Energy Loss of Photoelectrons by Interaction with Image Charge

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By measuring the photoelectron spectra of the Cu(001) and Cu(110) surfaces excited by tunable-laser photons of very low energy (4.50–4.95 eV), we have found that the photoelectron can lose energy through interaction with its image charge. This energy loss occurs just outside the solid surface and appears as a spike structure at the vacuum edge in the photoemission spectra. The requirement for observing this energy loss structure is the absence of unoccupied states at the vacuum level at the $\bar{\Gamma}$ point to which zero kinetic energy electrons can return.

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The interaction between a static electron near the solid surface and its image charge plays an important role in a variety of phenomena such as surface-state formation [1], resonant electron scattering [2], and resonant tunneling conductance [3]. This interaction has been investigated by various means [4–8]. However, the dynamic interactions between a moving electron near a solid surface and its image charge has not yet been investigated in detail. The difference between the image force felt by a moving electron and that felt by a static electron is that the former depends on the dynamical response and the kinetic energy of the electron, while the latter does not [9,10]. Thus it is interesting to investigate the interaction between the moving electron and its image charge.

Recently, Mills reported an interesting prediction about the interaction between the moving electron and its image charge [11]. He predicted theoretically that the electron moving away from the solid surface can lose energy in vacuum by this interaction. According to this theory the lost energy is spent in creating surface excitations (surface plasmons, for example). As Mills pointed out [11], the energy loss structure cannot be observed or is too weak to be detected by electron energy loss spectroscopy. He concluded that the energy loss of the reflected electron is canceled by the energy gain of the incident electron, because the electron moving toward the solid surface is accelerated, while the electron moving away from the surface is decelerated by the image force. We expect that photoelectron spectroscopy is a suitable method for observing the energy loss by this mechanism, because there is no "incident electron" in this case.

The interaction between the moving electron and its image charge is important in determining the band structure by photoelectron spectroscopy, because it can affect the energy distribution of the photoelectrons. Photoelectron spectroscopy is widely used as a reliable method to determine the occupied band structure of various solids. Recent improvements in the resolution of electron energy analyzers have made it possible to analyze photoelectron spectra near the Fermi level in detail. For example, a pseudogap was observed in the spectra of a high temperature (T_c) superconductor by using high-resolution photoelectron spectroscopy [12]. The pseudogap can be observed as a loss of spectral intensity at the Fermi level. However, Joynt [13], who initially discussed the energy loss of the photoelectron by interaction with the image charge, argued that the photoelectron intensity at the Fermi level may decrease through this energy loss mechanism. On the other hand, Schulte *et al.* [14] and Noh *et al.* [15] have concluded that this energy loss can be neglected or treated as a weak structureless background from their experiments using a He discharge lamp as the excitation light source. Although Joynt's argument is very plausible qualitatively, there is no conclusive view about this interesting question. One of the reasons is that there has been no report that clearly shows the energy loss structure originating from the interaction between the photoelectron and the image charge.

In this Letter we present an experimental finding that the energy loss structure, resulting from the interaction between the photoelectron and the image charge, exists in the very low kinetic energy region of photoelectron spectra. Because of the following two reasons, we expect that the energy loss structure can be observed with a high signal-to-noise ratio by analyzing very low energy photoelectrons. (i) The energy loss probability increases as the photoelectron velocity (i.e., the photoelectron kinetic energy) decreases [11,13]. (ii) By using low energy photons as the excitation source, one can suppress the background of secondary electrons generated in the solid.

We have measured the photoelectron spectra with the excitation photon energy tuned slightly above the work function of the solid surface, making the difference between the work function and the photon energy less than 300 meV. The Cu(001) and Cu(110) single crystal surfaces were studied. Since the band structure of Cu is known experimentally from photoelectron spectroscopy [16] and inverse photoemission spectroscopy [17–19], we can distinguish the energy loss structure of interest from the spectral features originating from the band structure. We found a spike structure that appears at the vacuum edge in the Cu(001) spectra, while no such structure

appears in the Cu(110) spectra. We conclude that this spike structure arises from the photoelectrons that lose energy down to zero kinetic energy by interaction with the image charge and that cannot return into the sample due to the absence of available states in the solid.

The sample was cleaned by a well-known procedure [20] that consists of repeated Ar ion sputtering (600 eV, $\sim 1\ \mu A/cm^2$, 1 h) and annealing (670 K, 1 h) in ultrahigh vacuum. The cleaning cycle was performed more than 30 times in the preparation chamber with the base pressure better than 5×10^{-11} mbar. The sample surface structure was confirmed by low energy electron diffraction (LEED), which showed very sharp LEED spots for the (1×1) surface.

