A tight-binding study of the electronic structure of Pd/Ta(011) and related systems

A tight-binding study of the electronic structure of Pd/Ta(011) and related systems

Š Pick and P Mikušík

J Heyrovský Institute of Physical Chemistry and Electrochemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, Czech Republic

Abstract. We study the electronic structure of the epitaxially grown Pd monolayer on the Ta(011) surface as well as the electronic properties of other related systems (Pt overlayer; Nb, Mo and W substrate). To this end an s–d electronic tight-binding Hamiltonian is treated using the recursion method technique. The calculations confirm that the 'noble-metal' properties of the overlayer are mainly due to the overlayer–substrate electron hybridization in which the role of s electrons is not negligible. The possible contribution of initial-state effects to core-level shifts is also considered. For Pd adatoms we obtain a semi-quantitative agreement with experiment.

1. Introduction

Bimetallic systems are possible candidates for tailoring physical and chemical properties of solid surfaces and interfaces. A considerable effort has been devoted to the study of very thin Pd and Pt overlayers on the (011) surface of BCC transition metals. Let us briefly recall here some results. Comparison of the photoemission (PES) spectra with the calculated energy bands [1] shows that the electronic structure of the Pd monolayer on Nb(011) is similar to that of the corresponding free-standing Pd monolayer. Nevertheless, in the adlayer case the d band moves down to higher binding energies by about 2 eV. The Pd adatoms thus resemble noble-metal atoms, as reflected by their lower chemical activity [1]. Similar effects were observed experimentally also for Pt films on Nb(011) [2] and for Pd and Pt overlayers on Ta(011) [3,4].

Theoretical papers [1,5,6] are concerned mainly with the Pd/Nb(011) structure. According to [6] there is a small charge transfer onto Pd atoms mediated mainly by electrons of non-d character, and the hybridization of these electrons into the d band is the cause of its 'filling'. On the other hand, in the semi-empirical study [5] a non-negligible enlargement of the Pd d-electron count with respect to the bulk was postulated. To justify this idea it has been argued [5] that in the adlayer the Pd atoms partially approach the free-atom limit with the valence d shell filled. Besides the disagreement with the first-principles calculations [6], such a picture cannot be used for Pt adatoms which also show the d-band 'filling' [4].

In the experiment [4] considerable positive (i.e. to higher binding energies) core-level shifts (CLSs) were found for Pd and Pt adatoms. A systematic experimental investigation of CLSs for related systems and their correlation with the surface reactivity has been undertaken by Rodriguez et al; the reader is referred to their review article [7], see also [8].

Properties analogous to those described above are found for a number of transition-metal intermetallic compounds. The d band of the more electronegative element becomes bonding with respect to the hybridization between unlike atoms and the gross features in the local density of electronic states (LDOS) move to higher binding energies. Positive bulk CLSs are also common in alloys with split d bands [9–11]. Presently, there is no consensus

on the nature of CLSs in solids since at least two theories stressing the importance of the local geometry either in the final or in the initial state of the photoexcitation yield usually satisfactory results [12]. The third approach, based on the idea of charge transfer, has been criticized recently [13]. We also mention the paper [14] analysing the role of particular effects in the Auger spectra. If the initial-state origin of CLS is supposed (chemical shift) one can try to correlate it with the shift of the local d-band centre of gravity ϵ_d on the assumption that the localized d electrons feel a similar electrostatic potential as the electrons at the outer core level do [9–11]. In this model, CLS is expressed as the change

$$- \delta(\epsilon_d - E_F) \tag{1}$$

where E_F is the Fermi energy.

Recently, the present authors have studied [11, 15, 16] the bulk and surface electronic properties of several M–Ti systems (M = Ni, Pd, Pt) using a semi-empirical tight-binding model. Whereas the results were in approximate agreement with the available literature data, in our first (unpublished) attempts to apply this model to Pd and Pt overlayers on BCC substrates we failed to obtain the correct position of the adatom d band without making an assumption about its additional filling in analogy with [5].

