Angle-resolved photoelectron emission from isolated xenon atoms on W(100)

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High-resolution angle-resolved photoelectron spectra for isolated xenon atoms physisorbed on a W(100) surface are reported. The results show conclusively that splitting of the $5p_{3/2}$ level due to surface crystal fields and other mechanisms is smaller than previously believed.

Rare-gas atoms physisorbed on metal surfaces constitute a unique family of systems which can be used to study several interesting physical processes. Ground-state perturbations of rare-gas adsorbates and accompanying changes in metal surface electronic structure are minimal because of the relatively weak interactions associated with physisorption.[1] These systems are therefore particularly well suited for studying final-state effects associated with localized ionized levels and the attendant screening by neighboring conduction electrons.[2,3] Additionally, ordered physisorbed monolayers[4] and thicker crystalline films can be formed on metal substrates under suitable conditions. These structures provide a basis for studying two-dimensional band effects resulting from adsorbate coupling[5] and for studying the evolution of three-dimensional band structure.[6]

Waclawski and Herbst[7] conducted one of the first photoemission investigations of a rare-gas monolayer on a metal surface. They reported significant broadening of the $5p_{3/2}$ component of the spin-orbit split $5p$ level of xenon physisorbed on W(100). This broadening was attributed to the tungsten surface crystal field interacting with the excited state. Subsequent theoretical work[8,9] suggested an alternate mechanism based on induced image charges, and additional experimental work[5] has indicated the observed broadening could be a consequence of experimental conditions. More recent experimental work has revealed what appears to be anomalous behavior associated with photoelectron emission from xenon physisorbed on Pd(110).[10]

Herbst[11] has investigated theoretically the angular distributions of photoelectrons from atoms adsorbed on metal surfaces taking into account the crystal field of substrate atoms. The primary results pertaining to xenon on W(100) are summarized in Fig. 1. Gas-phase photoelectron emission from the $5p$ level of atomic xenon produces two narrow peaks corresponding to the ionization potentials of the $5p_{1/2}$ and $5p_{3/2}$ states. The spin-orbit splitting Δ is 1.33 eV and the peak intensity ratio is 1.80 (not 2.0 representing the statistical weight). When the xenon atom is placed at a fourfold site on a metal surface, two effects are predicted: a shift of all levels (V_0) and a splitting of the $5p_{3/2}$ level (2ψ). This splitting, estimated to be of the order of a few hundred meV, can be modeled by an electric field $\vec{E}_z$ normal to the surface (see Fig. 1). Emission from the $5p_{3/2}$ sublevels is not isotropic in polar angle, as one would judge from their charge distributions shown in Fig. 1. Herbst's prediction of the polar-angle intensity ratio I_2/I_3 is shown plotted versus the polar angle in Fig. 1. These results provide the basis for a rather straightforward experimental test for surface crystal-field effects as probed by a physisorbed atom on a metal surface.

This paper reports the results of a careful

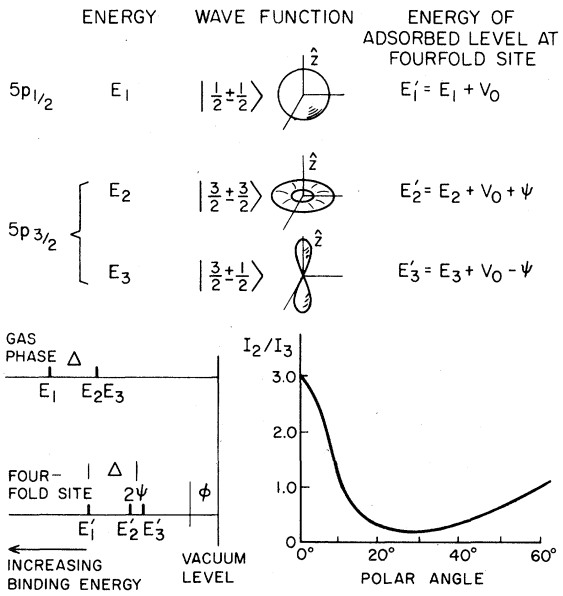

FIG. 1. Summary of theoretical predictions for xenon physisorbed at a fourfold site. The upper half of this figure illustrates $5p$ wave functions and energies. The lower half illustrates binding energy shift V_0 and crystal-field splitting 2ψ resulting from fourfold site. Graph shows predicted polar-angle variation of photoelectron intensity for E_2' and E_3' levels.

