Optical Dephasing in Cu(111) Measured by Interferometric Two-Photon Time-Resolved Photoemission

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The polarization dynamics induced by the optical excitation of the *s*,*p*-band derived occupied surface state on Cu(111) are studied by a new technique, interferometric two-photon time-resolved photoemission. The polarization decay due to phase breaking collisions of the charge carriers on an ~20 fs time scale is modeled by the optical Bloch equations. The optical phase resolution also allows direct observation of nonlinear polarization oscillations at the harmonics of the excitation frequency, which lead to the surface harmonic generation. [S0031-9007(97)02319-3]

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A medium exposed to an electric field will acquire polarization, which can decay by various scattering mechanisms or by coherent radiation into the vacuum by the process known as the free induction decay (FID). Time-resolved measurements of FID and related coherent phenomena have been performed in atomic [1] and excitonic systems [2], but not in metals. The FID gives the time scale on which materials preserve the memory of the optical phase of the excitation pulse, and therefore the time scale for coherent light-matter interactions. Linear and nonlinear (surface harmonic generation [3]) reflection of light are familiar manifestations of coherent phenomena at metal surfaces. However, these processes are generally thought to be instantaneous [4]. A technique for time-resolved measurement of polarization decay in a metal could permit direct measurements of scattering processes involved in photon absorption and establish the time scales for coherent light-metal interactions. A deeper understanding of polarization decay in metals also is necessary for the application of coherent control [5] to electron wave packets at metal surfaces and interfaces, which may be important for the development of ultrafast optoelectronic devices. This Letter presents a new technique, interferometric two-photon time-resolved photoemission (I2PTRP), which is used for the first optical phase resolved study of FID at a metal surface.

The common method for estimating phase relaxation in metals is the linewidth analysis in photoemission spectra [6,7]. Typical widths of bulk bands place a lower limit for phase relaxation times of $\ll$10 fs due to the ultrafast charge carrier scattering. However, the time scales for phase-breaking collisions can be considerably longer near the Fermi surfaces of metals [8] and in surface states that are weakly coupled to the bulk bands [9,10]. The recently developed two-photon time-resolved photoemission technique (2PTRP) is well suited for studying the dynamics of charge carriers with a specific energy and momentum rather than the traditional absorption and reflection techniques, which probe the total electronic response of a metal [11]. The possibility of time-resolved measurements of phase relaxation rates in metals was first suggested in 2PTRP studies of hot electrons at Cu(110), and Cu(100) surfaces [12]. Two distinct components in the two-pulse correlation measurements of hot-electron lifetimes were attributed to the coherent and sequential two-photon absorption processes. However, it was difficult to separate the polarization and hot-electron population dynamics since the measurements were integrated over the optical phase. Optical phase-resolved measurements of two-photon photoemission can be accomplished by interferometric, phase-locked scanning of the pump-probe delay, which was recently developed for coherent control studies of excitons in GaAs quantum wells [13]. This Letter introduces a general method for phase-resolved measurement of polarization dynamics, I2PTRP, which is used to measure the response of a two-dimensional electron gas, the occupied $n = 0$ surface state (SS) on Cu(111) to a 15 fs laser pulse excitation.

The apparatus for I2PTRP measurements is described in Ref. [12], except for the subfemtosecond resolution interferometric scanning of the pump-probe delay used for phase-resolved measurement of the polarization dynamics. A frequency doubled Ti:sapphire laser produces 15 fs, ~1 nJ pulses at an 82 MHz repetition rate. The excitation light is centered at $\omega_L = 400 \pm 1$ nm (3.1 eV) and it has a bandwidth of 110 ± 5 meV. An identical, pump-probe pulse pair with a variable delay of 100 fs is generated in a Mach-Zehnder interferometer. The delay is scanned at a 2 Hz rate by a piezoelectrically actuated stage. The timing of the delay scanning and data acquisition is synchronized by a feedback loop to allow the averaging of repetitive scans. Interference fringes at ω_L are monitored through a monochromator as the delay is scanned. A lock-in amplifier compares the phase of the fringes with a linear ramp driving wave form of the piezoelectric actuator, and outputs an error signal to a second

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(fast) piezoelectrically driven delay. The timing of the delay scanning relative to the data acquisition is stabilized to $<\lambda/20$ (<67 as delay) for repetitive scans. Photoemission is measured for electrons with specific energy and momentum by a hemispherical electron energy analyzer with nominal energy and angular resolutions of 25 meV and 5°. Angle resolved photoemission is measured by rotating the polar angle θ of the sample with respect to the analyzer. The experiments are performed under an ultrahigh vacuum, at room temperature, using standard surface preparation techniques [12].