The sample was transferred to the analysis chamber made of μ-metal after the cleaning procedure. The magnetic field at the sample position was less than 5 mG, and the base pressure was better than 8×10^{-11} mbar. The sample was cooled by liquid nitrogen. The incident laser beam was generated by a picosecond Ti:sapphire laser in combination with second and third harmonic generation crystals. The laser pulse width was 2 ps with the repetition rate of 82 MHz. The p-polarized laser beam was incident at 54° off normal to the sample surface. The spot diameter and the intensity of the laser beam at the sample surface were about 100 μm and 100 $\mu W/cm^2$-cw equivalent, respectively. To achieve high reproducibility of the photoelectron spectra, both the laser spot and the sample position were carefully controlled.

The photoelectrons emitted normal to the sample surface were analyzed by a hemispherical electron energy analyzer. The pass energy and the acceptance angle of the analyzer were set at 0.5 eV and 1° around the surface normal, respectively. To minimize spectral distortion due to stray electric and magnetic fields and to collect the very low energy photoelectrons effectively, a bias voltage of -7.0 V was applied to the sample with the analyzer entrance hole grounded. We measured the bias voltage dependence of the spectra up to -10 V. No significant dependence was found in the spectral line shape. The energy resolution of the analyzer, which was determined by fitting the low energy cutoff curve of the spectrum [21], was estimated at 7 meV. To verify that the nonlinear (multiphoton) effect [4,5,22] and the space charge effect [23] did not distort the spectral line shape, we measured the photoelectron spectra for various light intensities. The photoelectron intensity was proportional to the incident light intensity, and no significant dependence of the spectral line shape on light intensity was observed.

Figure 1 shows the very low energy photoelectron spectra of the Cu(001) surface taken at various photon energies. The sample temperature was 95 K. The vertical axis is the photoelectron intensity normalized by the cw-equivalent laser power and the photon energy. The horizontal axis is the final state energy, which is the energy of the electron relative to the Fermi level of the sample. In this energy scale the upper cutoff energy is equal to the incident photon energy. The spectral line shape of the high energy side is reproduced by the convolution of the Fermi-Dirac distribution, the instrumental resolution function, and the energy width of the incident photon. The lower cutoff energy (~ 4.65 eV) corresponds to the work function of the Cu(001) surface. The kinetic energy of the electron is also shown in the upper horizontal axis in Fig. 1. One sees a spike structure just above the lower cutoff energy (at zero kinetic energy). The energy position of this spike structure does not depend on the incident photon energy. As is discussed later, we believe that this spike structure originates from the energy loss of the photoelectrons in vacuum.

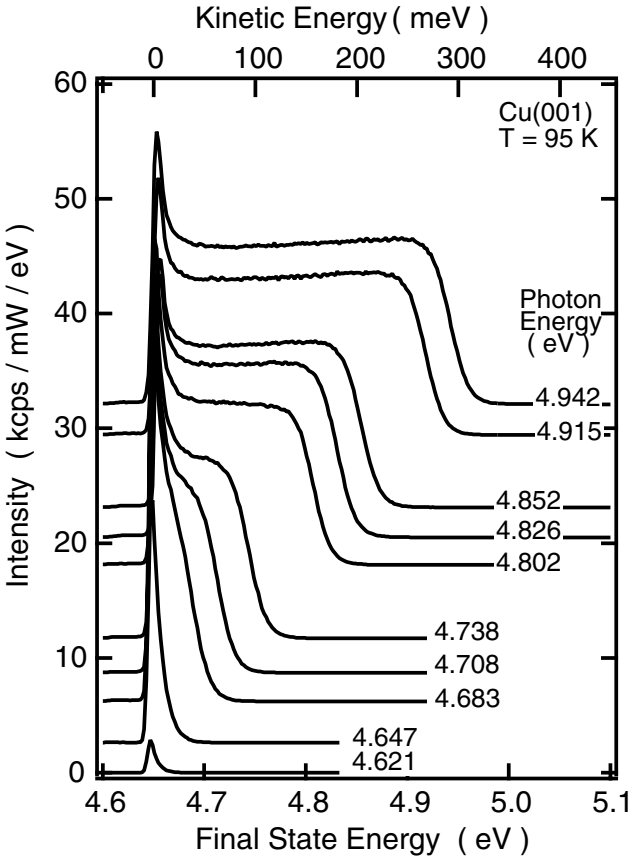

FIG. 1. Low energy photoelectron spectra of the Cu(001) surface taken at various photon energies. The intensity was normalized by the cw-equivalent laser power (mW) and the photon energy (eV). Note the presence of a spike structure just above the vacuum level cutoff (~ 4.65 eV).

