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Femtosecond dynamics of the $n=2$ image-potential state on Ag(100)

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We report the first time-resolved studies of higher-order image-potential states on Ag(100). Two-photon photoemission measurements are performed with femtosecond resolution using pump and continuum probe techniques. We measure the lifetime of the $n=2$ image state on Ag(100) to be ~ 180 fs, substantially longer than that of the $n=1$ state. These results have implications for theoretical models used for predicting the lifetimes of these states.

Image-potential states are an interesting class of surface states because they provide a system for studying the dynamics of a two-dimensional electron gas confined outside the bulk crystal. Image-potential states are somewhat analogous to quantum-well states in semiconductors, with potential barriers formed by the Coulombic potential on the vacuum side, and a band gap of states in the crystal lattice about the vacuum level. The states form a hydrogenic series approaching the vacuum level,[1] and are predicted to exist in a variety of material systems due to the fundamental nature of the binding potential. Since image states are localized in the vacuum, they are relatively insensitive to energy-loss mechanisms associated with the crystal. They are predicted to be long-lived relative to bulk states at comparable energies above the Fermi level.

Recent interest in image-potential states on metal surfaces has been motivated by the development of high-resolution measurement techniques. In the past few years, inverse photoemission[2-4] and two-photon photoemission[5,6] techniques have been used to accurately measure the binding energies and effective masses[7-10] of the $n=1$ and 2 states on various surfaces of Ag, Cu, and Ni. These results showed good agreement with theoretically predicted values based on a hydrogenic model.

Theoretical analyses have also been used to predict the lifetime broadening of these states, and the dependence of this broadening on the state number n. A hydrogenic scattering-resonance model proposed by Echenique and Pendry[11] predicts energy broadening scaling as n^{-3} (excited-state lifetime scaling as n^3). Higher-order states are expected to be longer lived since their wave functions are localized further in the vacuum. The n^{-3} scaling of the lifetime broadening has been confirmed by recent calculations employing a many-body self-energy formalism.[12] Similar calculations suggest excited-state lifetimes on the order of 10–100 fs.[13,14]

Previous experimental studies of image-potential states have been unable to provide conclusive information about the lifetimes of these states. As expected, the observed linewidth broadening is quite small, less than 100 meV, but measurement accuracy has been limited by instrument resolution and possible inhomogeneities in the surface work function.

Recently, femtosecond pump-probe techniques have been combined with two-photon photoemission spectroscopy to provide direct measurements of the lifetime of the $n=1$ image-potential state on Ag(100).[15] The lifetime of the $n=1$ state was measured to be in the range 15–35 fs, in reasonable agreement with theoretical predictions. In this paper, we report the extension of this technique using tunable femtosecond pulses to study the dynamics of the $n=2$ image-potential state on Ag(100). This represents the first direct lifetime measurement of a higher-order image-potential state. Comparisons with previous measurements of the $n=1$ state lifetime will be relevant in determining the accuracy of theoretical models. We observe an $n=2$ image-potential state lifetime ~ 180 fs. Furthermore, the relative lifetimes of the $n=1$ and 2 states are consistent with theoretical predictions.[11,12]

The femtosecond source for these investigations is a dispersion-compensated colliding-pulse mode-locked ring dye laser,[16] amplified at 8 kHz by a copper-vapor laser amplifier.[17] The system produces 55-fs pulses at 620 nm (2.00 eV) with pulse energies of a few microjoules. A standard pump-probe geometry is employed with the probe delayed relative to the pump by a translation stage. In contrast to previously reported measurements of the $n=1$ image-potential state,[15] it is necessary to produce tunable femtosecond pulses in order to excite the $n=2$ states. This measurement is performed by continuum generation and frequency doubling. Amplified pulses in the pump arm are focused in a jet of ethylene glycol to generate a broad-band femtosecond continuum via self-phase modulation. A portion of this continuum in the wavelength range of about 570 nm is then frequency doubled in a 300-μm crystal of potassium dihydrogen phosphate (KDP). Pulse durations as short as ~ 90 fs at 285 nm (4.35 eV) are achieved by using a pair of quartz prisms in the pump arm to compensate group-velocity dispersion in the uv due to the optical elements.

Measurements are performed in an ultrahigh vacuum (UHV) chamber with a base pressure of $\sim 10^{-10}$ torr. A single-crystal Ag sample is cut and polished in a (100) orientation with an accuracy of 2°. The sample is mount-

ed in the vacuum chamber, and the surface is prepared by sequentially sputter-ion cleaning and annealing. Auger spectroscopy and low-energy electron diffraction (LEED) are used to confirm the purity and quality of the surface. Ultraviolet pump and visible probe pulses enter the vacuum chamber collinearly, and are focused onto the sample by a curved mirror to eliminate chromatic abberation. Both uv and visible beams are P polarized to satisfy selection rules for populating the image-potential states. Photoelectrons are collected by a double-pass cylindrical mirror analyzer (CMA) with an energy resolution of ~ 180 meV.

