

Changes in Density of States Caused by Chemisorption: Monolayer of Adatoms on a Model Transition Metal

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The effect of chemisorption of a monolayer of atoms on the (001) surface of a model transition metal is investigated using the Green's function formalism and the phase shift technique. The electronic structure of the surface is obtained by the application of the Kalkstein and Soven method. For comparison, both a single and two peaked model of the surface density of states (DOS) are used. The change in the DOS upon chemisorption as well as the adatom DOS are calculated within the Newns-Anderson model for chemisorption. It is shown that the two peaked substrate DOS model can qualitatively account for the strong coverage dependence of the photoemission spectra observed in the H/W(100) system. In addition, it is shown that the direct interaction between the adatoms plays an important role in the monolayer chemisorption.

1. Introduction

There has been a considerable amount of work recently dealing with the light gas atom chemisorption on transition metal surfaces [1]. In order to develop a qualitative picture of the chemisorption process, simple model calculations have been very useful [2]. Using the Green's functions coupled with the phase shift technique, several authors [3, 4, 5] have investigated the change in the density of electronic states (DOS) due to the interaction of the adatom with the clean substrate. This approach has further been applied to the problem of the adatom-adatom interaction. Einstein and Schrieffer (ES) have studied the pairwise interaction energy of the adatoms as a function of the separation between the two adatoms and of the Fermi energy [6]. Burke [7] has extended the ES theory and studied the pair interactions between transition metal atoms adsorbed on the surface of a transition metal.

Other simple methods have also been used to study the chemisorption behaviour. Cyrot-Lackmann et al. [8] have used the moment method to calculate the local DOS for the adatom on the (001) surface of the simple cubic (sc) crystal in three different adsorption geometries. Haydock and Kelly [9], using a similar method, have studied the adatom DOS for (001) surface of a body centered cubic metal. Furthermore, Morán-López, Kerker and Bennemann [10] have calculated the local DOS

for the adatom on a disordered alloy surface, using the continued fraction technique.

Most of the previous calculations, however, have been concerned with the adsorption of a single gas atom on various crystal surfaces: Only a few investigations have been made on the problem of the adatom-adatom interaction. Therefore, it is desirable to investigate the integrated effect of many distant adatoms for the chemisorption system with monolayer or near monolayer coverages.

On the other hand, it is of experimental concern to investigate the change with coverage of the charge distribution, the heat of adsorption and the state density of the adatom. Thus it is very useful to carry out a theoretical calculation on the chemisorption behaviour of systems with monolayer or near monolayer coverages. At higher coverages, the effect of many distant adatoms becomes more important since the adatoms can interact with each other in two ways: In the following, we investigate both the direct and indirect (RKKY type) interactions between the adatoms. Here, it is noted that to describe the properties of the chemisorbed adlayers, treatments based only on pairwise interactions may not be sufficient.

The purpose of the present study is twofold. First, we investigate the above mentioned two interaction effects using a simple model calculation. Numerical calculations are performed for the (001) surface of an sc tightbinding metal using the Newns-Anderson model of chemisorption. This particular system has been chosen so that a direct comparison can be made with the results of Ref. [3],

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wherein a single adatom under the same assumptions was chemisorbed on the same surface.

Second, we study the effect of the form of the substrate DOS on the chemisorption behaviour (change in the DOS during chemisorption) for a monolayer coverage. In the present investigation, two models of the substrate DOS are used: One is the usual single peaked structure of the *sc* tight-binding metal and the other is the two peaked one introduced in Ref. [5] by the present author. As will be shown later, the effect of the form of the substrate DOS on the chemisorption behaviour is very large for the monolayer coverage and important in interpreting the photoemission spectra of the chemisorbed systems.

The format of the present paper is as follows. In Sec. 2, we present the Green's function theory for chemisorption of a monolayer of adatoms on a tight-binding substrate. Section 3 contains the results of the calculations and discussions. Finally, in Sec. 4, we summarize the results obtained and compare them with the available experimental results.

