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Charge state of adsorbate ions: I on Cu(001)

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We have used x-ray photoelectron spectroscopy to study iodine adsorbed on Cu(001). The change with coverage of the I-core-electron binding energy directly measures the charge state of the adsorbate atoms. We find a charge transfer of 0.04 electron to each I atom.

The charge state of the adsorbate atoms is naturally of great importance in the study of any adsorption system. This quantity has generally been inferred from the change in work function resulting from the formation of the surface dipole layer.[1] For the clean substrate, however, there is typically already a surface dipole, resulting from a distortion of the electron density at the surface, which may be subsequently modified by the adsorbate. This modification also contributes to the change in the work function, so that work-function measurements cannot unambiguously determine the charge state of the adsorbate atoms. This ambiguity can be avoided by using the technique of x-ray photoelectron spectroscopy (XPS). Here we report experiments on Cu(001) with well-characterized iodine overlayers, demonstrating that the adsorbate charge can be independently estimated from the coverage dependence of the binding energy of the adsorbate atom's core electrons. Experiments on other orientations of Cu, and on Ag and Ni, are in progress and are planned to be reported elsewhere.[2]

The experiments were carried out in a UHV sample preparation chamber with 10^{-8} Pa base pressure, attached to a Hewlett-Packard (HP) 5950A electron spectroscopy for chemical analysis (ESCA) spectrometer. An oriented Cu single-crystal slab was mounted in a special sample holder equipped for high-temperature annealing. Since some buildup of carbon contamination was noted after overnight runs, it was general practice to clean the sample before each exposure to iodine. The sample was cleaned by repeated argon-ion sputtering and annealing until no significant oxygen or carbon contamination could be discerned in 15-min ESCA scans. A good low-energy electron diffraction (LEED) pattern gave further evidence that a clean, well-ordered surface had been obtained.

The LEED pattern was observed as iodine was admitted into the preparation chamber through a leak valve while the chamber was pumped by a partially throttled turbopump. A pressure of 10^{-6} Pa was maintained during the adsorption process. Two distinct LEED patterns were sequentially observed with increasing exposure: A $p(2\times2)$ and a distorted $c(2\times2)$.[3]

A complete set of x-ray photoemission (XPS) scans was first taken on the clean, iodine-free sample. Particular emphasis was given to those regions where the iodine $3d$ and $4d$ signal were subsequently to be measured. XPS data were taken at a variety of coverages, including some so low (~0.1 monolayer) that no change in the original CU(001) LEED pattern could be discerned.

Both copper and iodine lines were recorded after each exposure, including spectra for the Cu $2p$, I $3d$, I $4d$, and valence-band regions. The valence-band spectra were used mainly for a direct determination of the Fermi energy, which is sensitive to sample position in the HP spectrometer. The iodine $3d$ cross section is sufficiently large[4] at 1.5 keV photon energy so that even a few percent of a monolayer of iodine could be detected. The I $3d$ data were not useful, however, for more detailed analysis because these spectra include a high background of Cu L Auger electrons. Most of the detailed information was obtained from the I $4d$ spec-spectra, which occur in a region of low background and which have a small lifetime width.

The experimental data were analyzed by least-squares fitting, using a theoretical representation of the XPS line shape which incorporates a two-parameter form of our resolution function,[5] the

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Doniach-Sunjic (DS) line shape,[6] and phonon broadening, all combined by convolution. In order to extend the fit over some distance from the peak of the line, it is necessary to include a representation of other sources of energy loss, e.g., plasmon excitation. For Cu, one has reasons to expect the DS function to give an adequate representation of the line shape up to the point where *d*-band excitation become energetically possible. We have consequently explored the use of a displaced integral background with a threshold energy near 2 eV. By including this background in the model function which is fitted to the data, the data can be represented both inside and outside of the DS range. The form of the background used in fitting the iodine spectra does not affect the important quantities, i.e., the binding-energy shifts, extracted in the data analysis.

