

Dynamics and Spatial Distribution of Electrons in Quantum Wells at Interfaces Determined by Femtosecond Photoemission Spectroscopy

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The dynamics of excited electrons in insulator quantum well states on a metal substrate were determined by femtosecond two-photon photoemission for the first time. Lifetimes are reported for the first three excited states for 1–6 atomic layers of Xe on Ag(111). As the image states evolve into quantum well states with increasing coverage, the lifetimes undergo an oscillation as the layer boundary crosses each node of the wave function. The lifetime data are modeled by extending the two-band nearly free-electron approximation to account for the presence of a dielectric layer. The lifetimes are shown to depend on the spatial distribution of the interfacial electron. [S0031-9007(97)04743-1]

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The transition of the electronic structure from two-dimensional atomically thin layers to the three-dimensional extended electronic structure of the bulk has implications in many fields including surface photochemistry, photoinduced charge transfer, and semiconductor device physics. Surface effects (e.g., chemisorption, band bending, surface reconstructions, and image potential states) as well as quantum confinement (which results in the discretization of momentum along the surface normal) affect the electronic characteristics of the composite interface. Femtosecond time-resolved two-photon photoemission (TRTPPE) has proved to be a useful technique for the determination of the energies and dynamics of interfacial electronic states for a variety of systems [1,2] including metal surfaces [3], semiconductor surfaces [4,5], and metal-insulator interfaces [6,7]. This Letter presents a new and general method for determining the evolution of electronic structure from two-dimensional states of a single atomic layer to three-dimensional quantum well (QW) states by analysis of the femtosecond dynamics of excited electronic states for a range of layer thicknesses.

Physisorbed multilayers of Xe on a noble metal surface [8,9] have recently been identified as an important model system for understanding carrier dynamics at interfaces and in quantum wells. Since solid Xe can be considered a wide-gap semiconductor, aspects of this model system are similar to those of a metal-semiconductor interface. Because the crystal and electronic structures of bulk Xe and Ag are experimentally [10,11] and theoretically [12] well characterized, models of the composite interface electronic structure and dynamics can be constructed and tested. Of fundamental importance to understanding electron behavior in quantum wells and at interfaces are the time scales and mechanisms for energy and momentum relaxation of carriers near the junction of two materials. A systematic study over a range of film thicknesses provides a unique probe of the interface since the evolution of the electronic structure can be monitored atomic layer by layer, allowing for the separation of the various factors which deter-

mine the electronic structure and dynamics of the composite interface. For the experiments described here, the first photon excites electrons from the valence band of the metal substrate into QW states derived from the Xe conduction band located in energy several eV above the Fermi level (Fig. 1). The second photon probes the dynamics in the image potential and QW states by photoemission. TRTPPE is well suited to the study of excited electrons at interfaces owing to the inherent surface sensitivity, good

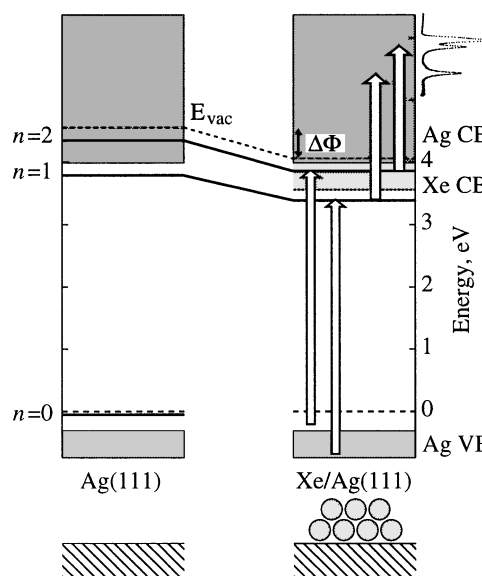


FIG. 1. The surface-projected band structure for (left) clean Ag(111) and (right) Xe on Ag(111). The zero of energy is set to the Fermi level. The adsorption of a monolayer Xe reduces the work function Φ by 0.5 eV. This lowers the image state energies with respect to the Fermi level since image states are pinned to the vacuum level. Adsorption of additional layers of Xe results in the formation of quantum well states. The Xe and Ag(111) bands are denoted by light and dark shading, respectively. A two-photon photoemission spectrum for a bilayer of Xe on Ag(111) containing the $n = 1, 2,$ and 3 peaks is shown on the right-hand side.

energy resolution (~ 30 meV), low background, and ultrafast time resolution afforded by the technique.