2. Green's Function Theory for Monolayer Chemisorption

In order to derive the Green's functions appropriate for the adsorbate and substrate of the chemisorbed (coupled) system, we need to know first the corresponding Green's functions for the uncoupled system. For simplicity we consider the (001) surface of an *sc* tight-binding metal and assume the commensurate adsorbate layer, i.e. a two-dimensional (2D) square lattice with the unit lattice constant. The Green's function for the uncoupled adatoms having a single nondegenerate energy level E_a is given by

$$G_{aa}^0(E, k_{\parallel}) = [E - E_a - 2t_a \cdot (\cos k_x + \cos k_y) + i0]^{-1}, \quad (1)$$

where E is the energy, t_a the direct hopping integral between nearest-neighbour adatoms and k_{\parallel} (k_x and k_y) the wave vector parallel to the surface plane. The direct interaction term in Eq. (1) is usually omitted in the literature. The direct interaction effect is expected to be as large as the indirect one for adatoms having a core size comparable to that of the substrate atom. Thus the inclusion of the direct interaction effect is much more important

for transition metal or halogen adsorbates than the hydrogen adsorbate.

The unperturbed Green's function for the semi-infinite clean substrate crystal can be obtained, in a mixed Bloch-Wannier representation, from the previous work of Kalkstein and Soven [11]. For the first layer (hereafter referred to as 0-th layer, $-1, -2, \dots$ denoting the interior planes) of the (001) surface of the *sc* tight-binding metal, the uncoupled substrate Green's function is given by

$$G_{ss}^0(E, k_{\parallel}) \equiv G_{ss}^0(E, k_{\parallel}; 0, 0) = -s/|t_m|, \quad (2)$$

where

$$s = \begin{cases} \mu - \text{sgn}(\mu)(\mu^2 - 1)^{1/2} & |\mu| > 1, \\ \mu + i(1 - \mu^2)^{1/2} & |\mu| < 1, \end{cases} \quad (3a)$$

$$|\mu| < 1, \quad (3b)$$

and

$$\mu = (E_0 - E)/2|t_m| - \cos k_x - \cos k_y. \quad (4)$$

Here, m and n in $G_{ss}^0(E, k_{\parallel}; m, n)$ label the layers parallel to the surface. t_m is the hopping integral between the nearest-neighbour substrate atoms and E_0 denotes the energy level of the bulk atom. In a mixed Bloch-Wannier representation, a knowledge of the Green's function gives us local DOS for a given value of k_{\parallel} : A numerical integration over k_{\parallel} would give us the atomic local DOS.

In order to derive the chemisorbed (coupled) Green's function, it is convenient to express the uncoupled (unperturbed) Green's functions in a matrix form:

$$G^0(E, k_{\parallel}) = \begin{pmatrix} G_{ss}^0(E, k_{\parallel}) & 0 \\ 0 & G_{aa}^0(E, k_{\parallel}) \end{pmatrix}. \quad (5)$$

The chemisorbed system is formed by coupling the uncoupled system via the adsorbate-substrate hopping interaction V_{as} (or V_{sa}). This interaction generates a flow of changes between the substrate and adsorbate atoms and thus shifts their orbital energies. These terms are treated as the perturbing potential V and expressed in a matrix form

$$V = \begin{pmatrix} \delta V_s & V_{sa} \\ V_{as} & \delta V_a \end{pmatrix}, \quad (6)$$

where V_{sa} ($|V_{sa}| = |V_{as}|$) is the on-site (The adatom sits directly over the substrate atom and is bonded only to it.) binding strength and δV_a and δV_s represent the changes in the orbital energies of the adsorbate atom and the substrate atom beneath it, respectively. The magnitudes of these shifts in the

orbital energies can be determined to satisfy the Fiedel sum rule. In Eq. (6), it is assumed that the perturbation δV_s is localized completely in the surface plane ($n=0$) of the clean substrate crystal. Under the assumption given by Eq. (6), the chemisorbed Green's function is obtained by solving the matrix-form Dyson equation:

$$G = G^0 + G^0 V G. \quad (7)$$

The explicit expression of the chemisorbed Green's function is written, in a mixed Bloch-Wannier representation, as follows:

$$\begin{aligned} G(E, k_{\parallel}; n, n) &= G_{aa}^0(E, k_{\parallel}) + G_{aa}^0(E, k_{\parallel}) \\ &\quad \cdot [\delta V_a \{1 - G_{ss}^0(E, k_{\parallel}; 0, 0) \cdot \delta V_s\} \\ &\quad + V_{as} \cdot G_{ss}^0(E, k_{\parallel}; 0, 0) \cdot V_{sa}] \\ &\quad \cdot G_{aa}^0(E, k_{\parallel}) / \Delta(E, k_{\parallel}), \\ &\quad \text{for } n = 1 \text{ (adsorbate layer),} \end{aligned} \quad (8)$$