attempt to observe effects in the photoemission spectra of physisorbed xenon on W(100) which could be unambiguously attributed to surface crystal-field effects. Lateral coupling effects have been established in previous work[5] and by our own work at monolayer coverages which will be briefly described in this paper. High-resolution angle-resolved spectra of *isolated* atoms are required to probe for the predicted characteristic angular properties produced by surface crystal fields. The angle-resolved spectra reported here were obtained using high resolution (50–100 meV), employing substrate temperatures low enough to guard against island formation, and using carefully calibrated coverages from ~0.1 monolayers to thick films. The crystal was also oriented so that lateral coupling could be investigated at full monolayer coverages by sweeping reciprocal space along a symmetry direction. These experiments clearly identify the unique properties associated with each of three regimes describing physisorbed xenon on W(100) which occur at submonolayer, saturated monolayer, and multilayer coverages.

Experiments reported here were conducted using an Auger-photoelectron spectrometer which has been described previously.[12] The spectrometer incorporates a commercial twin-pass cylindrical-mirror analyzer (CMA) equipped with an angle-resolving drum ($\Delta\Omega = 4°$ or 12°) and a cold-stage manipulator utilizing a closed-cycle refrigerator which permits samples to be heated to ~1200 K and cooled to below 40 K. The sample geometry permits sweeping crystal momentum along symmetry directions by either rotating the crystal in the plane of light incidence or by rotating both the crystal and CMA drum.[12]

The tungsten crystal was spark cut and aligned to approximately ±1° using x-ray Laue techniques, and then mechanically polished to a mirror surface using various grades of alumina powder down to 0.05 μm. Most of the bulk carbon was removed from the tungsten crystal in a separate chamber by extended heating in oxygen (1800 K at $\sim 1 \times 10^{-6}$ Torr O_2) and flashing to 2500 K. After being mounted in the photoelectron spectrometer, the samples were cleaned by gentle argon ion sputtering (500 eV energy), annealing in oxygen and flashing in vacuum. Surface purity was monitored by Auger analysis.

Figure 2 shows normal-emission angle-resolved photoelectron spectra for low coverages of xenon physisorbed on W(100). Angular resolution for this data is 4° and energy resolution is about 100 meV as judged from the tungsten Fermi edge. The crystal temperature was maintained at 40 K.

Accurate determination of *relative* coverages

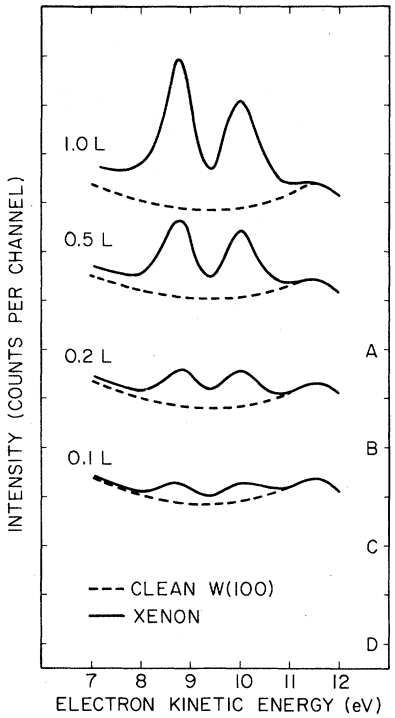

FIG. 2. Normal-emission angle-resolved photoemission spectra for low-coverage xenon on W(100). Angular resolution $\Delta\Omega = 4°$, energy resolution 100 meV, and substrate temperature 40 K. *A*, *B*, *C*, and *D* indicate the zero reference for the four spectra.

was obtained from careful monitoring of the gas dose. This technique is valid because the first monolayer sticking coefficient for xenon gas at 300 K on a tungsten surface below 60 K is unity.[13] The area under the $p_{1/2}p_{3/2}$ photoemission peaks normalized to the tungsten emission background as well as the work function change were also found to be roughly proportional to the dose at low coverages ($\lesssim 1$ monolayer). These parameters provided a consistency check on relative coverages. Absolute calibration of the coverage in terms of both peak area and dose was established as follows: The desorption temperature for the second layer of xenon on tungsten is 50–55 K.[14] A saturated coverage of $4.2 \times 10^{14}/\text{cm}^2$ is easily achieved by annealing a thick film above 55 K but below the first monolayer desorption temperature which is over 80 K at 10^{-10} Torr. Single and double monolayers were easily produced by adsorption followed by annealing, and these two coverages could be distinguished by measuring the *NOO* Auger line positions.[3,15] Single monolayer films yielded *NOO* Auger peaks at kinetic energies of 35.5, 37.7, and 40.1 eV; second-layer *NOO* peaks were found to be shifted to lower kinetic energy by about 2.2 eV.

