretically determined structures. In particular, the two

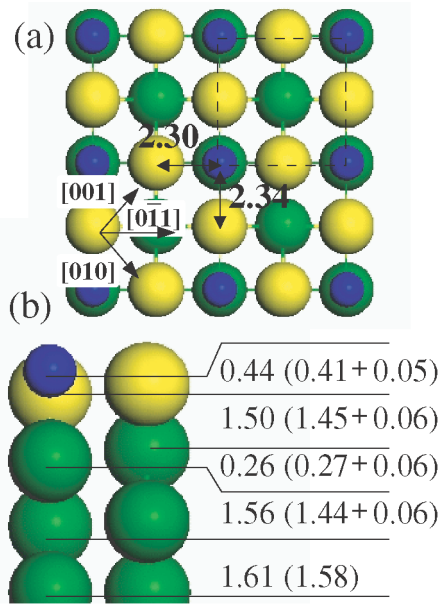

FIG. 1 (color online). Top (a) and side (b) views of the $(\sqrt{2} \times \sqrt{2})R45°$ N overlayer on W{100}. Large spheres are W atoms with the light grey ones being top layer W. Small black spheres are N atoms. The unit cell is indicated by the dashed square in (a). (b) is annotated with calculated and experimental (Ref. [10]) values for the interlayer spacings in Å. There is buckling in the first and third layers: the average values for these layers are displayed, however, in order to facilitate direct comparison with Ref. [10]. The distances in (a) are calculated N-W bond lengths in Å.

key characteristics of Bessent's structural model, namely, a large interlayer buckling of the second W layer (0.27 ± 0.06 Å) and the N height above the surface (0.41 ± 0.05 Å), are remarkably well reproduced by DFT. The DFT values for these two distances are 0.26 and 0.44 Å, respectively. Further, the nearest-neighbor W-N bond length, at 2.19 Å to the W atom in the second layer, immediately beneath N, is in reasonable agreement with the experimental value (2.13 ± 0.05 Å). The only discrepancy with experiment is some rumpling in the first and third W layers, which was not identified experimentally. A consequence of this buckling for the topmost W layer is that the fourfold symmetry of the N adsorption site is broken and there are two distinct W-N bond lengths. The calculated W-N distances are 2.30 and 2.34 Å and the experimental value is 2.27 Å [10]. Similar symmetry breaking rumpling has recently been observed upon N adsorption on Cu{100} [13].

The calculated Φ for clean W{100} is 4.34 eV and for the $(\sqrt{2} \times \sqrt{2})R45°$ N overlayer it is 3.75 eV, which yields a $\Delta\Phi$ upon N adsorption of -0.59 eV [14]. At 0.5 ML and when confirmed with LEED to correspond to the $(\sqrt{2} \times \sqrt{2})R45°$ overlayer the experimental $\Delta\Phi$ is -0.6 [7] or -0.65 eV [9]. Thus our theoretical value is in excellent agreement with experiment and we conclude that the structural model proposed by Bessent *et al.* and confirmed here for N adsorption on W{100} does indeed account for a large Φ decrease.

We now investigate why N lowers the Φ of this surface. On the basis that a Φ decrease implies adsorbate to substrate electronic charge transfer it has been argued that N must carry a positive charge on W{100} [6,7]. However, the results of two separate population analyses of the charge density indicate that this is not the case. The atom resolved electronic charges obtained from Mulliken [15] and Bader [16] population analyses are shown in Table I. Both approaches, which employ conceptually diverse partitioning strategies of the charge density, reveal that N is likely to be negatively charged when adsorbed. The Mulliken and Bader charges on N are approximately $-1e$ and $-1.5e$, respectively. As with any electronic charge partitioning scheme the absolute magnitude of the charges in the particular system under consideration are of less importance than their relative charges. From Table I, however, it is obvious that in this adsorption system a substantial amount of electronic charge flows from the W substrate, in particular, the W atoms in the top layer to the N adsorbate. The simplistic, yet otherwise very successful, procedure of equating a Φ decrease with adsorbate to substrate electron flow therefore fails for this system.

In order to understand why the negatively charged N adatoms induce a Φ decrease a careful analysis of the electron density redistribution upon adsorption has been performed, from which the surface dipole change has been explicitly calculated. Figure 2(a) displays the planar averaged charge density change upon N adsorption:

$$\Delta\rho_{(z)} = \rho_{(z)}\mathrm{N/W\{100\}} - \rho_{(z)}\mathrm{W\{100\}} - \rho_{(z)}\mathrm{N}, \qquad (1)$$

where z is perpendicular to the surface plane; $\rho_{(z)}$N/W{100} is the density of the adsorption system; and $\rho_{(z)}$W{100} and $\rho_{(z)}$N are the densities of the isolated clean W{100} slab and N atoms, respectively, each in the precise position they adopt in the adsorption system. Figure 2(a) reveals substantial electronic charge depletion at the surface, corresponding to the top layer of W atoms, and a large charge accumulation region just outside the surface, centered slightly above the N atom. This

TABLE I. Atom resolved electronic charges obtained from Mulliken and Bader population analyses of the $(\sqrt{2} \times \sqrt{2})R45°$-N/W{100} adsorption system. Two values are given for each W layer, corresponding to the two atoms in each layer.