Figure 1 shows a schematic of the projected band structure at the (100) surface of Ag. Electrons are confined in the orthogonal direction, resulting in discrete states with binding energies of 0.53 and 0.16 eV for $n=1$ and 2, respectively.[10] The bands are nearly free-electron-like in the $k_{\parallel}$ direction, with an effective mass of $1.15m_0$ for $n=1$ electrons.[10] Femtosecond pulses at 4.35 eV are used to populate the image states via transitions originating below the Fermi level in the bulk. The high photon energy required to excite the $n=2$ state also generates an electron population in the $n=1$ state with several hundred meV of excess energy. This excess electron energy is in the form of parallel momentum $k_{\parallel}$ along the crystal surface.

Electrons in the $n=2$ state as well as the $n=1$ state are photoemitted to the vacuum by a visible femtosecond pulse at 2.00 eV. The visible pulse is delayed in time relative to the uv pulse, thus providing information about the transient dynamics of the image states. Using two different photon energies for populating and photoemitting provides a substantial advantage over standard two-photon photoemission because it allows the effects of the pump to be distinguished from the effects of the probe. Furthermore, by using relatively low photon energies for photoemission, background signals due to bulk transitions are reduced.

Figure 2 shows photoelectron spectra generated by uv-visible two-photon photoemission at various time delays. Visible and uv fluences of $\sim 600\ \mu J/cm^2$ and $\sim 30\ \mu J/cm^2$ are used to avoid space-charge effects. At these fluences, we estimate nonequilibrium electron heating of only a few hundred degrees, which should have a negligible effect on our measurements. Positive delay corresponds to visible probe pulses arriving after the uv pump pulses. Electron energies are measured relative to the vacuum level which is determined by the onset of the photoemission signal. We observe a peak at ~ 1.5 eV which corresponds to the $n=1$ image state with a binding energy of ~ 0.5 eV. Because of the very short lifetime of this state, ~ 25 fs, the $n=1$ peak disappears very rapidly. However, at longer time delays, a second peak emerges at an energy of ~ 1.8 eV. This corresponds to the $n=2$ state with a binding energy of ~ 0.2 eV. With increasing time delay, the height of the $n=2$ peak relative to the $n=1$ peak is observed to increase, suggesting that the $n=2$ state is longer lived.

Though electrons are excited in the $n=1$ band with as much as 400 meV excess energy, the measured energy width of the photoelectron peak due to the $n=1$ state is only ~ 200 meV. This effect is due to collection angle limitations in our CMA. Since the analyzer used in these experiments has an acceptance angle of only 15°, our measurements are most sensitive to electrons near the bottom of the $n=1$ band. However, the $n=1$ peak in the photoelectron spectra of Fig. 2 shifts slightly to lower energies with increasing time, suggesting that electrons with

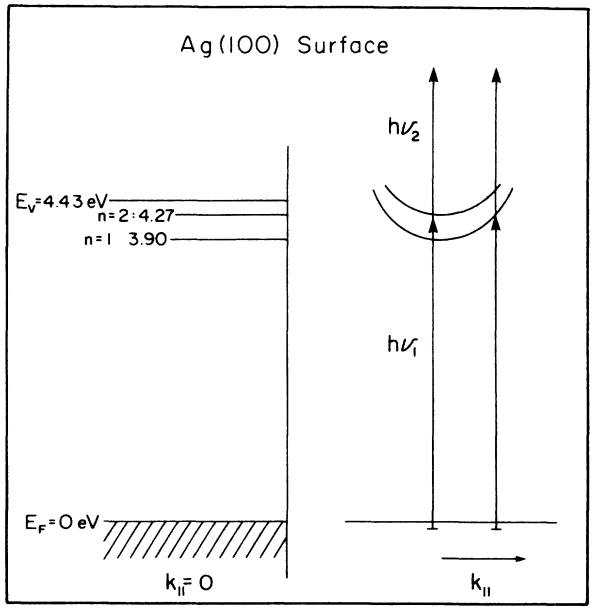

FIG. 1. Energy-level diagram for Ag(100) surface for $k_{\parallel}=0$ and $k_{\parallel}\neq 0$. Ultraviolet femtosecond pulses, $h\nu_1=4.35$ eV, populate both the $n=1$ and 2 states via nonresonant transitions originating below the Fermi level. Visible pulses, $h\nu_2=2.00$ eV, photoemit excited electrons to the vacuum.

