Ultrafast Dynamics at Semiconductor and Metal Surfaces

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A variety of important dynamical phenomena at metal and semiconductor surfaces are now being investigated with the use of new ultrafast measurement techniques involving lasers and nonlinear optics. Understanding of the rates and mechanisms for relaxation of optical excitations of the surface itself as well as those of adsorbates on the surface is providing new insight into surface chemistry, surface phase transitions, and surface recombination of charge carriers in semiconductors.

ULTRAFAST LASER SPECTROSCOPY HAS BEEN USED TO great advantage in the study of dynamical behavior in solids on picosecond and femtosecond time scales. A great variety of relaxation and transport phenomena have been examined in detail in bulk materials as well as in artificially layered structures (*1*). An important area of solid-state physics that has only recently been addressed by ultrafast laser techniques is the study of dynamical phenomena at surfaces and interfaces. Some of the processes of interest that occur at surfaces and interfaces include vibrational and electronic energy relaxation; adsorption, desorption, and surface diffusion; catalysis and chemical reactions; surface phase transitions; and the transport and recombination of charge carriers in semiconductors.

Before it was possible to use ultrafast lasers for the study of surface dynamics, the only means available for obtaining information about these processes was the measurement of spectroscopic linewidths. Such experiments rely on the assumption that the spectroscopic line being observed is purely lifetime-broadened. This approach has been used, for example, to determine the lifetimes of electronically excited atoms (*2*) and molecules (*3*) on metal surfaces as well as the lifetimes of vibrationally excited molecules on metal surfaces (*4*). Mechanisms leading to the observed vibrational (*4*) and electronic (*5*) line broadenings have been a subject of intense theoretical interest. The principal difficulty with linewidth measurements lies in the underlying assumption that the line is lifetime-broadened. Unfortunately, inhomogeneous broadening is often encountered, which gives rise to complicated and unexpected behavior (*4*). Wherever possible, direct, time-domain measurements of dynamics are greatly preferred. However, progress in the use of ultrafast lasers to uncover these fundamental mechanisms has been hampered by the low sensitivity of most optical techniques to surface phenomena.

Time-Resolved Laser Experiments on Surfaces

The first time-domain studies of the effect of a metal surface on an electronically excited molecule located hundreds or thousands of angstroms away were done by Drexhage (*6*). Langmuir-Blodgett layers were used as a spacer for luminescent molecules, and the lifetime of the molecular emission could be measured as a function of its distance from the metal surface. Considerable progress in the understanding of nonradiative electronic energy transfer from excited atoms and molecules to metals at the ≥ 50 Å distance scale was made with the use of this general method (*7*). As molecules begin to come into contact with a metal surface, the lifetimes become too short to measure with conventional fluorescence decay apparatus. It then becomes necessary to use a nonlinear optical technique to investigate the picosecond time domain.

For example, transient infrared bleaching experiments have been successfully used (*8*) to measure vibrational relaxation dynamics of carbon monoxide (CO) molecules chemisorbed on the surfaces of small metal particles (particle diameter of ~15 to 40 Å). Such experiments are made possible because of the large surface-to-volume ratio of the large collection of metal particles. However, the surface structure is not well controlled or characterized in such samples. The vibrational energy relaxation time for the first excited vibration of CO on Pt and Rh particles was found to be sample-dependent, in the range of 5 to 10 ps.

Because they can be reproducibly prepared and characterized, samples consisting of flat, low-index faces of single crystals are strongly preferred for surface physics experiments. At present, three nonlinear optical laser techniques have demonstrated monolayer and submonolayer surface sensitivity on well-characterized, flat surfaces: (i) surface-enhanced Raman scattering, (ii) surface second-harmonic generation, and (iii) two-photon photoemission spectroscopy.

Surface-enhanced Raman scattering (*9*) has been extensively exploited for the study of molecular vibrations on surfaces. However, the enhancement is greatly reduced, if not eliminated, on smooth, flat surfaces (*9*), and, in any event, its extension into the picosecond domain for the study of dynamics has not yet been accomplished.

Surface second-harmonic generation and the related surface sum-frequency generation are now beginning to be used for ultrafast studies. The initial stages of laser melting of Si (*10, 11*) have been investigated with the use of second-harmonic generation. These experiments exploit the sensitivity of second-harmonic generation to surface structural symmetry via the tensor properties of the surface nonlinear susceptibility. The uppermost 75 to 130 Å of a crystalline Si surface loses cubic order only 150 fs after the Si is excited by an intense, 100-fs optical pulse, whereas the properties of the subsequently produced liquid Si phase were not obtained for several

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hundreds of femtoseconds (*11*). This result was interpreted to suggest that disorder can be induced directly by electronic excitation, before the excited electronic states heat the lattice to the equilibrium melting temperature.

