Femtosecond photoemission study of ultrafast electron dynamics on Cu(100)

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The energy dependence of the relaxation of photoexcited electrons in copper was measured using femtosecond time-resolved photoemission spectroscopy to within 0.3 eV above the Fermi level. By performing lifetime measurements under different surface conditions, several surface dynamical processes were investigated. In particular, an anomalous long lifetime feature, which cannot be explained with Fermi-liquid theory, was observed in the lifetime-energy curve. This feature was found originating from the photoexcitation of the strongly localized Cu $3d$ electrons. [S0163-1829(97)01227-7]

The transient behavior of excited electrons at or near metal surfaces is fundamental to many important surface processes, such as chemical reactions, transport, and surface phase transitions. The advent of ultrafast laser makes it possible to time-resolve these dynamical processes, and the measurement techniques based on ultrashort laser pulses become now the most powerful tools in elucidating such ultrafast dynamics. In contrast to optical measurements of transmission and reflection that rely on the dynamic changes in macroscopic optical constants, time-resolved two-photon photoemission (TR-TPPE) provides a direct measurement of the temporal evolution of the photoexcited electron distribution. The lifetimes of the $n=1$ and $n=2$ image states for Ag(100) has been determined by TR-TPPE to be 25 ± 10 and 180 ± 20 fs.[1,2] Time-resolved photoemission measurements have shown that the thermalization of the hot electrons to a Fermi distribution occurs on a time scale comparable to the electron-phonon relaxation time (~1 ps).[3] Several recent studies of the energy dependence of photoexcited electron relaxation in metals were reported.[4–7] However, there still exist some discrepancies in the results.

Here, we report femtosecond time-resolved photoemission studies of electron dynamics in Cu(100). Alkali metals (Cs and K) were used to lower the surface work function, which enables us to probe low excitation states, less than 0.3 eV above E_F, with photon energies smaller than the intrinsic surface work function. It is found that the relaxation of the lower excited states (less than 1 eV above Fermi level) is not a simple exponential decay but includes the effects due to the repopulation from the relaxation of the higher excited states. A fitting routine incorporating this cascade process was used to extract the lifetimes of these states. The results show that the measured energy dependent relaxation cannot be fitted well by the Fermi-liquid theory (FLT). In particular, an anomalous long lifetime feature that is associated with the creation of Cu $3d$ holes was observed, and we interpreted as a transient exciton resonant state formed by strongly localized d holes and excited electrons.

The laser system used in the experiment is a self-modelocked Ti:sapphire laser pumped by a cw Ar^+ laser. It produces 40 fs pulses with a pulse energy of 10 nJ at a repetition rate of 82 MHz. The laser wavelength can be tuned from 730 (1.70 eV) to 850 nm (1.46 eV). Both the fundamental and frequency-doubled beams, which are obtained with a 250-μm-thick beta barium borate doubling crystal, are used in lifetime measurements employing the one color pump/probe protocols. In both cases, the laser pulse is first split by a nonpolarizing equal-intensity beam splitter. After one beam is sent through a variable delay line, the two beams are focused and realigned to have both spatial and temporal overlap on the sample surface. The spot size on the surface is estimated to be about 150 μm and the polarization of the pump and probe beams can be adjusted independently by using half wave plates. The photoelectrons were detected by an angle-integrated hemispherical energy analyzer with resolution of 0.1 eV at 10 eV transmission energy. A -10-V bias was applied between the sample and energy analyzer to reduce the effects of stray fields, and a normal emission geometry was used.

The laser pulse energy was kept very low, at about 0.5 nJ/pulse, and on the average less than one electron per pulse was photoemitted. This low-pulse-energy and high-reparation-rate measurement provides high sensitivity and a more reliable detection by eliminating the ambiguities that might arise in a highly excited electron distribution, thermionic emission, or space-charge effects. The time resolution is laser-pulse-width limited, and a 50 fs pulse width and 10 fs time resolution were achieved with a pair of external prisms