The schematic band structure and wave functions in Fig. 1 are relevant to the interpretation of the photoemission spectra and polarization dynamics. The $n = 0$ surface state in the Shockley-inverted band gap of Cu(111) forms a natural quantum well, where the electrons are localized by crystal and image potentials at the metal/vacuum interface. The SS has been of interest for studying surface effects and broadening mechanisms in photoemission spectra [14,15]. The Lorentzian width of the SS at 30 K is 30 meV and it increases with temperature to ~55 meV at 300 K due to hole-phonon scattering [16,17]. The width has been attributed to the inverse hole lifetime. However, extrinsic effects such as scattering of the outgoing photoelectrons with impurities and defects at the surface also may contribute to the widths [15]. Since the SS has been extensively studied by high-resolution photoemission measurements, it is possible to compare the polarization dynamics observed in the interferometric two-pulse correlation (I2PC) measurements with dephasing rates deduced from linewidth analysis. Figure 1 shows that for $k_{\|} = 0$ the $L_{2'} - L_1$ band gap extends between -0.85 and 4.3 eV, the SS is at -0.39 eV, and there is an image potential (IP) state series starting with $n = 1$ (IP) at 4.1 eV [7,14–17]. Lifetimes of SS and IP are determined in part by their coupling to the bulk. The coupling strength depends on the penetration of surface state wave functions, which are exponentially damped in bulk due to the $L_{2'} - L_1$ band gap [7,10]. The excitation laser is detuned by 1.4 eV from the SS⟶IP resonance. Thus, the two-photon absorption proceeds through a virtual intermediate state. The final state for photoemission is a portion of a continuum of free-electron-like—outward going low-energy electron diffraction (LEED)—waves that is transmitted through the electron energy analyzer. The photoemission of the SS at 6.2 eV is dominated by the surface photoelectric effect; thus scattering of outgoing electrons in the bulk may not be significant [14].

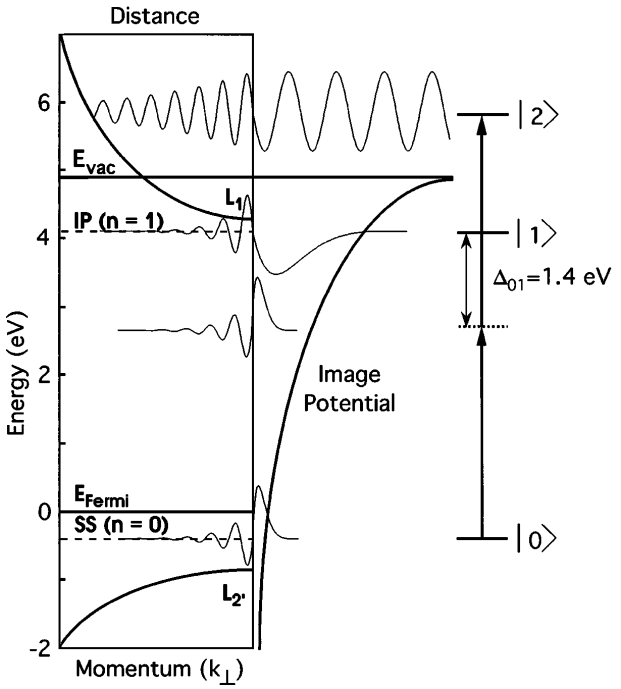

FIG. 1. The schematic diagram of the $k_{\|} = 0$ band structure and relevant wave functions for two-photon photoemission from the SS. The initial and intermediate states are localized mostly at the surface due to the $L_{2'} - L_1$ band gap [7]. The 2PP proceeds through a virtual state at 1.4 eV below the $n = 1$ IP state. The final state is an outgoing free-electron wave. On the right is the three-level scheme for the optical Bloch equation simulation of the polarization dynamics.

