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Experimental test of the photoemission of adsorbed xenon model

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This paper explores the prospects of utilizing the photoemission from adsorbed xenon (PAX) technique to characterize the surface composition of an ordered binary alloy. Photoelectron binding energies of Xe, Kr, and Ar adsorbed on β-NiAl(110) yield work-function results which are internally consistent, but which do not agree with the work function obtained directly from photoemission, and which further do not agree with the observed surface composition changes inferred from other parameters that are sensitive to the stoichiometry. These results imply that the PAX technique should be used with caution when applied to binary systems.

Characterizing the surface stoichiometry of a multicomponent surface constitutes an important and long-standing problem in surface science. Recently, a new surface-sensitive technique has been developed and has become known as the photoemission of adsorbed xenon (PAX)[1] technique. This technique appears to offer unique opportunities for probing selected properties of heterogeneous surfaces. The PAX technique is based on the experimental observation that valence and core-level electron binding energies E_v^b (measured with respect to the vacuum level) of rare-gas atoms physisorbed on surfaces are independent of the substrate on which they are adsorbed. The invariance of E_v^b leads to a model for the PAX mechanism and to a spectroscopic probe of the "local" work function F_{local} at the adsorption site. The local nature of the effect renders the technique a potentially useful tool for characterizing heterogeneous surfaces on an atomic scale. In the present study, the β-NiAl(110) alloy surface was investigated with the PAX technique in an attempt to determine the suitability of the PAX technique for quantitative analysis of surface stoichiometry.

The physical basis of the PAX model can be understood based on the potential energy near the surface region, as discussed by Lang and Williams.[2] The key point is that the surface potential may be considered to consist of two parts: a short-ranged electrostatic and a longer-ranged exchange-correlation part. The electrostatic part of the surface potential does not significantly perturb the rare-gas-atom electron wave functions or energy levels. While the exchange-correlation part of the surface potential does affect valence orbitals of the adsorbed rare-gas atoms, it produces only a minor initial-state shift in the rare-gas-atom electron energy levels. The result: The binding energies of the rare-gas-atom electronic energy levels measured relative to the vacuum level are independent of the substrate on which they are adsorbed.

E_v^b can be equated to the work function F and the electron binding energy relative to the Fermi level (E_F^b) as follows:

$$E_v^b = F + E_F^b \ . \tag{1}$$

Since E_F^b is the experimentally measured quantity, and E_v^b is known, the work function (F) can be deduced directly. This analysis has been termed the photoemission of adsorbed xenon model. The model has proven successful in several systems.[1] The technique has demonstrated an ability to detect surface defects. Work on stepped surfaces[3,4] clearly shows that the spin-orbit-split doublet in the rare-gas photoemission spectrum is shifted in energy. Typically, what one observes is a pair of doublets, corresponding to terrace and step sites.

β-NiAl(100) has a bcc crystal structure of the CsCl (B_2) type. A significant amount of work has been reported on the electronic and crystallographic properties of this system.[5-8] Sputtering of ordered NiAl alloys results in preferential loss of Al, producing a near-surface composition different from the bulk. We also found that the Al content of the near-surface region could be enriched by annealing to high temperature. The pertinent result of these studies[5] is that the surface and next several layers below the surface have been shown to have essentially the same composition. As a result, the fraction of Ni or Al obtained from Auger electron spectroscopy is also the fraction of Ni and Al at the surface layer. Further, NiAl surfaces have been uniformly reported as well behaved, without precipitation of Ni or Al clusters, and representative of ideal bulk termination, except as discussed below. The NiAl(110) surface was selected because this surface contains a 1:1 stoichiometric ratio of Ni and Al atoms. The work functions of Ni(110) and Al(110) differ by 0.96 eV; thus, a probe such as the PAX technique which is sensitive to the local work function should prove quite useful in examining the NiAl(110) surface.

