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Image-potential state lifetimes in Ar/Cu(1 0 0)

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Abstract

Time-resolved two-photon photoemission experiments performed on the Cu(1 0 0) surface with one or several layers of argon reveal image state lifetimes unusually long compared with those obtained for the clean surface. The interaction of the image state electron with the metal surface is thus dramatically altered by the adsorbed layers, which induce a decrease in the overlap between the image state wave function and the bulk states. We report a calculation of the $n = 1$, 2 image-potential state lifetimes in the Ar/Cu(1 0 0) system, obtained within the GW approximation of many-body theory. Image state wave functions are calculated from a one-dimensional model potential which describes the surface band structure and incorporates the modified interaction in the adlayer region. Results obtained from this model are in fairly good agreement with the experimental data.

Keywords: Many body and quasi-particle theories; Surface electronic phenomena (work function, surface potential, surface states, etc.); Copper; Noble gases; Insulating films; Metal–insulator interfaces

1. Introduction

Experimental and theoretical studies of image-potential states have led to considerable progress in understanding fundamental aspects of the inelastic decay of excited states at surfaces. On clean metal surfaces, with a band gap near the vacuum level, the electron in an image-potential state is mainly located in the vacuum. The penetration of the wavefunction into the bulk and its amplitude at the surface are small [1–5]. This leads to lifetimes of tens of femtoseconds which can be measured accurately in the time domain by means of two-photon photoemission (2PPE) [6–13]. At the same time, realistic many-body calculations of the decay process are feasible because the potential necessary to describe the Rydberg-like series of states is one-dimensional in nature [14–17]. This allows to calculate the lifetimes of inelastic decay with high predictive accuracy.

Recently, it has been shown by several groups that in the presence of adsorbate layers with either

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a negative or a small positive electron affinity, image-potential states are still observable [7,9,18–22]. In the former case, the adlayers act as insulating spacers that decouple the electrons from the metal and prolong the lifetimes [19,22–24]. Rare-gas films on metal surfaces are best suited for this purpose, because they exhibit epitaxial growth, a wide band gap, and a repulsive interaction of an excess electron with the closed valence shell. In particular Ar, with an electron affinity of EA $= -0.25$ eV, is most interesting for the theoretical understanding of the effect of adsorbates on the dynamics of image-potential states. For the system Ar/Cu(1 0 0), Berthold et al. [22] observed, as a function of the film thickness, a continuous decrease of the binding energy and a dramatic increase of the lifetime of the first two image-potential states. The lifetime of $n = 1$ e.g. increases from 40 fs for the clean surface to as much as 10 ps in the presence of five monolayers (ML).

Previous calculations of inelastic lifetimes in the presence of rare-gas layers have been based on two approximations. On the one hand the so-called bulk penetration model was employed which assumes that the decay rate is proportional to the probability density of the electron inside the metal [4]. In some cases, this model gives a satisfying estimate of the change of lifetimes depending on the adsorbed material and layer thickness. However, it does not yield absolute lifetime values but relies on scaling of an empirical bulk decay rate. Even more severely, it ignores most of the many-body effects that have been shown to play a decisive role in the decay processes on clean surfaces [14,17]. While the bulk penetration picture is implicitly based on a local nature of electronic decay, in reality, the imaginary part of the self-energy has a strong non-local character at metal surfaces [15,25]. The other approximation is the dielectric continuum model [23,26,27]. It neglects the influence of the periodic, corrugated potential inside the adsorbate layer and considers it as a homogeneous dielectric slab. Screening is treated by classical electrostatics and an effective mass is introduced by hand. It was shown that this model fairly reproduces the experimental trends [24,28], but quantitative agreement could not be achieved [22]. Only recently, the atomic corrugation of the potential inside the Ar layer was calculated by Marinica et al. [29] based on the mutual polarization of the Ar atoms and their interaction with the metal. With this parameter-free potential the experimentally observed increase of the lifetimes upon Ar adsorption could be reproduced by using the bulk penetration approximation.