Figure 2 shows the two-photon photoemission (2PP) spectrum relevant to the discussion of time-resolved measurements. The spectrum is measured at $\Theta = 15°$ since this gives the highest SS intensity relative to the bulk bands. The energy of the SS at $\theta = 15°$ is -0.15 eV due to $k_{\|}$ dispersion. Its intensity is maximum at this angle due to its E^4 dependence on the perpendicular component of the electric field at the surface. For $\Theta > 15°$, the SS density of states extends above the Fermi level (E_F) and hence its intensity decreases.

Figure 3 shows I2PC measurements at $\Theta = 15°$ when photoemission is detected from the SS and *s-p* band (-1.2 eV relative to E_F). The I2PC scans near zero delay are dominated by interference fringes with a period of ~1.33 fs, which corresponds to one optical cycle of 400 nm light. The origin of the interference fringes may be the modulation of light intensity by the interference

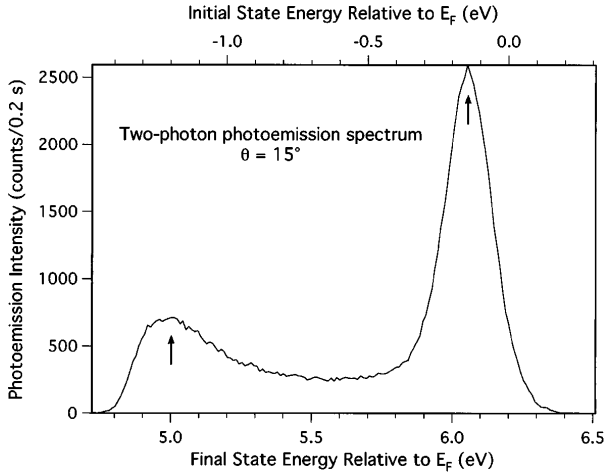

FIG. 2. 2PP spectrum measured at $k_{\|} = 0.15$ Å^{-1} ($\Theta = 15°$) from Cu(111). Arrows indicate the measurement energies in Figs. 3(a) and 3(b).

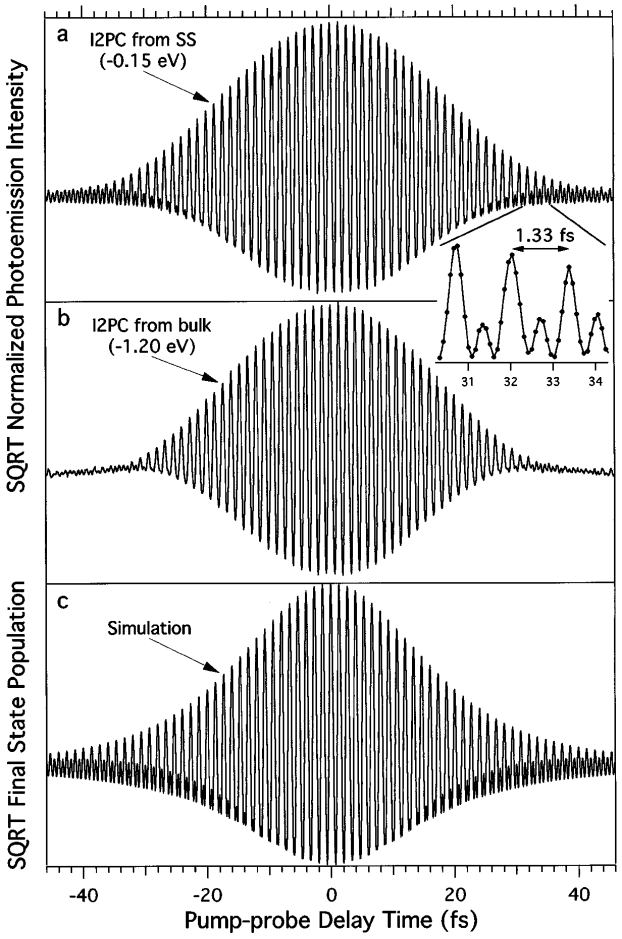

FIG. 3. (a) I2PC measurement from the SS (-0.15 eV). (b) The *s-p* band (-1.2 eV). (c) Simulation of the data in (a) The I2PC data are averaged for 5000 scans. The ordinate for the I2PC scans is the square root of photoemission counts to emphasize the interference fringes at long delay times ($\tau > \tau_p$). The inset shows an expanded view of the oscillations at $2\omega_L$, and highlights the subfemtosecond resolution in the delay scanning.