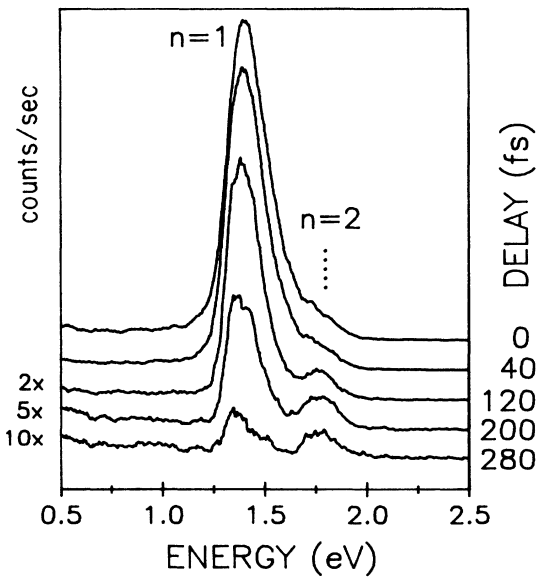

FIG. 2. Photoelectron spectra from Ag(100) using uv-visible two-photon photoemission. Positive delay corresponds to visible pulses arriving after the uv pulses. The peak photoemission signal is ~ 0.1 electrons/pulse (800 electrons/sec).

excess parallel momentum are relaxing to $n=1$ image states with lower $k_{\parallel}$, and/or escaping into the crystal by coupling to bulk bands or surface excitations.

More quantitative information about the relative lifetimes of the $n=1$ and 2 states is obtained by taking time-resolved scans with the energy analyzer tuned to the peak of each state at 1.5 and 1.8 eV, respectively. These measurements are shown in Fig. 3. The solid lines indicate the transient response of each state, with positive delay corresponding to visible probe pulses arriving after the uv pump pulses. The response of the $n=1$ state is nearly instantaneous, relative to our resolution, although a slight asymmetry toward positive delay is clearly evident. The transient response of the $n=2$ state indicates a lifetime that is substantially longer, approximately 180 fs. This is consistent with theoretical predictions since higher-order image states have wave functions localized further in the vacuum.[11,12]

An estimate of the $n=2$ image-state lifetime is obtained by assuming a simple exponential relaxation. Under this assumption, we model the transient response by convolving the uv-visible cross correlation with a single-sided exponential. To get an accurate measure of the cross correlation at the sample, the sample surface is roughened by ion sputtering. The roughening process effectively quenches both the $n=1$ and 2 image-state lifetimes. Thus, the nearly instantaneous transient response provides a reasonable approximation to the uv-visible cross correlation.

Because of instrument limitations in our angular resolution, the measured response of the $n=2$ state also includes electrons from $n=1$ image states with excess parallel momentum. Thus, our model for the $n=2$ transient response also includes some component of the $n=1$ response. This model is described by the following expression:

$$n_2(t)=A(t)\otimes\exp(-t/\tau)+\alpha n_1(t)\,,$$

where $n_2(t)$ is the predicted response, $A(t)$ is the uv-visible cross correlation, τ is the predicted lifetime of the $n=2$ state, and $\alpha n_1(t)$ describes the component of the $n=1$ transient response which contributes to the measurement. Since high-energy electrons, $k_{\parallel}\neq 0$, in $n=1$ states decay nearly instantaneously, we approximate the $n=1$ response at high energies by the uv-visible cross correlation, $n_1(t)_{k_{\parallel}\neq 0}\approx A(t)$.

The numerical fits to the $n=2$ response are shown by the dashed lines in Fig. 3. The parameters used in these fits are $\alpha=0.8$ and time constants, $\tau=160$, 180, and 200 fs. The best fit is obtained assuming a lifetime of 180 fs. The $\tau=160$ and 200 fs fits are plotted to show the sensitivity of the fitting procedure. Thus the $n=2$ image state lifetime on Ag(100) is significantly longer than that reported for the $n=1$ state. Using a lifetime of $\tau\sim 25$ fs for the $n=1$ lifetime is roughly seven times longer.

This result is consistent with previous theoretical predictions by Echenique and Pendry.[11] Using a hydrogenic model, Echenique and Pendry predict lifetimes which scale as n^3 for the higher-order image states. More recent calculations using a many-body self-energy formalism predict n^3 lifetime scaling for states $n\geq 5$.[12] For lower-order states, the model predicts a lifetime scaling of somewhat less than n^3, with $\tau_{n=2}/\tau_{n=1}\approx 4$. This model overestimates $\tau_{n=1}$ since the hydrogenic model neglects wave-function penetration into the bulk. Thus we expect the ratio of the lifetimes $\tau_{n=2}/\tau_{n=1}$ to be between four and eight, which is in good agreement with our experimental measurements.