Our sample-preparation method for NiAl(110) and instrumentation have been described previously.[9] The chamber includes the capability to perform low-energy electron diffraction (LEED), Auger electron spectroscopy, and angle-resolved and angle-integrated photoemission studies to cool the crystal to 30 K, and to heat it to 1100 K. Work-function data characteristic of the clean surface were obtained by measuring the angle-integrated photoemission energy distribution curve (EDC) width

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(E_W) and subtracting E_W from the photon energy. All data reported herein were obtained from samples with less than 1 at.% contamination, primarily oxygen.

Figure 1 displays typical angle-integrated photoemission spectra for low-coverage Xe, Kr, and Ar adsorbed on a clean and well-ordered NiAl(110) surface. The data presented in Fig. 1 correspond to a surface composition of 50 at.% Ni as judged by the main Ni and Al Auger peaks. This particular surface composition represents an ideal termination of the bulk lattice and is the surface most extensively studied.[8] The structural properties, electronic properties, and Ni-to-Al Auger peak intensity ratio corresponding to 50 at.% Ni (Ref. 5) are all well established. The inset in Fig. 1 summarizes the measured work functions of the rare-gas-covered surface at the stated coverage as determined by both the width of the photoemission EDC's (E_W) and by using the PAX model. The average work function obtained from photoemission was found to be 4.6 eV. (All work-function values are uncertain to 0.1 eV unless otherwise stated.)

Local work-function values obtained from binding energies of adsorbed Xe, Kr, and Ar were mutually consistent, and yielded a work-function value of 5.1 eV. This value is

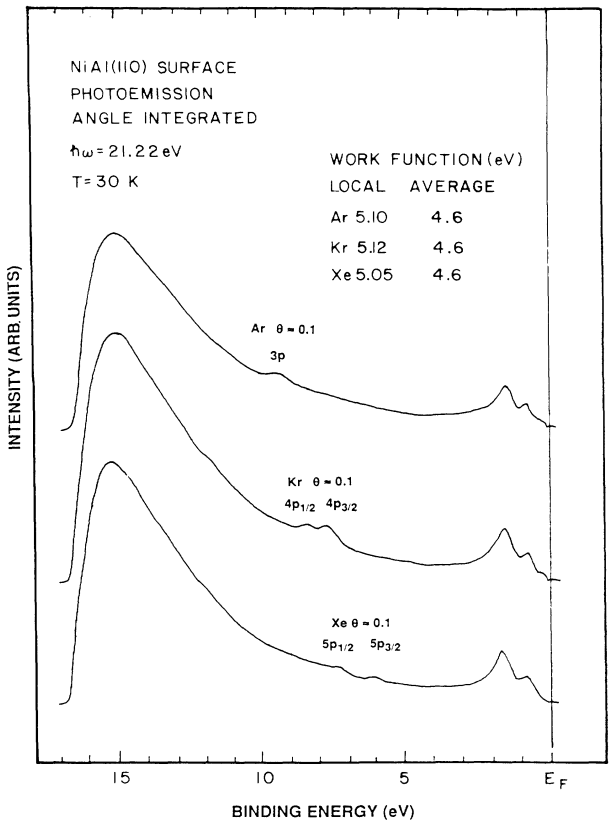

FIG. 1. Angle-integrated HeI (21.22 eV) photoemission spectra for low coverage (0.1 monolayer) of Xe (lower curve), Kr (center curve), and Ar (upper curve) on NiAl(110). Substrate temperature was approximately 30 K. Inset: value of work function obtained from EDC widths (average) and from PAX formula [Eq. (1)] (local) for these three cases.

0.5 eV higher than the corresponding work-function value of the clean surface, and the 0.5 eV difference is well outside the uncertainty in the work-function values.

This result is quite surprising for several reasons. Our expectation in performing the above measurements was that the work function obtained from PAX would be the same as that obtained from the photoemission EDC, due to the size of the Xe atom and the presumed random distribution across the surface at dilute coverage and low temperatures. In addition to this unexpected result, we noted that the Xe $5p_{3/2}$ photoemission feature exhibited a further lifting of the $J=3/2$ degeneracy, as previously reported.[9,10] We first confirmed the difference, repeating the measurement a total of more than 20 times. The result was unambiguous: There was always a difference of 0.5 eV in the two work-function values and for a coverage regime where the values should have been the same, within experimental error.

