

Work function of metals upon alkali-metal adsorption: Overlayer relaxation

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The work function of metals is lowered upon alkali-metal adsorption and this lowering ($\Delta\Phi$) is known to be coverage dependent. Using standard jellium-model calculations, we show that if the metal-overlayer distance is assumed to increase with coverage, the experimental behavior of $\Delta\Phi$ is much better reproduced. In particular the minimum work function is increased and shifted to higher coverages, in agreement with experimental results. The increase of distance with coverage also leads to an energetically more stable configuration.

The adsorption of alkali metals on metal surfaces has been studied for a long time.¹⁻¹⁰ A rather complete list of references can be found in a recent paper by Wimmer *et al.*¹⁰ The change in work function $\Delta\Phi$ depends on coverage Θ and shows universal behavior on almost all metallic substrates.¹ On semiconducting substrates the behavior may be somewhat different¹¹ but it is not yet fully established. Alkali-metal adsorption at low coverage leads to a rapid decrease of the work function. Then at a critical coverage Θ_c the curve shows a minimum. Eventually at higher coverages one reaches the characteristic value of the overlayer. The correct physics of this behavior is contained in the model proposed by Gurney¹² in 1935. At low coverage the valence level of the alkali-metal adatom is only partially occupied leading to a large dipole moment which lowers the work function. With increasing coverage the adatom valence-level occupancy increases and hence the work-function lowering goes through a minimum. The general shape of the work-function-change curve is thus reasonably explained.

A fundamental understanding of the work function of clean surfaces and the changes occurring due to adsorption has been provided by the density-functional calculations of Kohn, Lang, Smith, and Ying.^{3,4} Quantitative values have been obtained using the simplified scheme of the jellium model.⁵ The full-potential linearized augmented-plane-waves (FLAPW) method for slabs of real atoms has been applied by Wimmer *et al.*¹⁰ More recently Ning *et al.*⁶ have used a combination of slab and jellium approaches. Whereas the general shape of $\Delta\Phi$ as a function of coverage is quite well reproduced, the critical coverage at which $\Delta\Phi$ goes through a minimum is usually underestimated.

In the present report we present results based on standard jellium-model calculations. A crucial new element, however, is the introduction of a coverage-dependent metal-overlayer distance. At low coverages, where the alkali-metal atom is more or less an ion, we choose the ionic radius to estimate the metal-overlayer distance. At high coverages, when metallization sets in, it is more ap-

propriate to use the atomic radius. At intermediate coverages our results are based on a linear interpolation.

Our motivation for choosing such a model is derived from a recent first-principles total-energy calculation for the Al-Ge system.¹³ The calculation was done for two different coverages and it was concluded that the overlayer metallization was in fact accompanied by overlayer-substrate distance relaxation. More recently experimental evidence for such a distance relaxation has also been presented.¹⁴ Furthermore, Muscat and Batra,¹⁵ using an Anderson model Hamiltonian approach, have also studied non-self-consistently the effect of distance relaxation. Wimmer *et al.*¹⁰ have noted an almost linear dependence of the change in work function with overlayer distance at a fixed coverage. Thus the evidence seems to be rather persuasive to incorporate the overlayer-substrate vertical distance as a parameter in the work-function calculations. This is the subject of the present Brief Report.

In our calculation the substrate is described by the jellium model.³ The alkali-metal adatom is also replaced by a jellium slab of width d with coverage dependence obtained from

$$d(\Theta) = d_{\text{ion}} + (d_{\text{atom}} - d_{\text{ion}})\Theta, \quad (1)$$

where d_{ion} is twice the alkali-metal ionic radius and d_{atom} is the distance between the most compact planes in the bulk alkali metal. The adatom slab is centered at $\frac{1}{2}d(\Theta)$ and the height of the jellium increases according to the increase of Θ . We notice that the model of Lang⁵ is simply obtained by taking $\Theta=1$ in Eq. (1), as the value of d is kept fixed in his model. The results are obtained by solving for the system of two jellium materials (substrate and adsorbate) self-consistently in the local-density approximation (LDA).