An example of an I 4*d* spectrum fitted with this line shape and background is shown in Fig. 1. Below the data we display the residuals, i.e., the difference between the fitted curve and the data. The absence of systematic fluctuations indicates that the model provides an adequate representation of the data. The two spin-orbit components were constrained to have the same shape. The I 4*d* spin-orbit splitting was found to be 1.71 eV and the $4d_{3/2}$-to-$4d_{5/2}$ intensity ratio 0.694, a value in good agreement with Ref. 4. The lifetime width is 0.3 ± 0.1 eV, and the singularity index is comparable to that of Cu. The Gaussian width increases with coverage, especially beyond the $p(2\times2)$ range where it approaches 0.5 eV. We take that as an indication of inhomogeneous broadening due to inequivalent iodine atoms occurring in the coverage region of the distorted $c(2\times2)$ LEED pattern.

Analysis of the Cu $2p_{3/2}$ line at 932.7 eV is complicated by the I $3p_{1/2}$ line at 931 eV. The latter is relatively broad and weak, but cannot be ignored if meaningful parameters are to be obtained for the Cu line. By explicitly including both lines in the fit a consistent lifetime width of ~0.6 eV was obtained for the Cu $2p_{3/2}$ line independent of iodine coverage. The overall Gaussian width, which includes instrumental, phonon, and inhomogeneous broadening, was found to decrease slightly with increasing iodine coverage, while the Cu $2p_{3/2}$ peak evinced a small but reproducible shift of ~0.06 eV to higher binding energy. The singularity index for the Cu did not change significantly with iodine adsorption. The Cu 3*s* and 3*p* signals at 122.2 and 74.0 eV were not useful for detailed analysis because they are both relatively wide — 1.9 ± 0.1 eV and 2.0 ± 0.1 eV, respectively. The Cu 3*p* spin-orbit splitting is 2.44 ± 0.02 eV.

Upon analysis of the data for a wide range of

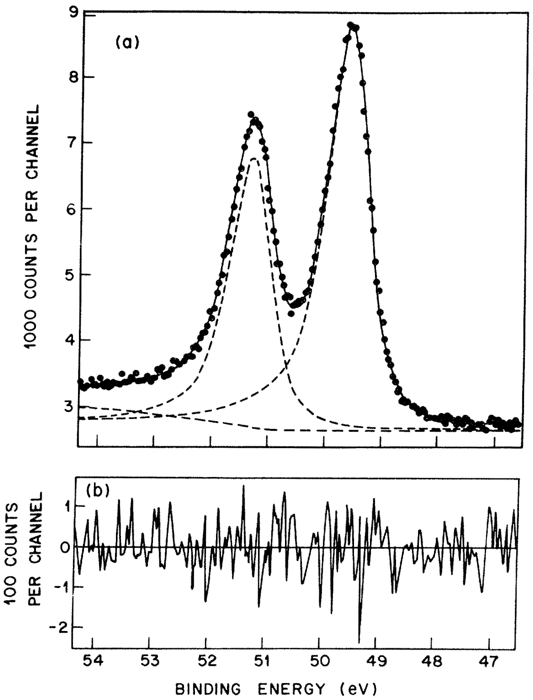

FIG. 1. (a) The I 4*d* x-ray photoemission spectrum for a $p(2\times2)$ overlayer on Cu(001). The solid line is a least-squares fit using the model described in the text. The components are shown as the dashed curves. (b) The residuals.

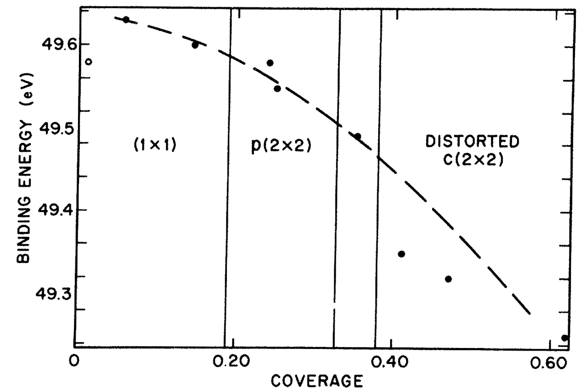

FIG. 2. The coverage dependence of the I $4d_{5/2}$ binding energy (see text). The open circle indicates the binding energy of a small amount of iodine remaining after sputtering and annealing the sample several times.

