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Temperature and adsorbate dependence of the image-potential states on Cu(100)

Z. Wu
Department of Physics, Rutgers University, Newark, New Jersey 07102

B. Quiniou, J. Wang, and R. M. Osgood, Jr.
Columbia Radiation Laboratories, Columbia University, New York, New York 10027

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We report a systematic study of the dependence of image-potential states on surface temperature and oxygen adsorption on Cu(100) using two-photon photoemission spectroscopy. The binding energy of the $n=1$ image-potential state is found to be insensitive to temperature, in agreement with inverse-photoemission measurements. In the temperature range 300–963 K, the image-peak amplitude is found to have a weak temperature dependence. The exposure of Cu(100) to oxygen (1.5×10^{-6} Torr s) reduces the intensity of the image-potential peak and causes a shift of the position of this peak toward higher kinetic energy by an amount comparable to the change in the work function. A technique is described for eliminating space-charge effects, which can be a problem in pulsed-laser two-photon measurements.

Image-potential states are unique surface (actually near-surface) states with very narrow energy widths (a few tens of meV[1,2]). They are bound states between the image potential and the surface barriers. Like the hydrogen atom, the image-potential states from Rydberg progressions, with the $n=1$ state having about 0.5–0.8 eV binding energy for most of the metal surfaces that have been studied.[3] Since these image states are normally unoccupied, inverse photoemission spectroscopy[4,5,6,7] and two-photon photoemission spectroscopy[8,9] have been used to investigate these image states, although only the latter method offers measurement resolution comparable to the actual lifetime-limited width. Because of this resolution, two-photon photoemission spectroscopy allows the use of slight shifts in the image state to probe surface conditions, such as surface adsorption or temperature.

Previous experiments on image-potential-state binding energies, using inverse photoemission,[10] have reported that the binding energies are relatively insensitive to temperature; that is, the state appears pinned to the vacuum level. The purpose of this work is to investigate this observation more closely by using the high resolution available from two-photon photoelectron spectroscopy. Our study focuses on the temperature dependence of the Cu(100) surface, and our measurements are thus complementary to inverse photoemission experiments, although we report a somewhat larger temperature range. An important secondary result of our work is that space-charge effects, which are known to be an important limitation in two-photon photoemission spectroscopy, particularly using a low-duty-cycle pulsed source, can be obviated by simple adjustment of the optical source intensity.

In selecting a copper surface for our study, we initially considered Cu(111) because of its well-known resonant enhancement using two-photon excitation.[3] However, this enhancement results from the excitation from a narrow occupied surface state just below the Fermi level E_F, thus any measurement of the temperature dependence of the two-photon signal will reflect thermal alteration of both the surface state and the image-potential state. In fact, previous observations have shown that the resonantly enhanced image-state photoemission on Cu(111) is strongly quenched at the relatively low temperature of 200 °C.[11] This temperature dependence is unexpectedly strong since the electron wave function of the image state is a few Å outside the crystal surface.[12] In order to study the properties of image states without being affected by surface states, we chose the Cu(100) surface in which there is no occupied surface state just below E_F so that the image states would be populated only by nonresonant excitation from the bulk states.

In two-photon photoemission, a photon excites an electron from the valence band to an excited state, the image-potential state in our case, which is then ionized by a second photon. The light source was a frequency-doubled excimer-pumped dye laser. The intensity of the laser beam was low enough that sample heating due to laser irradiation was negligible. The (100) surface of single-crystal copper (99.999% purity) was chemically cleaned before being loaded into an ultrahigh-vacuum chamber. The sample was then sputtered and annealed ($\sim$850 K) until a sharp (1×1) low-energy electron-diffraction pattern appeared. The pressure in the chamber was normally below 3×10^{-10} Torr, although for the highest-temperature ($\sim$1000 K) measurements it rose to $\sim2\times10^{-9}$ Torr. For variable-temperature experiments, the sample was heated using a button heater. The wiring of the heater and the leads were such that the magnetic field due to the heating current was less than $\sim$0.2 G. The sample was biased at -5 V with respect to the electron energy analyzer in order to reduce the effect of the stray magnetic field ($\sim$0.5 G). The electron energy was analyzed using an electrostatic, 160° spherical-sector energy analyzer, with a resolution of about 200 meV for the conditions of our experiment. The analyzer was positioned normal to the sample surface and the collection angle was 0.002 sr. A multichannel plate detector was used to detect photoelectrons. Both the sector energy analyzer and the multichannel plate detector were enclosed in a μ-Metal box to reduce any stray magnetic fields.

