Time-Resolved Two-Photon Photoemission of Buried Interface States in Ar/Cu(100)

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We demonstrate the existence of buried image-potential states at the interface between thick Ar films and a Cu(100) substrate. The electron dynamics of these solid-solid interface states, energetically located above the vacuum level in the band gaps of both materials, could be investigated with time-resolved two-photon photoemission for an Ar layer thickness up to 200 Å. Relaxation on time scales between 40 and 200 fs occurs via two distinct channels, resonant tunneling through the insulating layer into the vacuum and electron-hole pair decay in the metal.

During the last decade, the application of time-resolved two-photon photoemission (2PPE) has led to an enormous progress in our understanding of ultrafast electron dynamics at surfaces [1–7]. In particular, the investigation of image-potential states has provided deep insights into the many-body processes responsible for the inelastic decay of electronic excitations at metal surfaces [8]. It has even been possible to perform more accurate experimental tests of the theory of electron-hole (e-h) pair decay than available in bulk metals [9]. For many technological applications, however, the dynamics of electronic states located at solid-solid interfaces, rather than at the solid-vacuum surfaces, is of great importance. Direct spectroscopic information about buried solid-solid interfaces is scarce. In semiconductor technology, the characteristics of electronic devices themselves are frequently used to deduce dynamical properties of interface states [10]. In the emerging field of molecular electronics, much scientific progress has been achieved by performing transport measurements at the single-molecule level [11], whereas the application of 2PPE, which could access individual factors entering present theories of metal-molecule contacts, is still at its very beginning [12].

In this Letter, we show that insulating Ar films grown on a Cu(100) substrate support a series of states at the Ar/Cu interface very alike the image-potential states at clean metal surfaces (Fig. 1). We demonstrate that time-, energy-, and angle-resolved 2PPE experiments are possible despite the fact that these interface states are buried under Ar films as thick as 200 Å. The existence of such buried image-potential states makes it possible to investigate electron transfer and decay processes, which are of general relevance to metal-insulator interfaces, in a simple and well-defined model system. It will be shown that the lifetimes of electrons excited into the Ar/Cu interface states are limited by two distinct decay channels: elastic transfer through the Ar film and inelastic decay by e-h excitation in the metal.

In bulk Ar the lowest energy of an excess electron would be the conduction band minimum $E_{\text{CBM}}$. Close to the metal, however, the electron is attracted by screened image forces. In the limit of thick layers an approximate expression of the resulting potential perpendicular to the interface is simply

$$V_{\text{int}}(z) = V_{\text{Ar}}(z) - \frac{e^2}{4\epsilon z^2}, \quad z > 0. \quad (1)$$

$V_{\text{Ar}}$ is a parametrized corrugated potential that reproduces the correct position of the conduction band minimum $E_{\text{CBM}}$ and the effective electron mass $m_{\text{eff}}$ of bulk Ar [13], and $\epsilon$ is the dielectric constant of Ar. The solution of the Schrödinger equation results in a series of states, denoted by $n' = 1, 2, \ldots$, that are localized at the boundary between the Cu(100) crystal and the Ar layer with energies

$$E_{n'} = E_{\text{CBM}} - \frac{0.85 \text{ eV}}{(n' + a)^2} \times \frac{m_{\text{eff}}}{e^2} \cdot \quad (2)$$

$a$ is the quantum defect resulting from the matching of the wave functions at the interface [14,15].