$$\begin{aligned} G(E, k_{\parallel}; n, n) &= G_{ss}^0(E, k_{\parallel}; n, n) \\ &\quad + G_{ss}^0(E, k_{\parallel}; n, 0) \\ &\quad \cdot [\delta V_s \{1 - G_{aa}^0(E, k_{\parallel}) \cdot \delta V_a\} \\ &\quad + V_{sa} \cdot G_{aa}^0(E, k_{\parallel}) \cdot V_{as}] \\ &\quad \cdot G_{ss}^0(E, k_{\parallel}; 0, n) / \Delta(E, k_{\parallel}), \\ &\quad \text{for } n = 0, -1, -2, \dots \\ &\quad \text{(substrate layers),} \end{aligned} \quad (9)$$

where

$$\begin{aligned} \Delta(E, k_{\parallel}) &= \{1 - \delta V_s G_{ss}^0(E, k_{\parallel})\} \\ &\quad \cdot \{1 - \delta V_a G_{aa}^0(E, k_{\parallel})\} \\ &\quad - G_{ss}^0(E, k_{\parallel}) \cdot V_{sa} G_{aa}^0(E, k_{\parallel}) V_{as}. \end{aligned} \quad (10)$$

The local DOS of the chemisorbed system can be calculated by the usual formula

$$\rho_n(E) = - (1/\pi N_{\parallel}) \sum_{k_{\parallel}} \text{Im } G(E, k_{\parallel}; n, n), \quad (11)$$

where N_{\parallel} is the total number of atoms in each plane and the sum is over the surface Brillouin Zone (SBZ).

In order to find the change in the DOS due to chemisorption, it is convenient to introduce the k_{\parallel} dependent phase shift function $\eta(E, k_{\parallel})$ in the SBZ. This phase shift function is related to the Fredholm determinant $\Delta(E, k_{\parallel})$ as

$$\begin{aligned} \eta(E, k_{\parallel}) &= - \text{Arg det} \| I - G^0 V \| \\ &= - \text{Arg } \Delta(E, k_{\parallel}), \end{aligned} \quad (12)$$

where I is the identity matrix. For the adsorbate atoms with one valency, the Friedel sum rule is

expressed in terms of the total phase shift function as

$$\eta(E_f) = -\pi/2, \quad (13)$$

where E_f is the Fermi energy and the total phase shift function is given by

$$\begin{aligned} \eta(E) &= (1/N_{\parallel}) \sum_{k_{\parallel}} \{ \eta(E, k_{\parallel}) \\ &\quad - \pi \theta(E_a + 2 t_a (\cos k_x + \cos k_y) - E) \}. \end{aligned} \quad (14)$$

Here, $\theta(E)$ is the Heaviside theta function. Once the total phase shift function $\eta(E)$ is known, the change in the DOS, $\Delta \rho(E)$, is given by

$$\Delta \rho(E) = (1/\pi) \partial \eta(E) / \partial E. \quad (15)$$

In Eq. (14), the theta function is added so that $\Delta \rho(E)$ directly gives the difference in the DOS between the chemisorbed system and the clean substrate. $\Delta \rho(E)$ in Eq. (15) is the quantity of experimental interest since photoemission difference spectra are obtained by subtraction of the clean substrate spectrum from the chemisorbed system spectrum. The magnitudes of the diagonal matrix elements of V , δV_s and δV_a , are in principle obtained from Eq. (13) under appropriate assumptions such as $\delta V_s = -\delta V_a$.

3. Calculation Results and Discussion

In this section we present numerical results of the adsorbate DOS, $\rho_a(E)$, and the change in the DOS due to chemisorption, $\Delta \rho(E)$, using the method described in Section 2. The computation is performed for two different substrate DOS models; the single peaked DOS model and the two peaked one introduced in Ref. [5] by the present author.

3.1. Single Peaked Model for the Substrate Density of States

In order to perform the numerical calculations on the chemisorption behaviour, we need to adopt a specific form for the substrate DOS. Recently, there have been a number of theoretical calculations of the substrate DOS for sc (or bcc) s-band metals, transition metals [12] and especially for tungsten or molybdenum [13]. However, detailed information on the substrate DOS of the specific transition metals is still lacking. In view of this we attempt to use two different models for the substrate DOS showing only the gross feature of the substrate DOS. First, we perform the numerical calculations

using a single peaked substrate DOS model, i.e. the KS model for the s-band tight-binding metal surface. It is noted that the tight-binding model gives a better idea of the narrow-band properties of transition metals than electron-gas models.

