THE METALLIC BOND FOR MONOLAYER TRANSITION METAL LAYERS ON TRANSITION METAL SURFACES

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APR 16 1983

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ABSTRACT. This present work discusses changes in the electronic and chemical properties of some transition metal layers on transition metal substrates, and presents a simple framework for understanding the results.

1. Introduction

It is the purpose of this present work to present a coherent picture of how the electronic properties of transition metal layers on transition metal substrates are modified. The study of bimetallic overlayer systems has a long history of both experimental¹⁻⁵ and theoretical work⁶⁻⁸ of which we reference only a few representative papers. Some new data and a simple picture are presented here for the Pd/Ta system and various other data is discussed to present framework for understanding bilayers in the limit of strong binding. Contrary to recent results,⁹ it will be argued, and evidence will be presented which shows that charge transfer between the overlayer and the substrate is not the dominant factor in modifying the properties of Pd/Ta and related bilayers and, furthermore, the bilayer properties and systematics are not greatly modified from those of bulk alloys.¹⁰ Of course, there are always modifications due to the different number of nearest neighbors at the surface, and also surface related electronic modifications that form the basis of surface core level shifts¹¹. Surface energies which are generally much less than the cohesive energies also can lead to stable surface layers in situations where there are no stable bulk alloys and the two elements are immiscible. This happens, for example, in the case of Ag on Nb¹².

In the discussion, the Pd/Ta system is taken as a prototypical strong binding bilayer system. In some of our work, studies were also made on Pd/Nb with few noticeable differences from Pd/Ta, and in some of the discussion these results will be used interchangeably. In this paper we will present both new data and theoretical work in addition to previously published work to present a coherent picture of why the properties of metal bilayers are greatly changed from the properties of the bulk elemental metal.

2. Results

2.1 CHEMICAL PROPERTIES AND ELECTRONIC STRUCTURE

To illustrate the unusual properties of such bilayer systems, we show data for CO adsorption on Pd/Ta(100) as a function of the amount of Pd¹³ (Figure 1) showing greatly reduced adsorption near

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Figure 1. Variation in the intensity of C 1s or CO photoemission features as a function of Pd film coverage on Ta(100).

Figure 2. Photoelectron valence spectra for Pd/Ta(110) showing the evolution of Pd-derived d-states as a function of Pd coverage (θ).

one monolayer. Similar results are also found for Pt covered Ta(110)¹⁴ and, in addition, reduced adsorption was also found for Rh on Mo(110)¹⁵. In the case of the pure Ta surface, CO chemisorbs dissociatively and the amount of C and O is shown to be a function of the Pd coverage for a constant exposure of CO. At one monolayer there is no detectable CO, C or O and the system is qualitatively like a noble metal. The data in Figure 1, are for a room temperature sample; as the temperature is lowered there is weak adsorption of CO on the monolayer surface¹⁶. This problem has been studied in detail by Koel and co-workers¹⁷. As more Pd is deposited CO builds up non-dissociatively and finally saturates at a few monolayers of Pd where the electronic properties are similar to bulk Pd.

The corresponding electronic properties of the surface as Pd is deposited onto Ta(110) is shown in Figure 2 and it is clear that the Pd states, up to one monolayer coverage, are shifted significantly below E_F ¹⁸. As Pd coverage exceeds one monolayer, the electronic states start to approach those that of bulk Pd, as is to be expected in the thicker layers. It is our intuitive view that this movement of the Pd d states below E_F is the crucial factor in the change of chemistry of the monolayer. In the regime below one monolayer, the decrease in dissociative chemisorption can be explained by the relatively low density of states near the Fermi level in the Pd islands covering the Ta, until at one monolayer the Ta is covered by a commensurate layer of Pd in the Ta(110) structure¹. With increasing Pd coverage, the structure of the Pd layer transforms to the Pd(111)¹ structure and the density of states starts approaching that of Pd¹⁸. The greatly changed chemistry of the monolayer system, and the correlation with the number of states near E_F , was also found for the case of hydrogen uptake through the Pd into the bulk Nb or Ta crystal¹⁸.