The first direct, time-resolved vibrational relaxation measurement for a molecular monolayer on a metal surface (*12*) was recently demonstrated; the technique used was surface sum-frequency generation. The lifetime of the first excited state of the C–H stretching mode in the terminal methyl group of cadmium stearate on Ag was measured by saturating the $\nu = 0$ to $\nu = 1$ vibrational transition with an intense, resonant 3-ps infrared laser pulse. The subsequent vibrational relaxation was probed with a time-delayed infrared-visible pulse pair to generate a sum-frequency mixing signal, which was resonantly enhanced by the same $\nu = 0$ to $\nu = 1$ transition. The magnitude of the resonance-enhanced probe signal was used as a measure of the population difference between the $\nu = 1$ and $\nu = 0$ vibrational levels. The recovery time of the probe signal to its equilibrium value is a measure of the $\nu = 1$ to $\nu = 0$ population relaxation rate. The recovery of the symmetric stretching mode was characterized by a complex multicomponent decay involving time constants of 2.5 ps, 165 ps, and >1 ns. Surprisingly, the asymmetric stretching mode showed only a single, fast recovery of 2 to 3 ps. The different relaxation behavior of the symmetric and antisymmetric stretching modes for the ordered monolayer film is in sharp contrast to the analogous behavior in liquids, where it is believed that the C–H stretching modes of small molecules undergo rapid internal equilibration before energy flows into other vibrations of the molecule (*13*).

The greatest success thus far in the study of ultrafast dynamics on surfaces has been obtained with time-resolved, two-photon photoemission spectroscopy (TPPE). This technique is fundamentally an electron spectroscopy and therefore achieves the high surface sensitivity that is characteristic of electron emission spectroscopies, as described in the introduction to most texts on surface science (*14*). TPPE has been used to measure carrier relaxation times at ZnTe(110) surfaces (*15*) and surface electron dynamics at InP(110) surfaces (*16*). TPPE techniques were used to perform the first direct, time-domain measurement of a surface-state lifetime, that of the mid-gap, π^* state on the cleaved Si(111) surface (*17*). This result led to a detailed study of surface recombination dynamics of bulk carriers at cleaved Si(111) surfaces (*18*). Further TPPE studies of electronic surface-state dynamics have included the measurement of surface intervalley scattering processes on GaAs(110) surfaces (*19*) and image-potential dynamics at Ag(100) surfaces (*20*). The latter experiment was performed with the highest time resolution achieved to date in TPPE, yielding a lifetime of 25 fs for the lifetime of the $n = 1$ image state.

Time-Resolved TPPE

Measurement of the kinetic energy of electrons photoemitted from a solid is one of the most effective methods available for the determination of the electronic structure of its surface (*21*). Ultraviolet photoelectron spectroscopy (UPS) involves the use of photons in the range of 5 to 150 eV and is best suited for the study of the structure of the valence energy bands. A special case of UPS is angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) (*22*), in which both the kinetic energy and the vector momenta of the photoemitted electrons are simultaneously measured. This technique allows for the mapping of the dispersion, that is, the wave vector dependence of the energy, of individual energy bands.

The ultraviolet radiation source in a conventional UPS (or ARUPS) experiment is either a discharge lamp or synchrotron radiation. Advances in nonlinear optics and ultrafast laser technology now provide laser-based ultraviolet radiation sources capable of producing ultrashort pulses at a large selection of photon energies in the range of interest for UPS experiments (*23*). These sources can provide time-averaged total photon flux comparable to that obtained at typical synchrotron bending magnet beam lines. Although synchrotron radiation is also pulsed, typical pulse widths are >100 ps. Ultrafast laser technology is capable of generating pulses in the femtosecond regime.