![Figure 1](https://example.com/fig1.png)

**FIG. 1.** Schematic energy diagram of a 20 ML Ar film on Cu(100) indicating (from left to right) the pseudopotential of $sp$ electrons in Cu, the screened corrugated potential of a single electron in Ar [Eq. (1)], and the vacuum image potential. Filled and empty electronic bands are marked by dark and light shades. $|\Psi_{n=1}^2\rangle$ and $|\Psi_{n=1}^2\rangle$ denote calculated probability densities of the first Cu/Ar interface and the first Ar/vacuum image-potential state, respectively.
A potential of the form of Eq. (1) has been used previously to describe the decoupling of image-potential states from metal surfaces by insulating spacer layers or the occurrence of quantum-well states in thin films with positive electron affinity [13,16,17]. However, it had not been observed that insulators with negative electron affinity, such as Ar, give rise to a second series of states at the metal-insulator boundary in addition to the image-potential states at the insulator-vacuum boundary (Fig. 1, right). As will be shown below, the energies of the Ar/Cu interface states are higher than the vacuum energy. Most likely, this fact has prevented an earlier experimental detection of these states because one usually avoids pump photon energies larger than the work function in 2PPE experiments [1].

The setup of the present experiment was similar to that of our previous studies of Ar monolayers [13] except that the third harmonic of the Ti:sapphire oscillator used for excitation of unoccupied states was set to a photon energy of $\hbar \omega_a = 4.71$ eV, which is 0.34 eV higher than the work function of Ar/Cu(100). The fundamental pulses ($\hbar \omega_b = 1.57$ eV) served as probe pulses. The cross correlation between pump and probe pulses had a full width at half maximum of 85 fs. The experiments were carried out in ultrahigh vacuum at 18 K sample temperature. Ar films of varying thicknesses were prepared by metered dosing at 23 K on top of an annealed and highly ordered monolayer [13]. The layer thickness was calibrated using temperature-programmed desorption.

Energy-resolved 2PPE spectra for different Ar coverages recorded in normal emission are plotted in Fig. 2. For clean Cu(100) and for a coverage of 1 ML (monolayer) only image-potential states $n = 1, 2, \ldots$ were observed. When the layer thickness is increased, the energies of these states shift upwards and their intensity gets weaker, as shown previously [13]. Starting at a coverage of 2 ML, a new broad feature appears at the high-energy side of the spectrum. With increasing coverage it grows in intensity and shifts down in energy. At 10 ML a smaller second peak emerges above the first one. We identify these peaks with the interface states $n' = 1, 2$. Their energies saturate in the limit of thick layers at $0.076 \pm 0.005$ eV and $0.199 \pm 0.015$ eV, i.e., 0.17 and 0.05 eV below the conduction band minimum of Ar ($E_{\text{CBM}} = 0.25$ eV [18]). From angle-dependent 2PPE measurements [19], we determine an effective mass of $0.6 \pm 0.1$ for the converged $n' = 1$ state in 25 ML Ar.

Using $m_{\text{eff}} = 0.6$ and the quantum defect $a = 0.15$ from Ref. [7], we find that the measured energies of the $n' = 1, 2$ states are given by Eq. (2) with $\epsilon = 1.5$. This value is only slightly smaller than the dielectric constant of bulk Ar ($\epsilon_{\text{bulk}} = 1.7$) [20]. Since also the measured $m_{\text{eff}} = 0.6$ lies very close to the effective mass at the CBM of bulk Ar, $m_{\text{eff}} = 0.53 \pm 0.01$ [18], and agrees with recent theoretical results for resonance states in very thin Ar films [22], we conclude that the observed interface states are indeed derived from the conduction band of Ar and that their basic physical properties are given by Eqs. (1) and (2).

To our knowledge the 2PPE spectra presented above are the first from electronic states buried deeply under an insulating layer and we would like to comment on the feasibility of such 2PPE measurements. In a usual surface 2PPE experiment the probe photon lifts the electrons from the intermediate state, e.g., an image-potential state, directly into unbound vacuum states (Fig. 2, bottom right). In case of the interface states $n' = 1, 2$, the probe pulse promotes the electrons into the Ar conduction band (Fig. 2, top right) from where it escapes to the vacuum by ballistic transport through the layer. Our spectroscopic results indicate that this transport occurs without appreciable loss of energy or momentum for layer thicknesses up to roughly 100 Å. We observe sharp peaks and an almost constant maximum count rate of 5000/s. For thicker Ar layers, however, the count rate decreases and peak broadening is noticeable (spectra for 40 and 70 ML in Fig. 2). The use of a pump photon energy well above the work function of Ar/Cu(100) did not pose a serious limitation in the present measurements because the one-photon background was efficiently blocked by the insulating layer.