between the pump and probe pulses in the interferometer, or coherent interaction between the pump induced polarization in the sample and the probe pulse. The analysis of the coherent response of the conduction band electrons in Cu from the I2PC measurements requires the knowledge of laser pulse amplitude and phase. This can be obtained with an interferometric autocorrelation measurement (IAC) of the laser pulse; however, at present there is no method for measurement of IAC of 3.1 eV light at an $\sim$1 nJ level. An upper limit of the pulse width, $\tau_p = 15$ fs, for the purpose of discussing the polarization dynamics associated with the SS [Fig. 3(a)] can be obtained from I2PC measurement from the *s-p* band [Fig. 3(b)] [18]. The slower polarization decay rate when the initial state is the SS as compared with the IAC results in a significantly broader envelope of the interference fringes for the I2PC from the SS. There is a clear trend that the interference fringes persist on a longer time scale ($>$100 fs) as the initial state approaches E_F. This trend is consistent with a hole-hole scattering mechanism for the phase relaxation, which has a $(E - E_F)^2$ dependence [13,16].

While interference fringes at ω_L dominate the I2PC scans, there also are weaker oscillations at $2\omega_L$ (Fig. 3 inset). Oscillations at even higher harmonics of ω_L can be deduced by Fourier transforming the I2PC data. The harmonic oscillations clearly are due to the material response, since they are not present in the interferometric electric field autocorrelations of the excitation pulses. *Thus the evidence that the I2PC scan in Fig. 3(a) measures the polarization dynamics upon excitation of the SS is that the interference fringes persist for much longer than in the IAC and the presence of oscillations at the harmonics of* ω_L. The observation that the polarization at ω_L and its harmonics persist for a longer time than the excitation pulse implies that linear and nonlinear reflection (surface harmonic generation) from a surface, under some circumstances, may *not* be instantaneous.

To further understand these observations, the I2PC scan from the SS is simulated with a phenomenological model based on the optical Bloch equations [19]. This analysis helps to identify the necessary conditions to reproduce the observed phenomena, but cannot treat many-body effects, coherent interactions involving continuous bands, or nonlocality and coupling of surface and bulk bands. Optical Bloch equations are solved for the three-level scheme in Fig. 1, where the initial, intermediate, and final states for the 2PP process are, respectively, the SS, virtual state continuum at -1.4 eV from the IP, and a free electron wave propagating to the detector. Although all states with the correct symmetry contribute to the virtual state absorption, the IP state has the smallest detuning and largest overlap.

The final state population is calculated as a function of pulse delay where the excitation by a two-pulse sequence is described by $E(t)\cos[\varpi t] + E(t - \tau)\cos[\varpi(t - \tau)]$, where $E(t)$ is the electric field amplitude with assumed sech(t) profile and 15 fs width. The wave function $\psi(t)$ is a linear combination of the basis functions of the undisturbed system (without E field), $\psi(t) = \sum_k a_k \varphi_k$. After transformation into a rotating set of coordinates the wave function can be written as $\psi(t) = \sum_k c_k \varphi_k$, where $c_k = a_k e^{ik\omega t}$. The differential equations for motion of c_k are

$$\frac{dc_k}{dt} = -i\Delta_k c_k + \frac{i}{2\hbar} p_{k,k-1}\tilde{E}^*(t)c_{k-1} + \frac{i}{2\hbar} p_{k,k+1}\tilde{E}(t)c_{k+1}, \quad (1)$$

where $p_{n,m}$ are transition dipole moments and $\tilde{E}(t) = E(t) + E(t - \tau)e^{-i\varpi\tau}$. The time-dependent populations are $\rho_n = c_n^* c_n$ and polarizations are $\rho_{nm} = c_n^* c_m$. Equation (1) is used to derive nine coupled differential equations, which describe the time evolution of populations and polarizations associated with the three levels. The energy (T_1) and phase (T_2) relaxation of ρ_n and $\rho_{n,m'}$ respectively, are included in the usual manner [19]. The

