Electronic structure and atomic positions of metallic surface alloys

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Abstract

Photoemission spectra collected over a large solid angle give information about the form and energies of spectral features, which are related to the underlying electronic structure of the sample. Spectra measured as a function of exit angle reflect the phenomenon of photoelectron diffraction, which is related to the underlying crystallographic structure of the sample. We report applications of these techniques by our group to the study of a number of systems involving ultra-thin metallic layers on surfaces, which can be true surface alloys, whose properties are often very different from those in the bulk. The surface systems we chose manifest surfactant behavior, catalytic activity and intercomponent effects. Our electronic structure results were derived from photoemission and X-ray excited Auger spectroscopies: interpretation of these data requires inclusion of the phenomena of relaxation and screening. Our crystallographic results were derived from photoelectron diffraction in combination with LEED: derivation of the results requires comparison with multiple scattering theoretical simulations and involves considerable computational effort. We have studied In, Sn and Sb on Pd(1 1 1) and Ni(1 1 1), Cu on Pd(1 1 1) and Pd on Cu(1 1 1), Sb on Ag(1 1 1) and Pd and Mg oxides on Ag(1 1 1)—we present representative results of these studies.

1. Introduction

In heterogeneous catalysis, information regarding the electronic structure and the atomic positions of the component atoms of the catalyst, often in the form of a metallic alloy, is of fundamental importance in order to facilitate correlation of the reaction and catalyst characteristics. X-ray photoelectron spectroscopy (XPS) is one of the most commonly used experimental techniques in the field for characterization: the spectral peak energy positions permit chemical identification and the spectral peak intensities allow composition determination. It has long been recognized that another feature of the XPS spectra, the chemical shift of the core level peak energy, reflects the chemical environment of the corresponding atom: extraction of quantitative electronic structure information from the shifts, however, is hardly a routine procedure.

Although random metallic alloys, of great importance in catalysis, represent one of the simplest situations beyond that of perfect crystals, the problem of determining their electronic structure presents difficult challenges for electronic structure theory. We have shown elsewhere [1] that it is possible to extract electronic structure of bimetallic random alloys from the XPS and X-ray excited Auger electron spectroscopy (XAES) core level shifts [2] of both components.

When we consider metallic surfaces, however, the situation becomes even more complicated. In many cases, such as those of Pd and the other 4d metals, the core level XAES kinetic energies are very high, so that the electron mean free path is relatively large, and the spectra are weak, so that it is very difficult to separate the surface XAES shift. Consequently, the techniques we have developed for bulk alloys [1–19] are difficult to apply to surface alloys [20–22]. Nevertheless, as we show below, it is possible to draw some rather strong conclusions regarding the changes in electronic structure of surface alloys by considering the XPS shifts, and the behavior of such spectral features as XPS shake-up satellites and line shape asymmetries.

Metallic surface alloys can be produced by appropriate treatment of an ultra-thin film deposited on a metallic substrate. In many cases, the bulk versions of these alloys do not exist. The formation of such alloys is associated with various phenomena, such as surface reconstruction, relaxation, charge transfer and charge redistribution [20–22]. It is clear, therefore, that the

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surface electronic and crystallographic structures are intimately related. Since the energy and intensity of a photoelectron spectrum is a function of the photon energy as well as the direction of the photoelectron, spectra collected over a large solid angle give information about the form and energies of spectral features, which are related to the underlying electronic structure of the sample and spectra measured as a function of exit angle reflect the phenomenon of photoelectron diffraction, which is related to the underlying crystallographic structure of the sample. XPS, therefore, is an appropriate tool for investigating both electronic and crystallographic structures.

In this paper, we report a systematic body of work by our group at Unicamp on metallic surface alloys. The motivation of these studies is that of correlating the electronic and crystallographic structures of the alloys with the properties of the atoms composing the adsorbates and substrates. We chose our first substrate, Pd(1 1 1), because of its unusual catalytic properties [23,24], and we have completed measurements and structure determinations for Cu [25,26], In [27], Sb [28], Sn [27] and Ni [29] on Pd(1 1 1) (as well as the complementary systems Pd on Cu(1 1 1) [30] and Pd on Ni(1 1 1) [31]). In consonance with our objective of performing a systematic study, we have also studied In, Sb and Sn on Ni(1 1 1) [27], and Sb and oxides of Pd and Mg on Ag(1 1 1) [27]. We should mention that analysis of the data involves a great deal of work and lengthy computations—a reliable structural determination can involve months of analytic work.