The evolution of an $n = 1$ image potential state into a QW state was recently observed by Fischer *et al.* [13] for Au/Pd(111). Similarly, it was determined that conduction band QW states can form with increasing layer thickness for an insulating overlayer such as Xe which has a positive (attractive) electron affinity [9]. The energy levels of excess electrons in these states were measured, and it was shown that the binding energies are quantized according to the layer thickness. It was also demonstrated that the quantized energy levels are in good agreement with the Xe conduction band dispersion. Here, these measurements are extended to the time domain, providing the first direct measurement of the lifetime of QW states at a metal-insulator interface. The results are shown to yield the spatial distribution of the QW electron through its effect on the lifetime.

In general, the electronic states of the interface depend on contributions from the electronic structure of the substrate, the overlayer material, polarization or image effects, and quantum confinement effects. As shown below, all of these effects are important in Xe/Ag(111). QW states occur in a layered sample when the states of one material are confined by band gaps in the neighboring layers. The relevant bulk bands of the materials under study are the surface-projected Ag(111) valence and conduction bands (VB and CB, respectively) and the Xe $6s$ CB (Fig. 1). In addition, the polarizability of the metal surface supports a Rydberg series of image potential bound states converging to the vacuum level. The lowest members of that series are also plotted in Fig. 1. The work function shift of $\Delta\Phi = -0.5$ eV due to the adsorption of monolayer Xe places the vacuum level at approximately 0.07 eV above the Ag CB minimum. The Xe CB minimum is at approximately -0.5 eV with respect to the vacuum level. Electrons promoted to the CB of a Xe slab on the surface will be subject to confinement by the projected band gap in the metal and the image potential in the vacuum. Previous work has shown that the manner in which an image state evolves with coverage depends on its energy relative to the band structure of the Xe slab. The $n = 2$ and 3 image states, which are above the Xe CB minimum, become QW states of the layer at 7–9 layers of Xe and exhibit a mixed QW-image state behavior at intermediate coverage. These exhibit a discrete perpendicular dispersion corresponding to the Xe CB, whereas $n = 1$ does not [9].

Details of the experimental apparatus are published elsewhere [1,6,14] and are only briefly described here. A coherent Ti:sapphire oscillator-regenerative amplifier system produces a 200 kHz train of 200 fs pulses at 800 nm. Optical parametric amplification of white-light continuum yields 70 fs visible pulses which are frequency doubled to yield UV pump pulses. The residual fundamental is used as a probe pulse and is optically delayed with respect to the pump pulse. The two pulses are focused collinearly on the sample. The energy of the photoemitted electrons is de-

termined by time of flight. Using 300 and 600 nm pulses as pump and probe, our measured instrument function is ~ 110 fs FWHM. The wavelength was selected to place the pump photon energy (4.13 eV) close to the vacuum level but to avoid producing background counts from one photon photoemission. The sample was cooled to 45 K by means of a liquid helium cryostat in a UHV chamber with background pressure at $\sim 1 \times 10^{-10}$ torr. Xe was adsorbed on the sample by Langmuir dosing using a leak valve. Xe/Ag(111) x-ray structure results [15] show Xe to form an ordered incommensurate hexagonal layer on the Ag(111) surface.

The lifetime of the clean Ag(111) $n = 1$ image state was determined to be 30 ± 10 fs [1,6] in agreement with other published results [3]. Time-resolved TPPE spectra were acquired for each of one to six layers of Xe. The $n = 1$ trace corresponds to an exponential decay convolved with a Gaussian instrument function, as shown in Fig. 2. The $n = 1$ lifetime increases monotonically with each additional layer of Xe while the lifetime of the $n = 2$ state initially increases

