Work Function of Transition-Metal Surface with Submonolayer Alkali-Metal Coverage

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The film linearized-augmented-plane-wave method with a refined set of basis functions in the jellium-vacuum region is used to calculate the electronic structure of a model system simulating a W(100) surface covered by a Cs overlayer from zero to monolayer coverage. The work function decreases rapidly with coverage at the initial stage of adsorption, reaches a minimum at $\theta = 0.22$, and rises again at higher coverage, in good agreement with experiment. The changes of the electron distribution and potential reveal that the initial decrease of the work function is caused by electron transfer from the Cs to the W surface.

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It has been discovered years ago and widely used in the development of cathode materials that the deposition of an alkali-metal overlayer on a transition-metal surface may greatly reduce the work function.[1] Lang[2] gave a qualitatively successful theoretical account of this phenomenon by a jellium model; however, this model cannot describe the localized surface states which have been shown to exist on the transition-metal surfaces and which strongly interact with adsorbates (for the W surface; see, e.g., Posternak *et al.*,[3] Wimmer *et al.*,[4] and Soukiassian *et al.*[5]). So it is not expected that the jellium model will give quantitatively good results.

On the other hand, calculations for a slab model containing both atomic layers of adsorbate and substrate have been carried out in recent years to describe the overlayer-substrate system. For example, a very good film linearized-augmented-plane-wave (LAPW) calculation of a hypothetical $c(2\times2)$ Cs/W(100) system was given by Wimmer *et al.*[4] In this type of slab calculation, which requires 2D translational periodicity in the film plane, it is obviously impossible to change the coverage of the adsorption layer continuously, and investigate the coverage dependence of the physical properties of concern.

In order to give a better description of the adsorption of an alkali-metal overlayer on a transition-metal surface, a model system consisting of a jellium layer and an atomic slab is proposed in this Letter. This is called a "jellium-slab" model system (Fig. 1). With the use of a suitable band method (e.g., LAPW), this model can take the substrate characteristics, namely the d-electron states, into consideration, and at the same time address the coverage dependence by a continuous variation of the jellium density. As an example, the results of the coverage dependence of the work function are given below for a jellium-slab model system simulating a Cs-covered W(100) surface.

A slab containing three layers of W atoms is used to simulate the W(100) substrate with the parameters of an ideal W crystal ($a = 5.98$ a.u.). A jellium layer, i.e., a uniform positive-charge region, is put on the substrate instead of the discrete nuclei (or ion cores) of the adsorbate. Below monolayer coverage, the thickness of the jellium layer, d_j, is set equal, independently of the coverage, to 8.08 a.u., i.e., the spacing of the most densely packed lattice plane of bulk bcc Cs as given in Ref. 2. It is also assumed in this model that, below monolayer coverage, the charge density of the jellium layer, ρ_j, depends on the coverage θ (the ratio of the number of adsorbed Cs atoms to that of surface W atoms) as

$$\rho_j = \theta n_j,$$

where n_j is set equal to the average valence-electron

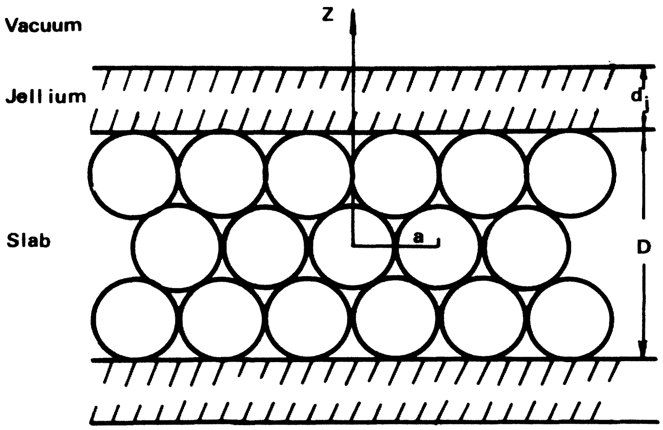

FIG. 1. A jellium-slab model system simulating a W(100) surface covered by a Cs overlayer.

density for $\theta = 1$, i.e., $n_j = 0.003\,46$ a.u.$^{-3}$ The calculation is carried out for $\theta = 0$ to $\theta = 0.4$, which corresponds to about the highest coverage that one could achieve in experiments within the monolayer region, because Cs atoms are much larger than W atoms. A corresponding number of electrons of the adsorbate (jellium) is added to the valence electrons of the metal slab to fill the bands.