To elucidate the situation, we deliberately altered the surface composition by using both sputtering and extended annealing to alter the Ni-to-Al concentration ration. We determined experimentally that there was a limited range of Ni or Al surface enrichment for which excellent crystallographic order was retained as determined by LEED. A large number of experiments similar to those just described were performed over this limited composition range. An additional calibration point at 100% Al was obtained by vacuum deposition of a thin Al layer onto the NiAl(110) surface. These results are presented in Fig. 2. The shaded region of the figure indicates the range over which the surface composition could be varied while retaining an excellent LEED pattern. The results demonstrate several interesting trends: (1) the work function obtained by the PAX model is consistently higher than that determined by photoemission EDC widths, independent of surface composition; (2) the work-function values determined by EDC widths fall near a straight-line extrapolation between work-function values for Ni(110) and Al(110); (3) for the Al-covered surface, the photoemission-derived work-function value matches the continuation of this extrapolation, denoted by the dashed line. The work-function values determined from photoemission EDC widths indicate a well-behaved surface for which the work function increases monotonically with Ni concentration.

Quite a different picture emerges from the work-function values obtained from Xe, Kr, or Ar physisorption. Despite larger (conservative) error bars for the Ni- or Al-rich samples (0.2 eV typical uncertainty), due to broadened features, and more scatter in the data, several noteworthy points emerge: (1) The work-function values obtained from physisorption are *always* larger than those obtained from photoemission EDC widths; (2) the work function obtained from physisorption does not change systematically over the range of Ni composition for which good LEED patterns were obtained. In sharp contrast to the photoemission-derived work-function values just reported, there does not seem to be any marked change with composition, although the photoemission-derived values change from 4.3 to 4.7 eV over the composition range investigated; (3) the work-function values of any one of the

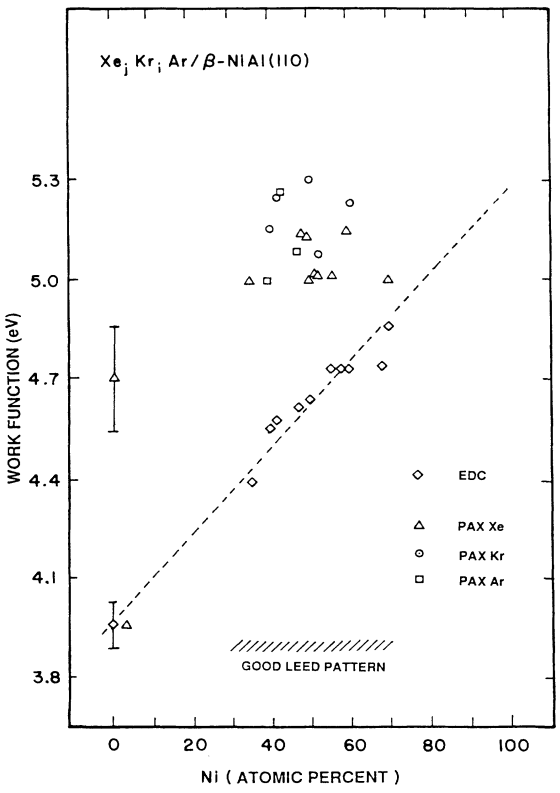

FIG. 2. Work function vs at.% Ni on surface. The work function was measured by photoemission energy distribution curve (EDC) (◇) or by physisorption of Xe (△), Kr (○), or Ar(□).

rare-gas atoms do not lie consistently higher than the values obtained from the others; (4) for the Al-covered surface, there were two pairs of Xe features observed. One pair corresponds to a work-function value equal, within experimental error, to the value obtained from the photoemission EDC width.

As a further check, we performed angle-integrated photoemission measurements at a variety of coverages, including one monolayer (data shown in Ref. 11). The one-monolayer data confirm the difference in work-function values obtained from photoemission and from the PAX model.