In order to discuss the general behaviour of $\rho_a(E)$ and $\Delta\rho(E)$, it is convenient to begin with the numerical calculation of the localized electronic states outside the energy band. This is mainly due to the fact that the existence of localized states can alter the chemisorption behaviour considerably. For the single adatom chemisorption, the localized states exist as delta functions, i.e. the split-off states from the band edge. For the monolayer chemisorption, however, the behaviour of the localized states is quite different; the delta function like localized states are broadened by the interaction between adatoms and the localized states are wave vector k_{\parallel} dependent. Thus the localized states for the monolayer chemisorption are not the split-off states in the energy spectra as shown later in Figs. 3 and 4. The localized states exist if there are solutions of the following equation:

$$\begin{aligned} & \{1 - \delta V_a G_{aa}^0(E, k_{\parallel})\} \{1 - \delta V_s G_{ss}^0(E, k_{\parallel})\} \\ & - V_{sa} G_{aa}^0(E, k_{\parallel}) V_{as} G_{ss}^0(E, k_{\parallel}) = 0 \quad (16) \end{aligned}$$

for values of E which lie outside the bands when plotted in k_{\parallel} space.

In Fig. 1, we show the positions of the localized states with respect to the substrate energy band along the (10) and (11) directions of the SBZ. As shown in Fig. 1, localized states exist both above and below the energy band. For the present case, the inclusion of self-consistency ($\delta V_s = -\delta V_a \neq 0$) causes minor changes in the positions of the localized states. The values of the model parameters are shown in the caption in units of $|2t_m|$. The energy unit of our calculation is everywhere $|2t_m|$. To relate our model to actual crystals, we assume that $|2t_m| \sim 1.6$ eV. This gives a substrate band-width of 10 eV, simulating the tungsten d-band.

The position of the adsorbate energy level E_a ($= -0.3$) in the band is taken for the following two reasons:

(1) This choice of E_a facilitates a direct comparison of the present results with those for the single adatom chemisorption of Reference [3].

(2) From the self-consistent calculation [14] of the adatom (single) charge, it is known that the positions of E_a for gas atom adsorbates such as

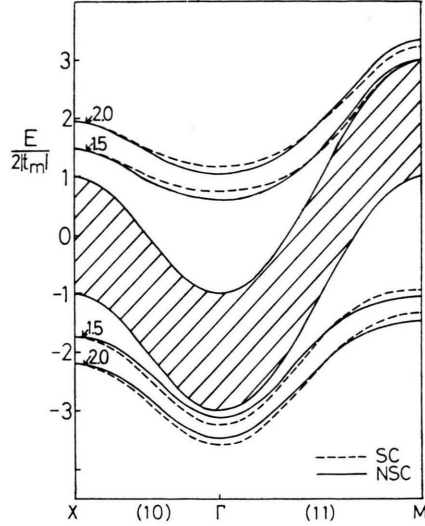


Fig. 1. The positions of the localized states for monolayer chemisorption (on-site) in relation to the energy band along the (10) and the (11) directions of the surface Brillouin zone. All energies are expressed in units of $|2t_m|$, where t_m is the nearest-neighbour hopping integral of the bulk metal. The magnitude of the adsorbate-substrate coupling strength $|V_{as}|$ is shown in the figure (1.5 and 2.0) and the adsorbate energy level E_a is -0.3 . The dashed curves show the effect of self-consistency ($\delta V_s = -\delta V_a \neq 0$).

hydrogen or halogens on W(100) substrate are slightly below the band center.

The magnitude of the adsorbate-substrate coupling strength $|V_{sa}|$ is often estimated from the experimental binding energy. However, as the binding energy is not a purely electronic property, it is difficult to obtain the magnitude of the coupling strength accurately for specific chemisorption systems. Therefore, it is desirable to perform the numerical calculations for a wide variety of $|V_{as}|$: In the present investigation, the magnitude of the coupling strength is taken as $|V_{as}| = 1.5 \sim 2.5$ (in units of $|2t_m|$).