In this case the smallest amount of uptake into the bulk occurred for the monolayer and it is only with increasing amounts of Pd that the uptake of hydrogen increases by several orders of magnitude. It is thought that hydrogen molecules do not dissociate on the monolayer surface and, hence, the uptake into the bulk is greatly reduced. Again, it was suggested that this property is related to the changed electronic structure. The results for Pd on Nb or Ta(100) are not unique and, as mentioned previously, similar trends are seen for Pt on Ta as well as Rh on Mo(110)¹⁵.

The main point of this present work is to present further data and a simple framework for understanding how the properties of the bilayer are modified and why the chemistry of simple molecules on this surface is so greatly changed. The view we will develop below considers the density of d states near E_f to be crucial to the bonding of molecules to the surface and this view has already been advanced in the work of Hoffman¹⁹ and Zangwill²⁰, and has been pointed out in several experimental papers^{13,18}. Zangwill discusses this problem on the basis of a picture of "covalent" bonding proposed by Gadzuk²¹ and the formation of a bonding level formed by the hybridized metal d states. Although this picture is oversimplified, it is our view that in the Pd/Ta system, it has more of the essential physics of the changed properties than models based on charge transfer between the overlayer and substrate⁹. This point will be expanded in the following sections which critically discuss the interpretation of experimental and theoretical results obtained from such systems.

2.2 CORE LEVEL SHIFTS

The question of core level shifts and their meaning has been a subject of controversy in both metals and in clusters on various substrates. Most would agree with the idea that as charge is removed from a site, the core level shifts to higher binding energy. For metals; final state effects are usually taken to the same for dissimilar systems even though this effect approaches 10 eV in various calculations. In the discussion here, final state effects will be assumed to be equal in magnitude and similar for the various metal systems.

Initial state core level shifts have been studied in bulk alloys and an excellent summary of results for numerous alloy systems can be found in the work of Steiner and Hufner¹⁰. What is important in this data is the variety of behavior and the result that core levels in similar bimetallic systems can either shift in opposite directions or both core levels can shift in the same direction. In the PdZr and PdTi systems, the core levels of both alloy components actually shift in the same direction. There are many additional examples of this phenomenon and, in fact, this happens in the Pd/Ta system. Of course, from simple notions of charge transfer from one element to another, this is difficult to understand. Charge removed from one site must add to the charge on the other site and it would be expected that the core levels would move in opposite directions. Hence, other phenomena are involved in causing core level shifts than charge transfer. In general, there are various effects that contribute to core level shifts. These include: (1) interatomic charge transfer, (2) intraatomic charge transfer, i.e. d $\rightarrow$ sp interchange, (3) final state effects, (4) extra-atomic (Madelung) potential terms, (5) covalent bonding contributions over and above their contributions to site electron count changes, including volume effects due to deviations from Vegard's law, and (6) charge tailing, i.e., the effective medium due to an atom's neighbors that affects electron site counts.

In various alloy systems, the role of the above factors can vary and there are many discussions in the literature²². In recent work^{9,23} showing correlations between core level shifts and the chemical properties in bilayer systems, charge transfer was identified as the dominant factor and

the direction of the charge transfer for the bilayer systems is opposite to charge transfer in bulk alloy. Of course, there is a great danger in making any simple model for a complex phenomena

Figure 3. Core level photoemission from the Ta 4f levels for Pd-covered Ta(110) and Pd/Ta surface phases created by heating said overlayers. (B) indicates bulk core level.....notice it does not shift. (S) indicates surface feature.

Figure 4. Pd 3d core level data showing the shift to higher binding energy for the Pd monolayer.

and we intend to argue that at least in the Pd/Ta system the dominant mechanism is not charge transfer and the properties can be understood by an alternative picture based on hybridization of the d orbitals.