	Mulliken charge	Bader charge
N	−0.97	−1.48
W layer 1	0.39, 0.30	0.55, 0.37
W layer 2	0.11, 0.05	0.29, 0.16
W layer 3	0.04, 0.03	0.07, 0.01
W layer 4	0.07, 0.02	0.07, 0.00

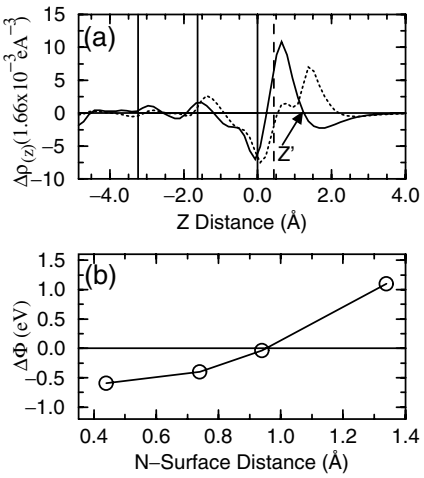

FIG. 2. (a) Planar averaged charge density change $\Delta\rho$ upon N adsorption for N at its equilibrium height (solid line) and for N fixed at 1.34 Å (dotted line) above W{100}. The average location of each of the top three W layers and the N atom at its equilibrium height (0.44 Å) are indicated by the solid (dashed) vertical lines. (b) Work function change ($\Delta\Phi$) upon N adsorption on W{100} for N at different heights above the surface.

is consistent with the electronic charge analysis discussed above and implies an increase in the surface dipole upon N adsorption. However, further into the vacuum, at 1–2 Å from the surface, there is a small region of charge depletion and we find that this region is of crucial importance to the surface dipole.

The dipole moment change ($\Delta\mu$) induced by N adsorption on either side of our symmetric slab is given by

$$\Delta\mu = \int_{-a}^{-a+z/2} z\Delta\rho(z)dz, \qquad (2)$$

where $\Delta\rho$ is the density change upon N adsorption; a is the distance from the center of the slab to the surface plane; and $z/2$ is half the length of the unit cell. By integrating over the Fourier transform grid in the z direction of our supercell $\Delta\mu$ is obtained. The calculated $\Delta\mu$ upon N adsorption is -0.40 D, which, satisfyingly, is consistent with a Φ decrease upon N adsorption. We find that the shallow electronic charge depletion layer at $\sim$1.5 Å outside the surface is entirely responsible for the reduction in the surface dipole. This becomes immediately apparent if we discount the contribution made by this region from the calculation of $\Delta\mu$. We do this by omitting the region of electronic charge depletion from the integration in (2) and simply summing from the center of the slab to the point labeled Z' in Fig. 2(a). For this hypothetical situation $\Delta\mu$ upon N adsorption is large and positive (3.6 D), which corresponds to a significant Φ increase. Clearly the small electronic charge depletion layer at 1–2 Å outside the surface has a dramatic effect on the magnitude of the surface dipole. Although small compared to the electron accumulation layer nearer the surface it is sufficiently far from the surface to carry with it a large enough weight in Eq. (2) to govern the sign of $\Delta\mu$ upon adsorption. Ultimately, this electronic charge depletion region, relatively far from the surface, is responsible for the observed Φ decrease upon N adsorption.

We find that the crucial layer of density depletion at 1–2 Å from the surface is associated with W surface atoms. Specifically W $5d$ orbitals, which extended out into the vacuum before adsorption, have been depopulated. Figure 3 displays a 2D electron density difference plot that runs along the $\langle 0\bar{1}1\rangle$ plane, perpendicular to the surface. It clearly reveals depletion of W $5d$ orbitals in the surface layer. Moreover, the regions of electronic charge depletion extend up to 2 Å into the vacuum, which is farther out than the region of electronic charge accumulation located on N. Overall then, in a planar averaged difference plot [Fig. 2(a)], as one moves from the surface towards the vacuum, electronic charge accumulation associated with the N atoms is encountered. This is followed by electronic charge depletion associated with the $5d$ spillout electron density. A schematic diagram of the physical picture that has emerged is shown in Fig. 4(a).