The hybridization in alloys leads generally to the formation of a low-density tail in the LDOS of the late-transition-metal element which extends above E_F. Our computational experience shows that the effects we are interested in are sensitive to the tail description. Roughly speaking, the tail accommodates some holes. The better developed the tail, the more the d band has to move down from E_F to avoid large departure from local charge neutrality. For surface atoms with a lowered coordination the familiar band-narrowing mechanism works against this trend. Guided by these remarks and by the discussion in [6] we have decided to check whether the inclusion of s electrons into the tight-binding scheme could facilitate the LDOS tail formation and thus remove the problems in the description of the Pd overlayer mentioned above. We obtained in this manner a significant improvement. It appeared, however, that the problem has also been partly caused by yet another effect. In the original model [5] as well as in our preliminary tests a d-band tight-binding parametrization for BCC structures was used in which the ratio of hopping integrals between the first- and second-nearest neighbours, respectively, was slightly overestimated in comparison to most other parameter sets [17]. When the nearest-neighbour interactions were fitted to the FCC Pd crystal and transferred to the BCC-like overlayer the band narrowing was also overestimated. Hence, the picture in which the hybridization between the adatom and substrate electrons is the decisive mechanism [6, 18] is recovered in the improved model. A brief account of our results for Pd/W(011) and Pt/W(011) has been published elsewhere [19]. Results for the substrate pairs Nb, Ta and Mo, W are similar.

2. Model

It is our aim to study the Pd or Pt epitaxial monolayers on the (011) faces of Nb, Ta, Mo and W. We start from an s–d-electron tight-binding Hamiltonian treated by the standard recursion method technique [20] in a similar way as in our previous studies [15]. Namely, the charge self-consistency is controlled by adjustable on-site (Coulomb) integrals, supposing that starting from the fourth layer the bulk situation is reached. The quantity ϵ_d in (1) is obtained by taking the mean of the on-site integrals over the five d orbitals. The moments are evaluated to the 24th order for s and d orbitals on all non-equivalent atoms.

The s–d-electron tight-binding Hamiltonian is met regularly in calculations of transition-metal systems [21–25]. The inclusion of the s–d hybridization should improve the description especially for late transition metals. On the other. hand, the omission of

p electrons allows us to reduce drastically the volume of calculations, which has enabled us to make a number of numerical tests, and it offers the prospect of applying the s–d model to other systems that are difficult to treat by more elaborate methods. Below we use the s–d part of an spd Hamiltonian. The universal most-localized two-centre Slater–Koster parameters for BCC and FCC metals, respectively, are rescaled by parameters $\bar{\Delta}_s$, $\bar{\Delta}_d$ (tables II, III and equations (90), (91) of [17]). That is, the blocks of the universal hopping intergrals between orbitals i and j (i, j = s, d) scale as

$$H_{ij} = (\bar{\Delta}_i)^{1/2} h_{ij} (\bar{\Delta}_j)^{1/2}. \tag{2}$$

For hopping integrals between unlike atoms we suppose in analogy to the Shiba geometrical-mean approximation that the formula (2) holds true also when the two $\bar{\Delta}$ values refer to different atoms. We postulate the R^{-1} and R^{-5} distance dependence of $\bar{\Delta}$ for s and d electrons, respectively [17].

The on-site matrix elements are fixed to yield the desired s- and d-electron occupations N_s and N_d, respectively, on particular atoms. Due to the omission of p electrons the bulk charges cannot be taken directly from the first-principles calculations; we have found N_d from the comparison of LDOS and E_F position with the literature data. For bulk Pd and Pt atoms we obtain $N_d = 9.2$ and 9.0, respectively, and we take $N_d = 3.6$ for Nb and Ta, $N_d = 4.6$ for Mo and W. Since all the results are quite insensitive to N_s we simply take the values listed in [17]. For the Pd and Pt overlayers we postulate a small charge transfer from the first substrate layer onto adatoms. Based on elementary electronegativity arguments and the values from [6], we put $\delta N_s = 0.1$, $\delta N_d = 0.05$ for Nb and Ta substrates and $\delta N_s = 0.05$, $\delta N_d = 0$ for Mo and W. The results, however, are not too sensitive to δN_d smaller than about 0.1 and become at odds with PES for values higher than about 0.2. The results are not sensitive to δN_s.

For crystals of the metals considered here, LDOS and also surface CLS from (1) calculated within the s–d model agree with the predictions based on the d-band model [11, 15], the main difference lying in a smoothing and the LDOS-peak height reduction at the bottom of the d band, cf. also [25]. It appears, however, that in comparison to common d-band model parametrizations, the crystal-field splitting [17] has to be included in the s–d model in order to obtain the correct LDOS for the BCC substrates. (Let us note that the BCC lattice is very anisotropic for s–d interactions since the nearest-neighbour s–e_g hopping integrals vanish because of the symmetry.) For Pd and Pt, both in the FCC and adatom BCC geometries the crystal-field splitting is included as well, although it is of lesser importance (see below). For the surface atoms with a rather high coordination we use the bulk values.

