Momentum-resolved dynamics of Ar/Cu(1 0 0) interface states probed by time-resolved two-photon photoemission

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Abstract. The electron dynamics of buried Ar/Cu(1 0 0) image-potential states was investigated by time-resolved two-photon photoemission (2PPE) as a function of parallel momentum. The first interface state shows a parabolic dispersion with an effective mass of 0.6. Its lifetime of 110 fs at the $\bar{\Gamma}$-point decreases with increasing parallel momentum. The momentum dependence of the decay can be understood by intra- and inter-band decay processes mediated by Cu electrons, just as the decay of image-potential states on the clean Cu(1 0 0) surface.

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1. Introduction

Time-resolved two-photon photoemission (2PPE) is an ideal experimental tool for the investigation of electron dynamics at solid surfaces. It allows one to monitor the temporal evolution of energy, parallel momentum and, by exploiting coherence phenomena, the phase relationship of excited electrons \[1\]–\[3\]. In the last decade, several groups have used this technique to study the dynamics of image-potential states at clean and adsorbate-covered metal surfaces \[4\]–\[19\]. These hydrogen-like states have simple and well-defined physical properties \[20\]–\[22\] which have made realistic many-body calculations of the electronic decay possible \[23\]–\[26\]. The close collaboration between experiment and theory has led to enormous progress in our understanding of the fundamental physics of electronic decay processes at clean metal surfaces \[27\].

Recently, we have shown for the system Ar/Cu(1 0 0) that similar electronic states exist at the boundary between a metal and an insulator \[28\]. In bulk Ar, the lowest energy of an excess electron would be the conduction band minimum located 0.25 eV above the vacuum level. Close to the metal interface, such an excited electron is attracted towards the metal by image forces while the projected band gap of the Cu(1 0 0) crystal hinders it from penetrating into the metal (figure 1). Analogous to the case of image-potential states on clean surfaces \[20\], this gives rise to an infinite series of electronic states located at the Ar/Cu interface with energies

\[
E_{n'} = E_{\text{CBM}} - \frac{0.85 \, \text{eV}}{(n' + a)^2} \times \frac{m_{\text{eff}}}{\epsilon^2}, \quad n' = 1, 2, \ldots ,
\]

where \(n'\) denotes the quantum number and \(a\) the quantum defect \((0 \leq a \leq 0.5 \ [22, 29])\).

Compared to the usual series of image-potential states that converge towards the vacuum level \(E_{\text{vac}} = 0\), the reference level for the Ar/Cu interface states is the Ar affinity level or the conduction band minimum \(E_{\text{CBM}} \approx 0.25 \, \text{eV}\). The binding energy of the interface states with respect to \(E_{\text{CBM}}\) is lowered by a factor \(m_{\text{eff}}/\epsilon^2\) because the image potential is screened by the Ar overlayer with its dielectric constant \(\epsilon\) and because the potential is periodically modulated by the Ar atoms which leads to an effective electron mass \(m_{\text{eff}} \cdot m_0\), where \(m_0\) is the mass of the free electron. In \[28\], we have shown that interface states can be studied with time-resolved 2PPE even if they are buried under Ar layers as thick as 100 Å. After a pump pulse has populated the interface states \(n' = 1, 2\) with an electron from the metal, the probe pulse promotes the electrons into the Ar conduction band (figure 1, top right) from where it escapes to the vacuum by ballistic transport through the layer.

The dynamics of electrons located at buried solid–solid interfaces is not only of vast technological significance but also of great fundamental importance. Interesting issues are, e.g., the elastic or quasi-elastic transfer of electrons across the boundary of two materials with different geometric and electronic structure or the dynamical many-body response of interface electrons leading to inelastic decay. Buried image-potential states such as those in Ar/Cu provide a simple model to address these problems. As we have shown by experiments using Ar films of varying thickness, the lifetimes of electrons excited into the Ar/Cu interface states are limited by two distinct decay channels \[28\]: inelastic decay by electron–hole-pair (e–h) excitation in the metal and by elastic tunnelling through the Ar layer. This second channel is a consequence of the negative electron affinity of Ar which results in \(E_{n'} > 0\), i.e. in the language of atomic physics the states are autoionizing resonances.