Here, we present examples of our results. In Section 2, we describe the experimental details. In Section 3, we argue that the changes in the Pd 3d spectrum for In on Pd(1 1 1) imply that the Pd local surface electronic structure is significantly different for the alloy from that of the pure metal surface, a result valid for Sb and Sn on Pd(1 1 1) also. In Section 4, we discuss our X-ray photoelectron diffraction (XPD) results for the atomic positions and present the findings for Sb on Pd(1 1 1).

2. Experiments

Our photoemission experiments involved both conventional Al Kα radiation (1486.6 eV) and synchrotron radiation at the Brasilian Synchrotron Radiation Laboratory (LNLS). The experiments were conducted in an ultra-high vacuum chamber (throughout the experiments, a base pressure lower than 2×10^{-10} Torr was maintained in the chamber) equipped with LEED optics, a fixed geometry high-resolution hemispherical energy analyzer (Omicron HA125HR with multi-detection) mounted in the plane of the storage ring when synchrotron radiation was used, a differentially pumped argon ion sputter gun for *in situ* sample cleaning and a two axis (θ, φ) sample manipulator equipped for heating the sample to 1300 K by electron bombardment. The electro-polished 10 mm diameter Pd(1 1 1) crystal was mounted on a thick Ta foil support that could be aligned by three set screws. Sample heating was accomplished either by directly irradiating the backside of the crystal (for low temperatures) or by electron bombardment (for high temperatures). To protect the crystal from deformation, a Pd phantom of exactly the same dimensions as the crystal with an Alumel/Cromel thermo-

couple spot welded to its edge was used to measure a calibration curve (applied power × temperature) in order to determine the sample temperature during annealing. The sample mounted in the system was aligned precisely with a He–Ne laser so that its surface plane was normal to the axis of the electron analyzer (the alignment was also verified after the system was baked and always varied less than 2°).

Argon ion bombardment (1.5 kV accelerating potential and 2.0 mA/cm² current density on sample) and subsequent annealing up to approximately 1100 K for 5 min was used for sample cleaning. The process was repeated until no impurities could be observed with XPS using Al Kα radiation. After cleaning, the sample was annealed to get a sharp LEED pattern in order to check the crystallinity, and also to determine precisely the initial azimuthal angle. The clean Pd(1 1 1) surface displayed $p(1 \times 1)$ reconstruction after annealing [25].

Ultra-thin films of In and Sb were evaporated, using a previously degassed Knudsen type cell. The film growth was monitored by XPS and the pressure in the chamber was kept under 4.5×10^{-10} Torr. The deposited films (of thickness ~3.6 ml) were heated to a temperature of around 530 K for around 30 min. The LEED patterns had $(\sqrt{3} \times \sqrt{3})R30°$ symmetry after heating.

The XPD data was measured in the angular mode. The azimuthal angle (ϕ), was varied in steps of 3° over a range of almost 150°. Since the LEED patterns for all structures showed threefold symmetry, this range was adequate to guarantee that we measured all the structures, and replication of the data set could be used to obtain 360° azimuthal scans. The polar angle (θ), defined by the analyzer axis and the normal to the surface, was varied in 5° steps from 20° to 70° in most cases. The analyzer's axis subtended an angle of 60° relative to the propagation direction of the linear polarized photon beam, so that the electrical polarization vector was at 30° to the analyzer axis. The samples were excited with photons with energies in the range of 530–700 eV, which was high enough to ensure little multiple scattering for Pd 3d photoelectrons. A 90% transmission Au grid monitored the intensity of the radiation and the data was normalized appropriately. After each full angular scan, we verified the absence of contaminants with XPS.

We used a modified version of the MSCD package [39] that is able to treat ordered and random alloy phases to analyze the data. The method used to describe random alloy phases is based on the average T-matrix approximation (ATA) [40] and was successfully applied to Cu/Pd(1 1 1) [25] and Pd/Cu(1 1 1) [30]. In this model, each lattice site is occupied by an atom whose atomic scattering amplitude is equal a weighted combination of the atomic scattering amplitude of each element in the alloy.