The results of normal-emission low-coverage experiments are summarized in Table I. The experimental data indicate that at low coverages there is no coverage dependence in binding energy of either the $p_{1/2}$ or $p_{3/2}$ level with respect to the Fermi energy, and that the ratio of peak intensity (area under the peaks) remains constant. The data also show that there is a significant increase in amplitude of the $p_{1/2}$ level in relation to the $p_{3/2}$ level as coverage approaches one monolayer. This effect is attributed to lateral interactions between xenon atoms which eventually leads to evolution of bulk band properties of solid xenon. At low coverages the peak width results from screening of the xenon ion by conduction electrons. Gas-phase spectra taken using our photoelectron spectrometer show very narrow $p_{1/2}p_{3/2}$ linewidths limited by spectrometer resolution. It is interesting to note that our angle-resolved spectra for one monolayer coverage is in fairly good agreement with the angle-integrated results reported by Waclawski and Herbst,[7] and the fixed binding energies we find at low coverages agree with similar work on Pd(100) (Ref. 5) but disagree with results for Pd(110) (Ref. 10).

To check for evidence of crystal-field effects predicted by Herbst,[11] angle-resolved photoelectron spectra for low coverages were obtained as a function of polar angle along symmetry directions of the W(100) crystal. Figure 3 shows results for one coverage. To illustrate the effect attributable to crystal fields acting on the excited state of a xenon atom, Herbst's predictions of the angular variation of crystal-field split $p_{3/2}$ components were used to obtain the curves shown as an inset of Fig. 3. The "predicted" curves were obtained by modeling the three peaks associated with E_1', E_2', and E_3' using a three-Gaussian function with parameters chosen to represent the correct spin-orbit splitting $\Delta = 1.30$ eV, to simulate a crystal-field splitting $2\psi = 0.3$ eV, and to simulate our experimental observation that the $p_{1/2}$ and $p_{3/2}$ levels have similar intrinsic widths and strengths at low coverages.

It is clear that if $2\psi \approx 0.3$ eV, and the I_2/I_3 ratio prediction is approximately correct, the effect of crystal fields should have easily been observed in this experiment. A shift as small as 50 meV would have certainly been detected with the energy resolution used in these experiments. The unmistakable conclusion is that any crystal-field-induced shifts must be very small, i.e., less than 50 meV. This result supports the primary objection raised by Antoniewicz[9] in discussing the crystal-field explanation of the splitting which required a rather large positive charge to be associated with tungsten surface atoms.

A number of monolayer films were studied as well as several thick films. Low-energy electron diffraction (LEED) was not available to characterize our films and no LEED work for the xenon-W(100) system seems to have been reported. Ordered films were produced by annealing at ~80 K, and reproducible angular dispersion of the $p_{1/2}p_{3/2}$ bands were obtained along the [11] direction of the W(100) crystal. The results are similar to what has been found[5] for Pd(100) and are compatible with the assumed existence of hexagonal antiphase domains on W(100). We find dispersion of both $p_{1/2}$ and $p_{3/2}$ levels equaling about 0.3 eV along the [11] axis of W(100). This would correspond to the $\bar{\Gamma}$–$\bar{H}$ direction of the

TABLE I. Summary of experimental results for four low-coverage systems. [μ and full width at half maximum (FWHM) in eV.]