Figure 1 shows our typical calculated results for the work function as a function of coverage. The example chosen corresponds to the substrate $r_s=2.07$ a.u. (Al) and with Cs as the overlayer. It is well known that jellium-

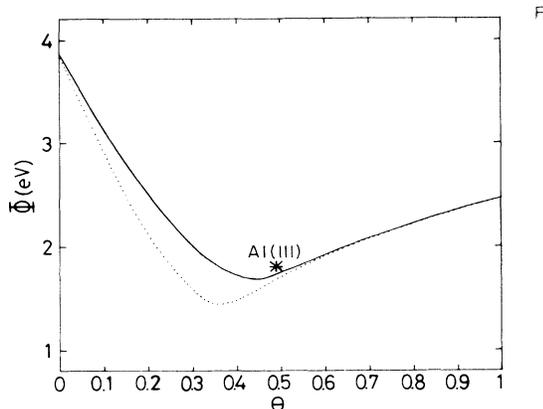


FIG. 1. Aluminum work-function change with cesium adsorption (in units of one monolayer) using the variable-width slab model (solid line) and the fixed-width slab model of Lang (Ref. 5) (dotted line). The recent experimental result (Ref. 16) on Al(111) has been shown by the asterisk. Notice the agreement between the adsorbate relaxation coverage-dependent theory and experiment.

model calculations to not give, in general, the correct absolute value of the clean-substrate work function but for Al the results are close to experimental values. The corresponding results obtained without relaxing the substrate-adsorbate distance are shown by the dotted line. There are three noteworthy differences when d is allowed to vary with coverage: (i) the initial falloff near $\Theta=0$ is more moderate, (ii) the Φ_{\min} value is higher, and (iii) the critical coverage Θ_c at which Φ_{\min} is reached is larger.

The initial reduction of slope noted upon making d a function of Θ can be understood in a qualitative fashion from the following simple argument. If the ionic picture is valid, which is believed to be the case at $\Theta \approx 0$, then

$$\delta\Phi/\delta\Theta \approx d(\Theta)[\delta\mu(\Theta)/\delta\Theta] + \mu(\Theta)[\delta d(\Theta)/\delta\Theta], \quad (2)$$

where μ is some effective charge transfer which decreases with coverage. The first term in the varying-width slab model is thus negative giving the negative slope in Fig. 1. The second term is positive (d increases with Θ and $\mu \geq 0$) and is responsible for reduction of the initial slope if d is allowed to increase with Θ . The presence of the second term of Eq. (2) implies that Φ_{\min} is increased and Θ_c is displaced to higher coverages, in better agreement with experimental data (see Figs. 1 and 2). The precise values of Φ_{\min} and Θ_c are determined by detailed calculations which have been done for all alkali metals deposited on substrates with $r_s = 2.07$ and 3.02 a.u. representative of Al and Ag, respectively. Essentially the results show similar characteristics to those shown in Fig. 1.

In Fig. 2 we have compiled results for critical coverage Θ_c and Φ_{\min} for four different alkali-metal overlayers (Li, Na, K, Cs). The calculated results refer to a substrate with $r_s = 2.07$ a.u. but the experimental data are from several surfaces.^{7,8} It is clear from this figure that when d is allowed to vary with coverage a much better

agreement with experiments is obtained and the trend of Θ_c goes in the same direction as the experimental data.

