Angular dependence of uv photoelectron distributions for oxygen adsorbed on W(100)

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Recent theoretical work has suggested the possibility of determining chemisorption bond geometry by the use of uv photoemission. This possibility is being investigated experimentally in an apparatus developed at NBS. The apparatus is described, and preliminary results are presented which show energy distributions as a function of emission angle for electrons photoemitted from W(100), both clean and with adsorbed oxygen. The results obtained at $h\nu = 21.2$ eV for several emission angles indicate substantial angular dependence of the photoelectron distributions, not only for the clean (100) surface, but also, more dramatically, with an oxygen adlayer.

INTRODUCTION

Fundamental to an understanding of the nature of the surface bond is a determination of its electron energy levels for a given adsorbate–substrate system. Ultraviolet photoemission already has demonstrated its utility for such a surface spectroscopy.[1,2] Additionally, it has been proposed[3,4] that information regarding types of bonds and bond directions might become accessible if one could measure the angular dependence of the uv photoemission from an adsorbate fixed on a two-dimensional array of substrate atoms. The angular dependence of uv photoemission has been investigated for clean surfaces,[5] and, more recently, for hydrogen adsorbed on W(100).[6] In this paper we report our first attempt to measure energy distributions as a function of emission angle for electrons photoemitted from oxygen adsorbed on W(100). Previous work[2] indicated that when W(100) was exposed to $\sim 5\times10^{-6}$ t·s of oxygen, heated to $\sim$1500 K, and then cooled to room temperature, two distinct peaks in the photoelectron distribution were observed at $\sim$5 and $\sim$6 eV below the Fermi level, E_F. The purpose of the present investigation was to determine whether there existed any differences in the angular distributions for emission from these (assumed) different states of oxygen on W(100) by observing these two peaks at several emission angles. The results of a rather limited sampling of emission angles show substantial angular dependence of the photoelectron distributions, not only from the oxygen adlayer, but also for the clean tungsten surface.

EXPERIMENTAL

The experimental apparatus,[7] Fig. 1, consisted of an ultrahigh vacuum chamber (ultimate vacuum $\sim 5\times10^{-11}$ Torr), a triple-grid, ac-modulated ($\sim$500 Hz), retarding potential energy analyzer, and a microwave-excited, helium resonance lamp which was isolated from the chamber by two stages of differential pumping. Photons of $h\nu = 21.2$ eV were incident at 45° to the sample normal. Electrons photoemitted from the sample passed through the analyzer grids and struck a 76-mm diam channel plate positioned so as to intercept electrons emitted into a cone of solid angle $\sim 0.6\ \pi$sr about the sample normal. A flat, fluorescent screen positioned behind the channel plate provided a visible ($\sim$0.11 fL max) display-in-angle of the amplified photoelectron current. A spot photometer was used to measure the intensity at a small, selected area of the screen.[8,9] The spot photometer (Fig. 2) consisted of a Wray 4:1 copying lens ($f/1$, 51-mm focal length) coupled to an RCA 931A photomultiplier. With a lens-to-screen distance of $\sim$28 cm, the image reduction was about 1/5.3. A circular aperture of $\sim$1 mm diam, located in the image plane, defined an area at the center of the screen of about 5 mm diam. At this position, the light from this sampled area corresponded to electrons photoemitted into a solid angle of $\sim 1.2\times10^{-2}$ sr ($\sim$3.5° half-angle). Because of the flat screen presentation and the fixed aperture size, the sampled solid angle decreased toward the edge of the screen to $\sim 4\times10^{-3}$ sr ($\sim$2° half-angle). The direction of emission was selected by a horizontal or vertical translation of the aperture and the multiplier parallel to the image plane. The ac-modulated component of the screen intensity within the sampled area was converted by the photomultiplier to an ac voltage which was coupled to a lock-in amplifier. The output of the lock-in amplifier was fed to a voltage–to–frequency converter, and thence to a multichannel analyzer whose channel address was converted to a proportional dc voltage and amplified to provide the retarding potential applied to the grids.