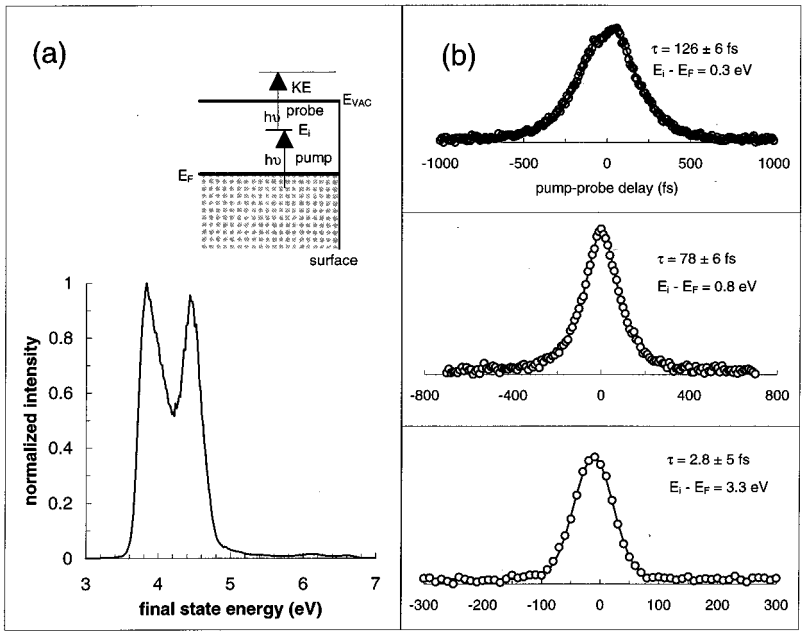

FIG. 1. (a) Two-photon photoemission spectrum of Cs/Cu(100) taken with a photon energy of 3.38 eV. (b) Pump-probe scans taken at three different energies at 3.3, 0.8, and 0.3 eV above the Fermi level. Open circles are data taken with cross-polarized beams. Solid lines are obtained from model fit to the experimental data. The error is calculated with $\sigma=(\sigma_1^2+\sigma_2^2)^{0.5}$, where σ_1 is the one standard deviation generated in the fitting and σ_2 is the estimated experimental error.

to compensate for the pulse broadening resulting from the positive group velocity dispersion[8] after the beam propagating through the subsequent optical elements after the doubling crystal.

The Cu(100) surface was cleaned by cycles of Ar^+ sputtering at 1 keV and subsequent annealing at 850 K inside an ultrahigh vacuum chamber with a base pressure of 5×10^{-11} torr. After each treatment, the surface quality was checked with both x-ray photoelectron spectroscopy (XPS) and reflection high-energy electron diffraction until an atomically clean and well-ordered surface was obtained. Then the surface was dosed with alkali metals (Cs or K) to reduce the sample work function. The final alkali-metal coverage is estimated to be less than 0.1 ML by measuring the work-function change[9,10] and the XPS peak intensity calculation.[11] After the alkali-metal deposition, the lowest excited state that can be probed with frequency-doubled pulses is usually within 0.3 eV above the Fermi level.

A two-photon photoemission spectrum from a Cs covered Cu(100) surface obtained with 3.38 eV photons is shown in Fig. 1(a). The flat part in the high-energy side is the two-photon photoemission from Cu 4*s* electrons, and the peak is from Cu 3*d* electrons with its rising edge at about 2.0 eV below E_F. Lifetime measurements are carried out by conducting pump-probe measurements at each fixed kinetic energy (E_K) throughout the two-photon photoemission spectrum. The corresponding energies of the intermediate states (E_i) are then determined by assigning the Fermi edge in the two-photon photoemission spectrum (E_{KMAX}) as the highest excited intermediate state, with one-photon energy above the E_F, i.e., $E_i=E_K-E_{\mathrm{KMAX}}+E_F+h\nu$. In Fig. 1(b) we present three pump-probe scans taken at the highest energy accessible, an intermediate energy, and at the lowest energy accessible (3.3 eV, 0.8 eV, and 0.3 eV above E_F, respectively). Each curve was obtained with the polarizations of the pump and the probe beams perpendicular to each other in order to eliminate the coherence peak.[12]