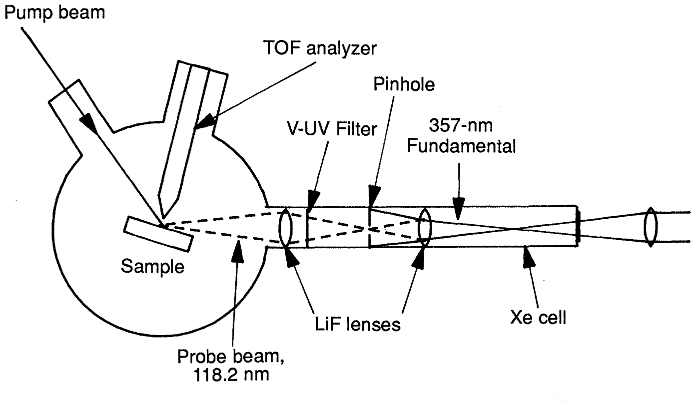

Fig. 1. Schematic diagram of experimental apparatus used for picosecond time- and angle-resolved photoemission spectroscopy; TOF, time of flight; V-UV, visible-ultraviolet.

In a time-resolved UPS experiment, a surface is first excited by absorption of a short "pump" pulse. Then the photoemission spectrum of the excited surface is recorded with a short ultraviolet "probe" pulse, which is derived from the same laser system by nonlinear optical techniques. Thus the photoelectrons of interest are produced by the absorption of two separate photons. By varying the relative time delay between the arrival of the pump and the probe pulses, one can obtain information on the dynamical behavior of the excited surface. Williams *et al.* were the first to directly time-resolve excited-state dynamics at a surface with TPPE (*15*). In their experiment, the second (2.35 eV) and fourth (4.7 eV) harmonics of a neodymium phosphate glass laser were used to excite and probe single-crystal ZnTe surfaces. The pulses produced by this laser were 5 ps in duration, and carrier relaxation times of several hundred picoseconds were measured.

The technique was further advanced by the use of higher energy (10.5 eV) radiation and angle-resolved detection. A schematic diagram of the apparatus presently used for such experiments is shown in Fig. 1. Experiments based on the use of various versions of this apparatus have been performed on the clean InP(110) (*16*), GaAs(110) (*19, 24*), and Si(111) (*17, 18*) surfaces cleaved in ultrahigh vacuum. States within the band gap of some of these materials formed during the deposition of various gases and metals have also been observed. Two stages of harmonic generation beginning with an Nd:YAG (yttrium-aluminum-garnet) laser were used to produce the 10.5-eV probe photons used in these studies. The pulses produced by this system were 60 to 70 ps in duration.

Semiconductor Surface Recombination

According to the phenomenological Stevenson-Keyes (*25*) model, semiconductor surface recombination is mediated by trap states that lie in semiconductor band gap in analogy with bulk indirect recombination. These surface recombination traps have heretofore been inaccessible to direct study. However, a series of TPPE

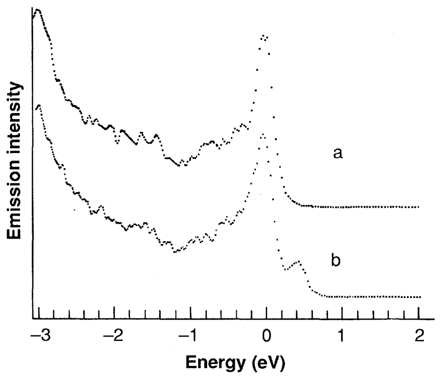

Fig. 2. Photoemission spectra of the cleaved Si(111) surface (*17*). The zero of energy corresponds to the position of the valence band maximum on the equilibrium surface. Curve a, equilibrium surface; curve b, 2.8-μm photoexcited surface, at zero time delay between pump and probe pulse.

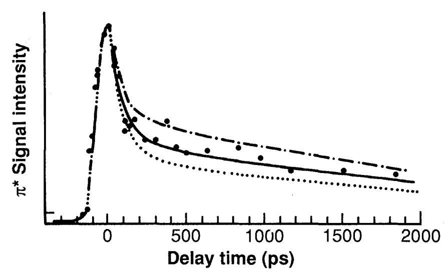

Fig. 4. Time dependence of the π* surface-state population on Si(111) when excited with resonant, 2.8-μm pulses (*17*). The experimental data are shown as bold dots. The results of a model calculation for three values of τ_h are also shown. Values of B_r and τ_e were fixed at 0.004 cm²/s and 2.5 ns, respectively. Solid curve, τ_h = 300 ps; dotted curve, τ_h = 400 ps; dotted-dashed curve, τ_h = 200 ps.

experiments performed on Si surfaces cleaved in ultrahigh vacuum has now allowed for the full characterization of the electronic structure and dynamics of mid-gap surface states and their mode of participation in surface recombination of bulk electrons and holes.

