Ultrafast dynamics of electrons in image-potential states on clean and Xe-covered Cu(111)

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Lifetimes of electrons in the $n=1$ and $n=2$ image states on Cu(111) are studied with femtosecond time-resolved photoemission. Adsorption of one monolayer of Xe results in a pronounced increase of the image-state lifetime, which for the $n=1$ state changes from 18 ± 5 fs at clean Cu(111) to 75 ± 15 fs at the Xe-covered surface. The slower relaxation rate induced by the Xe layer is attributed to a reduced overlap of the image-state wave function with bulk states. A density-matrix calculation reveals the importance of dephasing in the excitation process. [S0163-1829(96)51032-5]

The termination of the crystal periodicity by a surface gives rise to new electronic states whose wave functions are localized at the surface and decay exponentially into the bulk. Such surface states may influence the surface reactivity and growth kinetics because adsorption energies and diffusion barriers depend critically on the electron density in front of the surface.[1] A particular class of surface states is created by the Coulombic tail of the image potential, which gives rise to a Rydberg-like series of states. The binding energies of these image states range from 3.7 meV at the surface of liquid helium to 0.85 eV at metal surfaces and converge with $\sim 1/n^2$ towards the vacuum level ($n=1,2\ldots$ being the quantum number of the Rydberg series).[2] Compared with electronic excitations in the bulk, image states are expected to have long lifetimes, because their wave function is located in front of the surface. In the past, image states on single-crystal metal surfaces have been extensively studied using inverse photoemission[3] and more recently by two-photon photoemission (2PPE).[4] Combined with ultrafast lasers 2PPE provides a powerful technique to *directly* probe the time evolution of nonequilibrium electron distributions in metals[5–7] and semiconductors[8,9] as well as the dynamics of image states on a femtosecond time scale.[7,10]

In this paper we examine the influence of a dielectric adsorbate on the surface electron dynamics directly in the time domain. The interaction between an adsorbate and the surface, i.e., a change of the *chemical* state, causes a perturbation of the surface potential, which frequently leads to a quenching of image states.[4] However, Harris and co-workers have recently observed that image states may persist in the presence of physisorbed rare gases and alkane overlayers.[11] Here we show for the $n=1$ and $n=2$ members of the Rydberg series on Cu(111) that *the image-state lifetime strongly increases in the presence of a monolayer of xenon.* Our study demonstrates that the relaxation dynamics of image states is governed by the penetration of the wave function into the bulk where the population of photoexcited electrons can decay into substrate excitations. The decrease of the substrate work function in the presence of the Xe layer lowers the energetic position of the image state with respect to the bulk band structure. As a consequence, the wave function of the $n=1$ image state decays more rapidly into the crystal and, hence, the lifetime increases due to the reduced overlap with bulk states. This is discussed on the basis of a simple phase

analysis calculation.[12] We also show that dephasing plays a crucial role in the two-photon photoemission process. Based on a density-matrix calculation we propose a new excitation mechanism where ''pure'' dephasing during *off-resonant* excitation from the occupied surface state on Cu(111) induces a transient population in the image state. Subsequent *resonant* photoemission from the image state to the final state continuum gives rise to the image state feature in the 2PPE spectra.

The experiments are performed with a 200-kHz femtosecond Ti:sapphire laser system pumping an optical parametric amplifier (OPA). The visible OPA output (pulse duration 60 fs) is used to probe the image-state dynamics following excitation with the frequency-doubled UV pump pulses, as described previously.[7,13] The Cu(111) sample is mounted in an UHV chamber[13] and can be cooled to 20 K with a helium cryostat. The Xenon monolayer (ML) is prepared by exposure at 55 K up to saturation, which decreases the work function by (0.50 ± 0.05) eV.

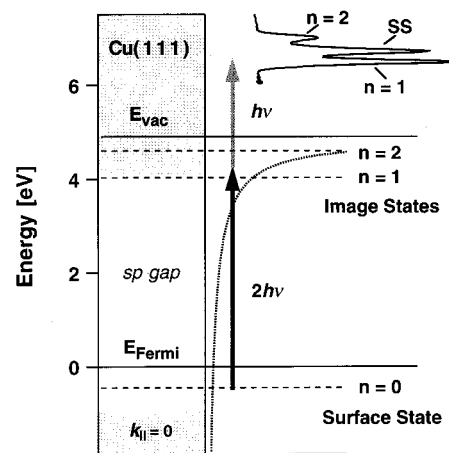Figure 1 displays a schematic diagram of the electronic structure of the Cu(111) surface for zero parallel momentum

FIG. 1. Schematic energy diagram of the Cu(111) surface for ($k_\parallel=0$) and two-photon photoemission (2PPE). The dashed lines indicate the first two image states and the occupied $n=0$ surface state (SS) in the sp-band gap of the bulk projected band structure (shaded). The 2PPE spectrum ($2h\nu=4.77$ eV) shows pronounced peaks due to the image and surface states, respectively.