Whereas the usual image-potential states have energies slightly below the vacuum level, the Ar/Cu interface states lie above it. These states are therefore unstable with respect to electron transfer to the vacuum. The states thus offer the possibility to perform time-resolved experiments of electron transfer through an insulator. Apart from this elastic
FIG. 3. 2PPE signal at the peak maxima of the $n' = 1, 2$ states recorded as a function of pump-probe delay for different Ar film thicknesses. Lifetimes were obtained from fits using rate equations. The dotted lines indicate the cross correlation between pump and probe pulses.

channel, the states decay inelastically by the creation of electron-hole pairs in the metal, similar to the image-potential states of clean surfaces. In the following, we analyze each of these decay processes.

Figure 3 displays time-resolved 2PPE data for various thicknesses of the Ar film. The lifetimes of the excited $n' = 1$ and $n' = 2$ states deduced from these and other data are plotted in the main panel of Fig. 4(a) as a function of layer thickness. The lifetime of the $n' = 1$ state increases strongly with increasing Ar coverage and reaches a saturation value of 105 ± 10 fs near 15 ML. The lifetime of the $n' = 2$ state is shorter for thin Ar films than that of the $n' = 1$ state but reaches a higher saturation value of 180 ± 20 fs near 30 ML. The large scatter in the $n' = 2$ lifetime above 30 ML probably originates from the contribution of energetically close-lying and long-living higher states $n' \geq 3$, which are experimentally difficult to separate.

Since thick layers effectively suppress the elastic decay by electron transmission, we identify the saturation values of the measured lifetimes $\tau_{\text{sat}}$ with the inelastic decay channel due to $e$-$h$ excitation. This relaxation mechanism is virtually independent of coverage, only confinement to extremely thin films may enhance the coupling of the wave functions to the metal. We can therefore obtain the thickness-dependent rates of elastic transfer $\Gamma_{\text{tr}}$ by subtracting the nearly constant contribution of inelastic decay $\Gamma_{e-h} = \hbar/\tau_{\text{sat}}$ from the measured total decay rate $\hbar/\tau$ [inset of Fig. 4(a)]. The resulting transfer rates $\Gamma_{\text{tr}}$ of both states decrease exponentially with layer thickness, the transfer through all films being faster for $n' = 2$ than for $n' = 1$. This dependence on layer thickness and electron energy is characteristic for tunneling through the band gap of Ar.

In a simplified but illustrating approximation the transfer rates may be analyzed with the WKB formula for tunneling through a square barrier of height $\Delta E$ and width $w$, $\Gamma_{\text{tr}} = \Gamma_0 \exp[-2w\sqrt{2m\Delta E/\hbar^2}]$. From best fits to the data of Fig. 4(a), using $m = 0.6m_e$, we obtain $\Delta E = 0.092$ eV (0.024 eV) for $n' = 1$ ($n' = 2$). These energies are smaller than the measured energy differences $E_{\text{CBM}} - E_{n'} = 0.17$ eV (0.05 eV) of $n' = 1$ ($n' = 2$). Obviously the screened image potential increases more gradually than the rectangular potential used in the WKB formula. The attempt rates $\Gamma_0 = 0.55$ eV (0.27 eV) lie within the same order of magnitude, as expected from the classical oscillation time of an electron in the image potential [7].