In this paper, we investigate the momentum dependence of the states and compare it with the clean surface. We show that the Ar/Cu states disperse less than the image-potential states on...
clean Cu due to the lateral corrugation of the Ar layers. The lifetime of the interface states due to e–h decay decreases with increasing parallel momentum but the dependence is smaller than the one found on clean Cu(1 0 0).

2. Experiment

In our 2PPE experiment, we used the third harmonic of a Ti : sapphire oscillator for the excitation of the normally unoccupied interface states. The photon energy was set to $\hbar \omega_a = 4.71$ eV which is 0.34 eV higher than the workfunction of Ar/Cu(1 0 0). The fundamental pulses ($\hbar \omega_b = 1.57$ eV) served as the time-delayed probe pulses. The cross-correlation between pump and probe pulses had a full-width at half-maximum of 85 fs. Details of sample treatment and layer preparation have been published elsewhere [18, 28]. The sample was kept in an ultra-high vacuum chamber with a base pressure at room temperature of $6 \times 10^{-11}$ mbar and was cooled to 18 K by means of a liquid helium cryostat.

Most of the experiments were performed using a new hemispherical analyser (Specs Phoibos 150) equipped with a two-dimensional (2D) charge-coupled-device (CCD) detector and an angle-resolved lens mode. It allowed for single-shot $E(k_{\parallel})$ measurements. Typically, a pass energy of
Figure 2. (a) \( E(k_\parallel) \) 2PPE spectrum for the clean Cu(1 0 0) surface recorded with a pump–probe delay of 67 fs using an exposure time of 8 s. Bright areas indicate a high 2PPE intensity. Energy zero denotes the vacuum level. (b) 2PPE energy spectrum for \( k_\parallel = 0 \) obtained from a cut through the 2D spectrum with a width of about 0.013 Å\(^{-1}\). 10 eV was chosen. A kinetic energy range of 1.3 eV was visible along the energy-dispersive axis of the spectrometer under these conditions and gas-phase UPS measurements of the Ar 3p\(_{3/2}\) level showed that the energy resolution (FWHM) was 14 meV at \( E_{\text{kin}} = 1 \) eV. The low-energy cutoff of the 2PPE spectra had a width of 29 meV or less. The full acceptance angle of the electron lens was \( \theta = \pm 16^\circ \). For a kinetic energy of \( E_{\text{kin}} = 1.5 \) eV, this corresponds to parallel momenta in the range of \( \pm 0.14 \) Å\(^{-1}\) \((k_\parallel = \hbar^{-1}(2m_0E_{\text{kin}})^{1/2}\sin \theta = 0.5123 \) Å\(^{-1}\) \(\sqrt{E_{\text{kin}}(\text{eV})}\sin \theta\). The angular resolution was characterized by placing a regular slit array in front of the electron lens which yielded 0.3° (FWHM).

Figure 2 displays 2PPE-data for clean Cu(1 0 0) acquired within 8 s without a sample bias voltage. The lowest three image-potential states are clearly visible. The picture shows a cut-out of the raw data with a size of 500 x 460 pixel. The calibration of the energy scale was determined to 1.56 meV/pixel with a linearity of \( \pm 1 \) pixel. All energies are given with respect to the vacuum level. The linearity of the detected intensity has been checked by varying the UV-laser power by a factor of 35 up to the saturation of the CCD-camera which has a dynamic range of about 4000. No change in the linewidth of the states has been observed. The parallel momentum scale has been calibrated by measuring the dispersion \( E(k_\parallel) \) of the \( n = 1 \) and \( n = 2 \) state in the conventional way by rotating the sample. The result is a simple linear dependence between the value of \( k_\parallel \) and the horizontal position on the screen. Furthermore, the parallel momentum is approximately independent of energy due to a slight energy dependence of the
Figure 3. (a) $E(k_{||})$ 2PPE spectrum for 25 ML Ar/Cu(1 0 0) using an exposure time of 100 s. The blue dots along the dispersion parabola of the $n' = 1$ interface state mark the points used for evaluation of the time-resolved pump–probe traces. The faint parabola of the $n' = 2$ state is also visible. (b) 2PPE energy spectrum for $k_{||} = 0$ obtained from a cut through the 2D spectrum with a width of about 0.018 Å$^{-1}$.