In the close-packed FCC-like bimetallic systems the interatomic distance can be assessed from metallic radii values (Vegard law). In BCC lattices the assumption of the mean atomic volume conservation (Zen law) is usually better [6, 26]. For Pd (Pt) overlayers we obtain in this way on Nb, Ta, Mo and W substrates moderate surface–subsurface distance relaxations of 3%, 3%, 0% and 1%, respectively, with respect to the ideal BCC geometry.

3. Results and discussion

We have used the s–d-electron model to study the Pd and Pt epitaxial monolayers grown on the (011) surface of Nb, Ta, Mo and W. To obtain an idea of the importance of the s–d-electron mixing the pure d-band model has also been considered. Below we present the results for the Ta substrate, for which the PES data are available [3,4]; the W substrate has been considered elsewhere [19]. In figures 1 and 2 we show the LDOS for Pd and Pt overlayers, respectively. The 'filling' of the adatom d band leading to the 'noble-metal' character is apparent as well as the low-density LDOS tail at higher energies. (We present
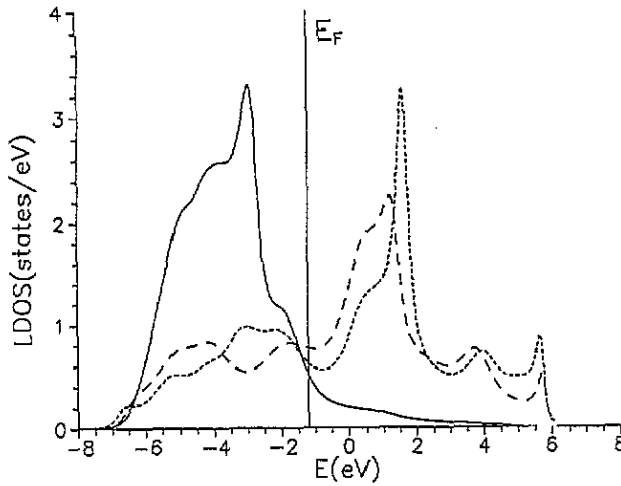
Figure 1. The local density of d-electron states (LDOS) for Pd adatoms (full curve), interface Ta (long-dashed curve) and bulk Ta atoms (short-dashed curve) for the Pd/Ta(011) system.
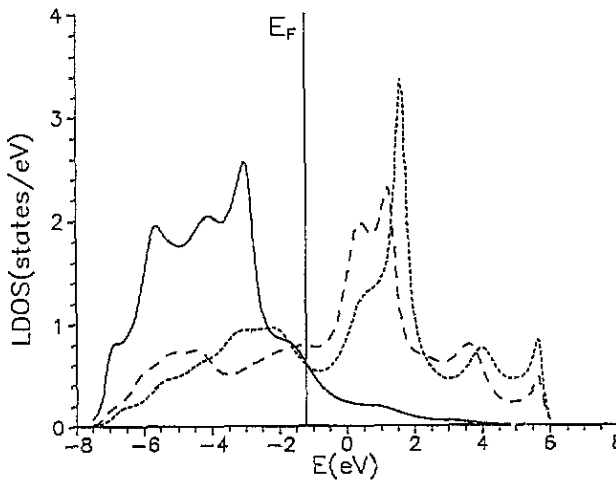

Figure 2. LDOS in the Pt/Ta(011) system. Details are as in figure 1.
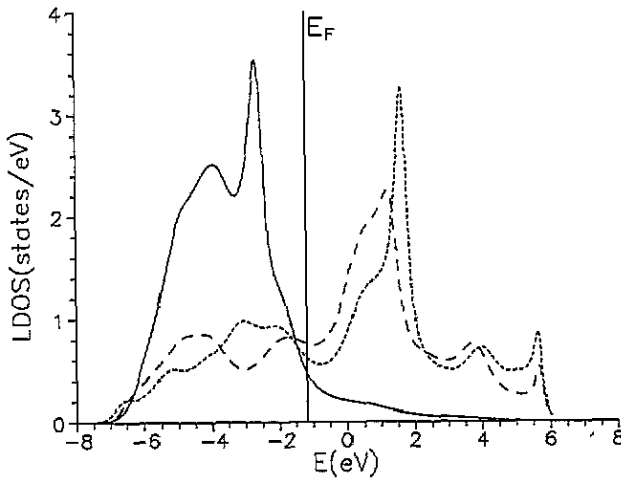