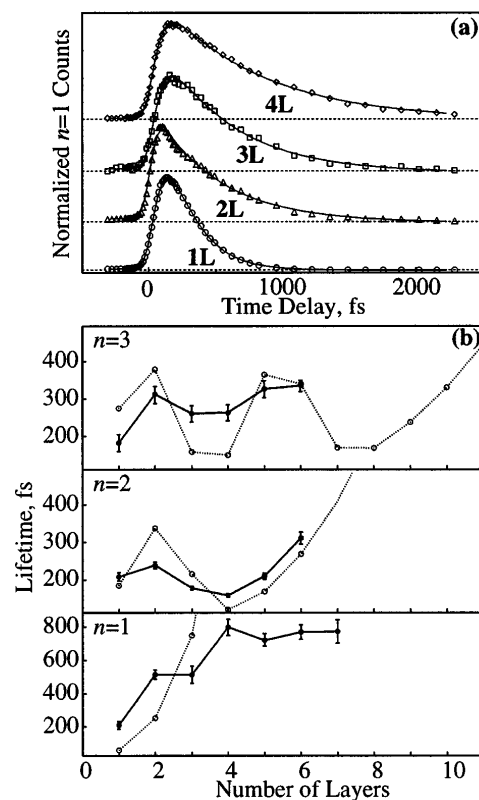


FIG. 2. Ultrafast time-resolved two-photon photoemission traces (a) for the $n = 1$ state for one to four layers of Xe (symbols) along with a fit obtained by convolving a single exponential with a Gaussian instrument function. Lifetimes (b) of the $n = 1, 2$, and 3 states for 1–6 layers of Xe extracted from the time-resolved data (filled circles). Lifetime predictions taken from the 1D model (open circles) are in qualitative agreement with the oscillations in lifetime apparent in the data. The experimental error bars are calculated for a 95% confidence limit.

with the addition of a monolayer of Xe, decreases slightly at three layers, then increases again at five and six layers (Fig. 2). The $n = 3$ state lifetime possesses a similar oscillation at three layers and remains approximately constant from five to six layers, suggesting a second oscillation.

In order to quantify the possible contributions to the binding energies of the image potential and QW states, a 1D quantum-mechanical model which explicitly includes the polarizability of the metal substrate and adlayer, as well as the substrate and adlayer band structure, is used [9]. The model is in good agreement with experimental binding energies. Implicit in this model is the quantum confinement due to the band gap of the substrate and the image potential barrier in the vacuum. A simple extension yields lifetime predictions for Xe QW states based on wave function penetration into the substrate (see below). The Ag(111) substrate bands are treated within the two-band nearly free-electron (NFE) approximation. The two-band NFE approximation was chosen since it had been successfully applied [16] to describe the substrate for the related case of surface states in the band gap of a metal. The two-band parameters were taken from calculations of clean Ag image and surface state binding energies [17]. In the overlayer the potential was set to the Xe CB minimum of -0.5 eV and the effective mass was set to $0.55m_e$. In the vacuum the potential was taken from the continuum dielectric model [6,18]. The continuum dielectric model yields the image potential outside a dielectric slab on a metal surface, accounting for the polarizability of the metal and adlayer. The dielectric constant of the layer was set to the literature value [19] of $\epsilon = 2$. The eigenstates of the model potential were determined by numerical integration, and binding energies and wave functions were determined for 1–11 layers of Xe. The probability densities are shown in Fig. 3.

Lifetime predictions were obtained from this model as follows. Since Xe has a large gap, it can be assumed that very few decay channels are present within the Xe layer, and therefore the primary decay pathway for excited electrons at the Xe/Ag(111) interface is a recombination with a vacancy in the substrate. Based on this assumption, the lifetime should depend on wave function overlap with the substrate. A model which has proven successful in obtaining qualitative lifetime predictions from calculated wave functions starts by assuming that the coupling to the crystal is related to the penetration p of the image state into the bulk, where p is defined as the probability density in the bulk [20–23],

$$p = \int_{-\infty}^0 \psi^* \psi dz.$$

The lifetime broadening Γ of the image state is related to the linewidth of the bulk crystal conduction band $\Gamma_b(E)$ by $p\Gamma_b(E)$. Calculated lifetimes using a value of Γ_b based directly on independent photoemission data [24] are shown in Fig. 2.

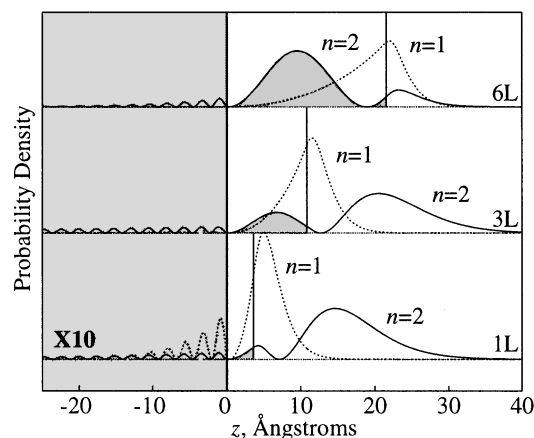


FIG. 3. The electron probability density $\psi^* \psi$ for the quantum well model for the $n = 1$ and 2 states for 1, 3, and 6 layers of Xe. The model predicts that the probability density in the layer increases for the $n = 2$ state as the number of layers increases. The vertical lines represent the layer–vacuum boundary.