Using infrared (0.45-eV photon energy) pump pulses to selectively excite the mid-gap, π* surface state on the cleaved Si(111) surface and 10.5-eV ultraviolet photons for the probe, Bokor *et al.* conducted a detailed study of the relaxation dynamics of this surface state (*17*). The photoemission spectra obtained from both the equilibrium and the infrared pumped surface are shown in Fig. 2; the relevant energy levels are shown in Fig. 3. The additional peak at ~0.5 eV seen in the spectrum from the excited surface arises from transient population in the mid-gap, π* surface state. The time dependence of the transient π* population is shown in Fig. 4. To understand this decay curve, it is necessary to consider both the surface electrons excited into the π* state and the surface holes that are simultaneously pumped into the normally occupied π state. The decay dynamics are then determined by two mechanisms. At high densities, two-body radiative recombination of the surface electrons and holes dominates. This leads to the fast initial decay. At lower densities, the electrons nonradiatively decay into defect or step states. We obtained values for the two-body radiative recombination parameter, B_r, and the surface electron and hole lifetimes, τ_e and τ_h, respectively, by fitting a numerical solution to two coupled differential equations to the data. The measured lifetimes were found to vary by up to an order of magnitude from cleave to cleave, indicating that steps and defects play an important role in the dynamics.

In a subsequent experiment (*18*), Halas and Bokor investigated the role of these surface states in the surface recombination of bulk electrons and holes. In this case, 532-nm visible (pump) radiation was used to excite a bulk electron-hole plasma in the near-surface region (~1 μm) at cleaved Si(111) surfaces. We then observed the surface recombination dynamics by monitoring the time dependence of population changes in the surface states and in the bulk conduction band, using TPPE. The spectra obtained were very similar to those shown in Fig. 2.

Only the transient population in the π* state could be detected in this way; the sensitivity to bulk conduction-band electrons with the 10.5-eV probe photons was found to be too low. Following Long *et al.* (*26*), we used lower energy (4.68 eV) probe photons to monitor the time-dependent density of bulk conduction-band electrons. The lower energy probe photons were more effective because of the much longer mean free path for the lower energy photoelectrons. The photoemission process integrates the population over a depth near the surface corresponding to the mean free path for electrons with a kinetic energy equal to the photon energy. The mean free path for 10-eV electrons in Si is ~15 Å (*27*) but for 5-eV electrons it is 200 to 300 Å (*28*).

The time dependence of this photoexcited conduction band signal was measured for a variety of cleaves and conditions (*18*). In particular, the results for a clean and partially oxidized surface are shown in Fig. 5. The oxidized surface shows a reduced surface recombination rate relative to the clean surface. Analysis of the data showed that the conventional Stevenson-Keyes (*25*) model of surface recombination was inadequate to describe the results. A revised model of surface recombination appropriate to the transient regime was developed. In this model, the complicated surface dynamics are expressed in terms of a set of rate equations (involving k_1, k_2, τ_h, τ_e, and B_r) for the surface dynamics. These equations are then imposed as a boundary condition on the bulk transport

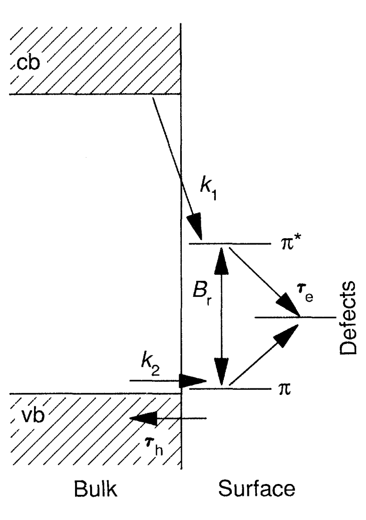

Fig. 3. The energy levels and recombination processes for the cleaved Si(111) surface (*18*); cb, conduction band; vb, valence band.

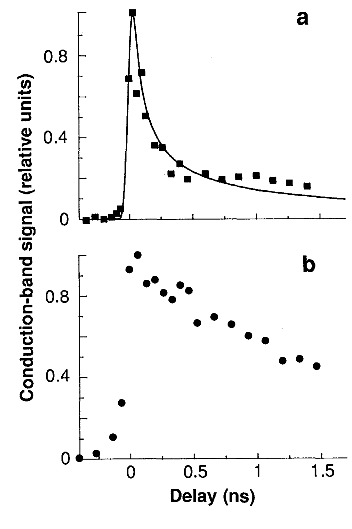

Fig. 5. Conduction-band photoemission as a function of time delay between the photoexcitation and the probe pulse (**a**) for the clean, cleaved Si(111) surface and (**b**) for the vacuum-oxidized Si(111) surface (*18*).

equations. This approach provides a fully self-consistent treatment of transient surface-charging effects on the bulk transport of carriers toward the surface.