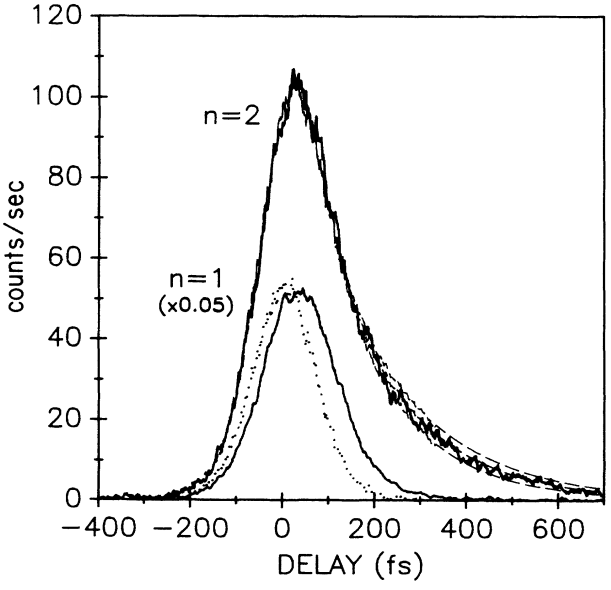

FIG. 3. Transient responses of the $n=1$ and 2 image-potential states on Ag(100) (solid lines). Dashed lines are convolved exponentials with decay times of 160, 180, and 200 fs and $\alpha=0.8$ according to the response model. The dotted line is the normalized uv-visible cross correlation.

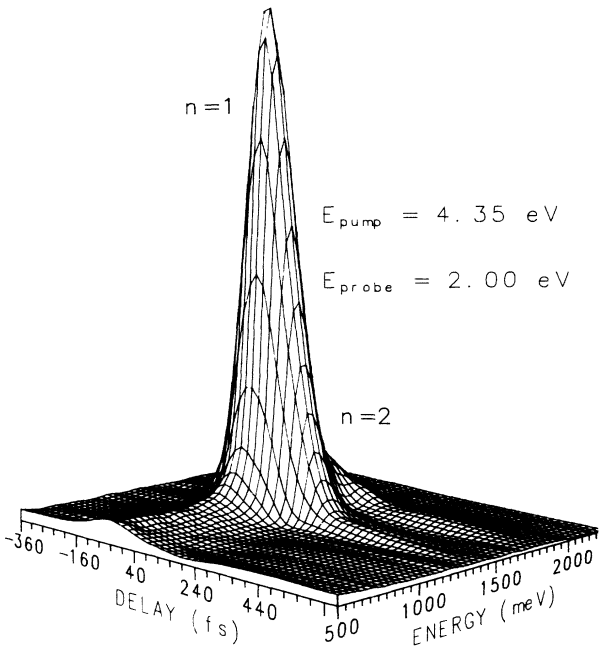

FIG. 4. Relaxation dynamics in time and energy of the $n=1$ and 2 image-potential states on Ag(100).

In addition, since our measurements monitor the occupancy of the $n=1$ and 2 states simultaneously, we should be sensitive to population transfer from the $n=2$ state to the $n=1$ state. This type of relaxation process is not evident in our results. Figure 4 shows the transient dynamics of the $n=1$ and 2 states in time and energy. This manifold is constructed from photoelectron spectra taken at various time delays, and provides an overview of the excited-state dynamics. In order to clarify the surface features, a grid is superimposed over the data using a cubic spline interpolation algorithm. The large peak at ~ 1.5 eV is the response of the $n=1$ state, which decays quite rapidly. The $n=2$ response is initially obscured by the shoulder of the $n=1$ state, but is more pronounced at later times after the $n=1$ state has decayed. On this longer time scale, we observe an electron population primarily in the $n=2$ state. The correlation signal observed at low energies is attributed to nonequilibrium electron heating, and two-photon photoemission.

In summary, the transient dynamics of the $n=2$ image-potential state on Ag(100) have been investigated using femtosecond pump-probe techniques combined with two-photon photoemission spectroscopy. Optical pulses of less than 100-fs duration at 4.35 eV are generated via self-phase modulation and frequency doubling. By exciting the image states with the uv pulses, and then photoemitting with visible pulses, the transient dynamics of the $n=1$ and 2 states can be studied simultaneously, under nearly background-free conditions. Our results show the population and decay of the $n=1$ state on a time scale comparable to the pulse duration. This is consistent with our previously reported measurement of an excited-state lifetime between 15 and 35 fs.[15] In contrast, the $n=2$ state is shown to be much longer lived. The measured lifetime is ~ 180 fs and is consistent with theoretical models which predict that image-state lifetimes scale as $\leq n^3$ for the lowest states. Our results do not indicate substantial population transfer from the $n=2$ to the $n=1$ state, although there is evidence of an energy relaxation process within the $n=1$ band. Extension of this approach to other surfaces may enable further refinement of the theoretical model, and provide additional information about the dynamics of a two-dimensional electron gas.

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