Figure 3. The same as figure 1 with zero crystal-field splitting at Pd adatoms.

only the d-state LDOS in our figures since the s-like contribution is very small and uniform with some features at the bottom of the s–d band and at rather elevated energies only, as a rule.) The comparison with the angle-integrated valence PES spectra [3, 4] is quite satisfactory—we reproduce correctly both the position and the overall PES intensity profile
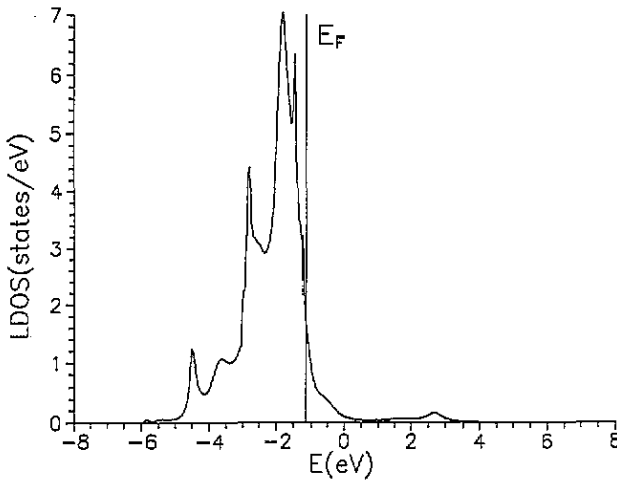
Figure 4. LDOS for the free-standing BCC Pd(011) monolayer with the Ta–Ta interatomic distances.
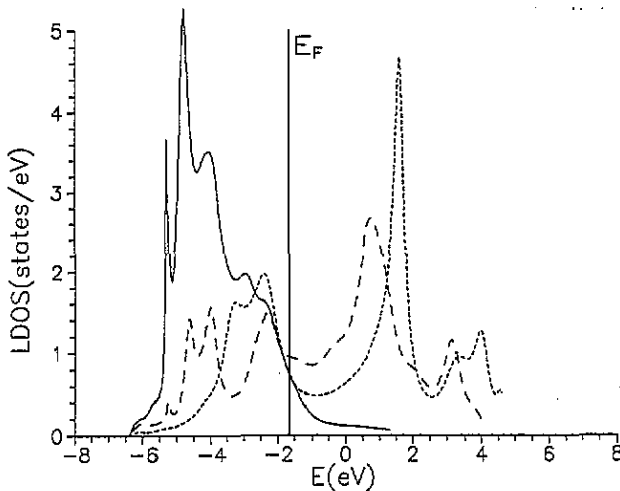

Figure 5. The same as figure 1 for the pure d-band model.

of valence bands for both the Pd and Pt overlayers. The Pd/Ta(011) LDOS with zero crystal field on Pd atoms is shown in figure 3. It is seen that only some details are slightly affected. Figure 4 represents the result for a free-standing BCC (011) Pd monolayer. In analogy to [1] we verify that the specific behaviour of the d band does not take place in the absence of the substrate. Finally, let us consider the LDOS obtained within the pure d-band picture (figure 5). Let us note that the limited accuracy of the d-band model has also been demonstrated by other authors [27] for Mo–Ru systems. We take here a higher occupation $N_d(Pd) = 9.45$ (including charge transfer 0.05) which seems to be more suitable in the d-band model; however, the resulting effect is small in this case. The d-band position is again in a reasonable accord with experiments, but matching with the intensity profile is less satisfactory. The shoulder one finds at about 0.8 eV below E_F develops for Pd/W(011) in a distinct peak at E_F in the d-band model. Unfortunately a relevant experiment is missing. However, no such feature is found in PES spectra for Pd/W(001) which are claimed to be similar to those for the Pd/W(011) system [28].

Let us turn to the CLS predictions (table 1) based on (1) and let us consider first the overlayer atoms. For Pd deposited on Mo and W the positive CLSs we obtain are slightly lower than the experimental values whereas the core-level shift of 0.2 eV we find for Pd on Ta underestimates the measured CLS by 0.4 eV [7, 8]. The fact that the overlayer CLSs in table 1 are higher for Mo and W substrates is due to the short adatom–adatom bond

Table 1. Core-level shifts (CLSs) for the overlayer Pd (Pt) atoms and first-layer substrate (s) atoms in eV. CLSs are calculated from (1) and are taken with respect to corresponding bulk atoms.