Clearly a central tenet of this model is the relative height of the W charge depletion to the N charge accumulation regions. One would therefore anticipate a strong Φ dependence on the height of the N atoms above the surface. Figure 2(b), which plots $\Delta\Phi$ induced by N for N adsorbed at various heights above W{100}, confirms this: as N is moved from its equilibrium height (0.44 Å) to a distance of 1.34 Å above the surface $\Delta\Phi$ changes from -0.59 to $+1.10$ eV. This dramatic dependence of the height of N above the surface implies that if N atoms were to adsorb further from the surface ($>$ 1Å) then a Φ increase upon adsorption would indeed be observed.

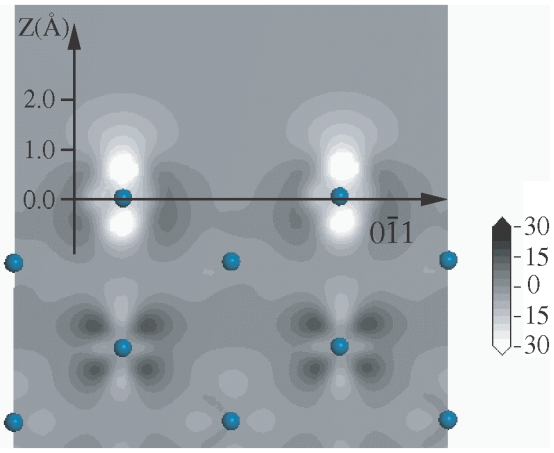

FIG. 3 (color online). 2D electron density difference plot from the $(\sqrt{2}\times\sqrt{2})R45°$-N/W{100} adsorption system. Light (dark) regions correspond to electronic charge depletion (accumulation) upon N adsorption. The spheres are W atoms and the units are $1.66\times10^{-3}e$ Å^{-3}.

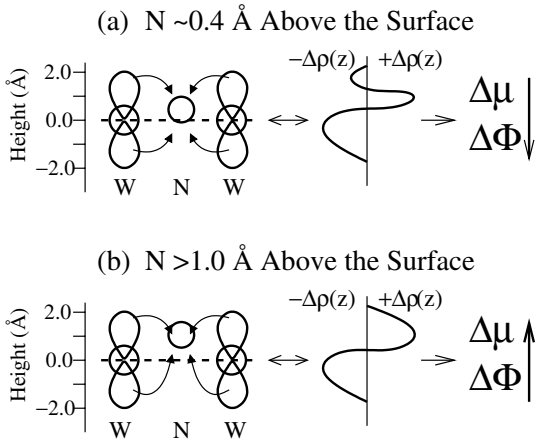

FIG. 4. Schematic diagram illustrating the physical basis of the work function (Φ) decrease upon N adsorption on W{100} (a) and the effect of moving the N atom farther from the surface (b). In (a) the N adsorbate is located beneath the electron spillout density of the W *d* orbitals. This results in a dipole (μ) and Φ decrease. In (b) the N adsorbate is far enough from the surface that μ and Φ increases are observed.

Analysis confirms that the increase in Φ along with an increase in N height is associated with a diminution of the W electronic charge depletion layer in the planar averaged density difference plot [dotted line in Fig. 2(a)]. As N moves farther from the surface its associated charge accumulation layer overwhelms the small stationary (and still present) depletion layer in the W overspill electron density. A schematic illustration of this process is shown in Fig. 4(b).

To summarize, it has been shown that despite carrying net negative charges and residing outside the surface, N atoms do lower the Φ of W{100}. The resolution of this long-standing quandary has resulted in fundamental new insight into the nature of the $\Delta\Phi$ induced by atomic adsorbates on metal surfaces. In this system equating a Φ decrease with adsorbate to substrate electron flow is grossly misleading. It is essential to consider the electronic charge redistribution over the entire surface region and not just on the adsorbate. In particular, the height of the adsorbate and its associated electronic charge accumulation region must be compared to the overspill electron density of the surface. Here, because the N adatoms are very close to the surface, the adsorbate electronic charge accumulation layer is located beneath this overspill density. This results in a small layer of charge depletion outside the surface, which is responsible for a net dipole and Φ decrease.

We have demonstrated that for N the height of the adsorbate above the surface has a dramatic effect on $\Delta\Phi$ and that at distances of > 1 Å the expected Φ increase for the adsorption of an electronegative adsorbate is observed. It is anticipated that analogous relationships between $\Delta\Phi$ and adsorbate height exist in many other systems. It appears that correlations between $\Delta\Phi$ and electronic charge transfer are generally successful because the adsorbate is far enough from the surface that depletion in the metallic spillout density is not the overriding factor. This is clearly the case for O atoms that sit > 1 Å above W{110} and are responsible for a 0.7 eV Φ increase [17]. Only when the electron density associated with an electronegative atom resides beneath the layer of spillout density is there a net reduction in the surface dipole. Nonetheless depletion of spillout electron density that accompanies the adsorption of electronegative adsorbates will always affect the absolute magnitude of the surface dipole and is a key aspect of the physics of the work function that should not be overlooked.

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