Two modes of operation were possible with the spot photometer: (1) The emission angle was selected by positioning the movable image plane aperture. A scan

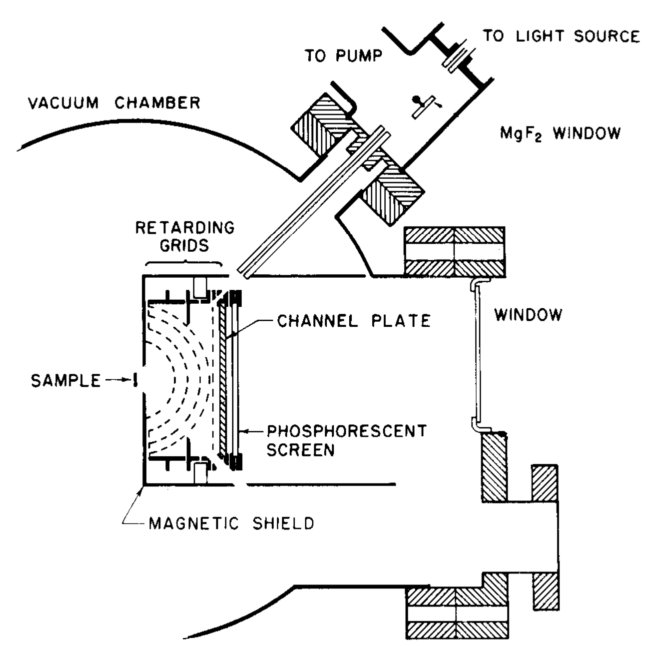

FIG. 1. Schematic diagram of the photoelectron spectrometer (top view).

of the retarding potential then provided the full electron energy distribution at the selected angle of emission. (2) A particular feature in the distribution could be chosen by using a fixed retarding potential, and then the aperture could be scanned across the image of the screen. In this mode, the variation of the selected feature with angle of emission was measured. A typical sequence for mode (1) was as follows: With the detector positioned at a selected emission angle, the sample was flashed to >2500 K, and a clean distribution taken. This consisted of three summed scans of the energy distribution and took a total time of $\sim$2.5 min. Oxygen was then admitted into the chamber to a total exposure of $\sim 5\times10^{-6}$ t·s and another spectrum was taken for this room-temperature exposure. Finally, distributions were taken after the sample was heated to 1500 K and cooled to room temperature. This sequence of cleaning, exposure, and heating was repeated at each of the selected emission directions.

RESULTS

Photoelectron distributions for five emission directions and with different surface conditions are displayed in Figs. 3–5. The angles shown in the figures were calculated from the geometry of the system and can only be taken as approximate since the electron optics has not been fully investigated. Also, calculations show that a flat screen presentation of the intensity for an isotropic distribution will fall off with angle as $\cos^3\theta$, where θ is measured away from the sample normal (center of screen). Thus, the (uncorrected) curves shown in the figures should be amplified for increasing angles. Earlier data,[2] obtained for total screen distributions (i.e., averaged over $\sim 0.6\ \pi$ sr) are shown as the lowest curve in each figure for comparison with the angle-resolved distributions. The curves marked 0° are for the center of the screen, and correspond to emission in the [100] direction. The other curves were measured away from the (horizontal) plane of incidence by translating the spot photometer vertically. A "posthumous" x-ray analysis of the crystal revealed that the [001] axis (in the crystal face) was rotated clockwise about 36° from the plane of incidence (cf. Fig. 2).

For clean W(100), the distributions in Fig. 3 for the total screen and for 0° show considerable similarity in energy location of the structure. A marked difference is in the relative amplitudes of the -2 and -0.4 eV (surface state) peaks. The dip in the distributions at -12.5 eV is seen to deepen for emission in the [100] direction. The band structure calculations of Christensen[10] show a $\sim$2 eV gap along the [100] direction which corresponds to this dip $\sim$4 eV above the vacuum level. For the remaining distributions in Fig. 3, shifts of $\sim$1 eV occur for the -2 and -4.5 eV peaks, indicating that a more comprehensive study of the angular distributions may prove helpful in elucidating the shapes of the energy bands in directions away from the symmetry directions.

Figure 4 shows distributions obtained after exposure to 5×10^{-6} t·s of oxygen at 300 K. The oxygen peaks at -5.2 and -6.3 eV are almost resolved in the total screen distribution. However, as a function of angle, the dominance of one peak over the other alternates as the emission direction is moved away from the sample normal. In addition, in Fig. 4, the peak near -2 eV narrows somewhat in the [100] direction.