Data for the Ta core levels in the Pd/Ta system are already in the literature²⁴, and in Figures 3 and 4 we show that in this system both core levels are shifted to higher binding energy in the bilayer system, in much the same way as the alloy systems already mentioned. Overlayers of Pt on Ta also show similar behavior²⁵. Besides the monolayer system itself, it is also evident that heating thicker layers of Pd on Ta causes a shift to higher binding energy. In the case of heating samples with several layers of Pd, there is no doubt that there is a region of a few layers where alloying occurs²⁶ and in this case both core levels also shift to higher binding energy. There are two important features to emphasize. First, there is no qualitative difference between the monolayer or the alloyed region at the surface. Second, both Pd and Ta core levels shift in the same direction with alloying and we have already emphasized that this is not unusual. However, it is well to point out that this cannot be understood by a simple charge transfer picture.

2.3 THE WORK FUNCTION

Another issue to be briefly mentioned here is the behavior of the work function. It has been suggested⁹ that the work function also fits nicely into the picture of charge transfer between the overlayer and substrate. However, caution is also necessary in discussions of the work function. For small enough amounts of overlayer, there should always be a decrease in the work function due to the polarization of the adatom. This has been discussed by Lang²⁷ for the case of rare gases. Another issue is the fact that the work function depends on orbitals that are less tightly bound such as s and p orbitals whereas core levels are most affected by the more tightly bound d levels. Hence, any correlations between core level shifts and work function systematics in d metals is not obvious. A good example of the fortuitous nature of work function correlations can be found in the case of both Pt and Pd on Ta²⁸. Both systems, as already discussed, have deeper core levels for both the monolayer and the substrate component. However, for the monolayer system whereas Pd on Nb or Ta has a lower work function, Pt has an increased work function to this regime. Hence, there is no simple correlation in this case. In fact for Pt, except for very small coverages, the work function is always above the substrate value. Other published data for monolayer coverages likewise clearly demonstrates caution is necessary when making correlations between core level shifts and work function changes²⁹.

2.4 SURFACE ENERGIES AND ALLOY FORMATION

Recent theoretical calculations can now predict the stability of the Pd/Nb system¹². It is interesting that the surface energy term that predicts that Pd will form a stable monolayer also predicts that Nb should not form a stable layer on Pd¹². In such a case, agglomeration would occur. However, measurements show that alloying occurs for the Nb on Pd case and intuitively this is reasonable because of the large alloy heat of formation. This alloying is of particular interest since it allows us to determine the density of states and study the bonding of molecules to the alloy surfaces. In Figure 5 we show an ion scattering study of Pd on Ta and Ta on Pd³⁰. The Ta/Pd system was studied rather than Nb since the greater Z values between Ta and Pd provided greater selectivity in the ion scattering study. Ion scattering was used since this technique is sensitive to the composition of the topmost layer of atoms. It is immediately clear that the Pd layer completely covers the Ta and, in fact, this was found to be true even at 1000K.

However, when Ta was deposited on Pd, complete Ta coverage is not attained until much greater amounts of Ta (> 1 monolayer) and it is thought that this is indicative of alloying at the surface. Photoemission studies³⁰ with Nb deposited on Pd shows a shift of the d states below E_F with coverages near one monolayer of Nb, and it is, therefore, clear again that alloying is occurring rather than agglomeration. This is the case because agglomeration would show sharp Nb states near E_F rather than the movement of the Pd d states below E_F which shows bonding between Nb and Pd. The similarity of these d states below the Fermi level to the bilayer case is evident, and it is observed that CO does not chemisorb on this alloy surface at room temperature³⁰. This, of course, is also similar to the bilayer case. Thus, these results show the important role played by the density of states of the outermost layer in the chemistry of molecules. In this case where non-dissociative chemisorption occurs, the "averaged" density of states at the surface is the important quantity. When dissociative adsorption occurs, it is probable that specific reactions to atomic sites will occur.

Figure 5. Low energy ion scattering data for Pd/Ta(110) and Ta/Pd(111).