TABLE I. Binding energies and lifetimes of the $n=1$ and $n=2$ image states for clean Cu(111) and for 1 ML Xe on Cu(111). Experimental data are compared with results of a phase analysis model (Ref. 12).

		Cu(111)		1 ML Xe/Cu(111)	
		$n=1$	$n=2$	$n=1$	$n=2$
Binding	expt.	0.82 ± 0.05	0.25 ± 0.07	0.68 ± 0.05	0.20 ± 0.05
energy (eV)	calc.	0.82	0.21	0.71	0.21
Lifetime (fs)	expt.	18 ± 5	17 ± 5	75 ± 15	40 ± 10
Penetration	calc.	35–40 %		12%	

($k_\parallel = 0$). The $n=0$ surface state is located 0.42 eV below E_F (at 40 K in the sp-band gap along the Γ-L line of the bulk band structure.[14] The first ($n=1$) image state is located slightly below the upper edge of the sp-band gap with a binding energy of 0.82 eV with respect to the vacuum level.[4] The second ($n=2$) image state is in resonance with the bulk continuum. The corresponding 2PPE spectrum ($2h\nu=4.77$ eV) exhibits three peaks originating from the occupied surface state and the first two image states (see Fig. 1). Note that image states are observed in 2PPE, albeit no initial states can be accessed by *resonant* excitation at $k_\parallel=0$. This is explained by an off-resonant excitation scheme from the $n=0$ state as discussed below.

Image states on Cu(111) are found to persist in the presence of a Xe monolayer in agreement with previous work on Ag(111).[11] For 1 ML, Xe on Cu(111) the binding energy of the first image state is reduced by (140 ± 50) meV to $E_{b,\mathrm{Xe}} = (0.68 \pm 0.05)$ eV. This can be attributed to the lowering of the work function by 0.5 eV, which moves the $n=1$ state towards the center of the gap (see Fig. 1). Inside the crystal the wave function changes from s-like to p-like character when going from the top to the bottom of the gap. The matching condition of the wave function at the surface pushes the probability density away from the surface where the image potential is weaker and, hence, the binding energy decreases.[4] For the $n=2$ state no change in binding energy is observed within the experimental accuracy, while the occupied $n=0$ state is shifted by (100 ± 20) meV towards the Fermi level. A simple phase analysis model that combines a multiple-reflection picture with the two-band approximation for the crystal reflectivity is able to reproduce most of the experimental findings.[12] Using the band-structure parameters of Ref. 4 we calculate a binding energy of 0.82 eV for the first image state on clean Cu(111) (work function $\Phi_{\mathrm{Cu}(111)} = 4.90$ eV) and $E_{b,\mathrm{Xe}} = 0.71$ eV on the Xe covered surface (for $\Phi_{\mathrm{Xe/Cu}} = 4.40$ eV) in agreement with our 2PPE data. The results are summarized in Table I.

The image state dynamics was studied by recording the 2PPE signal of the surface state and the ($n=1$) image state as a function of the pump-probe delay. Such cross-correlation curves are shown in Fig. 2 (left panel) for clean and Xe-covered Cu(111). 2PPE from the surface state is a nonresonant two-photon process that allows us to determine the cross correlation and time delay of the UV pump and visible probe pulses.[7] Due to the finite lifetime of the image state the corresponding correlation trace reaches its maximum *after* the signal from the surface state has passed its maximum at $\Delta\tau = 17$ fs with respect to the surface-state re-

sponse. After adsorption of 1 ML Xe the cross correlation trace of the $n=1$ state becomes clearly asymmetric and is shifted by $\Delta\tau = 55$ fs.