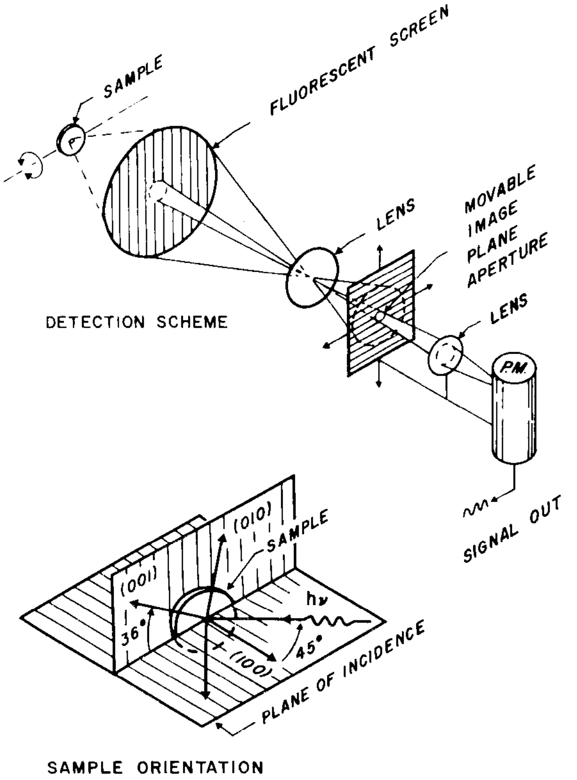

FIG. 2. Top—schematic diagram of the spot photometer configuration. Bottom—the sample orientation referred to the (horizontal) plane of incidence.

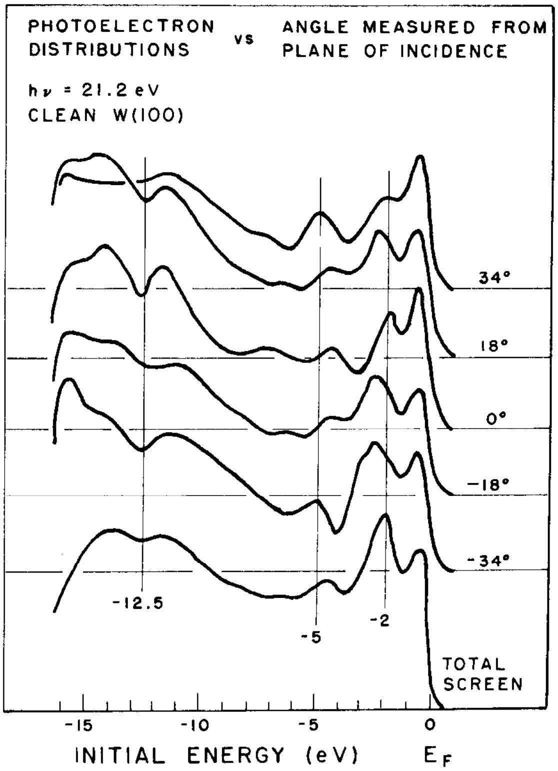

FIG. 3. Angular photoelectron distributions from clean W(100). The angles shown in the figure are measured from the sample normal. The same azimuthal angle about the sample normal was used for each of the five upper curves. The lowest curve (for comparison) shows the distribution measured for the total solid angle ($\sim 0.6\ \pi$ sr) subtended by the screen.