Dose	Peak area	μ_1	μ_2	$FWHM_1$	$FWHM_2$	Ratio
0.1L	0.048	8.70	10.00	1.00	0.990	60:45
0.2L	0.112	8.70	10.00	0.860	0.990	60:50
0.5L	0.26	8.70	10.00	0.750	0.980	60:60
1.0L	0.50	8.70	10.00	0.690	0.940	60:60

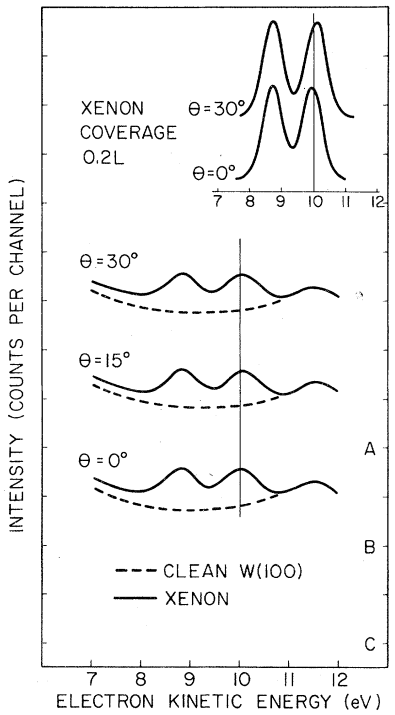

FIG. 3. Angular resolved photoelectron emission polar plots for low-coverage xenon on W(100). Angle is varied along the [11] direction of the W substrate. Angle resolution $\Delta\Omega = 4°$, energy resolution 100 meV, and substrate temperature 40 K. Inset shows predicted peak shift based on $2\psi = 300$ meV.

two-dimensional Brillouin zone of antiphase hexagonal domains, but could also correspond to the $\bar{\Gamma}-\bar{X}$ direction of a $(\sqrt{2}\times\sqrt{2})45°$ ordered structure. There is some evidence that such a structure is stable on W(100) at $T=65$ K.[13] In any event, we have observed lateral coupling at one monolayer coverages on W(100), and the effects are qualitatively different from our results at low coverages. This clearly distinguishes the two regimes.

Thick xenon layers yielded normal-emission photon energy dependence ($\hbar\omega=16.85$, 21.22, 40.81) of energy distribution curves similar to those reported for xenon crystals grown on Pd(100).[6] This behavior is consistent with interband transitions between bulk bands as probed along the $\Gamma-L$ direction of the Brillouin zone.

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[1]G. G. Kleiman and U. Landman, Phys. Rev. B 8, 5484 (1973).
[2]J. A. Cunningham, D. K. Greenlaw, J. L. Erskine, and C. P. Flynn, Phys. Rev. Lett. 42, 328 (1979).
[3]G. Kaindl, T.-C. Chiang, D. E. Eastman, and F. J. Himpsel, Phys. Rev. Lett. 45, 1808 (1980).
[4]T. Engel, P. Bornemann, and E. Bauer, Surf. Sci. 81, 252 (1979).
[5]K. Horn, M. Scheffler, and A. M. Bradshaw, Phys. Rev. Lett. 41, 822 (1978); M. Scheffler, K. Horn, A. M. Bradshaw, and K. Kambe, Surf. Sci. 80, 69 (1979).
[6]K. Horn and A. M. Bradshaw, Solid State Commun. 30, 545 (1979); N. Schwentner, F. J. Himpsel, V. Saile, M. Skibowski, W. Steinman, and E. E. Koch, Phys. Rev. Lett. 34, 528 (1975).
[7]B. J. Waclawski and J. F. Herbst, Phys. Rev. Lett. 35, 1594 (1975).
[8]J. A. D. Matthew and M. G. Devey, J. Phys. C 9, L413 (1976).
[9]P. R. Antoniewicz, Phys. Rev. Lett. 38, 374 (1977).
[10]J. Kuppers, F. Nitschke, K. Wandelt, and G. Ertl, Surf. Sci. 88, 1 (1979).
[11]J. F. Herbst, Phys. Rev. B 15, 3720 (1977).
[12]J. L. Erskine, Phys. Rev. Lett. 45, 1446 (1980).
[13]C. Wang and R. Gomer, Surf. Sci. 84, 329 (1979).
[14]T. Engel and R. Gomer, J. Chem. Phys. 52, 5572 (1970).
[15]Kaindl *et al.* excited the *NOO* Auger electrons using 90-eV photons. Our *NOO* Auger spectra were obtained by operating the spectrometer in a pulse-counting mode and using a low-intensity 100-eV electron beam from the CMA coaxial gun.