3. Discussion

3.1 A SIMPLE PICTURE FOR UNDERSTANDING THE RESULTS

The simplest concept to interpret the results is the intuitive idea of the surface molecule proposed by Gradzuk and discussed by Zangwill. For transition metals, the d orbitals in the bilayer system are localized enough to form a bonding and anti-bonding level just as in the case of the diatomic molecule. This view is, of course, oversimplified, but explains the movement of the hybridized Pd/Ta d band below E_F . It is this movement of the d band below the Fermi level that dramatically affects the chemistry of molecules on the surface and we will return to this point in the next section. In this model there is very little charge transfer and tight binding calculations by Kumar and Bennemann³¹ indicated that the charge transfer involved in the Pd/Nb system was

on the order of 0.02 electron charges. More recent calculations of Pd/Nb¹² and Pd/Ta basically confirm this picture. It is important to mention that this magnitude of charge transfer is not enough to give core level shifts approaching 1 eV. Generally, changes of 0.1 electrons are necessary for 1 eV shifts.

If hybridization of the d states dominates, it can be immediately understood how both core levels shift in the same direction due to

Figure 6. Plot of 3d-derived bonding and anti-bonding state wave function densities for a linear atomic chain.

redistribution of charge. A simple diatomic molecule already demonstrates this charge redistribution effect, but in the Figure 6, we use the results of an infinite linear chain of atomic 3d orbitals to show the difference in charge density due to quantum mechanical effects. The bonding (antibonding) density is increased (decreased) between the atoms relative to the overlapped atomic density. Thus, the bonding density has a larger effective radius than does the antibonding density, resulting in a less repulsive electron-electron interaction, or more attractive potential at the nucleus ($V_e \sim q/R$), and this causes the core levels to shift to higher binding energy. If different atoms are allowed to interact, similar types of on-site charge rearrangements occur, although the densities will not be symmetric about the atomic positions. The changes in hybridization upon alloying will affect the density in the bond region significantly and simple calculations using the above model and reasonable parameters corresponding to transition metals show that core level shifts of the order of 1-2 eV are easily obtained. In cases where there is strong increased bonding between the constituents, there can be increased density between the atoms, resulting in both core levels increasing in binding. Note: that with different assumptions on the wavefunction taking part in the bonding between the atoms, this model can describe the cores shifting in opposite directions, as well as both to lower binding energy without invoking intrinsic charge transfer.

3.2 THE CHEMISTRY OF MOLECULES ON BILAYERS

It has already been pointed out that the chemistry of CO on bilayer surfaces as well as hydrogen uptake in the bilayer systems can be related to the density of states near E_F . Zangwill discusses this phenomena, again, in terms of the surface molecule picture and this gives a simple intuitive picture without a discussion of particular molecular orbitals. Similar ideas are also found in the work of Hoffman¹⁹. The basic idea is that the molecular orbitals form bonding and anti-bonding levels with the metal d states. When there is a high density of d states near E_F , the bonding level

falls below the Fermi level and the anti-bonding level above. The anti-bonding level is emptied when electrons transfer out of the level to the empty states at the Fermi level. In this case a chemisorption bond can be formed. With a filled d band below E_F , charge cannot transfer out of the anti-bonding state, and the bond is weakened. Hence, in this picture it is not charge transfer between the overlayer and substrate that affects the bonding of molecules, but rather the redistribution of charge and the altered density of d states at the surface, at E_F , of the bilayer system.

4. Summary

The systematics of strongly bonded monolayers can be understood on a model where there is hybridization of overlayer and substrate orbitals, with charge transfer playing a minor role. In systems which do not interact as strongly, it is possible that small amounts of charge transfer are more important relative to the much smaller hybridization; this issue is not discussed here. It is interesting that in the Pd/Nb or Pd/Ta systems for both alloy surfaces and bilayer surfaces, the chemistry of molecules is determined by the position of the d band with respect to E_F .

6. Acknowledgements

The authors are pleased to acknowledge the contributions of P. D. Johnson, L. Q. Jiang and X. Pan to the research discussed in this paper. This research is supported by the U. S. Department of Energy under contract DE-AC02-76CH00016. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

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