In our experiments, the hot-electron density generated by the absorption of a laser pulse (with 50 fs pulse width, 0.5 nJ/pulse energy, 150 μm spot size, and skin depth 17 nm for a 3.3 eV photon) is estimated to be $\sim10^{18}$ electrons/cm^3, which is much smaller than that of the conduction-band electrons in copper (8.47×10^{22} electrons/cm^3).[13] Under this low-excitation condition, the excited electrons relax mainly through scattering with cold conduction-band electrons. Theoretical calculation of this energy-dependent relaxation process is provided by Landau's FLT,[13–14] and the lifetimes τ_{e-e} are given by $\tau_{e-e}=a(E_i-E_F)^{-2}$ (in femtoseconds), where the energy is in electron volts, and a is a function of E_F and the density of conduction-band electrons. The calculated value of a by using the jellium model and the Lindhard dielectric function is given by Quinn[15] as 24.01 fs eV^2 for copper. On the average, electrons will lose half of their energies after each scattering through exciting electrons from below E_F into the unoccupied states above it. Consequently, secondary electrons generated from these scattering processes will populate states with energies $E-E_F<h\nu$. The time evolution of the electron distribution is, therefore, not only determined by the decay of the initial photoexcited electron population but also by the repopulation process from the secondary electrons.

The dynamics of these excited states can be adequately modeled with a simple kinetic process with a one rate constant describing the population flowing into a state and another one out of it, in the scheme $A\rightarrow B\rightarrow C$, where state B is being monitored. The population of state B with energy E_i is[16]

$$B=\int_{E_i}^{h\nu}\frac{A_0(E)\tau_2}{[\tau_1(E)-\tau_2](E-E_F)}\left[\exp\left(-\frac{t}{\tau_1(E)}\right)-\exp\left(-\frac{t}{\tau_2}\right)\right]dE+B_0\exp\left(-\frac{t}{\tau_2}\right), \quad (1)$$

where A_0 and B_0 are the initial populations of state A and B, τ_1 and τ_2 refer to the time constants of electron relaxation

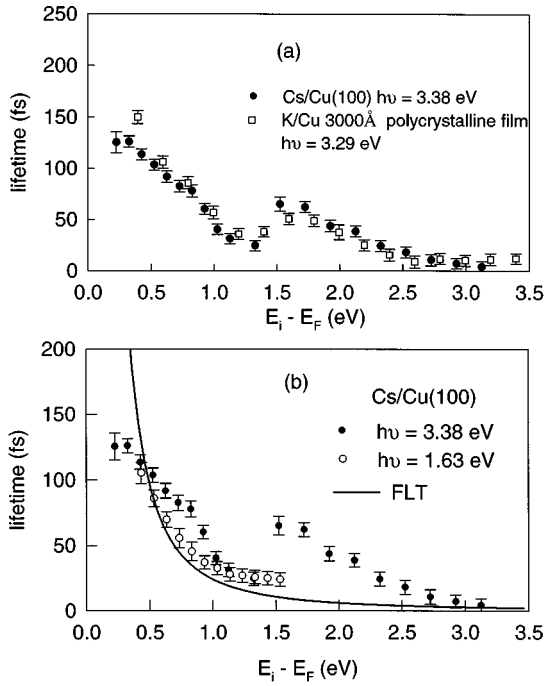

FIG. 2. Comparison of lifetime measurements of copper under different surface conditions and with different photon energies. The error bars are one standard deviation. (a) Filled circles and open squares represent lifetime measurement data taken from cesiated Cu(100) and K covered 3000 Å polycrystal copper film, respectively. (b) Filled circles are data taken with 3.38 eV photon energy causing the excitation of Cu $3d$ electrons. The open circles are results obtained with 1.63 eV photon energy, without the excitation of Cu $3d$ electrons. The solid line is the Fermi-liquid theory prediction.

into and out of the intermediate state B, and $h\nu$ is the maximum energy of the distribution populated by the excitation pulse. Since the variation of the density of states from one-photon to two-photon energy above E_F is small in copper, the initial population distribution $A_0(E)$ is approximated by the energy spectrum taken at time zero. The lifetime of state B, τ_2, is optimized in a nonlinear least-squares fit of data to Eq. (1). In the fitting, Eq. (1) is also convoluted with the Gaussian autocorrelation function to take account for the finite laser-pulse width. To determine the lifetimes for a set of data, the optimization proceeds from the highest to the lowest energy, since the distribution $\tau_1(E)$ (which is fitted by a polynomial) that describes the population flowing into lower energy levels needs to be constructed from the higher energy levels. The assumptions of this analysis is that a higher energy state E relaxes to any lower state weighted by the initial population distribution and repopulates all the states below it with the same probability through the weighting factor $1/(E-E_F)$. The fitting results for the three pump-probe curves taken with cross-polarized laser beams are shown in Fig. 1(b). It is seen that this model gives satisfactory fitting results.