detected emission angle which nearly cancels out the dependence of the parallel momentum on the kinetic energy. The energy spectrum in figure 2(b) is obtained at $k_{||} = 0$ by averaging over a width of 20 pixels which corresponds to $\Delta k_{||} = 0.013$ Å$^{-1}$. The signal-to-noise ratio of this data is about 100 corresponding to a minimum count rate of 10 000 in a single electron detection experiment.

Figure 3 shows the corresponding 2D spectrum of the Ar/Cu(1 0 0) interface states. These data were recorded with a negative bias voltage of $-6.4$ V applied to the sample. This ensured that the complete dispersion parabola up to the conduction band minimum of the Ar layer was visible within the detection window of the analyser. We have used the same pass energy of the analyser which leaves the energy calibration unchanged compared to figure 2. The momentum scale was calibrated by comparison with angle-resolved spectra at zero sample bias that were obtained in the conventional way by rotating the sample (compare figure 5). This procedure of applying a bias and calibrating the momentum-axis has the advantage of giving us access to the full $E(k_{||})$-dependent dynamics by just recording 2D-images as those as shown in figures 2 and 3 as a function of pump–probe delay.

For the time-resolved experiments on the clean surface, a complete 2D spectrum was recorded within 2 s in steps of 6.7 fs pump–probe delay as illustrated in the video sequence clean2d. The upper figure in the video sequence shows the 2D data using a logarithmic intensity scale. The coloured rectangles mark the areas whose integral intensities are plotted in the lower figure as a function of the pump–probe delay. The areas are centred at the energies of the $n = 1, 2$ and 3 image-potential states at the $\bar{\Gamma}$-point illustrating the increasing lifetime with quantum number $n$. The time-resolved measurement of the Ar/Cu states is illustrated in the
Figure 4. Lifetime of the $n' = 1$ interface state of Ar/Cu(100) measured in normal emission as a function of the thickness of the adsorbed Ar layer. Insets: computed probability density of state for thin (a) and thick (b) layers (the adlayer region is marked by shades, $z$ is the distance from the metal [28]).

3. Results

3.1. Layer-resolved lifetimes

The interface states in Ar/Cu(1 0 0) lie energetically above the vacuum level (see figure 1) because their binding energy with respect to the conduction band minimum is small. For this reason, the states are principally able to decay by resonant charge transfer into the vacuum. For thick layers, however, the Ar band gap represents a sufficient tunnelling barrier in order to suppress this decay channel with respect to inelastic e–h decay [28].

In the case of the $n' = 1$ state, elastic tunnelling can compete with the e–h decay only for a layer thickness up to 15 ML (45 Å). For thinner layers, the spatial spread of the state normal to the interface becomes comparable to the thickness of the layer. Consequently, the wavefunctions leak out across the Ar/vacuum boundary and the resonance lifetime becomes small (figure 4(a)). The measured lifetimes displayed in figure 4 show a steep initial rise at low Ar coverage and saturation between 100 and 110 fs above a coverage of 15 ML.

video sequence if2d. Here, the acquisition time for one spectrum was 7 s. The two integral regions are centred at the $\bar{\Gamma}$-point and at a $k_\parallel = 0.18 \, \text{Å}$. At large delays, a feature appears at an energy of about $-0.1 \, \text{eV}$ and $k_\parallel = 0$. We attribute this to a UV radiation-induced defect in the Ar film which does not have any influence on the time-resolved data of the interface state.
For the present experiments, we chose an Ar coverage of 25 ML corresponding to a layer thickness of 75 Å. At this coverage, the \( n' = 1 \) interface state is completely confined to the Ar layers (figure 4(b)). The 2PPE spectra reveal a well-resolved peak which arises from this state. In addition, the \( n' = 2 \) state becomes already visible at the spectra taken for this coverage.

