Chemisorption on a Model Transition Metal

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The effect of chemisorption on the (100) surface of a model transition metal is investigated using Green's functions coupled with the phase shift technique. A change in the electronic density of states (DOS) is obtained for two different binding sites, the on-site and the bridge-site; strong steric-effects are present. The importance of the substrate DOS for chemisorption is pointed out.

The electronic properties of chemisorbed systems have been the subject of recent studies[1]. In order to understand the complex process of chemisorption, it has been necessary and often desirable to deal with simple models. Using Green's functions coupled with the phase shift technique, Einstein and Schrieffer[2] have studied the adsorption of gas atoms on the (100) surface of tight binding sc crystals. The binding energies were obtained as functions of the filling of the energy band for three binding positions, the on-site, the bridge-site, and the centered four-fold site. More recently, the change in the electronic density of states (DOS), $\Delta\varrho(\varepsilon)$, due to chemisorption on the (100) surface of an s-band sc crystal was investigated by Davenport, Einstein and Schrieffer (DES)[3] and by Einstein[4]. Further, Ho, Cunningham and Weinberg[5] have studied chemisorption of a single adatom on the (100) surface of an s-band bcc metal.

The physical process considered by these authors is the adsorption of light gas atoms (H, O, N, C, etc.) on transition metals. Therefore, it would be more appropriate to use the realistic d-band model for the substrate DOS. It should be noted that the s-band fcc or bcc lattice model[5] is not better than the sc lattice model, and in many ways worse. The aim of the present note is twofold. First, we want to study chemisorption using a more realistic substrate DOS. By comparing with previous results[4] of chemisorption on a single-peaked (100) surface of an sc metal, we will investigate the sensitivity of $\Delta\varrho(\varepsilon)$ to the substrate DOS. Second, we investigate the sensitivity of $\Delta\varrho(\varepsilon)$ to the binding site configuration.

To reproduce the gross features of the DOS for low index surface planes of transition metals[6] we introduce a minimum at the center of the band bounded by two prominent peaks on each side within the band. Recent calculations[7] have indicated that, for the (100) surface of tungsten, the two-peaked structure is more appropriate than the single-peaked one. Now, let us recall the formalism of Kalkstein and Soven[8]; the DOS for the sc (100) surface, $\varrho_s(\varepsilon)$, is calculated as

$$\varrho_s(\varepsilon) = \frac{-1}{\pi t} \operatorname{Im} \int_{-\pi}^{\pi} \frac{1}{2\pi} \mathrm{d}k_x \int_{-\pi}^{\pi} \frac{1}{2\pi} \mathrm{d}k_y \, [(\alpha^2-1)^{1/2} + \alpha - E_s]^{-1} , \tag{1}$$

where $\alpha = \varepsilon/2t - \cos k_x - \cos k_y$, and E_s refers to the surface potential. Furthermore, t is the hopping matrix element between nearest-neighbour lattice sites. The integral over k_x and k_y can be converted into an integral over two-dimensional DOS[9], $\varrho_2(\varepsilon)$. For the present purpose, we introduce the following form for $\varrho_2(\varepsilon)$:

$$\varrho_2(\varepsilon) = \begin{cases} p/t & -4t < \varepsilon \leqq -2rt , \\ \mathrm{p}/t & -2rt < \varepsilon \leqq 2rt , \\ q/t & 2rt < \varepsilon \leqq 4t , \\ 0 & \text{otherwise} . \end{cases} \tag{2}$$

Here, r and $s \equiv p/q$ are parameters which are chosen to approximate the metal bulk DOS. In Fig. 1 we show $\pi \cdot \varrho_s(\varepsilon)$, π times the surface DOS or imaginary part of the surface Green's function $G_s(\varepsilon)$, for $r = 1$ and $s = 6$. The Green's function $G_B(\varepsilon)$ appropriate for the bridge-site is a sum of two surface Green's functions[2, 8], and its imaginary part is plotted in Fig. 1c; one notices that this curve is strongly skewed downward. This is due to the fact that $\Delta\varrho(\varepsilon)$ depends strongly on the binding site configuration, as will be seen in Figure 2. Using $\varrho_s(\varepsilon)$ thus obtained, we have calculated $\Delta\varrho(\varepsilon)$ for the two cases that the adatom is bound to a single substrate atom in the onsite configuration and that it is bound to two substrate atoms in the bridge-site configuration. In principle, $\Delta\varrho(\varepsilon)$ can be related to the results of photo- or field emission measurements.