To compare experiment and theory, normalized PED intensities χ [39,40] were used and the degree of agreement was quantified by considering the reliability factors Ra and Rb [39,40]. Small values of Ra and Rb indicate good agreement between simulations and experiment. We used a parabolic cluster type model with a radius of around 11.5 Å and a depth of around 12 Å with typically 280 atoms distributed in six layers. The parabolic format of the cluster, the number of atoms, the

number of layers, and distribution of emitters in the layers were chosen to minimize boundary effects.

3. Electronic structure of In on Pd(1 1 1)

As we mentioned, the present study is part of a larger program of research into the crystallographic and electronic structure of surface alloys. In particular, we performed photoemission, Auger, LEED and XPD experiments on thin films for sp-metals (In, Sn and Sb) deposited on transition metals (Pd and Ni) [27,28]. Here, we present a very clear portion of the data which suggests strongly that the surface Pd electronic structure undergoes an unusual change. In Fig. 1, we present a Pd 3d XPS spectrum taken at a polar emission angle of 85° with respect to the surface normal for clean Pd(1 1 1) and for In deposited on Pd(1 1 1) for a photon energy of 450 eV: the spectra in Fig. 1, therefore, correspond to a short photoelectron mean free path and, so, are surface sensitive. We would like to call attention to three features of the spectrum. First the binding energy shifts between clean Pd and the deposited sample are negligible in Fig. 1 (spectra measured using the Al Kα source, which involve a longer mean free path and are more bulk sensitive, display small, but measurable shifts [28]). Next, the satellites in Fig. 1 are sizeable for clean Pd, but have vanished for the deposited sample (spectra measured with $\hbar\omega = 1486.6$ eV always display visible satellites [28]). Finally, the clean Pd spectrum is asymmetric, whereas the spectrum for the deposited sample in Fig. 1 is symmetric (clean Pd and deposited samples measured with the conventional X-ray source always display asymmetries [28]).

The Pd core level spectra in the bulk metals manifest satellites and asymmetries, which reflect how the system responds in time to the creation of a core hole. The satellites and peak asymmetries arise because the potential felt by the valence electrons in the final state is not the same as that in the initial state so that transitions to more than one final state are possible. Since Pd has a partially full d-band, the satellites and main lines are

explained, in the terminology of Kotani and Toyozawa [37], as arising from two different final states, those corresponding to s- and d-electron screening, respectively: that is, the final state for the main line is a $4d^{10}5s^1$ configuration, whereas that for the satellite is $4d^9 5s^2$. The intensity of the satellite is determined by the density of unoccupied Pd 4d-states in the ground state of the system and by the position of its maximum above the Fermi energy (E_F) [35,38]. A reduction of the density of states (DOS) at E_F leads to weaker satellites because there are fewer final states into which the electrons can scatter. Another measure of the intensity of the DOS at E_F is the asymmetry of the line shape: for example, core spectra in Cu, with a full d-band, are symmetric, while those for Pd are asymmetric.

Decreasing Pd concentration in Pd bulk alloys produces satellites which diminish in intensity and are increasingly removed in energy from the position of the bulk Pd satellite, which is accompanied by a decrease of the Pd spectral asymmetry [32-34]. Elsewhere [27], we consider the Pd 3d spectra measured with $\hbar\omega = 1486.6$ eV, which manifest bulk-like behavior and make connections to the bulk alloys. Here, we concentrate on the behavior of the "surface" spectra measured with $\hbar\omega = 450$ eV. That the satellites vanish and the line shapes become symmetric in the In-deposited sample in Fig. 1 would seem to indicate, from our discussion above, that the Pd surface d-band has become full: that is, that the DOS at the Fermi energy becomes very small. Filling of the Pd surface d-band would require a gain of more than one d-electron, which would imply an enormous shift in the Pd-binding energy. But, the shift is almost zero in Fig. 1. Reconciliation of these findings requires a model where the initially filled Pd states are pulled below the Fermi level and the initially empty states are pushed above: that is, the model would suggest a sort of d-band splitting at the surface in the deposited samples. According to this model, the total number of d-electrons stays almost the same as in pure Pd(1 1 1), as it must in order to be consistent with the small binding energy shift, but the DOS is small at the Fermi energy, as indicated by the satellite and asymmetry disappearance. Such a model was proposed by Fuggle et al. to explain satellite suppression in alloys of Pd and Ni with electropositive metals [35,36]. The form of the model, that corresponding to a full d-band, would suggest an atomic Pd Auger MVV line shape [37,38], as for Ag. Simulations indicate that the Auger line shape is consistent with the model [27].