### 3.2. Band dispersion

The electronic bands of the interface states were mapped parallel to the surface by rotating the sample, while only electrons that left the sample along the direction of the electron lens were recorded by the analyser. The binding energy of the \( n' = 1 \) state with respect to the Ar conduction band minimum is 0.17 eV and thus sufficiently large to follow the dispersion of this state over a reasonable range of emission angles \( \theta \). The angle-resolved 2PPE spectra of figure 5 reveal a parabolic dispersion of this state which can be described by

\[
E(k_\parallel) = E_0 + \frac{\hbar^2 k_\parallel^2}{2m_{\text{eff}}}m_0,
\]

where \( E_0 \) is the energy at the band bottom and \( m_{\text{eff}} \) is the effective mass. By using

\[
E(k_\parallel) = E_{\text{kin}}(k_\parallel) - \hbar \omega_b,
\]

we find that the effective mass of the \( n' = 1 \) interface state is \( m_{\text{eff}} = 0.61 \pm 0.1 \) (inset). For comparison, we measured the effective mass of the \( n = 1 \) image-potential state of clean Cu(100) in a similar way and deduced 0.98 ± 0.1. The latter value is in good agreement with earlier measurements [30]. Since image-potential states on clean Cu(100) are mainly located in the vacuum region in front of the surface, they disperse with the free-electron mass.

The smaller effective mass of the \( n' = 1 \) interface state can be readily understood if one considers that these states are derived from the conduction band minimum of bulk Ar. There, an effective mass of 0.53 ± 0.01 has been measured using low-energy electron-transmission
Figure 6. Time-resolved 2PPE data of the $n' = 1$ Ar/Cu(1 0 0) interface state for three different values of parallel momentum compared to data of the $n = 1$ image-potential state on clean Cu(1 0 0) and the pump–probe cross-correlation (dashed line). The solid lines indicate numerical fits using rate equations. Positive delay times correspond to IR probe pulses arriving at the sample after the UV pump pulse.

spectroscopy [31]. This value is very close to our result. The small difference may arise from the energetic position of the $n' = 1$ state inside the band gap of Ar, 170 meV below the conduction band minimum. Our result agrees also with recent theoretical work on resonance states in very thin Ar films [32] which gave an effective mass of 0.6. The small effective mass inside the Ar film is a consequence of the strong corrugation of the atomic potential by the screened ion cores.

3.3. Momentum-resolved dynamics

Figure 6 displays a selection of time-resolved 2PPE data for different values of $k_{\parallel}$. The curves were retrieved from a complete series of 2D $E(k_{\parallel})$ spectra such as the one displayed in figure 3 that were recorded in 6.7 fs time steps of the pump–probe delay. The full data set is illustrated in the video sequence if2d. The data points for a given $E(k_{\parallel})$ along the dispersion curve were obtained by averaging over a 31 meV×0.018Å$^{-1}$ rectangular area, equivalent to $20 \times 20$ pixels of the CCD array. Variation of the area for averaging from $20 \times 10$ to $20 \times 30$ pixels had only a negligible influence on the results.