In this paper we extend our previous theory of image-potential states on clean Cu(1 0 0) and consider their inelastic decay in the presence of one–four monolayers of argon. The atomic corrugation inside the Ar layer is approximated by a one-dimensional parameterized potential [30] that allows us to make full use of the self-energy formalism of many-body theory within the GW approximation [25]. This permits to examine how the fundamental factors that determine the lifetime, i.e. the coupling between initial and final states, the available decay channels, and the imaginary part of the screened Coulomb interaction, are altered by the presence of a dielectric adlayer. Our calculated lifetimes agree well with the experiment and show an exponential increase depending on the thickness of the adsorbate layer, caused by repulsion of the wavefunction into the vacuum. We also find an accidental cancellation of different terms in the non-local self-energy leading to an approximately local character of inelastic decay in the Ar/Cu(1 0 0) system.

Unless otherwise is stated, atomic units ($\hbar = m = e^2 = 1$) are used throughout this paper.

2. Theory

A general description of our theoretical method can be found in Refs. [14,25]. Here we will focus on the specific expressions used in this work. Within the non-self consistent GW approximation [31,32], and considering translational invariance in the plane parallel to the surface, the inverse lifetime of an electron in an image or surface state is given by:

$$\tau^{-1} = -2 \sum_{E_F \leqslant E_f \leqslant E_0} \int \frac{d^2\mathbf{q}_\parallel}{(2\pi)^2} \int dz \int dz' \phi_0^*(z)\phi_f(z) \times \operatorname{Im} W(z, z'; \mathbf{q}_\parallel, E_0 - E_f)\phi_0(z')\phi_f^*(z') \quad (1)$$

where E_0 and E_f are the energies of the initial image-potential state and final metal state, respectively. The summation in E_f extends over all available states between the initial state and the Fermi level. $\mathrm{Im}W(z,z';\mathbf{q}_{\|},E_0-E_f)$ is the two-dimensional Fourier transform of the imaginary part of the screened Coulomb interaction [25,33]. It is obtained from the response function of the system, which we calculate within the random phase approximation (RPA) [25].

Eq. (1) makes use of the translational invariance parallel to the surface, which greatly reduces the computational effort. Performing a full three-dimensional calculation of the inelastic lifetime would be very time-consuming [34] and has been performed so far only for the relatively simple Be(0 0 0 1) surface [35]. In order to calculate lifetimes for the more complex noble-metal surfaces, Eq. (1) has to be applied. This expression relies on free-electron wave functions parallel to the surface. As a consequence, the localized valence bands of the adsorbate layer cannot be described correctly and unrealistic additional decay channels inside the layer would appear. We avoid this problem by approximating the response function of the metal/adsorbate system by that of the clean surface. We estimate the resulting error to be small, since the Ar levels lie quite deep in energy and are only weakly coupled to the Cu substrate. For this reason they do not represent a significant source of excitation of low-energy electron-hole pairs in comparison to the clean metal surface and thus do not provide new channels for inelastic decay. Also the wave functions of the metal states are only slightly altered by the adsorbate film. The one-particle wave functions needed for calculating the response function were obtained by solving the Schrödinger equation for a well established one-dimensional potential in the direction normal to the surface [36]. This parameterized potential reproduces the width and position of the energy gap, as well as the binding energies of the $n=0$ surface state and the $n=1$ image-potential state at the $\bar{\Gamma}$ point. The potential has been proven to accurately predict the lifetimes of surface and image-potential states on metal surfaces [3,14,33,37].

The wave functions ϕ_0 of the image-potential states, on the contrary, are strongly affected by the adsorbate layer, as these are localized in front of the surface. They have to be calculated from a potential that describes the electronic structure of the Ar film. We used a one-dimensional atomic model that gives a good description of the image-potential states for a variety of rare gases and noble-metal surfaces. This parameterized potential has been explained in detail in Ref. [30] and is of the form

$$V(z) = V_{\mathrm{DCM}}(z) + V_{\mathrm{atom}}(z)$$

$$V_{\mathrm{atom}}(z) = V_0 - \sum_{i=1}^{n_{\mathrm{rg}}} V_{\mathrm{core}} \exp(-|z - d_{\mathrm{rg}} \times (i - 1/2)|/l_{\mathrm{scr}}). \tag{2}$$

The first term V_{DCM} accounts for the screened image potential within the dielectric continuum model (DCM) [23,26,27], which is based on classical electrostatics. The second term V_{atom} describes the electronic structure. It was obtained by assuming a screened Coulomb potential for a single Ar atom and by averaging the contributions of all atoms in the surface plane. In the limit of very thick layers it generates a localized core state and valence band, and a delocalized conduction band. $d_{\mathrm{rg}} = 3.04$ Å is the interlayer spacing, n_{rg} is the number of Ar layers.