In Fig. 2(a and b), we present the changes in the DOS due to monolayer chemisorption for the parameters $E_a = -0.3$, $|V_{as}| = 1.5$ (a) and 2.0 (b). The solid curves in Fig. 2(a and b) represent the non-self-consistent results of $\Delta\rho(E)$ and can be compared with those for the single adatom chemisorption of Reference [3]. One notices that the general behaviour of $\Delta\rho(E)$ for the monolayer coverage is similar to that for the single adatom case of Refs. [3] and [4]; there are two prominent peaks corresponding to a bonding and an anti-

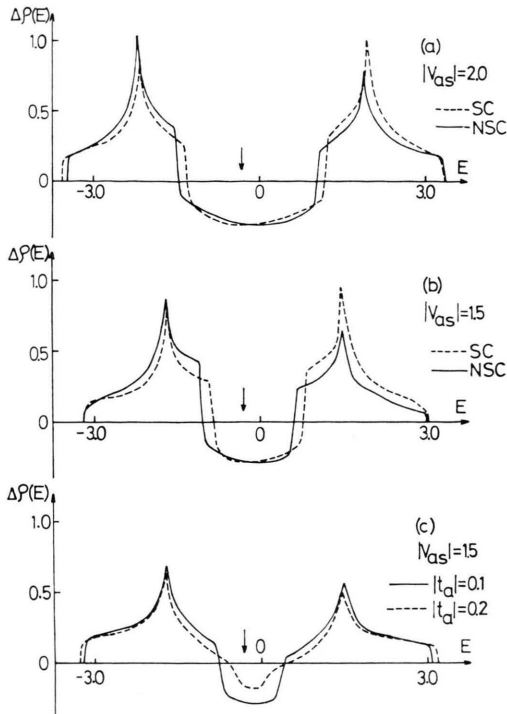


Fig. 2. The change in the density of states per adatom on the (001) surface of a simple cubic tight-binding metal (single peaked DOS model) for monolayer chemisorption. The arrow points to the adatom energy level; $E_a = -0.3$. $|V_{as}| = 1.5$ (b) and 2.0 (a). In Fig. (a) and (b), the solid and dashed curves represent the non-self-consistent and the self-consistent results, respectively. Figure (c) shows the effect of the direct interaction between adatoms (non-self-consistent results).

bonding resonances and a depletion region near the band center. However, there are some differences between the single adatom and the monolayer chemisorption. For the monolayer coverage, the resonance peaks are strongly skewed while the resonances for the single adatom chemisorption are nearly symmetric (see Refs. [3], [4], [5]). This comes from the fact that the localized states are wave vector k_{\parallel} dependent for the monolayer coverage. Such a characteristic is observed in the photoemission experiments [15] for the H/W(100) system.

Using the single peaked DOS model for the substrate, we have also investigated the effects of the direct interaction between the adatoms and the self-consistency on the chemisorption behaviour. As shown in Fig. 2(a and b), the effects of the self-consistency on the behaviour of $\Delta\rho(E)$ are rather small as far as the resonance peaks are concerned. However, the effects of the direct interaction

between the adatoms on the chemisorption behaviour are larger than expected: In general, it has been believed that the effect of the direct interaction is simply to broaden the adatom energy level and is thus of little importance. These ideas are in fact incorrect as explained below. One can observe in Fig. 2c that, as the magnitude of the direct interaction parameter $|t_a|$ increases, the depletion region near the band center decreases rapidly. Since the depletion region in the photoemission difference spectra is as important as the resonance peaks, the effect of the direct interaction has to be included in the calculation of the chemisorbed system with tightly packed overlayers. However, it must be noted that the importance of the direct interaction effect is closely related to the core size of the adatom relative to that of the substrate atom. In this respect, the direct interaction effect may be much more pronounced for halogen (the core radius of halogens is much larger than that of the transition metal atom) or transition metal adsorbates than hydrogen adsorbate.

3.2. Two Peaked Model for the Substrate Density of States

In the previous subsection 3.1, we have studied the general behaviour of monolayer chemisorption using the single peaked substrate DOS model. In this subsection we investigate the coverage dependence of the chemisorption behaviour using a substrate DOS model which has two peaks with a minimum in the region of the band center. The choice of this substrate DOS model is based on the following reasons:

(1) It is because of the low DOS near the Fermi level that we are able to see a distinct peak near the Fermi level in the photoemission difference spectra of the chemisorbed system such as H/W(100) for low coverage [15].