For the data analysis we have employed a density-matrix approach to time-resolved 2PPE where two electronic levels (i.e., the $n=0$ and $n=1$ state) are coupled to a continuum of final states where the electron leaves the surface. The formalism based on the Liouville–von Neumann equation allows us to account for energy *and* phase relaxation and is described in detail elsewhere.[15] Our treatment provides a consistent picture of both the spectroscopy and dynamics. In Fig. 2 (right panel, solid line) we compare calculated and experimental 2PPE spectra for Xe/Cu(111) ($2h\nu=4.3$ eV). Interestingly, we find that the feature associated with photoemission from the image state is *only* obtained in our calculation if ''pure'' phase relaxation contributes to the decay of the coherence between the $n=0$ and $n=1$ states. If dephasing is exclusively due to energy relaxation (e.g., given by the image-state lifetime) we obtain only a *single* 2PPE feature
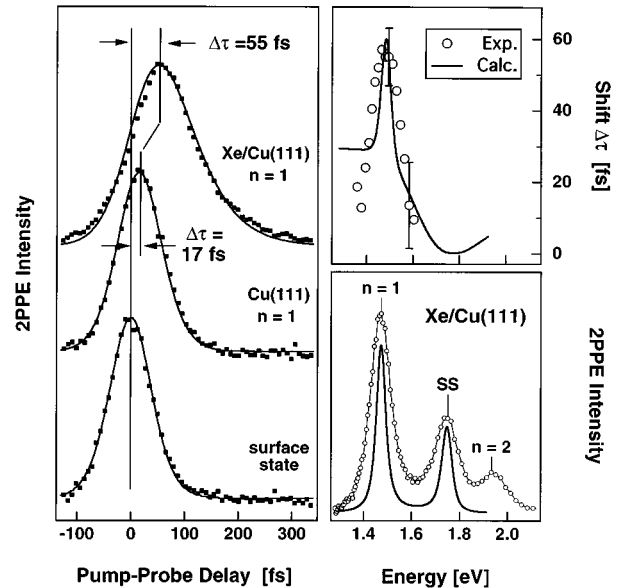

FIG. 2. Left panel: Cross-correlation traces obtained for the surface state (SS) and the $n=1$ image state on clean Cu(111) ($2h\nu=4.2$ eV) and for 1 ML Xe/Cu(111) ($2h\nu=3.8$ eV). The time response of image-state signal is delayed by $\Delta\tau$ with respect to the surface, corresponding to a lifetime of 18 and 75 fs for clean and Xe-covered Cu(111), respectively. Right panels: Results of a density matrix calculation of 2PPE spectra (bottom) and the shift $\Delta\tau$ (top) for 1 ML Xe/Cu(111) are in nice agreement with experimental curves (circles) which are broadened by spectrometer resolution.
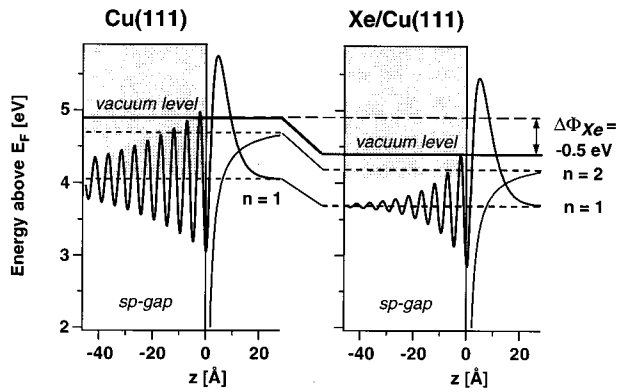
FIG. 3. Energy diagram and calculated wave function of the first image state based the phase analysis model for a work function of $\Phi_{Cu(111)}=4.9$ eV on Cu(111) and $\Phi_{Xe/Cu(111)}=4.4$ eV for 1 ML Xe/Cu(111). Within the projected band gap the imaginary part of the electron wave vector increases towards the center of the gap, leading to a stronger damping and hence a smaller penetration of the image-state wave function.

originating from a two-photon transition from the $n=0$ state. For off-resonant excitation from the $n=0$ to the $n=1$ state the coherent coupling with the radiation field induces recombinative contributions at times when the exciting laser pulse has passed its maximum strength.[7] However, if rapid phase relaxation occurs *during* excitation, the phase-breaking scattering events destroy the coherence and generate an (incoherent) population of the image state.[16] Subsequent excitation of this population by the probe pulse give rise to the image-state feature in 2PPE. This explains very well the appearance of the image state in 2PPE spectra from Cu(111) [and also Ag(111)] at photon energies were no resonant transitions at $k_\parallel=0$ are accessible.[15]