A typical photoemission signal with exciting photon energy 4.55 eV is shown in Fig. 1, in which the energy distribution curve (EDC) is shifted by 5 eV due to the -5 V bias. The large peak at ~5 eV is due to single-photon photoemission from the tail of the Fermi distribution.[2] An expanded view of the image-potential-state signal around 9 eV is shown in the inset of Fig. 1, where the two peaks correspond to the hydrogenic image-potential states $n=1$ and $n=2$, respectively, as have been seen by Giesen *et al.*[8] Shown in Fig. 2 is the temperature dependence of the $n=1$ image-potential-peak position. It is important to emphasize that the data in Fig. 2 were taken with the integrated area of the first low-energy peak (see Fig. 1) held constant by adjustment of the incident laser flux. This step was necessary since it was found that the image-peak position was affected not only directly by temperature but also by the space charge created by the large low-energy electron peak. While space charge broadening of the EDC's has been reported by several groups,[13,14,15] there has not been a previous discussion of the fact that the energy position of photoemission peaks can be easily shifted due to the presence of high electron densities in other features, a phenomenon of particular importance in pulsed-laser photoemission experiments. In our case, the space charge and temperature variation shift the image-peak position in opposite directions. However, by keeping the total number of low-energy electrons constant, the shift due to the space charge was kept constant, and we were able to observe the direct variation in the peak position with temperature. A linear fit to the data in Fig. 2 yielded the rate of change in kinetic energy with temperature $\Delta E_K/\Delta T = -(2.5\pm0.7)\times10^{-4}$ eV/K. The experimental uncertainty was mainly due to the fluctuation in the laser flux. According to the calculation of Herzfeld,[16] the slope of the work-function variation with temperature for Cu is $\Delta\phi/\Delta T = -2.5\times10^{-4}$ eV/K. Using $\Delta E_K = \Delta\phi - \Delta E_b$, with E_b being the binding energy of the image state, we conclude that, within our experimental uncertainty, the binding energy of the $n=1$ image-potential state is insensitive to the temperature variation within the temperature range 300–715 K. In view of the fact that the available experimental data on the temperature dependence of the work function are surprisingly scarce, it is interesting to note that data such as that shown in Fig. 2 provide an interesting method to measure the temperature dependence of the work function on certain clean metal surfaces. This method is expected to have advantages over the conventional technique of fitting the photoelectric yield near the threshold to a Fowler plot.

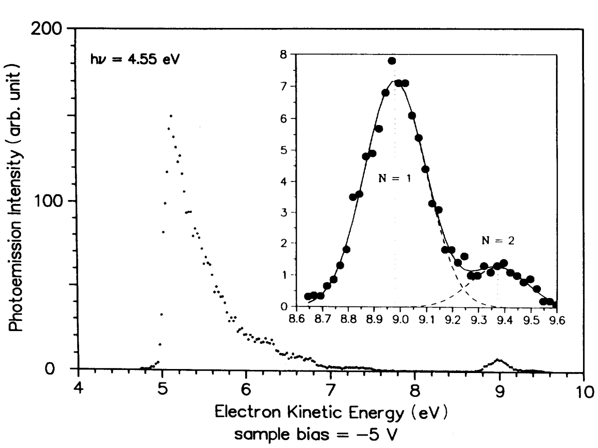

FIG. 1. Photoemission signal from Cu(100) with an incident photon energy of 4.55 eV. The sample was biased at -5 V. The inset is an expanded view of the same image-potential-state signal. The two peaks correspond to the hydrogenic image-potential states $n=1$ and $n=2$, respectively.

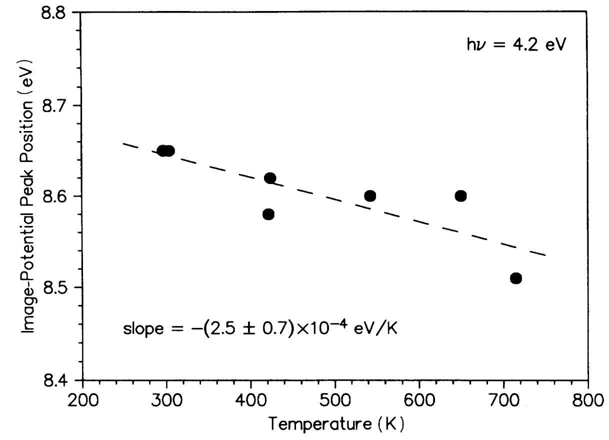

FIG. 2. Variation of the $n=1$ image-potential-peak position with temperature, with the integrated area of the low-energy peak being kept constant.