The time-resolved 2PPE signal from the Ar/Cu states is characterized by a steep rise and a slow exponential decay so that the lifetimes can be extracted by using simple rate-equations. As a reference we use the lifetime of the first image-potential on the clean surface which is $\tau = 40$ fs for $k_{\parallel} = 0$ [6, 19]. The lifetime of the $n' = 1$ interface state is significantly longer. It decreases
Figure 7. Decay rates of the first image-potential state (magenta) and the first Ar interface state (cyan) on Cu(100) as a function of the kinetic energy of parallel motion. The solid magenta line indicates the theoretical values for the clean surface from [17]. The dashed cyan and the dotted magenta lines represent the same curve but scaled by factors of 4.7 and 2.75, respectively (see text).

monotonically with increasing parallel momentum. We find $\tau = 110 \pm 5$ fs at the band bottom ($k_\parallel = 0$) and $\tau = 84 \pm 5$ fs at $E - E_0 = 171$ meV, i.e. at $k_\parallel = 0.18$ Å$^{-1}$.

In figure 7 the deduced decay rates $\Gamma = \hbar/\tau$ ($\hbar = 658$ meV fs) are displayed as a function of the energy above the band bottom, i.e. as a function of the kinetic energy of parallel motion $E_\parallel = \hbar^2 k_\parallel^2/2m_{\text{eff}}m_0$. The smaller decay rate of the Ar/Cu interface state goes along with a weaker $k_\parallel$-dependence as compared to the image-potential state on the clean surface. The present results obtained for clean Cu(100) agree with those published earlier [17].

4. Discussion

The physical properties of the interface states of Ar/Cu(100) are very similar to those of the image-potential states of clean Cu(100). Electrons in both states are subject to the same decay processes which occur via inelastic scattering with the electrons of the metal [27]. In comparison to the image-potential states of the clean surface, the interface states are modified by dielectric screening and by the atomic corrugation inside the layer. Both the screening and the smaller effective mass lead to a larger spatial spread of the states in the direction of the surface normal as compared to ordinary image-potential states located in vacuum. Since the $z$-dependence of the wavefunctions is basically that of hydrogen 1s-wavefunctions, it is straightforward to see that the characteristic length scale of the interface states is

$$a'_n = a_n \times \frac{\epsilon^2}{m_{\text{eff}}} = \frac{4\hbar^2}{(n^2 + a)^2m_0e^2} \times \frac{\epsilon^2}{m_{\text{eff}}}. \quad (2)$$
The larger spatial extent of the wavefunctions results in a reduced coupling of the interface states with the metal and should consequently lead to longer lifetimes as compared to the image-potential states of clean Cu(1 0 0). Since the decay rate depends on the probability density of the wavefunction in the interface region, we expect the decay rate to scale like

$$\Gamma_{n'} = \Gamma_n \times \frac{m_{\text{eff}}}{\epsilon^2},$$

(3)

where we assume that the interface states may be described by the same quantum defect $a$ as the states on the clean surface and that both states are located at a similar energy in the projected bandgap of Cu(1 0 0). This assumption appears justified because the lowering of the workfunction of Cu(1 0 0) in the presence of Ar ($\Delta \Phi = 0.25$ eV) partly compensates the upshift in energy of the first state. The resulting energy shift 0.43 eV relative to the bulk bands of Cu is small compared to the width of the sp-gap of 6.1 eV [21].

With the measured $m_{\text{eff}} = 0.61$ and the literature value for the dielectric constant of Ar $\epsilon = 1.7$ [33], equation (3) would predict the decay rates of the interface states to be smaller by a factor of 4.7. When we scale the calculated decay rate of the $n = 1$ state, which very well fits the data for clean Cu(1 0 0), by this reduction factor, the agreement with experiment is not satisfactory (dotted line in figure 7). Whereas the scaled theory predicts a lifetime of $4.7 \times 40$ fs = 190 fs at the $\bar{\Gamma}$-point, the measured lifetime is only 110 fs.