The screening length has only a minor influence on the computational result and was set to $l_{\mathrm{scr}} = 0.05 \times d_{\mathrm{rg}}$. The parameters $V_0 = -1.06$ eV and $V_{\mathrm{core}} = 538.8$ eV determine the electronic structure. V_0 was adjusted to give the correct value for the electron affinity of bulk Ar EA = +0.25 eV [38], V_{core} to reproduce the effective mass at the conduction band minimum $m_{\mathrm{eff}} = 0.47$ [39]. One should note that, although for very thin layers the concept of an effective mass in z-direction is ill-defined, in our case the corrugation is chosen such that the potential gives the correct effective mass for thick layers. The continuum part of the potential V_{DCM} depends on the dielectric constant that was treated as a free parameter. Fixing it to $\epsilon = 1.35$ results in very good agreement of the computed binding energies with the experiment. Although this value does not agree with the bulk dielectric constant of Ar, it gives a satisfying description of the image potential in the presence of the adsorbate layer.

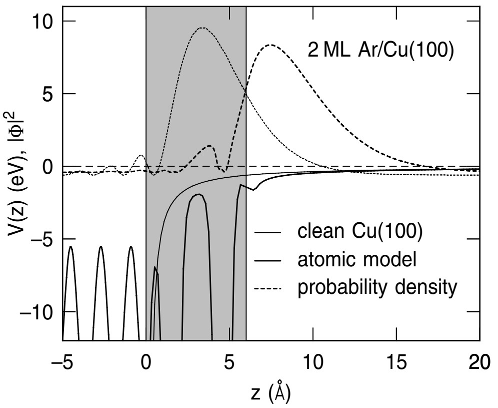

Fig. 1. Example of the model potential (thick solid line) and of the calculated $n=1$ probability density (thick dotted line) for Ar 2 ML. For comparison the potential and probability density of clean Cu(1 0 0) are also shown (thin lines). The shaded region indicates the adlayer, the metal jellium edge is at $z=0$.

The model potential is displayed in Fig. 1 for the case of 2 ML of Ar on Cu(1 0 0). It features two major modifications compared to the image potential of the clean surface. The enhanced attraction just in front of the layer stems from the polarization of the Ar film. Inside the layer, the potential is highly corrugated, giving rise to the electronic bands, while the envelope of the potential is image like.

3. Results and discussion

Fig. 2 shows our theoretical results for the lifetimes of the $n=1$ and $n=2$ image-potential states and compares them with the experiment. It is readily seen from the logarithmic scale of the plot that the lifetimes increase exponentially with increasing coverage. Very good agreement between theory and experiment is found for the $n=1$ state. Our calculation reproduces also nicely the smaller rise in lifetime of the $n=2$ state in comparison to $n=1$. Only the absolute values for this state lie slightly above the experiment. This deviation might be due to decay mechanisms outside many-body theory such as scattering off defects [40] or phonons [41] in the Ar layer. The dramatic increase of the lifetimes upon Ar adsorption reflects the strong decoupling of the image-potential states from the metal, caused by the repulsive interaction of the electrons with the 5s-derived Ar conduction band. This can be best seen from the wave functions of the states (Fig. 1), which undergo exponential damping inside the layer. As a consequence, the penetration of the $n=1$ wave function into the metal decreases with coverage, from 5.2% at Cu(1 0 0), to 1.24% for 1 ML and to 0.036% for 4 ML.

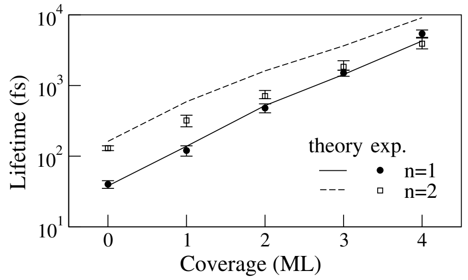

Fig. 2. Comparison of the calculated (lines) and experimental lifetimes (symbols) of the $n=1$ and $n=2$ states for 0–4 ML Ar/Cu(1 0 0).