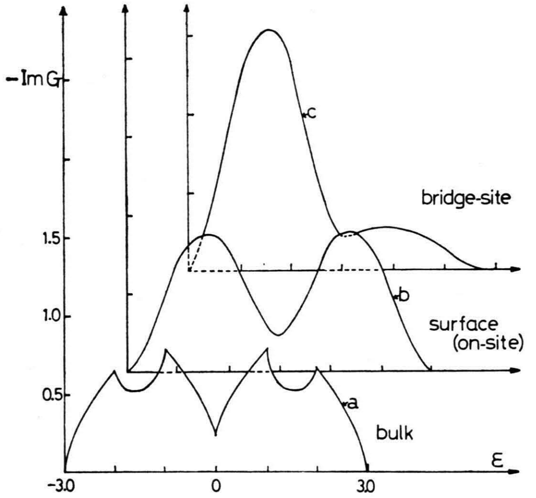

Fig. 1. Imaginary parts of the Green's functions (negative) appropriate for the bulk (a) and for on-side (b) and bridge-site (c) adsorption. Curve b (a) corresponds to π times the surface (bulk) DOS. Curve c indicates the downward shift (hybridization skewing) in energy of the symmetrized surface Wannier states.

For the adatom, we assume a single energy level of ε_a coupled to the surface with an interaction strength V_a. To obtain $\Delta\varrho(\varepsilon)$, we consider the adatom-substrate binding from the standpoint of the Anderson model and follow the Green's function method coupled with the phase shift technique[2-5]. This phase shift η is the negative of the argument of the complex determinant of the matrix $\mathbf{I}-\mathbf{VG}$, where $\mathbf{I}$ and $\mathbf{V}$ are the unit matrix and the perturbation matrix, respectively:

$$\eta = -\arg\det(\mathbf{I}-\mathbf{V}\,\mathbf{G})\,. \qquad (3)$$

$\mathbf{G}$ is the Green's function matrix appropriate for the adatom $G_a(\varepsilon)$ and substrate $[G_{ij}(\varepsilon)^{2,8}]$; $G_a(\varepsilon) = (\varepsilon-\varepsilon_a+i\,0^+)^{-1}$. Once the phase shift function is known, the change in the total DOS $\Delta\varrho_T(\varepsilon)$ is given by a simple differentiation,

$$\Delta\varrho_T(\varepsilon) = (1/\pi)\,\mathrm{d}\eta/\mathrm{d}\varepsilon\,. \qquad (4)$$

Here, it must be noted that the $\Delta\varrho_T(\varepsilon)$ given by Eq. (4) is the difference in the DOS between the adatom-substrate system and that of the clean semi-infinite crystal plus the free atom. However, following DES, we plot the difference in the DOS between the adatom-substrate system and the clean substrate, i. e., $\Delta\varrho(\varepsilon) = \Delta\varrho_T(\varepsilon) + \delta(\varepsilon-\varepsilon_a)$.

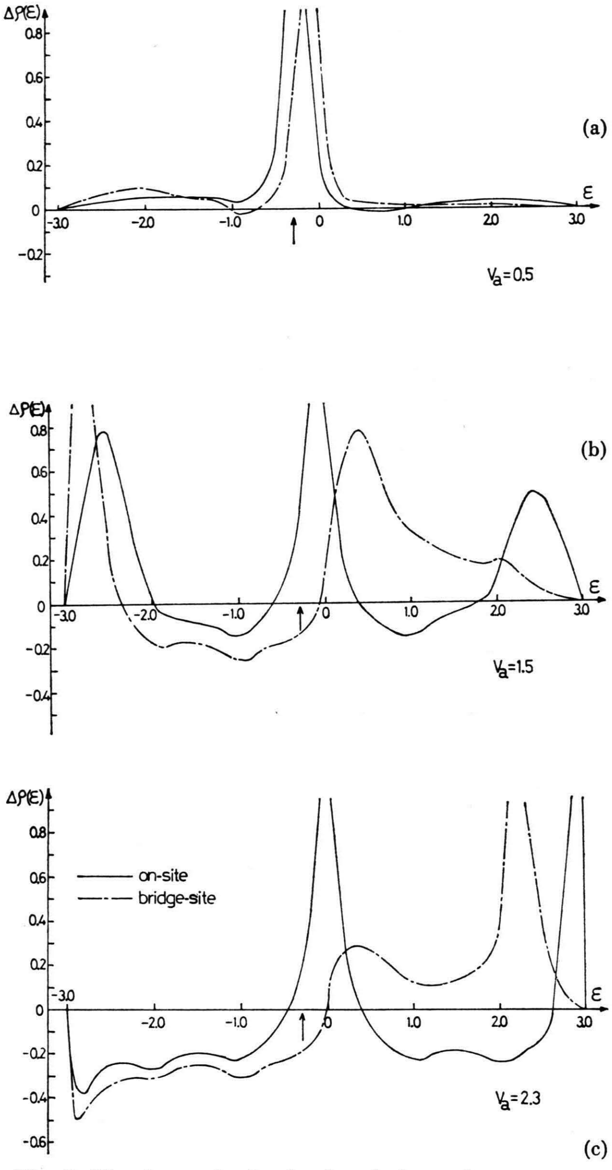

Fig. 2. The change in the density of electronic states as a function of energy due to chemisorption of a single atom of energy $\varepsilon_a = -0.3$ on the (100) surface of a model transition metal in two different binding sites; the solid (dot-dashed) lines indicate $\Delta\varrho(\varepsilon)$ for on (bridge)-site adsorption. (a) $V_a=0.5$, (b) $V_a=1.5$, (c) $V_a=2.3$.