(2) Recent theoretical calculations [13] indicate that, for tungsten (or molybdenum), the two peak structure is the more appropriate. The qualitative agreement between the chemisorption calculation for the single adatom case [5] and the peaks observed in photoemission spectra [15] indicates that this is indeed the case.

For the above mentioned reasons, it is of great interest to investigate the coverage dependence of the chemisorption behaviour using the two peaked

substrate DOS model. For this purpose, it is convenient to convert the integral over k_{\parallel} (k_x and k_y) appearing in Eqs. (11) and (14) into an integral over two-dimensional DOS $\rho_2(E)$ [16]. We introduce, as in Refs. [5] and [14], the following form for $\rho_2(E)$:

$$\rho_2(E) = \begin{cases} v/|t_m| & -4|t_m| < E \leq -2r|t_m| \\ & \text{and } 2r|t_m| < E \leq 4|t_m|, \\ u/|t_m| & -2r|t_m| < E \leq 2r|t_m|, \\ 0 & \text{otherwise.} \end{cases} \quad (17)$$

Here, r and $s \equiv v/u$ are parameters which are chosen to approximate the bulk metal DOS. The local DOS curves for the (001) surface and the bulk atoms have already been shown for $r=1$ and $s=6$ in Reference [5].

In Figs. 3 and 4, we present the changes in the DOS due to monolayer chemisorption on the (001) surface of the model transition metal mentioned

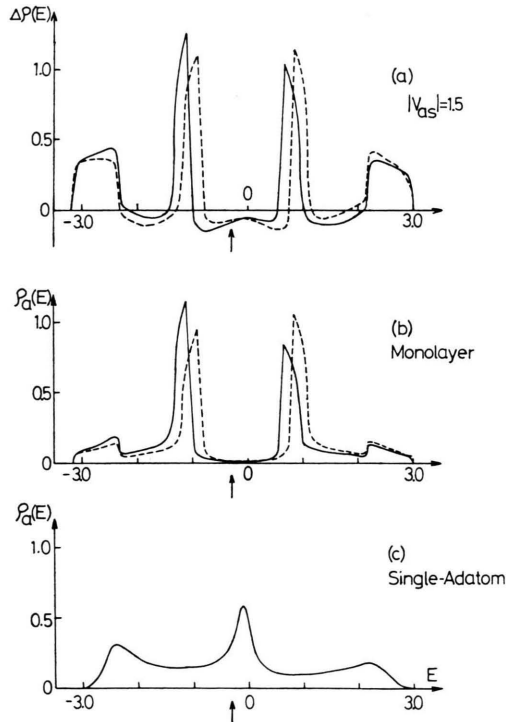


Fig. 3. (a) The change in the density of states per adatom on the (001) surface of the model transition metal (two peaked DOS model) for the monolayer chemisorption. $|V_{as}| = 1.5$ and $E_a = -0.3$. The dashed curve shows the effect of self-consistency. (b) Local density of states of the adatom for monolayer chemisorption. The model parameters are the same as in (a). The dashed curve shows the effect of self-consistency. (c) Local density of states of the adatom for single adatom chemisorption.

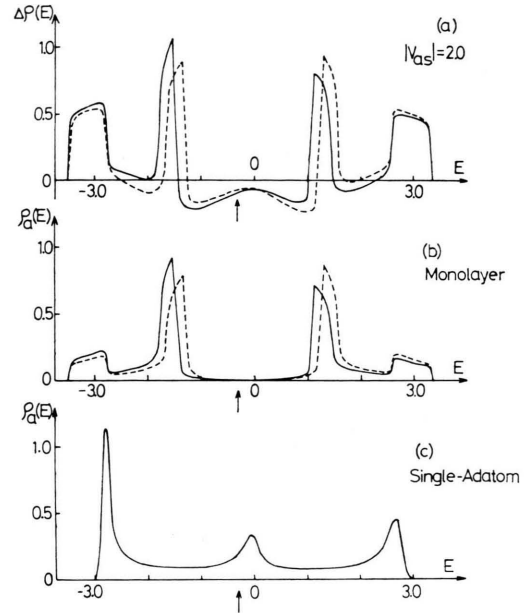


Fig. 4. The change in the density of states due to monolayer chemisorption and the local DOS of the adatom for $|V_{as}| = 2.0$ and $E_a = -0.3$. The substrate DOS model and notations are identical to Figure 3. Note that the general feature of $\rho_a(E)$ for the monolayer coverage is relatively insensitive to variations of $|V_{as}|$, in contrast to the single adatom case (see also Figure 3).