4. Atomic positions for Sb on Pd(1 1 1)

The objective of modifying and controlling the magnetic, electronic, and catalytic properties of a surface by utilizing such surface phenomena as lattice expansion and contraction, surface reconstruction, and alloy formation has motivated many studies of epitaxial growth of thin films and surface alloy formation [41]. In heterogeneous catalysis, for example, the possibility of fabricating surface alloy catalysts according to predetermined specifications for a reaction of interest is very attractive [42]. Here, the electronic structure, element concentrations, and geometric arrangement of the surface atoms are important, so that a prerequisite to understanding catalytic reactions involves com-
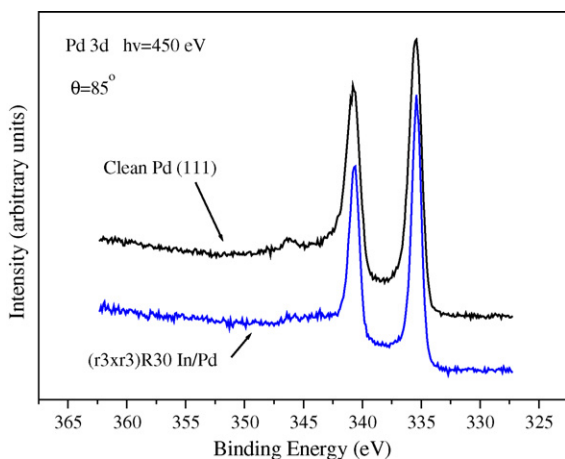

Fig. 1. Pd 3d XPS spectra for clean Pd(1 1 1) and for In on Pd(1 1 1) for excitation with synchrotron radiation of 450 eV and an 85° emission angle with respect to the surface normal. The spectra are surface sensitive because of the short photoelectron mean free path.

plete characterization of the surface of the catalytic agent: that is, understanding the mechanisms involved in surface alloy formation is fundamentally important.

We have studied a number of systems, as we have described in Section 1, in order to understand these mechanisms in function of the properties of the substrate and adsorbate constituent atoms. These studies, therefore, include systems apparently catalytically inactive: for example, besides the catalytically interesting Sn/Pd(1 1 1) [24], we have also studied In and Sb on Pd(1 1 1). In this section, we report some first results for Sb on Pd(1 1 1) [27], which is relatively simple to analyze and explain, since the Sb does not diffuse into the substrate.

The Sb/Pd(1 1 1) samples were prepared and the XPD results were obtained as described in Section 2: in particular, the LEED pattern is $(\sqrt{3} \times \sqrt{3})R30°$ after annealing. In Fig. 2(a), we present an experimental XPD pattern as a function of polar angle (θ) azimuthal angle (ϕ) for the Pd 3d photoelectron emitter measured with a photon energy of 650 eV (electron kinetic energy of 305 eV). A corresponding pattern for the Sb 3d photoemission does not manifest diffraction features, which would indicate localization of the Sb on the surface [27].

Analysis of the data proceeds in two steps for a system A/B. First, we choose a possible structural model and simulate it with a random alloy in the form A_xB_{1-x} in various layers, where x represents the A layer concentration; we then minimize the R factors (basically a least-square parameter for the difference between the experimental and theoretical spectra [39,40]) utilizing the same number of atoms, Debye temperature, and inner potential as for bulk-terminated Pd(1 1 1) in order to find the A layer concentrations [25,27]. In the next step, we use these A layer concentration as input and relax the parameters (including the structural parameters) in order to minimize the R factors once again [25,27]. When the both A and B photoemitters yield XPD patterns with diffraction features, both are used in the structural determinations. In the present instance, the featureless nature of the Sb XPD pattern made its use in the simulations difficult and only the Pd XPD patterns were relevant.

Our structural models included overlayer and substitutional HCP and FCC arrangements of Sb [27]. To give an idea of the quality of the results, the overlayer and substitutional HCP models yield Ra factors of 0.76 and 1.02, respectively, which indicate poor agreement with the data. The overlayer FCC model gives an Ra factor of 0.59, respectively, which is better than those for the HCP models. The best result, however, is for the model of substitutional Sb in the first layer, with an Ra of 0.27, which is consistent with the featureless Sb XPD pattern [27]. In Fig. 2(b), we display the theoretical XPD pattern for Pd 3d emission corresponding to this model.