coverage, the most important observation to emerge is a systematic change in the iodine core-electron binding energy with coverage. This is illustrated in Fig. 2 where the I $4d_{5/2}$ binding energy is plotted as a function of coverage. We attribute the systematic shift to an initial-state effect, that is, to the Coulombic interaction between adatoms. If this were a final-state effect reflecting the polarization of the neighboring I atoms in response to the new core hole, then the response of the substrate screening charge would be coverage dependent; as stated above, however, the asymmetry of the I peaks does not change with coverage as would then be expected. Thus, not surprisingly, the screening response of the Cu conduction electrons is seen to take precedence over the polarization of the adatoms. The observed iodine binding-energy shift indicates the sign of the charge transfer, and, as expected, the iodine becomes negative.

We can infer the charge transfer from the change in the I core-electron binding energy by calculating, at the site of one atom, the electric potential due to all the other adsorbate atoms. Of course, we include not only the charge on the adsorbate atoms but also the equal and opposite charge in the substrate. The charge distribution at large distances can be adequately represented as a collection of simple point-charge dipoles. In fact, explicitly locating the substrate charge at the sites of copper surface atoms has a negligible effect on the calculated potential. The calculation is easily carried out for the ordered $p(2\times2)$ overlayer, where the height of the adsorbate layer above the Cu surface is known from the surface extended x-ray absorption fine-structure (EXAFS) experiments of Citrin *et al.*[7] The measured shift in binding energy then implies a charge transfer of 0.04 ± 0.01 electron per adatom. In the case of I on Cu(001), then, we observe a charge transfer quite similar in magnitude to the values inferred from work function measurements in other systems.[1]

The inference of charge transfer to the adsorbate is confirmed by the analysis of the Cu $2p$ spectra. Because the $2p$ lines are rather broad we cannot resolve the contribution of the surface atoms in the bulk-dominated spectrum. However, the surface atoms in Cu are known to have core-electron binding energies lower by $\sim$0.25 eV than those in the bulk.[8] Thus both the narrowing of the Cu $2p$ peak and its small net shift to higher binding energies upon adsorption of I suggest an increase in the surface Cu electrons' binding energy. Charge transfer to the iodine would result in a decrease in repulsive energy, which accounts well for this increase in binding energy.

The surface EXAFS data indicate that, at the $p(2\times2)$ coverage, the iodine atoms are fourfold coordinated with the Cu atoms and the I—Cu distance is very close to the sum of the Cu and I covalent radii. We are inclined, then, to believe that in the $p(2\times2)$ structure each I atom is in a fourfold hollow on the 001 surface and is (weakly) covalently bonded to the surrounding Cu atoms. As θ is increased the simple $c(2\times2)$ structure is not observed. Instead, at coverages less than 0.5 monolayer, a "distorted" $c(2\times2)$ LEED pattern appears, indicating that the I atoms are no longer in the fourfold sites, having apparently moved along the grooves between rows of Cu atoms. This is consistent with the observed inhomogeneous broadening of the iodine XPS lines as described above. If the I atoms are still characterized by their covalent radii, as might be inferred for the $p(2\times2)$ structure, then this displacement from their previous lattice sites would not be due to I—I contact, but rather would result from an electrostatic interaction. Because the interaction of each slightly negative I atom with the dipole layer is only of the order of 0.01 eV, we would then infer that the iodine's affinity for the fourfold sites is very weak.

In summary, we have observed ordered, submonolayer coverages of weakly chemisorbed iodine atoms on the (001) face of Cu, with the coverage dependence of the I core-electron binding energy indicating a transfer of 0.04 electron to each I atom. This work demonstrates that XPS can be used to determine unambiguously the charge state of adsorbate atoms on metal surfaces. It will be particularly interesting to apply this method to systems in which the work function change upon adsorption has the "wrong" sign.[1,9]

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