One might of course argue that the scaling factor of 4.7 has been derived in a very approximate way, as (2) and (3) describe an asymptotic behaviour and are not strictly applicable to states with low quantum numbers. However, we find a very similar reduction of the decay rates by calculating the bulk penetration of the wavefunction using a 1D model potential [28, 34]. For this reason we believe that the deviation between the scaled theory and the experiment deserves further attention. There are three possible factors that could be responsible for the failure of the scaling law (3):

1. The electronic decay processes are very sensitive to the details of the $n' = 1$ wavefunction at the interface. If, e.g., the oscillatory character of the wavefunction in the Ar-layers close to the surface has a strong influence on the decay, neither the simple scaling law (3) nor the 1D model potential can be used to extrapolate lifetimes from the clean surface where this corrugation is not present.

2. The 3D corrugation of the wavefunction of the interface states in Ar is crucial for the quantitative description of the decay. In contrast to clean Cu(0 0 1), where the image-potential states are located mainly in vacuum, it is not clear whether the 3D corrugated Ar potential [32, 35] can be approximated by a 1D model potential even if such an averaged potential yields the correct energies of the states. The corrugation of the potential parallel to the surface will lead to a corresponding modulation of the coupling of the wavefunction. Since the coupling to the metal is determined only by a small fraction of the wavefunction, the averaged real coupling could be very different from the one calculated by an averaged potential.

3. The Ar/Cu interface states are subject to other decay processes such as those involving phonons or defects in the Ar layers which are not included in the theory of the decay on the clean surface.

In connection with appropriate many-body calculations for the decay of the interface states, the measured dependence on parallel momentum can help to resolve which of these factors (1)–(3)
is important. In the absence of such calculations we will comment here only on (3), the presence of other decay channels. On the clean Cu(1 0 0), the $k_\parallel$ dependence is due to the momentum dependence of the inter-band decay to bulk states and due to intra-band relaxation of electrons with finite parallel momenta towards the band minimum. Since both processes are mediated by the interaction of electrons in image-potential states with bulk electrons, both scattering processes will become weaker if the image-states are further decoupled from the metal. For this reason the decay of the $n = 2$ state on clean Cu(1 0 0) exhibits a much weaker $k_\parallel$ dependence than the $n = 1$ state [17].

When we introduce an empirical scaling factor and divide the calculated decay rates for clean Cu(1 0 0) by the experimentally measured ratio of rates for $k_\parallel = 0$, $\Gamma^\prime_{n=1}(\text{Cu}(1 0 0))/\Gamma_{n=1}(\text{Ar/Cu}(1 0 0)) = 110/40 = 2.75$, the calculation for the clean surface fits the $k_\parallel$ dependence for the interface states very well (dashed line in figure 7). In our opinion this good agreement between the theory scaled with this empirical factor and the present experiment indicates that the decay of the Ar/Cu(1 0 0) interface-states are subject to the same electronic decay mechanisms as the image-potential states on clean Cu(1 0 0). A decay process mediated by phonons in the Ar layer, such as those proposed for the decay of image-potential states in the system N2/Xe/Cu(111) [36] would, e.g., lead to a considerably steeper $k_\parallel$ dependence if they contributed significantly to the observed decay. On the other hand, decay processes mediated by defects are expected not to depend much on $k_\parallel$ [19].

5. Conclusions

In summary, we have shown that unoccupied electronic states located at the interface between argon and Cu(1 0 0) can be investigated by 2PPE with good time-, energy- and momentum resolution, despite the fact that the states are buried under relatively thick (75 Å) Ar layers. The states resemble the image-potential states of clean Cu(1 0 0) but are modified due to screening of the image-potential in the dielectric Ar layer and by the corrugation introduced by the Ar atoms. The states exhibit a parabolic dispersion at the $\bar{\Gamma}$-point with an effective mass of 0.6 that is only slightly larger than the effective mass of Ar conduction-band electrons. The lifetime of the interface states is shorter than expected from simple scaling considerations. However, absolute decay rates and momentum dependence differ by the same factor, which indicates that the interface states are subject to the same electronic decay processes at the Ar/Cu interface as the image-potential states on the clean Cu surface. The momentum dependence does not show any sign of phonon or defect-induced decay channels that are unique to the overlayer.

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