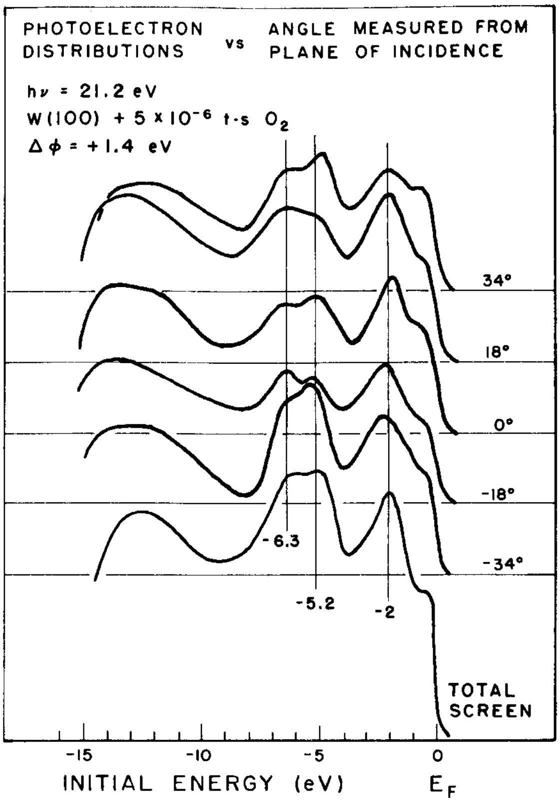

FIG. 4. Angular photoelectron distributions for W(100) exposed to $\sim 5\times10^{-6}$ t·s oxygen. The angular coordinates are the same as those in Fig. 3. The work function increase is referred to the clean (100) surface.

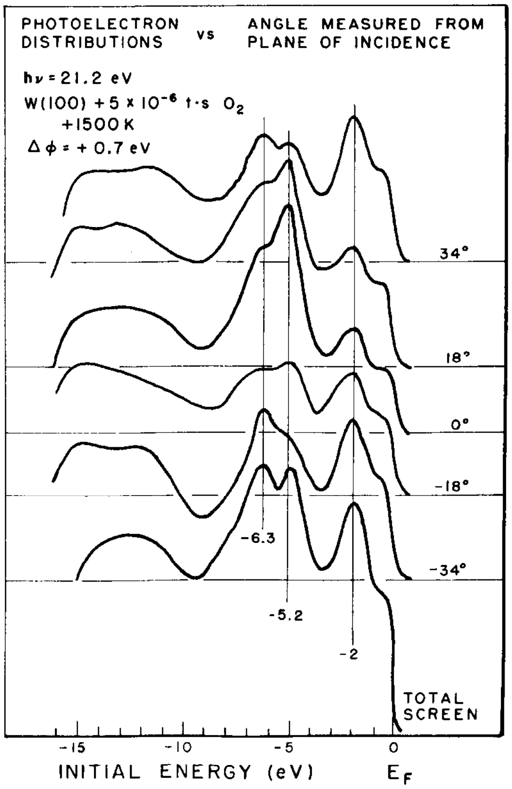

FIG. 5. Angular photoelectron distributions for W(100) exposed to $\sim 5\times10^{-6}$ t·s oxygen and subsequently heated to 1500 K. The angular coordinates are the same as those in Fig. 3. The work function increase is referred to the clean (100) surface. $h\nu=21.2$ eV; W(100)+$5\times10^{+6}$ t·s O_2+1500 K; $\Delta\phi=+0.7$ eV.

In Fig. 5, the total screen distribution shows a splitting, and a growth in amplitude of the -5.2 and -6.3 eV peaks when the sample is heated to 1500 K. It should also be noted that the work function (obtained from the width of the distribution) decreased after heating. The distribution for the [100] direction changes dramatically; the -5.2 and -6.3 eV peaks grow and completely dominate the spectrum, whereas the region from ~ -3.5 eV to E_F decreases. Also, the symmetry of the two peaks with respect to the sample normal has changed (compare Fig. 4). The -5.2 eV peak now remains dominant up to about ±18°, whereas the -6.3 eV peak assumes a dominance beyond ±18°. In the context of Gadzuk's calculations[11] of angular photoelectron distributions from oriented adsorbates, this would be suggestive of the -5.2 eV state possessing a p_z symmetry leading to a maximum emission normal to the sample in contrast to a different symmetry (bridge or four-fold bonding) indicated by the minimum in the normal direction for the -6.3 eV state. The region near -2 eV appears to have the symmetry of the -6.3 eV peak in that it maximizes towards the larger angles.

In conclusion, it has been demonstrated that uv photoelectron distributions possess angular dependence, not only for clean W(100) but, even more dramatically, also for an oxygen adsorbate. The extent to which the angular dependence reflects the geometry of the bonds for adsorbed species will be the object of a more comprehensive study.

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