Figure 2 shows the photoelectron spectra of the Cu(110) surface. The sample temperature was 90 K. The upper cutoff energy and the lower cutoff energy (~ 4.52 eV) correspond to the incident photon energy and the work function of the Cu(110) surface, respectively. No characteristic structure such as a spike was observed in the photoelectron spectra of the Cu(110) surface in contrast to those of the Cu(001) surface.

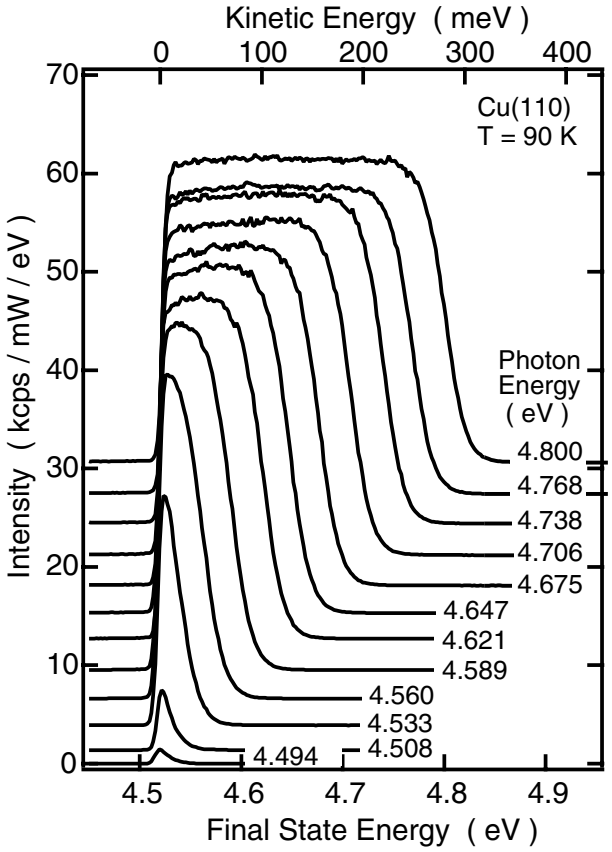

FIG. 2. Low energy photoelectron spectra of the Cu(110) surface taken at various photon energies. No spike structure is seen at the vacuum level cutoff (~ 4.52 eV).

Now let us examine the origin of the spike structure seen in Fig. 1. Since the nonlinear effect and the space charge effect were not observed in our measurements, we interpret these photoelectron spectra with single-photon photoemission processes. In the direct transition model of the photoemission process, the wave vector parallel to the surface $k_{\|}$ and the kinetic energy must be conserved. Thus $k_{\|}$ of the photoelectron excited by a low energy photon is very small. Accordingly, we will focus on the electrons at the $\bar{\Gamma}$ point in the surface Brillouin zone. Figure 3 shows the band structures [24] along the Γ–X ([001]) direction and the Γ–K ([110]) direction. The shaded areas in Figs. 3(a) and 3(b) indicate the projected bulk band structure for $k_{\|} = 0$ of the Cu(001) and Cu(110) surfaces, respectively. The dispersion curve of the free electron in vacuum is shown in Fig. 3(c). Since there is no unoccupied state just above the vacuum level of the Cu(001) surface, the spike structure cannot arise from interband transitions. The angle-resolved photoelectron spectra of the Cu(001) surface [16] also show no prominent peak structure in the vicinity of the Fermi level. In addition the inverse photoemission spectrum of the Cu(001) surface [7] does not show a sharp spike structure just above the vacuum level. Thus the spike structure in the Cu(001) spectra does not originate from the band structure of the Cu(001) surface. Hence we conclude that the spike structure must arise from the electrons that lose energy after excitation.