In order to cross check the above measurement of the pinning of the image state to the vacuum level, we measured the shift in the $n=1$ image state after exposing the Cu(100) surface to oxygen, since it is well known that oxygen adsorption increases the work function on Cu surfaces, i.e., moves the vacuum level upward. Note that the effect of oxygen adsorption on Cu(111) was studied by Rieger, Wegehaupt, and Steinmann.[17] However, in that case, no shift in the image peak could be observed since the resonant image-potential-state signal disappeared upon the adsorption of oxygen (1000 L). In our experiment, the exposure to the oxygen gas was done by backfilling the chamber with research-grade O_2, while the sample was at room temperature. Shown in Fig. 3 are the image peaks for clean and 1.5 L O_2 exposed Cu(100) (1 $\mathrm{L}=10^{-6}$ Torr s). The image-state signal was reduced after the exposure to O_2. A shift in the image-peak position by ~0.07 eV, towards higher kinetic energy, can be clearly seen. Both the direction and the magnitude of the shift are consistent with the increase of work function after the exposure to oxygen.[18] A similar shift of the image-potential energy level after the substrate was exposed to K and Cl has been reported in inverse photoemission experiments.[5,10]

Our temperature-dependent shift data as well as the oxygen-adsorption data are consistent with the phase-analysis model.[19,20,21] According to this model, the binding energy of the $n=1$ image state is determined from

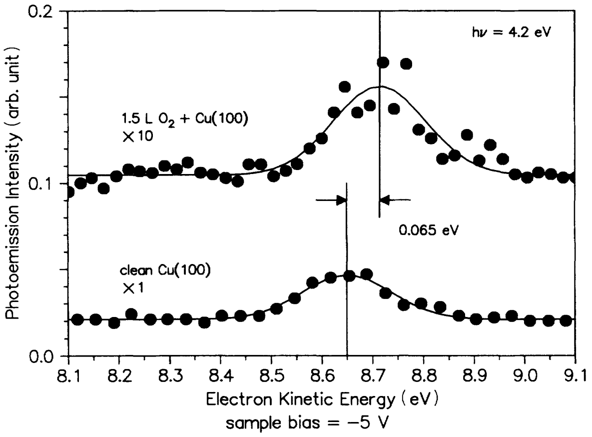

FIG. 3. Image-potential-peak position before and after 1.5 L oxygen-gas exposure.

the Bohr-like quantization condition $\phi_B+\phi_C=2\pi$. Here ϕ_B and ϕ_C are, respectively, the phase changes of the electron at the image potential and the surface barriers as it is reflected back and forth between these two potential barriers. The value of ϕ_B is a function of the vacuum energy level E_{vac} and the electron energy E and is given by $\phi_B=[(3.4 \text{ eV})/(E_{\text{vac}}-E)]^{1/2}\pi-\pi$. The value of ϕ_C depends on the energy band structure on Cu(100). Assuming that the only effect of oxygen adsorption is to shift the vacuum level upward with respect to the Fermi level, the phase model predicts that the $n=1$ level shifts upward by the same amount as the vacuum level does, which is consistent with what is observed.

However, when the surface temperature is raised, a small change occurs in the barrier at the crystal surface. In particular, according to the measurement by Knapp *et al.*,[22] the temperature coefficient for the bulk energy bands of Cu is of the order of 10^{-4} eV/K. This shift in the energy bands causes a change in ϕ_C, the magnitude of which is given by

$$\Delta\phi_C \approx \frac{\pi}{E_{X_1}-E_{X_4'}}\times 10^{-4} \text{ eV/K} \approx 5\times 10^{-5} \text{ rad/K} .$$

Here we have used $E_{X_1}-E_{X_4'}=6.1$ eV. The change in binding energy is given by

$$\Delta(E_{\text{vac}}-E)=-\frac{2(E_{\text{vac}}-E)^{3/2}}{\pi\sqrt{3.4}}\Delta\phi_B .$$

Noting that $|\Delta\phi_B|=|\Delta\phi_C|$ and that the binding energy of the $n=1$ image state at room temperature is 0.55 eV, we find that the change in binding energy is of the order of 10^{-5} eV/K, which is indeed quite small for our temperature range.