Semiconductor Surface Intervalley Scattering

The dynamics of surface-state electrons has recently been examined with subpicosecond time resolution on GaAs(110) surfaces by Haight and Silberman (*19*). Their experiment is a dramatic example of the power of the combination of picosecond time resolution with ARUPS. It directly shows that there is a surface analog to the well-known intervalley scattering process (*29*) in bulk GaAs. The existence of a satellite valley in an excited-state surface band was identified, and the scattering time from the central valley to the satellite valley was measured.

Sample photoemission spectra from this experiment are shown in Fig. 6, together with a band structure diagram. Pump radiation of 1.78-eV photon energy was used to selectively excite electrons to states near the conduction-band minimum at $\bar{\Gamma}$ (crystal momentum, $k_{\|} = 0$). These electrons appear in the angle-resolved photoemission spectrum taken with 10.7-eV probe photons as the peak near +1.5-eV binding energy emitted in the surface normal direction (top spectrum in Fig. 6). Momentum scattering of these surface electrons to the satellite minimum in the C_3 surface band at $\bar{X}$ ($k_{\|} = 0.786$ Å^{-1}) gives rise to another peak in the photoemission spectrum at about the same binding energy, emitted at an angle of 34° to the surface normal along the ($\bar{1}10$) azimuthal direction (bottom spectrum in Fig. 6). The time dependence of the signals from both $\bar{\Gamma}$ and $\bar{X}$ was then measured (Fig. 7).

These data were analyzed in a manner somewhat similar to the method used in (*18*), whereby rate equations involving the surface states are imposed as a boundary condition on the bulk continuity equation (*19*). A $\Gamma - \bar{X}$ scattering time of 0.4 ps was deduced. Because of the high carrier densities produced, effects owing to degenerate band filling in the two surface band minima were also involved. These high carrier densities also led to observable band-gap renormalization [a density-dependent narrowing of the band gap caused by exchange and correlation effects (*30*)].

Electronically Excited States at Metal Surfaces

The lifetimes of optically excited states at surfaces are now receiving attention because of the possibility of nonthermal photochemistry at surfaces. The simplest example is laser-induced desorption. In most cases of laser-induced desorption from metals, molecules are thermally (pyrolytically) desorbed from the surface after a temperature jump produced by the absorption of laser energy by the metal substrate. Although the absorption of laser photons initially produces electronic excitations of the substrate or molecule, or vibrational excitations of the molecule, these apparently degrade into heat before the desorption can take place. However, several recent laser-induced desorption experiments (*31–34*) suggest that under some circumstances the optical excitation can lead to molecular desorption before energy is equilibrated among all the available degrees of freedom (electrons, phonons, molecular vibrations).

The evidence for nonthermal mechanisms can take several forms. Laser-induced fluorescence has been used to measure the internal energy distributions of the desorbed molecules and time-of-flight mass spectroscopy has been used to measure the translational energy distributions (*31, 33*). The observation that the translational, vibrational, or rotational energy distributions are considerably different from Boltzmann distributions at the substrate temperature, calculated on the assumption that there is thermal equilibration among all modes, may reflect a nonthermal desorption process. Resonance effects in the wavelength dependence of the desorption yield can also indicate nonthermal mechanisms (*32, 34*). Continuous laser irradiation has been used to measure the time dependence of desorption on the time scale of seconds and to distinguish thermal from nonthermal desorption (*32*).

One of the key issues involved in this area is the lifetime of electronic excitations of adsorbates on metals. These lifetimes are well into the subpicosecond domain, and measuring them represents a formidable experimental challenge (*7*). There have, as yet, been no direct, time-domain measurements of the lifetime of an electronic excitation of a molecule adsorbed onto a metal surface. An indication that such measurements may soon be possible, however, is provided by the recent determination of the image-state lifetime on a clean Ag surface (*20*) made by TPPE.