The trends and overall magnitudes of the $n = 2$ and 3 lifetimes are reproduced by this simple model. These trends can be understood by considering two effects which have an opposite impact on lifetime. First, the semiclassical round-trip time in a simple square well varies as the width squared. Assuming the lifetime is inversely proportional to the attempt rate, the lifetime should increase as the square of the number of layers. The second effect is due to the presence of the soft image barrier in the vacuum: For a monolayer, the potential well in the vacuum is both wider and deeper than that of the layer. As the layer thickness increases, the increased distance from the metal substrate weakens the image potential in the vacuum while the layer potential gets wider. At a certain thickness, approximately when the Xe layer terminates near a node in the zero-order image state wave function, it is energetically favorable for the electron to move inside the layer, resulting in increased probability density in the layer, as can be seen by comparing the $n = 2$ wave function for one and three layers (Fig. 3). The expectation value $\langle z \rangle$ decreases, resulting in an increase in the probability density in the substrate which reduces the lifetime. A given image potential state effectively becomes a QW state in successive steps, the number of which is determined by the number of nodes in the zero-order hydrogenic wave function, i.e., the quantum number. For example, the calculations indicate that $n = 3$, having two nodes in the wave function, will have two oscillations in a lifetime before the simple square well behavior takes over.

Degeneracy of the image state with the substrate conduction band results in a decrease in lifetime relative to image states within the gap [3]. The fact that the lifetime of the $n = 3$ state in the presence of a monolayer of Xe is shorter (the lifetimes for $n = 1, 2$, and 3 are 210, 210, and 180 fs, respectively) than that of $n = 1$ and $n = 2$ could be explained in terms of the degeneracy of the $n = 3$ state with

the bulk. However, for the similar case of a monolayer of cyclohexane (C_6H_{12}) on Ag(111), the lifetimes of the $n = 1, 2$, and 3 states are 200, 220, and 660 fs. According to our measurements, the work function of Xe/Ag(111) is 30 meV lower than the value of 4.09 eV measured for cyclohexane on the same substrate, placing the $n = 3$ state in the presence of a Xe monolayer within the band gap, according to previous measurements of the Ag(111) band gap [13]. That the $n = 3$ lifetime in the presence of a monolayer of Xe is shorter than that of the $n = 3$ state in the presence of a monolayer of cyclohexane, despite the fact that the former is within the band gap of the substrate, rules out degeneracy as the cause of the difference in lifetime. Rather, this suggests that the difference in lifetime is due to differences in the potential within the layer. The main difference is that the alkanes possess a negative (repulsive) electron affinity, which prohibits the formation of quantum well states. No oscillations are observed or predicted in the lifetime for n -heptane/Ag(111) as a function of coverage [6]; the lifetimes increase monotonically, consistent with a picture in which the negative electron affinity excludes the electron from the layer. In contrast, appreciable electron density in the layer and the formation of quantum well states related to the band structure are observed for Xe layers [9].

The model results for the $n = 1$ state predict that its lifetime should also increase quadratically with layer thickness. This conflicts with the data, which indicate that the lifetimes for $n = 1$ reach limiting values by five or six layers. A possible interpretation is that the $n = 1$ state ceases to evolve as an image state at the Xe-vacuum interface [9] and becomes a screened image state of the metal inside the Xe slab. A more sophisticated, self-consistent approach to the potential in the overlayer should resolve this question and improve the agreement with the experimentally determined $n = 1, 2$, and 3 lifetimes.

Since the calculated wave functions successfully account for the lifetimes of the quantum well states, we conclude that the wave functions correctly describe the partitioning of conduction electrons between the three spatial regions of this model interface, i.e., between a noble metal, an insulator, and vacuum, as illustrated in Fig. 3. In addition, we have shown that the electron lifetime as a function of thickness displays a characteristic oscillation marking the onset of QW electronic behavior. Femtosecond layer-by-layer TPPE constitutes a new approach to understanding the complex dynamics of electrons at interfaces leading to stringent tests for theory of electronic structure and dynamics.

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