The results of excited electron lifetimes as a function of their energies above the Fermi level for Cu(100) is summarized in Fig. 2. The FLT prediction is also plotted in Fig. 2(b) for comparison. As one can see, the low-excited electrons very close to the Fermi level possess much longer lifetimes than those electrons high above the Fermi level. For higher photon energies ($h\nu=3.29$ and 3.38 eV), the excited electron lifetimes in most of the energy range being measured are longer than the FLT prediction, while the agreement to FLT gets better for the lower photon energy ($h\nu=1.63$ eV). In contrast to the FLT prediction, the extrapolation of the $\tau-E_i$ curve does not go to infinity when E_i approaches the Fermi level as predicted by the FLT. More interestingly, there exists an anomalous feature with a much longer lifetime at about 1.6 eV above the Fermi level (3.6 eV above the top of $3d$ band).

We have examined in several ways the origin of the anomalous feature on the electron lifetime-energy dependence curve. The possibilities of intrinsic surface states, surface defect states, and alkali-metal adsorbate states were investigated by comparing the lifetime measurement results from Cs and K covered Cu(100) and polycrystalline film surfaces, and the results are shown in the Fig. 2(a). These surface states tend to be strongly localized on the first few atomic layers and have very different electronic properties from those of the bulk. Therefore, one would expect that they will exhibit different relaxation behavior compared with bulk states. Inverse photoemission spectroscopy studies by Dudde and Reihl[17] show that adsorption induced surface states by alkali metals, such as K and Cs, are very different. These adsorbate states were observed at 0.6 and 1.1 eV above E_F for K and Cs, respectively. Because our lifetime measurements of Cs/Cu(100) and K/Cu show no difference within our experimental errors, the possibilities of alkali-metal adsorbate states for the observed feature can be excluded. This result also demonstrates that the effect of putting alkali metals on the copper surface is simply to lower its work function without interfering with the lifetime measurement. We also eliminated the possibilities of the intrinsic copper surface states and the surface defect states by comparing the lifetime measurements from the surfaces of single crystal Cu(100) and polycrystalline thin films.

Image potential states are formed by an attractive force experienced by a charge outside of a polarizable surface due to the surface charge redistribution that the charged particle induces. Image state lifetimes have been measured on several metal surfaces with TR-TPPE and found to be in the ten to hundred femtosecond range.[1,2] The characteristic of image states are that their energy positions are pinned with respect to the vacuum level. Since the position of the anomalous feature is only determined by the photon energy in our experiment, it cannot be attributed to the image state.

The copper $3d$ electrons are strongly localized[13] and the top of the d band is at about 2.0 eV below the Fermi level. $3d$ electrons in copper exhibit very strong non-free-electron-like behavior. Therefore the FLT calculation based on the jellium model (free electron) will not be adequate in describing the relaxation processes when $3d$ electrons are excited. In order to test the hypothesis that the anomalous feature is from the excitation of copper $3d$ electrons, we performed the lifetime measurements on a Cs/Cu(100) surface by using the fundamental infrared pulses of the Ti:sapphire laser. Unlike the pump-probe scans taken with doubled laser pulses, the Cu $3d$ electron are held unperturbed due to the smaller photon energy, which is 1.63 eV in this case. The results are shown in Fig. 2(b). The absence of the anomalous feature

with the longer wavelength excitation confirms that this feature is originated from the photoexcitation of the $3d$ electrons.

An interesting result is that the peak position of the feature is about 0.2 eV more than one-photon energy above the copper $3d$ band; thus it cannot be reached by a direct one-photon transition of $3d$ electrons. Furthermore, we also find slight modifications of the feature with different photon energies. This feature is centered at about 1.6 eV above E_F for 3.38 eV photons but is enhanced more at 1.3 eV above E_F when using 3.0 eV photons. We interpret the anomalous feature due to the resonant excitonic states arising from the photoexcitation of strongly localized Cu $3d$ electrons. The strongly localized $3d$ holes generated by photoexcitation of $3d$ electrons can trap excited electrons through attractive Coulomb interaction. The spatial localization of the excited electrons reduces their chances to scatter with other electrons, resulting in longer lifetimes compared with the nonlocalized excited electrons.