Next we determine whether the spike structure originates from energy loss processes *in the interior or the exterior of the Cu crystal.* Since the difference between the photon energy and the work function is less than 300 meV, the emitted electron is excited into the state 0–300 meV above the vacuum level. In Figs. 3(a) and 3(b), there is no unoccupied state around the vacuum level along the Γ–X direction, while the unoccupied states exist along the Γ–K direction. The photoexcitation to the unoccupied bulk states around the vacuum level occurs only in the Γ–K direction. On the other hand, the direct transition to the free electron states around the vacuum level occurs both at Cu(001) and Cu(110) surfaces. Consequently, the photoelectron emitted from the Cu(001) surface with very low kinetic energy is generated only at the surface, while the photoelectron emitted from the Cu(110) surface is generated at the surface as well as in the bulk [25,26]. If the electron lost energy in the interior of the Cu crystal, the spike structure should be observed also in the Cu(110) spectra. However, the spike structure was observed only in the Cu(001) spectra. Thus the spike structure does not arise from the energy loss of the photoelectron *in the interior of* the sample. From the above line of arguments we conclude that the spike structure arises from the photoelectrons that lose energy *after emission into vacuum.*

Now let us see why the spike structure appears only in the Cu(001) spectra and not in the Cu(110) spectra. We consider the kinetics of the photoelectron that loses energy immediately above the Cu surface. In the momentum space the photoelectron falls to the bottom of the dispersion curve of the free electron. This photoelectron cannot return into Cu, because the vacuum level lies in the band gap at the $\bar{\Gamma}$ point in the surface Brillouin zone of the Cu(001) [7,27]. In other words, the Cu(001) surface is a repulsive barrier for the very low energy photoelectron. Thus the photoelectrons that lose energy outside the surface remain at the bottom of the dispersion curve of the free electron in vacuum. Because a negative bias voltage is applied to the sample, these electrons are accelerated toward the detector.

In contrast the photoelectron emitted from the Cu(110) surface can return into Cu after the energy loss process, because the unoccupied states exist at the vacuum level for the Cu(110) surface. The very low energy photoelectron can fall back to the bulk states across the Cu(110) surface. The photoelectrons that lose energy in vacuum cannot remain at the bottom of the dispersion curve of the free electron, and hence the spike structure does not appear in the Cu(110) spectra. Thus we conclude that the spectral difference for these two surfaces can be explained by the presence or the absence of

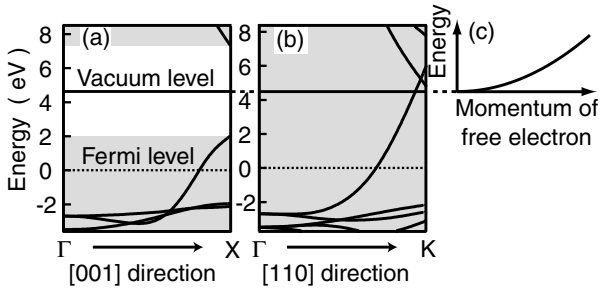

FIG. 3. Band structures of Cu along (a) the Γ–X ([001]) direction and (b) the Γ–K ([110]) direction [24]. (c) Dispersion curve of the free electron in vacuum. The shaded areas in (a) and (b) indicate the projected bulk bands for $k_{\parallel} = 0$ of the Cu(001) and Cu(110) surfaces.

the unoccupied states at the vacuum level at the $\bar{\Gamma}$ point. A similar spike structure has been observed in the Ag(001) spectra, which will be reported in a forthcoming paper [28].

Finally we discuss the energy loss mechanism of photoelectrons in vacuum. The only force that acts on the electron outside a nonmagnetic solid is a long-range electromagnetic force from the solid. Classically, this force is described by the interaction between the moving electron and its image charge [10]. Thus we conclude that the energy loss of photoelectrons in vacuum arises from the interaction with the image charge. Quantum mechanically, the energy loss of electrons involves the creation of elementary excitations in the solid (plasmons, polar phonons, electron-hole pairs, etc.). Unfortunately we cannot identify the elementary excitations involved in this energy loss mechanism from present experimental results alone. Although the microscopic mechanism is not clear, the present result is sufficient to demonstrate that the energy loss structure in the Cu(001) spectra does arise from the interaction between the photoelectron and its image charge.

In summary, we have measured the very low energy photoelectron spectra of the low index surfaces of Cu single crystal by using a tunable laser as the light source. A spike structure was observed at the vacuum edge in the spectra of the Cu(001) surface, while no such structure was found in those of the Cu(110) surface. The spike structure in the Cu(001) spectra arises from the photoelectrons that lose energy after emission into vacuum. For the spike structure to appear, an energy gap must exist at the vacuum level. We have demonstrated that the very low energy photoelectron spectrum does contain the energy loss structure by the interaction between the exiting photoelectron and the image charge.

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