Figure 2 shows $\Delta\varrho(\varepsilon)$ for the two binding cases, where all energies are expressed in units of $2t$ (the bandwidth is 6). We have chosen the zero of energy to be at the middle of the band and the adatom energy level ε_a to be -0.3 (this choice of ε_a is useful when comparing our results with those of Ref.[4]) as shown by the arrows. For the on-site adsorption, electron-hole symmetry gives self-consistency automatically for a half-filled band (e. g.

tungsten 5d band) and $\varepsilon_a = 0$. We therefore keep ε_a near the band center. The binding strength is chosen to be $V_a = 0.5$, 1.5, and 2.3 for the on-site adsorption. For the bridge-site adsorption, the adatom is assumed to interact directly with the two substrate atoms with a total strength of V_a; the hopping integral between adatom and each substrate atom is $V_a/\sqrt{2}$[10]. For small values of V_a (≈ 0.5), the adatom level is a single broadened resonance for the two adsorption sites.

For stronger binding ($V_a \approx 1.5$), however, the behaviour of the on-site adsorption differs significantly from that of the bridge-site adsorption; for the on-site adsorption one observers a distinct resonance near the band center in addition to the bonding and antibonding resonances. The appearance of the resonance near the band center is due to the minimum in the model surface DOS. If we use a single peak substrate DOS this resonance is washed out completely (see Reference [4]). This corresponds to the previous calculation by Lyo and Gomer[7], while the antiresonances are not observed in our calculations. Thus the results obtained are very sensitive to the form used for the substrate DOS. It is interesting to note that the gross feature of the on-site result in Fig. 2 b can be compared favorably with the observed photoemission spectra for the H-W(100) chemisorbed system[11]. For the bridge-site adsorption, the behavior for the region $0 \leqq \varepsilon \leqq \varepsilon_{\text{top}}$ is very different from that of the on-site adsorption; the separation between the anti-bonding resonance and the resonance near the band center is unclear and the depletion region is not observed.

Further, as V_a increases ($V_a \gtrsim 2.0$), the bonding and antibonding resonances move apart in energy and eventually become split-off states below and above the band, while the position of the resonance near the band center remains almost unchanged. The positions of the split-off states are presented in Table 1, with the corresponding values for the single peaked (100) surface of a sc metal. The steric-effects for the present two peaked substrate are more pronounced than those for the single peaked substrate.

Table 1. Energies of the split-off states due to on-site, ε_s^0, and the bridge-site, ε_s^B, adsorption for various values of the adatom energy, ε_a, and the binding strength V_a. Shown for comparison in parentheses are the corresponding values for the single peaked (100) surface of an sc metal.

ε_a	V_a	ε_s^0	ε_s^B
−0.3	2.5	−3.139(——)	−3.450(−3.166)
	3.0	−3.538(−3.384)	−3.893(−3.600)
−1.0	2.0	−3.017(——)	−3.272(−3.027)
	2.5	−3.404(−3.262)	−3.716(−3.452)
	3.0	−3.840(−3.714)	−4.183(−3.914)
−2.0	1.5	−3.076(——)	−3.275(−3.086)
	2.0	−3.480(−3.375)	−3.728(−3.520)
	2.5	−3.916(−3.819)	−4.197(−3.978)
	3.0	−4.367(−4.278)	−4.675(−4.447)

To summarize: We have studied gas atom adsorption on the (100) surface of a model transition metal using an improved substrate DOS and have demonstrated the importance of the substrate DOS in the study of chemisorption. To our knowledge, this is the first time that a two peaked substrate DOS, showing qualitative features * of the surface DOS, has been used to study chemisorption [calculations of $\Delta\varrho(\varepsilon)$]. The fact that the present bridge-site results differ from the on-site results is significant. We expect that strong steric-effects are also present for a realistic d-band substrate. This implies that it may be possible to predict the adsorption site by carefully analyzing the spectroscopic data (UPS, INS, SEE[12], etc.) of chemisorbed systems. Finally, we note that the simple model considered here will also be useful for the study of chemisorption on magnetic transition metals[9, 13].

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* Drastic modification of the Van Hove singularity characteristic of the bulk crystalline DOS and a decrease of the r.m.s. bandwidth (see Figure 1). This decrease is even more pronounced at an adatom.

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