The energy bands of this model system are calculated by use of the film LAPW method.[3,6] The treatment of the muffin-tin region and interstitial region is exactly the same as that described in Refs. 3 and 6 (for the notation used below, see these references, except for that explicitly given in this Letter). However, because of the existence of the jellium overlayer, the space outside the atomic slab now becomes the jellium-vacuum region, and an expression of the basis functions different from that used in Refs. 3 and 6 is required (for reasons explained below). The refined set of basis functions is, for the jellium-vacuum region,

$$\Phi_{mn}(\mathbf{k},\mathbf{r}) = [A_{mn} u_{km}(E_v^i,z) + B_{mn} u_{km}(E_v^{i+1},z)] \times \exp[i(\mathbf{k}+\mathbf{G}_m)\cdot\mathbf{r}].$$

Here $u_{km}(E_v^i,z)$ is the solution of the one-dimensional Schrödinger equation in the jellium-vacuum region,

$$[-\tfrac{1}{2}\delta^2/\delta z^2 + V(z) - (E_v^i - \tfrac{1}{2}|\mathbf{k}+\mathbf{G}_m|^2)] \times u_{km}(E_v^i,z) = 0,$$

for the ith vacuum energy parameter E_v^i. A_{mn} and B_{mn} are determined by the continuity of the basis function and its derivative at the film boundary ($z = D/2$). As a result of the existence of the jellium layer, the potential and the electron density do not decay exponentially in the jellium-vacuum region as found in the vacuum region of a clean surface. So it is not good to use a single energy parameter (as in Ref. 3) for the whole set of basis functions $\Phi_{mn}(\mathbf{k},\mathbf{r})$. Instead, a series of energy parameters (i.e., E_v^i, $i = 1, 2, \ldots N$) are chosen to cover the whole range of energy from the potential at the interface between the jellium and the atomic slab to approximately the vacuum potential,

$$V(D/2) = E_v^1 < E_v^2 < \ldots < E_v^N = 0.9\,V(\infty).$$

And for each basis function $\Phi_{mn}(\mathbf{k},\mathbf{r})$ two energy parameters E_v^i and E_v^{i+1} are chosen according to

$$E_v^i \le \tfrac{1}{2}(|\mathbf{k}+\mathbf{G}_m|^2 + k_n^2) \le E_v^{i+1},$$

to generate the z-dependent functions $u_{km}(E_v^i,z)$ and $u_{km}(E_v^{i+1},z)$. The linearized (with respect to energy E_v) basis function is thus given in terms of a linear combination of these two functions. This method for linearization is different from that used in Refs. 3 and 6, where the linearization is given by a summation of the wave function $u_{km}(E_v,z)$ of a single vacuum energy parameter and its energy derivative. A similar approach has been used by other authors, as given in a recent publication.[7]

It is crucial to use different energy parameters for a correct description of the wave functions of electron states having different energies, because they may have different z dependences, i.e., they either decay exponentially in the jellium region or oscillate, according to their energy. At higher coverage of the alkali-metal overlayer, the states near the Fermi surface belong to the latter case. The different schemes for linearization, i.e., with two wave functions of different energy parameters, as in the present work, or with one wave function and its energy derivative, as in Refs. 3 and 6, do not give a meaningful difference, as shown by test calculations, if they are derived in the same energy interval.

Fifty symmetrized (with respect to z reflection) LAPW's and three special $\mathbf{k}$ points[8] in the $\frac{1}{8}$ irreducible 2D Brillouin zone are used to solve the eigenvalue problem and generate the total charge density in the self-consistent iterations. More plane waves and $\mathbf{k}$ points are used in some test calculations which confirm the results given below. The self-consistency (difference between the input and output potentials) is better than 0.05 Ry.

The work function of a clean W(100) surface is 5.4 eV according to our calculation on this three-layer slab (Fig. 2). This is reasonably good in comparison with the experimental value, 4.61 eV,[9] and the accurate LAPW result, 4.6 eV.[10] It is slightly higher than these results because the W slab used in the present calculation is not thick enough. However, in the following investigation of the coverage dependence, this is kept unchanged, so that it should not influence the results given below.