In addition, the results in Fig. 2 reveal a striking dependence of the time response of the 2PPE signal on the final state energy (right panel, top). The calculated temporal shift $\Delta\tau$ (peak of the cross-correlation signal) passes a maximum at a final-state energy corresponding to the image state and approaches zero when the 2PPE signal originates from the surface state. This is in excellent agreement with experimental data obtained by recording 2PPE spectra at various delays (Fig. 2). Because the experiments always sample a finite energy interval a weighted average of the various contributions to the cross-correlation signal has to be included in the analysis. This procedure reveals a lifetime of 18 ± 5 fs for the first image state on the clean Cu(111) surface[17] and 75 ± 15 fs for 1 ML of Xe adsorbed on Cu(111). We have also studied the relaxation dynamics of the second image state, which is energetically located outside the sp gap and is strongly coupled to degenerate bulk states. On bare Cu(111) we measure a lifetime of (17 ± 5) fs for the $n=2$ state, which increases to (40 ± 10) fs on the Xe-covered surface (see Table I).

In the following we discuss the adsorbate-induced changes of the image-state dynamics based on a phase analysis model as described by Smith.[12] Figure 3 shows energy diagrams for clean and Xe-covered Cu(111) together with calculated wave functions of the $n=1$ image state. In the calculation the wave function is matched at the surface with

the solution of Schrödinger's equation for the image potential on the vacuum side. Our phase analysis calculation using the band-structure parameters of Ref 4 and $\Phi_{Cu(111)}=4.90$ eV places the $n=1$ state 4.08 eV above E_F, i.e., ~20 meV *below* the top of the band gap (4.1 eV). This is consistent with our observation that resonant excitation from the surface state (at 90 K) into the first image state occurs at a photon energy of $2h\nu=4.49$ eV. The small imaginary part of the complex wave vector near the top of the gap implies a large penetration of the image-state wave function into the bulk and hence a strong coupling to the continuum of substrate excitations. For the $n=1$ state of Cu(111) we evaluate a probability of 35–40 % for the electron being inside the crystal. Echenique and co-workers have calculated intrinsic linewidths of image states for (111) faces of noble metals and found a nearly linear relationship between the linewidth, Γ, and the penetration of the wave function into the crystal.[2,18] According to de Andres *et al.* a penetration of 35–40 % corresponding to a lifetime $\hbar/\Gamma$ of 8–10 fs.[18] The lowering of the work function induced by Xe adsorption moves the $n=1$ state towards the center of the gap where the wave function becomes more strongly damped. Allowing the vacuum level to drop by 0.50–4.40 eV above E_F and keeping all other parameters fixed, we calculate a penetration of 12% for the $n=1$ state. This corresponds to a lifetime of 30 fs according to Ref. 18. Thus, our phase analysis calculation clearly predicts an increase of the $n=1$ image-state lifetime upon adsorption of 1 ML Xe in agreement with the experimental trend (see Table I). In general, we expect that adsorption of different rare gases will allow us to alter the image-state lifetime via the induced change of the work function. We note, however, that the different lifetimes of the $n=2$ state on the clean and Xe-covered Cu(111) surface *cannot* be accounted for by a difference of penetration depths because this state is in both cases degenerate with bulk states.

We conclude by saying that image-state lifetimes are predominantly influenced by their wave-function overlap with bulk states. However, apart from the reduced penetration depth induced by a work-function change *additional* contributions may also lead to a decoupling of the image states from the substrate. First, the polarization of the Xe layer results in an outward shift of the image plane, which also moves the probability density of the electron away from the metal substrate. In addition, replacing the topmost layer of copper atoms by the xenon overlayer will decrease the relaxation rate within that layer. In fact, the electronic structure of solid Xe is characterized by a wide band gap ranging from 9.8 to 0.5 eV below the vacuum level,[19] suggesting that the available phase space for inelastic electron scattering is strongly reduced within the layer. Recently, Rous has shown that cross sections for resonant electron scattering are strongly enhanced when adsorbate resonance levels and image states interact.[20] We speculate that the interaction between the Xe 6s level and the image states might also effect image-state lifetimes. Finally, we discount that tunneling plays an important role, because the positive electron affinity of solid xenon ($E_a=+0.5$ eV, Ref. 19) argues against the existence of a tunneling barrier that might slow the relaxation rate. Such a tunneling scenario has been

proposed by Harris and co-workers for alkanes adsorbed on Ag(111) with reference to the repulsive affinity ($E_a < 0$) in that system.[21]

In summary, using time-resolved 2PPE we have demonstrated that the lifetime of photoexcited electrons in image potential states may be substantially longer in the presence of a rare-gas overlayer like xenon. For image states lying within a projected band gap this can readily be attributed to the reduced overlap of the image-state wave function with the substrate.

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