differential equations are solved numerically to give the calculated population in the final state, $\rho_2(\tau) = \int c_2^* c_2 \, dt$, as a function of pump-probe delay. The following approximations are made in the calculation: (i) Only the nearest state interactions are included, (ii) transition dipole moments are all set equal, (iii) $\Delta_{01} = 1.4$ eV, (iv) $T_{2_{mn}} = 2T_{1_{mn}}$, and (v) the $T_2 = 2\hbar/\Gamma$, where Γ is the inverse linewidth in photoemission spectra. The last approximation is based on the usual assumption that the linewidth of photoemission from a surface state is determined by the hole lifetime [6,7]. Thus, $T_{2_{1,2}}$ is set to 15.4 fs, corresponding to 85 meV width of the IP state [7,10], and $T_{2_{0,1}}$ and $T_{2_{0,2}}$ are set to 24 fs, corresponding to 55 meV width of the SS [17].

Figure 3(c) shows the calculated population in the final state vs the pump-probe delay $\rho_2(\tau)$. The calculation reproduces qualitative features of the I2PC scan from the SS: The interference oscillations persist on a longer time scale than those of IAC, and oscillations at $2\omega_L$ increase from a minimum at $\tau = 0$, and dominate at long pump-probe delays (>40 fs). The decay of oscillations at $2\omega_L$ corresponds to the decay of $\rho_{0,2}$ and is governed by $T_{2_{0,2}}$. Since the intermediate state is virtual, the decay of oscillations at ω_L due to $\rho_{0,1}$ and $\rho_{1,2}$ is faster than $T_{2_{0,1}}$ and $T_{2_{1,2}}$. The main effect of the decay time of $\rho_{1,2}$ is the ratio of intensities of oscillations at ω_L and $2\omega_L$. Setting $T_{2_{1,2}} \ll 15.4$ fs reduces the $2\omega_L$ amplitude relative to that of ω_L by $\sim$20%. The IP state makes a small contribution to the two-photon absorption cross section even though the detuning of the laser from the IP state is $\sim$16 times larger than its width. Differences between the experiment and simulated polarization dynamics can be attributed to (i) limitations of the model, (ii) the assumption of the T_2 parameters from the photoemission linewidths, (iii) washing out of interference fringes due to scan-to-scan fluctuations in $\Delta\tau$ and imperfect overlap of the beams, (iv) deviations of the pulse from ideal, transform-limited sech(t) profile, and (v) contribution of the sequential 2PP signal to the I2PC scans [12,18].

The following conclusions can be made from the comparison between the experiment and simulation: (i) The interference fringes at ω_L and $2\omega_L$ in the I2PC from the SS follow the time dependence of $\rho_{0,1}$, $\rho_{1,2}$, and $\rho_{0,2}$. The decay of fringes at $2\omega_L$ closely follows the decay of $\rho_{0,2}$ and is consistent with the SS hole lifetime implied by the photoemission lineshape analysis. (ii) The I2PTRP technique offers a unique way to measure linear and nonlinear polarization dynamics at metal surfaces with phase, energy, and momentum resolution.

In conclusion, the interferometric two-photon photoemission technique is developed and applied to coherent polarization dynamics associated with the $n = 0$ occupied surface state on Cu(111). This technique allows the first measurement of polarization dynamics at a metal surface with energy, momentum, and phase resolution. The decay in the induced polarization is consistent with the hole lifetime of the surface state. The observed oscillations in the I2PC scans at the excitation frequency and its second harmonic, which persist on a >100 fs time scale, indicate that under some circumstances linear and nonlinear reflection from a metal surface are not instantaneous. Observation of longer dephasing times than currently available laser pulse widths opens the way to coherent control experiments at metal surfaces. Since long dephasing times are observed even for emission from the bulk bands, similar observations and coherent control experiments may be possible for other surfaces of Cu, as well as for other metals. Finally, this Letter demonstrates the power of the interferometric two-photon time-resolved photoemission technique for studying coherent charge carrier dynamics at surfaces of solid state materials.

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[18] In Fig. 3(b) weak $2\omega_L$ oscillations indicate that polarization decay between the initial and final states is *not* instantaneous. The slowly varying "baseline" is due to the sequential two-photon absorption; the intermediate states are 1.9 eV hot electrons with a lifetime of $\sim$28 fs [S. Ogawa, H. Nagano, and H. Petek, Phys. Rev. B (to be published)].
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