For a more rigorous description of the rates $\Gamma_{\text{tr}}(w)$ we computed the profiles of the resonant states inside the overlayer by numerically solving the Schrödinger equation for the potential Eq. (1) while the energy was scanned in fine adaptive steps [23]. A resonance was identified as a

FIG. 4. (a) Summary of the experimental lifetimes (symbols) as a function of Ar layer thickness (1 ML = 3.04 Å). Simulated curves were calculated as $\tau = (\Gamma_{\text{tr}}/\hbar + 1/\tau_{\text{sat}})^{-1}$ from the theoretical rates of elastic transfer $\Gamma_{\text{tr}}$ and the experimental high-coverage lifetimes $\tau_{\text{sat}}$. Inset: elastic rates $\Gamma_{\text{tr}}$. (b) Computed probability densities of the $n' = 1$ state for different Ar coverages.
maximum of probability density inside the layer, and the resulting spectra were fitted by Beutler-Fano profiles. The resonance energies obtained in this way were found to reproduce the experimental peak positions of Fig. 2 very accurately. The widths of the resonances, which are equivalent to the transfer rates, are indicated by lines in the inset of Fig. 4(a). The calculated values differ only by a factor of 2 from the experimental ones. Considering the approximation of the truly three-dimensional corrugation of the Ar potential by a one-dimensional model, this agreement is satisfactory and confirms our interpretation of this decay channel.

For illustration purposes we compare in Fig. 4(b) probability densities calculated at the resonance positions of $n' = 1$ for different layer thicknesses. For thin films there is a considerable probability density in the vacuum region outside the layer. This leakage of the wave function is the origin of the elastic decay by electron transfer across the insulating Ar layer. It gets smaller when the adsorbate film grows and virtually vanishes for a thickness of 15 ML and higher. The probability densities of Fig. 4(b) also show a small amplitude at $z < 0$ inside the metal. This penetration of the wave functions reflects the coupling to the substrate and is therefore a measure of the rate of inelastic decay by the creation of $e$-$h$ pairs at the metal surface.

Today, many-body theory can very accurately predict inelastic lifetimes of image-potential states on clean noble-metal surfaces [8,9]. In the case of Cu(100) one can divide the different contributions into a pure bulk contribution, a near-surface contribution, and a cross term, all of which scale approximately with the amplitude of the wave function at the metal surface [9]. Dielectric screening in the Ar layer and the small effective mass of the interface states lead to a larger spread of the wave functions of the Ar/Cu interface states as compared to the image-potential states on clean Cu. One thus expects the interface states to interact less with the metal and to have the longer lifetimes. In fact, with $\tau_{n' = 1} = 105$ fs the experimental lifetime of the first interface state is larger than that of the first image-potential state $\tau_{n = 1} = 40$ fs [7,8]. However, the computed penetration values $p_{n' - 1} = 0.82$ and $p_{n - 1} = 3.9$ differ by almost a factor of 5, while the ratio of the lifetimes is only 2.6. At this point we can only speculate why the interface states decay faster than expected from penetration arguments. Enhanced screening of the Coulomb interaction inside the Ar layer should reduce rather than enhance the decay rate. Possibly the strong oscillatory character of the interface states in Ar enhances the near-surface contributions to the decay as compared to the smoother image-potential states. However, only a full many-body calculation can probably resolve this issue.

In summary, we have shown the existence of electronic states located at a metal-insulator interface that resemble image-potential states and have demonstrated the possibility to investigate such buried interface states with time-resolved 2PPE. The interface states in Ar/Cu(100) are located below the Ar conduction band and form metastable resonances above the vacuum level. They decay inelastically into the metal, and for layer thicknesses below 60 Å also by elastic transfer into the vacuum. Similar experiments should be possible at other interfaces between metals or semiconductors and dielectric materials.

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[20] Ar physisorption leads to the presence of static surface dipoles and an enhanced electric field at the Ar/metal interface [21], which is not included in Eq. (1). Probably, this is the main reason for the reduced value of $\epsilon$.
[23] For these calculations the image potential $-e^2/4\epsilon z$ in Eq. (1) was extended by small corrective terms that account for the finite layer thickness [13,16,17].