The work function of a W(100) surface is shown in Fig. 2, as a function of the Cs coverage (in fact, the jellium density ρ_j). The present results for the jellium-slab model (curve 1) show that, at the initial stage of adsorption ($\theta = 0$ to 0.2), the work function decreases rapidly with an increase of coverage. It reaches a minimum (of about 1 eV) at $\theta = 0.22$, and then rises slightly with a further increase of the coverage ($\theta > 0.25$). This is in good agreement with the experimental findings: The initial decrease in the experiment is almost the same as the theoretical one, and the lowest work function is achieved at the coverage of $\theta = 0.23$ to 0.25, corresponding to a $p(2\times2)$ structure.

In order to show the mechanism of the above phenomenon, the planar average of the potential and the charge density in the jellium-vacuum region are plotted in Fig. 3 against the vertical distance from the film center for $\theta = 0$, 0.2, and 0.4. As expected, for a clean W surface the electron density decays rapidly in

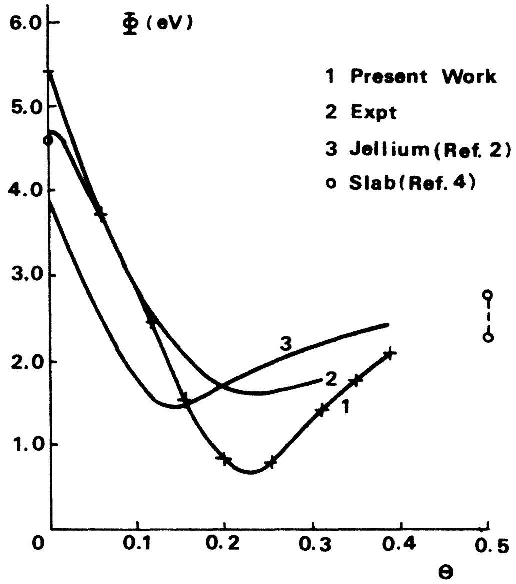

FIG. 2. Coverage dependence of the work function ϕ of a W(100) surface covered by a Cs adsorption layer. The experimental curve is from Swanson and Strayer, Ref. 11.

the vacuum region. However, up to the coverage $\theta = 0.2$ of the Cs overlayer, the electron distribution is still concentrated on the W surface [see Fig. 3(b)]. This means that the electron does not follow the positive jellium charge distribution, but is attracted to the W surface through its interaction with the surface states of the substrate. This can be seen more clearly from Fig. 3(c) which shows the differences of the electron density for different coverages. For example, the difference curve between $\theta = 0.2$ and $\theta = 0$ reveals that the jellium electron is strongly localized near the W surface region. So the total contribution from the jellium positive background and electrons is a negative dipole potential, and leads to the reduction of the work function.

However, the ability of the transition-metal surface to attract adsorption electrons is determined by its surface states. If the number of adsorption electrons is more than what the substrate surface can attract, the electrons in the adsorption layer can no longer be localized in the region near the substrate surface, and will spread over the whole adsorption layer or even spill out into the vacuum. The curve in Fig. 3(b) for $\theta = 0.4$ and the curve in Fig. 3(c) showing the electron-density difference between $\theta = 0.4$ and $\theta = 0$ clearly show this behavior. The dipole layer at the outer surface of the jellium layer (the electron in the vacuum region) explains the increase of the work function at coverages higher than $\theta = 0.25$. However, when comparing the curve for $\theta = 0.4$ to that for $\theta = 0$, one finds that a strong polarization of the electron distribution in the jellium region still exists, and so the work function is also lower than that of a clean W surface.