The shorter measured lifetimes than FLT prediction at low-excited states can be understood in two ways. First, for the low-excited electrons very close to the E_F, their lifetimes become very long. So other scattering mechanisms, such as electron-phonon scattering (e-p) and scattering with defects, become dominant in determining the excited electron lifetimes. In addition, these low-excited electrons have a very long inelastic mean-free path (MFP). The transport of these low-energy electrons with very long MFP out of the surface probe region could introduce additional relaxation channels.

There are several substantial differences between this study and the related work of Hertel *et al.*[5] on Cu(111). First, in the work of Hertel *et al.*, the optical Bloch equation, which considers only depletion of the initial photoexcited population, was used to calculate the electron lifetimes from each corresponding pump-probe data set. As a result, they can only rely on the fitting of the fast component in the decays to extract the lifetime. However, due to the 65 fs pulse width used in the experiment, their results are affected by the repopulation processes, which will result in the longer observed lifetimes for lower excited states very close to the E_F. While in our data analysis, a model incorporating this repopulation process was developed to extract the electron lifetime from each pump-probe curve, which is more reliable. Second, the $3d$ electron related feature was not detected in their two-color pump-probe (2.23 and 4.45 eV) experiment. Since Cu $3d$ band lies 2 eV below the Fermi level, the resonant excitonic states generated by the pump photons (2.23 eV) should be at 0.23 eV above the E_F, if they are present, which is lower than the lowest excited states that they can measure (0.3 eV above E_F). Even if the energy position of the states shift up, say by 0.2 eV as observed in our experiment, it will still stay very close to the Fermi level, about 0.4 eV above E_F. Since the excited states with this energy possess much longer lifetimes than those of the $3d$ band related resonant excitonic states, it is not possible to detect the $3d$ band related feature in the lifetime measurements in their experiment. Thus, the results are not consistent given the different experimental conditions. The main distinction in the present paper is that the FLT is not capable of properly modeling the dynamics when the $3d$ electrons are excited. Further theoretical work is needed to quantitatively account for the role of $3d$ states in the electron relaxation processes in copper.

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[1] R. W. Schoenlein, J. G. Fujimoto, G. L. Eesley, and T. W. Capehart, Phys. Rev. Lett. **61**, 2596 (1988).

[2] R. W. Schoenlein, J. G. Fujimoto, G. L. Eesley, and T. W. Capehart, Phys. Rev. B **41**, 5436 (1990).

[3] W. S. Fann, R. Storz, H. W. K. Tom, and J. Bokor, Phys. Rev. Lett. **68**, 2834 (1992); W. S. Fann, R. Storz, H. W. K. Tom, and J. Bokor, Phys. Rev. B **46**, 13 592 (1992).

[4] C. A. Schmuttenmaer, M. Aeschlimann, H. E. Elsayed-Ali, R. J. D. Miller, D. A. Mantell, J. Cao, and Y. Gao, Phys. Rev. B **50**, 8957 (1994).

[5] T. Hertel, E. Knoesel, M. Wolf, and G. Ertl, Phys. Rev. Lett. **76**, 535 (1996).

[6] S. Ogawa and H. Petek, Surf. Sci. **357/358**, 585 (1996).

[7] M. Aeschlimann, M. Bauer, and S. Pawlik, Chem. Phys. **205**, 127 (1996).

[8] R. L. Fork, O. E. Martinez, and J. P. Gordon, Opt. Lett. **9**, 150 (1984).

[9] C. A. Papageorgopoulos, Phys. Rev. B **25**, 3740 (1982).

[10] T. Aruga, H. Tochihara, and Y. Murata, Phys. Rev. B **34**, 8237 (1986).

[11] *Photoemission and the Electronic Properties of Surfaces*, edited by B. Feuerbacher, B. Fitton, and R. F. Willis (Wiley, New York, 1978).

[12] C. A. Schmuttenmaer, C. C. Miller, J. H. Herman, J. Cao, D. A. Mantell, Y. Gao, and R. J. D. Miller, Chem. Phys. **205**, 91 (1996).

[13] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976).

[14] D. Pines and P. Nozières, *The Theory of Quantum Liquids* (Benjamin, New York, 1966).

[15] J. J. Quinn, Phys. Rev. **126**, 1453 (1962).

[16] G. Friedlander, *Nuclear and Radiochemistry* (Wiley, New York, 1981).

[17] R. Dudde and B. Reihl, Surf. Sci. **287/288**, 614 (1993).