above, with parameters $E_a = -0.3$, $|V_{as}| = 1.5$ and 2.0. The familiar bonding and antibonding resonance peaks are seen near the bottom ($E = -3.0$) and the top ($E = 3.0$) of the substrate band, respectively for both cases. Note that the resonance peak near the band center in the single adatom chemisorption [Fig. 3(c) and Fig. 4(c)] splits into two peaks for the monolayer coverage: The separation between these two resonance peaks increases as the magnitude of the coupling strength $|V_{as}|$ increases. This splitting of the resonance peak results from the indirect interaction between the adatoms (effects of the long range order of adsorbate atoms) and drastically alters the chemisorption behaviour. In this respect, there might be a risk with the cluster model of losing some of the important features in the adsorbate DOS. The dramatic change in the chemisorption behaviour with coverage is in fact seen in the photoemission spectra [15] for the H/W(100) system, as shown in Figure 5. One can see that the overall chemisorption behaviour obtained by the model calculation is in accordance with the experimental results [15, 17].

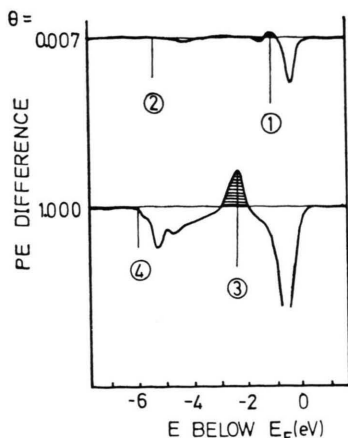


Fig. 5. Photoemission difference spectra for hydrogen chemisorption on W(100). θ gives the fractional coverage corresponding to the difference spectra. Photon energy, 10.2 eV. For the coverage $\theta = 0.007$, two adsorbate levels (marked 1 and 2) are observed at 1.1 and 5.4 eV below the Fermi level. For $\theta = 1.0$, the adsorbate level (marked 3) is observed at the energy of about 2 eV below the Fermi level. (From Feuerbacher and Fitton, Ref. [15]). Recently, the adsorbate energy levels have been found at energies of about 2, 6 (marked 4), and 12 eV below the Fermi level for a hydrogen (1×1) monolayer adsorbed on W(100) by angle-resolved photoemission (Ref. [17]).

The present numerical calculations are also performed with self-consistency. In general, the effect of the self-consistency on the chemisorption behaviour is small. However, it is worth pointing out that the self-consistency effect is much more pronounced for the resonance peaks near the band center than the bonding or anti-bonding resonance peaks.

4. Conclusions

We have presented a simple model calculation of the adatom DOS as well as the change in the DOS due to the chemisorption of a monolayer of atoms on the (001) surface of a tight-binding metal. The calculations have been performed both with and without self-consistency. In addition, the effects of the direct interaction between adatoms on the chemisorption behaviour have been investigated,

using the sc tight-binding substrate model (single peaked DOS model). We have found that the direct interaction effects on the chemisorption behaviour are larger than expected. In general, it has been believed that the direct interaction effect is simply to broaden the adatom energy level and of little importance. However, we have shown explicitly that for a chemisorption system with halogen or transition metal atom adsorbates, these ideas are not correct: The direct interaction effect is closely related to the depletion region near the band center and of great importance.

The present work has also shown that the results of the chemisorption behaviour are very sensitive to the form of the substrate DOS. For the single peaked DOS model, all the structure in the region of the Fermi level is washed out. In order to account qualitatively for the coverage dependence of the chemisorption behaviour for a system such as H/W(100), it is required at least to use the two peaked DOS model for the substrate. In this respect, the chemisorption calculation based on the single peaked DOS model [18] is less informative.

In the calculation using the two peaked DOS model we have found that, for the monolayer coverage, a resonance peak near the band center splits into two peaks. This splitting of the resonance peak is very important in interpreting the photoemission spectra of the chemisorbed system such as H/W(100). It is gratifying that the present two peaked substrate DOS model can qualitatively account for the coverage dependence of the photoemission spectra observed in the H/W(100) system. In addition, it has been shown that the asymmetry of the resonance peaks increases with coverage, in accordance with the experiments.

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