Finally, in Fig. 3 we show calculated results for the binding energy per adatom ΔE_a as a function of coverage Θ when d is also a function of Θ . The corresponding results when d is independent of Θ are shown by dotted lines. Keeping in mind the limitations of the jellium model, the trend is that the binding energy is

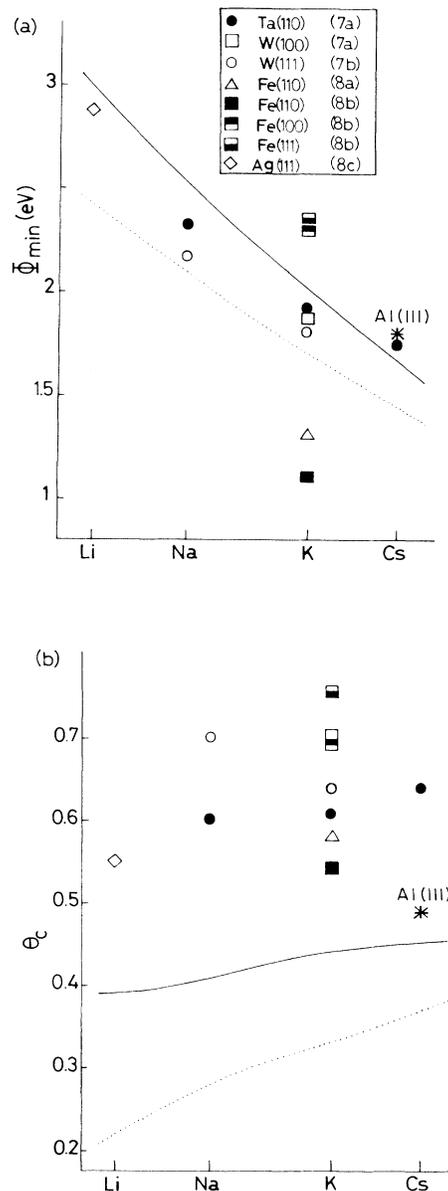


FIG. 2. Minimum work function Φ_{\min} (a) and critical coverage Θ_c (b) for four different alkali-metal overlayers (Li, Na, K, Cs) calculated with the variable-width slab model (solid lines) and the fixed-width slab model (dotted lines). We also show experimental results for different metal substrates and their references [see box in (a)]. Notice that the Φ_{\min} values for Fe(110) are too low. The data for Cs/Al(111) (Ref. 16) have been introduced.

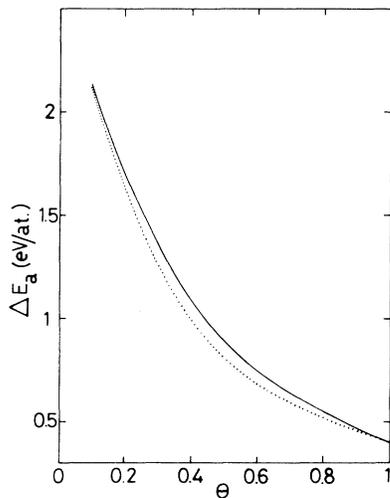


FIG. 3. Binding energy per adatom ΔE_a vs fractional coverage Θ for cesium on aluminum adsorption using the variable-width (solid line) and the fixed-width (dotted line) slab models.

higher when d is permitted to be a linear function of Θ . By relaxing away from the substrate with increasing coverage a stronger metallic bond may be formed with other alkali-metal species and hence higher overall binding energy results.

In conclusion it can be stated that the introduction of coverage-dependent metal-substrate overlayer distance leads to calculated quantities, like the change in work function, the critical coverage at which a minimum in work function occurs, and the minimum value of the work function itself, that are in overall better agreement with experiments. We should notice that the experimental values for Θ_c are still greater than our calculated ones by ≈ 0.15 of a monolayer. However, recent experimental results on work functions of Cesium adsorbed on Al(111) by Hohlfeld, Sunjic, and Horn¹⁶ show values of Φ_{\min} and Θ_c of 1.80 eV and 0.49 in excellent agreement with our calculations of 1.70 eV and 0.45 (see Figs. 1 and 2). That proves that our model is realistic and that the idea of the adsorbate relaxation with coverage has full physical significance. Also preliminary self-consistent calculations¹⁷ for Al surfaces using pseudopotential tend to support our basic idea in this paper. It is hoped that this information will be of value in metal-semiconductor interfaces as well, where the Schottky-barrier formation may take place at a coverage other than $\Theta \approx 0$.

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