Substrate	Pd	s	Pt	s
Nb	0.2	0.4	−0.1	0.4
Ta	0.2	0.3	−0.1	0.4
Mo	0.3	0.1	0.2	0.1
W	0.4	0.1	0.2	0.1

length, causing a more intense interaction that opposes the surface band narrowing. For Pt the calculated CLSs are small and can be of either sign. The only experiment gives, on the contrary, a large positive shift for Pt on Ta(011) [4]. For the interface Ta 4f CLS in Pd/Ta(011) and Pt/Ta(011) our results are again a little lower than the experimental values 0.5 and 0.75 eV, respectively [4, 29].

To summarize, our tight-binding analysis shows that in Pd/Ta(011) and similar systems the specific overlayer electronic structure is mainly due to the hybridization between the overlayer and substrate electrons. Together with the d electrons, s electrons participate in the hybridization. On the other hand our model does not support the possibility of an essential d-electron count change at adatoms with respect to the bulk value. The initial-state effect interpretation of CLSs is consistent with experimentally measured positive shifts in systems with Pd adatoms; the agreement has a semi-quantitative character. For the far less studied Pt overlayers our CLS prediction does not conform to the only available experiment.

References

[1] El-Batanouny M, Hamann D R, Chubb S R and Davenport J W 1983 *Phys. Rev.* B **27** 2575
[2] Pan X, Ruckman M W and Strongin M 1987 *Phys. Rev.* B **35** 3734
[3] Ruckman M W, Murgai V and Strongin M 1986 *Phys. Rev.* B **34** 6759
[4] Ruckman M W and Strongin M 1987 *Phys. Rev.* B **35** 487
[5] Kumar V and Bennemann K H 1983 *Phys. Rev.* B **28** 3138
[6] Weinert M, Watson R E, Davenport J W and Fernando G W 1989 *Phys. Rev.* B **39** 12585
[7] Rodriguez J A and Goodman D W 1991 *J. Phys. Chem.* **95** 4196
[8] Rodriguez J A, Campbell R A and Goodman D W 1992 *J. Vac. Sci. Technol.* A **10** 2540
[9] Oelhafen P 1981 *J. Phys. F: Met. Phys.* **11** L41
[10] Watson R E, Davenport J W and Weinert M 1986 *Phys. Rev.* B **34** 8421
[11] Pick Š and Mikušík P 1992 *Chem. Phys. Lett.* **189** 517
[12] Said M, Desjonquères M C and Tréglia G 1993 *Phys. Rev.* B **47** 4722
[13] Benesh G A and King D A 1992 *Chem. Phys. Lett.* **191** 315
[14] Darrah T T and Weightman P 1986 *Phys. Rev.* B **33** 5406
[15] Pick Š and Mikušík P 1991 *Solid State Commun.* **80** 897; 1992 *J. Physique* I **2** 121
[16] Pick Š and Mikušík P 1993 *Phys. Rev.* B **47** 15860
[17] Andersen O K, Jepsen O and Glötzel D 1985 *Highlights of Condensed Matter Theory* (Bologna: Società Italiana di Fisica) p 59
[18] Zangwill A 1988 *Physics at Surfaces* (Cambridge: Cambridge University Press)
[19] Pick Š and Mikušík P 1993 *Chem. Phys. Lett.* **208** 97
[20] Haydock R, Heine V and Kelly M J 1975 *J. Phys. C: Solid State Phys.* **8** 2591
[21] Bullett D W and Cohen M L 1977 *J. Phys. C: Solid State Phys.* **10** 2083
[22] Harrison W A 1980 *Electronic Structure and the Properties of Solids* (San Francisco: Freeman)
[23] Robbins M O and Falicov L M 1984 *Phys. Rev.* B **29** 1333
[24] Bruno P 1989 *Phys. Rev.* B **39** 865
[25] Phuong L Do, Pasturel A and Nguyen Manh N 1993 *J. Phys.: Condens. Matter* **5** 1901
[26] Mikušík P and Pick Š 1993 *Solid State Commun.* **86** 467
[27] Ferreira S, Duarte J Jr and Frote-Pessôa S 1990 *Phys. Rev.* B **41** 5607
[28] Graham G W 1986 *J. Vac. Sci. Technol.* A **4** 760
[29] Ruckman M W, Jiang L Q and Strongin M 1992 *J. Vac. Sci. Technol.* A **10** 2551