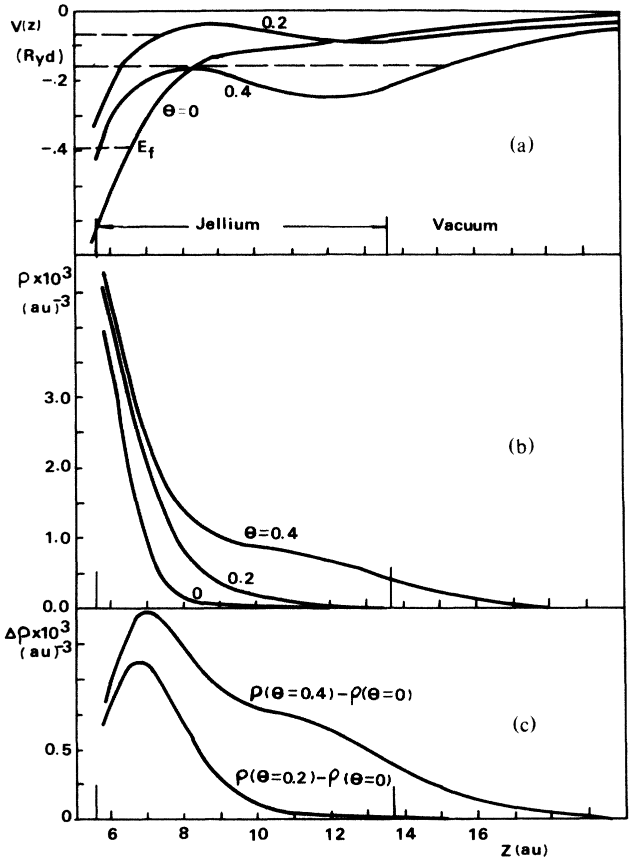

FIG. 3. Planar-averaged (a) potential and (b) electron density distribution in the jellium-vacuum region in a jellium-slab model system simulating the W(100) surface with Cs overlayer. (c) Difference in electron density for different coverages.

Wimmer *et al.*[4] have shown that the W d_{z^2} surface states at $\bar{\Gamma}$ form a strong bond (about a 1-eV shift to higher binding energy) with the Cs 6*s*-derived states in the Cs/W system. Experimentally, this was also shown for either the Cs/W or the Cs/Mo system by Soukiassian *et al.*[5] A detailed analysis of our results gives a closely similar picture, that is, a contour plot of the difference of the electron density distributions for $\theta = 0.2$ and for $\theta = 0$ (not given in this Letter) clearly shows d_{z^2} character.

A self-consistent potential is plotted in Fig. 3(a) for $\theta = 0$, 0.2, and 0.4. The electrostatic contribution of the negative dipole layer reduces the potential of the outer jellium region appreciably, and makes a very wide flat part of the potential curve for $\theta = 0.2$, going from the vacuum to deep in the jellium region. This effect is even stronger for higher coverage; for example, the curve for $\theta = 0.4$ shows an appreciable dip in the outer part of the jellium region. However, it rises again in the vacuum region because the electron is now spread widely in this part of space [Figs. 3(b) and 3(c)]. For $\theta = 0.4$, E_F is about 0.1 Ry higher than the potential in the jellium region [Fig. 3(a)], and so considerable care should be taken to describe the wave function of those occupied states near the Fermi surface. That is why a series of energy parameters have to be used to match the whole set of basis functions.

Obviously, a simple jellium model[2] cannot consider the localized *d* surface states of the transition-metal substrate, and underestimates the ability of the substrate to attract the adsorption (jellium) electrons. So it gives a much smaller θ for the minimum work function, $\theta = 0.15$, compared to the experimental value 0.25 (see Fig. 2, curve 3). Wimmer *et al.*[4] give a work function 2.3 to 2.8 eV (corresponding to different adsorption distances, from 2.9 to 2.6 Å, between Cs and the surface W plane) for their hypothetical $c(2\times 2)$ Cs on a five-layer W(100) slab, using an accurate LAPW slab calculation. The present results agree with this accurate slab calculation as one discovers by extrapolating curve 1 in Fig. 2 to the hypothetical case $\theta = 0.5$. This shows the validity of the proposed jellium-slab model, which replaces the Cs overlayer by a jellium layer. However, the value of the minimum work function is almost 1 eV too low as compared with experiments. This discrepancy is due to the neglect of the Cs $5p$ electrons, which are known to polarize oppositely,[4] or due to the uncertainty of the jellium thickness d_j used.

From the present calculation it is hard to say if the adsorption is covalent or ionic, but judging from Fig. 3(c) the peak of the net absorbed electron density $(\theta = 0.2)$ is much greater than $\rho_j(\theta = 0.2) = 0.69 \times 10^{-3}$ a.u.$^{-3}$, and well inside the jellium region, and it may be concluded that the absorption is similar to a covalent one in accordance with Ref. 5.

In summary, the advantage of the jellium-slab model is shown in the present study of the coverage dependence of the work function of a Cs-covered transition-metal (W) surface—it can simulate the adsorption of various alkali metals by changing d_j and n_j and can change the coverage continuously by changing $\rho_j = \theta n_j$. The mechanism for the reduction of the work function of the W surface upon the adsorption of Cs is elucidated from this coverage-dependence study. The attraction of the valence electron of the adsorption layer by the substrate surface to the interface region is responsible for this reduction.

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