Image-potential states are bound states of electrons trapped just

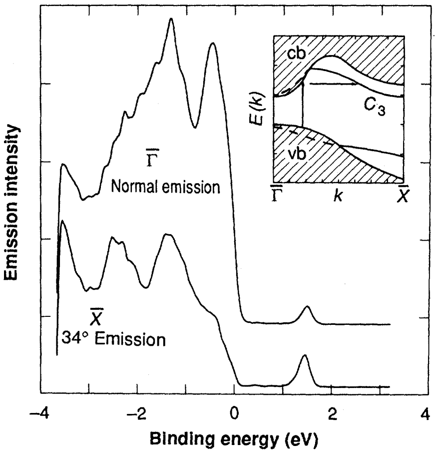

Fig. 6. Pump-probe photoemission spectra from cleaved GaAs (110). The bottom spectrum was collected at an emission angle of 34° relative to the surface normal. The top spectrum was collected along the surface normal. Inset: The relevant surface and bulk band structures. [Adapted from (*19*) with permission of the authors]

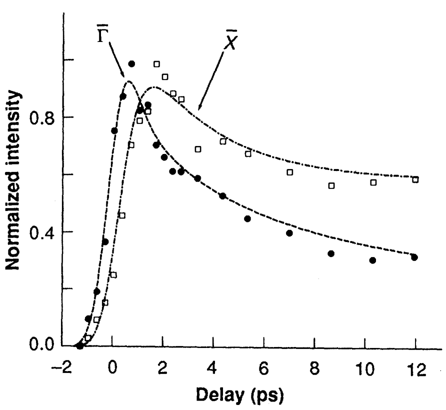

Fig. 7. Excite-probe delay curves for emission from the GaAs(110) surface satellite valley (open squares) and central valley (filled circles). [Adapted from (*19*) with permission of the authors]

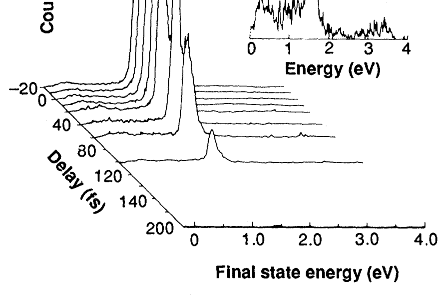

Fig. 8. Photoelectron spectra at various time delays showing the dynamics of the image-potential state on Ag(100). Inset (×100 vertical scale): the background spectrum at +200-fs delay. [Adapted from (*20*) with permission of the authors]

outside the surface of a metal between the Coulomb image potential on the vacuum side and a barrier at the surface created by a gap in the available bulk electronic states. These states are characterized by a Rydberg-like series. Many of the properties of these states were determined by TPPE with nanosecond laser pulses (non–time-resolved) (*35*). The binding energies, effective masses, and lifetimes of image states are of great theoretical interest because the relative simplicity of the image-state wave functions makes it possible to perform sophisticated calculations of these properties, including many-body effects on the surface response (*36*).

To achieve the extraordinarily high time resolution required to measure the image-state lifetime on Ag, it was necessary to modify the experimental strategies used in the previously discussed TPPE experiments to fit the highly specialized technology of femtosecond laser spectroscopy (*1*). In particular, the generation of vacuum ultraviolet pulses with harmonic generation has not yet been extended into the <100-fs regime. Instead, ~55-fs near-ultraviolet pulses at 4.0 eV were generated by frequency-doubling the ~55-fs pulses at 2.0 eV produced by an amplified colliding-pulse, mode-locked ring dye laser (*1*). The ultraviolet pulses were used in this case as the pump, and the visible pulses were used as the probe.

The femtosecond time-resolved photoemission spectra reported in (*20*) are reproduced in Fig. 8. By plotting the intensity of the image-state peak as a function of time delay, one can measure the lifetime of the state. The lifetime of the $n = 1$ image-potential state on the Ag(100) surface was measured to be 25 ± 10 fs, which lies within the range predicted by theory (*36*).

The successful extension of TPPE into the femtosecond regime now makes it possible to consider the study of other extremely short-lived excitations at metal surfaces. Ultrashort laser pulses are now available (*37*) with durations as short as 6 fs. This is of the same order as the lifetime of electronically excited N_2 on Al surfaces that was inferred by linewidth measurements (*3*). We therefore anticipate that it may soon be possible to directly observe the relaxation of electronically excited adsorbates on surfaces with the use of these new ultrafast techniques.

Conclusions

The combination of lasers and nonlinear optical techniques is now being brought to bear on the next frontier in surface physics, namely, surface dynamics. Ultrafast lasers allow for the study of picosecond and femtosecond processes directly in the time domain, circumventing the ambiguities attendant on linewidth measurements for the determination of lifetimes. One may anticipate continued growth in the diversity of applications of these techniques to the understanding of the complexities of surface dynamics.

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