The theoretical simulations yield not only the concentrations and structural symmetries, but also the atomic positions. For Sb on Pd(1 1 1), our first results [27] indicate a spacing between the centers of the surface and second layers of 2.20 Å; that between the second and third layers was 2.07 Å and all other spacings were the same as in the bulk (the bulk spacing for Pd(1 1 1) is 2.25 Å). These results indicate an oscillatory relaxation of the distances (the spacings in the planes were unchanged from Pd(1 1 1)).
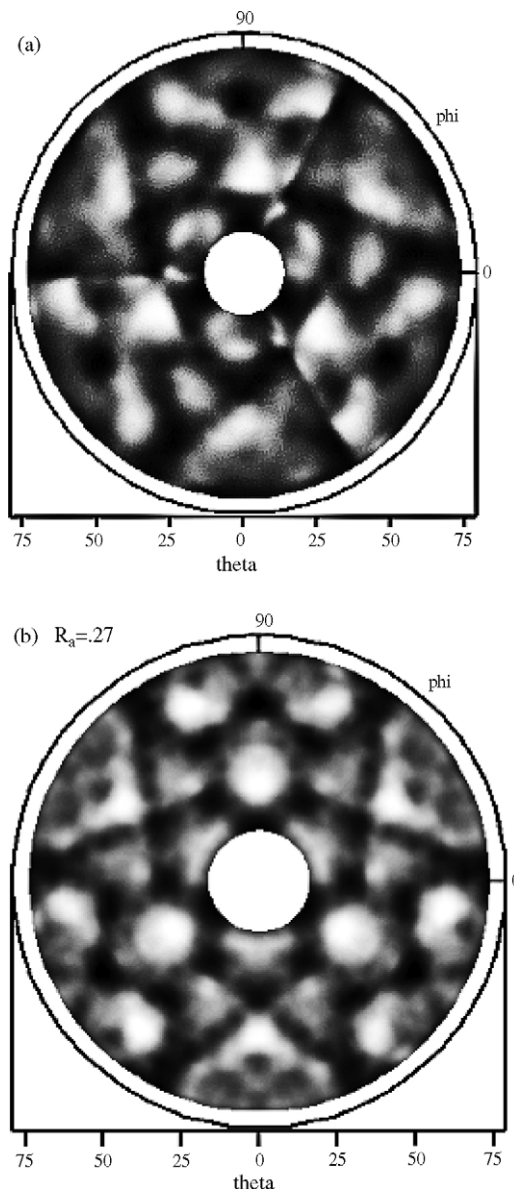

Fig. 2. (a) Experimental XPD pattern for Pd 3d emission from Sb/Pd(1 1 1), for a photon energy of 650 eV (photoelectron kinetic energy of 305 eV, consistent with little multiple scattering of the photoelectron). (b) Theoretical XPD pattern for Pd 3d emission from Sb/Pd(1 1 1), for a photon energy of 650 eV. The surface structure corresponds to substitution Sb in only the surface layer, in a $(\sqrt{3} \times \sqrt{3})R30°$ arrangement. Structural parameters are discussed in the text.

5. Conclusions

In this paper, we have reported work on the determination of electronic structure changes and atomic positions of surface alloys by our group at Unicamp. We present Pd 3d core level XPS satellites in surface alloys with In on Pd(1 1 1). The spectra from the surface region display an absence of satellites and asymmetries and almost zero binding energy shifts. These results are consistent with a Fuggle model [35,36], where the initially filled 4d-valence states are pulled below the Fermi energy and the initially unoccupied valence states are pushed above, leaving a very low density of states in the region of the Fermi energy: the small change in d-electron occupation in the initial

stat e explains the binding energy results. A simulation taking an atomic line shape (from Pd–Mg surface alloys [43,44]) into account, in accordance with the model, appears to describe our Auger spectra. The results appear to be valid also for Sb and Sn on Pd(1 1 1). The present problem will be addressed more completely in a future publication [27].

We also present data for Sb on Pd(1 1 1) in order to represent our results for surface structure determinations of surface alloys. The first results indicate that Sb remains on the surface (with no diffusion into the bulk), forms a $(\sqrt{3} \times \sqrt{3})R30°$ substitutional arrangement on the surface (from LEED), and displays an oscillatory behavior of the first and second layer spacings (deeper layers have bulk spacings).

Acknowledgments

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