Although the bulk-penetration model provides a qualitative explanation for the change of the lifetimes upon Ar adsorption on Cu(1 0 0), this is not necessarily the case for any given system. The effects of many-body theory go clearly beyond the local penetration picture. Firstly, relaxation of higher image-potential states to lower ones represents a significant source of relaxation. We compute that the decay of the $n=2$ state to $n=1$ amounts in average to as much as 28% of the total $n=2$ linewidth in the Ar/Cu(1 0 0) system. Secondly, the bulk penetration model fails in many cases, for example in predicting the difference in lifetime of the $n=1$ state for the Cu(1 0 0) and Cu(1 1 1) surfaces. While time-resolved 2PPE measures for the linewidth of this state 30 meV in Cu(1 1 1) [42] and 16.5 meV in Cu(1 0 0) [8,43], model potential calculations [36] yield penetration values of 0.22 and 0.05, respectively. Thus, the linewidths differ by a factor of 2, while the penetrations differ by a factor of 4. This discrepancy was resolved by a full calculation of the inelastic lifetimes [15] that showed that the size and position of the band gap and the coupling to the $n=0$ surface state are the crucial factors. Therefore, a many-body description, which takes into account not only the overlap between initial and final states, but also the available states for decay,

Table 1
Bulk, vacuum, and *cross-term* contributions to the linewidth $\Gamma = \hbar/\tau$ of the $n = 1$, 2 states for 0–2 ML of Ar/Cu(1 0 0)

	Γ (meV)		Γ_{bulk}		Γ_{vac}		Γ_{inter}	
	$n = 1$	$n = 2$	$n = 1$	$n = 2$	$n = 1$	$n = 2$	$n = 1$	$n = 2$
0 ML	17.75	4.02	17.61	3.58	10.34	2.90	−10.2	−2.46
1 ML	4.76	1.13	5.22	0.92	3.03	0.90	−3.49	−0.69
2 ML	1.26	0.41	1.44	0.31	0.80	0.33	−0.98	−0.23

the tails of bulk and surface states, and the screened interaction, is necessary in general. Only an accidental cancellation of the non-local contributions of the self-energy explains, as we show below, why the penetration approximation is applicable in favorable cases.

The non-local character of the screened interaction plays a decisive role in the decay process. It can be regarded, in a simplified picture, as the coupling of the initial states with the evanescent tails of bulk states in the vacuum region. In particular, the approximately local contribution from the bulk region to the total linewidth [15] and the non-local parts from the vacuum and cross-term regions can be analyzed. Each of these terms is obtained by confining the spatial integrals in Eq. (1) to $z < 0$, $z' < 0$ (bulk), $z > 0$, $z' > 0$ (vacuum) and $z < 0$, $z' > 0$ (cross-terms), $z = 0$ being the jellium edge. The resulting contributions Γ_{bulk}, Γ_{vac}, Γ_{inter}, and the total linewidth Γ for 0–2 ML are collected in Table 1. For the clean surface, the contribution from the cross-terms is of similar magnitude but opposite sign compared to the vacuum term. So the total linewidth is approximately the same as the bulk contribution, and one can use, with only a small error, the approximation $\Gamma \sim \Gamma_{\mathrm{bulk}}$. For 1 and 2 ML the cancellation is not complete, and the approximation would involve an error around 15–25%. However, this partial compensation explains why, for the system Ar/Cu(1 0 0), the bulk penetration shows the same scaling as a function of layer thickness as the experimental lifetimes.

4. Conclusions

We have reported on many-body calculations of the lifetimes of image-potential states in the Ar/Cu(1 0 0) system. We have demonstrated that the long lifetimes of these states can be described within the GW approximation and an appropriate one-dimensional potential. The repulsive interaction between the image-potential state and the closed Ar shells pushes the electronic wave function away from the metal substrate. This leads to an exponential rise of the lifetimes with increasing Ar coverage. Our calculated lifetimes show fairly good agreement with time-resolved 2PPE experiments, especially for the first image-potential state. Analysis of the different contributions to the non-local self-energy has served to understand the nature of inelastic decay. A close to complete cancellation of the non-local terms occurs, so that the self-energy is dominated by the approximately local term Γ_{bulk}. This explains why penetration arguments, although based on a simplified local description of the electronic interaction, give good results for the coverage dependence of the lifetimes. However, this cancellation is fortuitous, as it depends to a great extent on the particular form of the wave function of the initial state. Also, penetration arguments provide only scaling factors and no absolute lifetimes. Thus, more complex techniques such as the GW calculation that we presented here are needed, in general.

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