Returning to the motivation for this study, the NiAl(110) model system selected represents a limitation of the PAX model. Our remaining discussion will focus on the reasons for this surprising result and the precautions we have taken. By postulating a preferred site for the rare-gas atom, the results can be understood. The limited composition range investigated corresponded to a Ni:Al ratio ranging from 0.5–2.0. Such a limited range left at least half the sites with nominally no change in nearest-neighbor orientation, so a preferred site would (at dilute coverage) still be available. The difference in work-function values reported can be accounted for qualitatively by such a preferred-site hypothesis. The lack of change in the work-function values (deduced from the PAX model) with composition, in sharp contrast with the photoemission-derived values, is now explicable: The same site is always available and always occupied. We know the site is of C_{2v} symmetry, as previously reported.[9] We believe the cause is a charge transfer between the Ni and Al atoms on the NiAl(110) surface. In support of this view, we draw attention to a recent report by Davis and Noonan.[6] As Lang and Williams[2] have pointed out, the PAX model works well because the electrostatic part of the surface potential is too short ranged to affect the rare-gas-atom electronic energy levels. Such a conclusion is plausible for the jellium surface used by Lang and Williams, but must be reexamined for any alloy surface where charge transfer is a possibility. The report of Davis and Noonan[6] implies a local disturbance of the surface potential that may account for the breakdown of the PAX model reported here.

We are cognizant of several factors that must be included in a careful study and which have been taken into account in our work, including retaining a well-ordered sample at all times to avoid defect sites; accurately determining the actual rare-gas coverage; performing the measurements at dilute coverage so as to avoid lateral interaction; avoiding island formation for the same reason; selecting the proper values of E_v^b for Xe, Kr, and Ar; selecting the extrema of the clean NiAl(110) photoemission spectrum correctly so as to obtain an accurate value for E_W; carefully examining the adsorbed rare-gas photoemission spectra for the presence of two rare-gas doublets, which would indicate defect or other alternate sites; confirming a uniform surface; confirming the absence of rare-gas atom lateral interactions by obtaining angle-resolved photoemission and examining such spectra for indications of such interactions; multiple repetitions of the measurements to ensure reproducibility.

The actual rare-gas coverage is important in our study for several reasons. At dilute coverage, the rare-gas photoemission features reflect the local substrate environment. As the coverage approaches one monolayer, adatom-adatom interactions affect the photoemission features[12] and can cause misinterpretations.[13] We have performed angle-resolved photoemission studies[11] and have observed changes in the spectra for dilute and monolayer coverage of Xe and Kr. These changes (development of dispersing bands for one monolayer) and low-energy electron diffraction studies provide convincing evidence to exclude island formation. We have used the methods of Kaindl, Chiang, Eastman, and Himpsel,[14] Chiang, Kaindl, and Eastman[15] and LEED studies[11] to obtain an absolute exposure that corresponds to one monolayer.

The other two crucial decisions are selecting the correcting values of E_v^b for Xe(1), Kr, and Ar, and correctly measuring E_W. Since the values selected yield work-function values for Xe, Kr, and Ar adsorption that are internally consistent, we are confident of the values.

Measuring E_W correctly includes determining the Fermi edge and the cutoff of the secondary electrons. While the former is simple, the latter is not; many factors affect the cutoff. To establish an accurate method, we used elemental crystals, Ni(100) and Ag(110), scrupulously

cleaned them, and experimentally devised a procedure that yielded work-function values within 0.1 eV of the published values. We then used the same procedure for NiAl(110) and reported the results above.

In contrast to results reported for elemental and stepped surfaces,[1,3,4] we have found that the PAX method yields a value for the work function different from that obtained with angle-integrated photoemission. Further, we have found that the PAX-derived work-function values do not change systematically with surface composition over the limited range investigated. We have concluded that the rare-gas atoms occupy a preferred site and have given our reasoning in support of this view. We have noted that the β-NiAl(110) surface possesses sites of C_{2v} symmetry that the adsorbed rare-gas atoms preferentially occupy. Because of this preferred site, the work-function values obtained from the PAX model do not agree with those obtained from photoemission and do not accurately reflect changes in surface stoichiometry. This indicates that the PAX technique must be used with caution as a probe of heterogeneous systems.

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