While the temperature dependence of the image-peak position yields information about the binding energy of the image state, the temperature dependence of the amplitude of the image peak provides important insight into the dynamic properties of the image state. Since the image state interacts only weakly with the crystal, one would expect a weak temperature dependence of the image-peak amplitude. This weak temperature dependence was first observed using inverse photoemission.[10] The results of our two-photon photoemission study confirmed this observation, as can be seen from the data shown in Fig. 4. To avoid any possible effect on the collection efficiency due to the magnetic field of the heating current, all the data points were taken when the heating current was off. In order to discriminate between the change due to temperature and to spurious surface changes as a result of chemical reactions such as oxidation, the temperature was cyclically varied between 300 and 1000 K. The uncertainty in the data, as indicated by the representative error bars, is mainly due to the fluctuation in laser flux. The data points represented by open triangles were taken after the sample was heated to ~1000 K (~150 K above the annealing temperature) for a few minutes. Apparently, some permanent change in the surface condition occurred during the high-temperature treatment. It is, however, interesting to note that the temperature dependence of the image-peak amplitude is as weak on the modified surface as on the clean Cu(100) surface. The modification of the surface condition could be due to (1) surface disordering or (2) the segregation of sulfur to the surface[23] at high temperature (~1000 K). The first possibility, i.e., surface disordering, was ruled out based on the observation that the Cu(100) surface does not lose order even for temperatures as high as 1273 K.[24] In this connection, it would be interesting to study image-state photoemission on a Cu(110) surface, which was reported to exhibit strong surface disordering at temperatures as low as ~600 K. No such study has been reported yet. The sulfur-segregation hypothesis seems to agree with the observation that after the high-temperature treatment the position of the image peak is found to shift to higher kinetic energy by ~0.07 eV, indicating a change in the work function of the surface. Like oxygen, the sulfur atoms that have segregated to the surface are also expected to reduce the image-peak ampli-

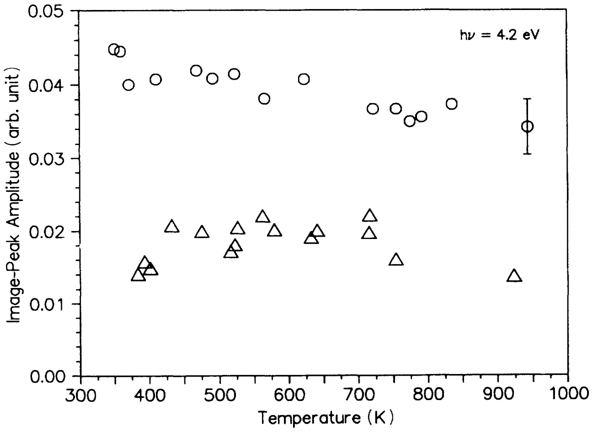

FIG. 4. Dependence of the image-potential-peak amplitude on temperature. The laser flux was kept constant. The data points represented by open circles were taken in the first temperature cycle. The sample was then heated to ~1000 K for a few minutes before the second temperature cycle started. The data points represented by open triangles were taken in the second temperature cycle.

tude. The fact that the same weak temperature dependence persisted on the sulfur-modified surface seems to indicate that the image-state electrons are still decoupled from this surface, even in the presence of an adsorbate system.

In conclusion, by using two-photon photoelectron spectroscopy, we confirmed and strengthened the observations of previous studies using inverse-photoemission spectroscopy. The image-potential state is pinned to the vacuum level, and the image-peak amplitude depends very weakly on the sample temperature. A method of measuring the temperature dependence of work function has been suggested. This method consists of measuring the kinetic energy of image-state photoelectrons while keeping the space charge fixed. Both the temperature and oxygen adsorption change the work function of copper and consequently the kinetic energy of image-state photoelectrons. However, whereas the temperature does not affect the image-state peak amplitude, oxygen adsorption drastically reduces the image-state peak amplitude. This same phenomena was observed on a Cu(100) surface modified by high-temperature heating. This modification was believed to be due to sulfur segregation to the surface. These observations seem to indicate that the unshielded charges on the adsorbed *O* or *S* atoms act as strong scattering centers for the image-state electrons.

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