Inelastic Decay of Electrons in the Shockley-type Metal-Organic Interface States

S. S. Tsirkin,1,2,3 N. L. Zaitsev,4 I. A. Nechaev,1,2 R. Tonner,4 U. Höfer,4 and E. V. Chulkov1,2,5,6,3

1Donostia International Physics Center (DIPC), 20018 San Sebastián/Donostia, Basque Country, Spain
2Tomsk State University, 634050, Tomsk, Russia
3Saint Petersburg State University, Saint Petersburg, 198504, Russia
4Philipps-Universität Marburg, D-35032, Marburg, Germany
5Departamento de Física de Materiales UPV/EHU, Facultad de Ciencias Químicas, UPV/EHU, Apdo. 1072, 20080 San Sebastián/Donostia, Basque Country, Spain
6Centro de Física de Materiales CFM - MPC, Centro Mixto CSIC-UPV/EHU, 20080 San Sebastián/Donostia, Basque Country, Spain

(Dated: July 28, 2015)

We present a theoretical study of lifetimes of interface states (IS) on metal-organic interfaces PTCDA/Ag(111), NTCDA/Ag(111), PFP/Ag(111), and PTCDA/Ag(100), describing and explaining the recent experimental data. By means of unfolding the band structure of one of the interfaces under study onto the Ag(111) Brillouin zone we demonstrate, that the Brillouin zone folding upon organic monolayer deposition plays a minor role in the phase space for electron decay, and hence weakly affects the resulting lifetimes. The presence of the unoccupied molecular states below the IS gives a small contribution to the IS decay rate mostly determined by the change of the phase space of bulk states upon the energy shift of the IS. The calculated lifetimes follow the experimentally observed trends. In particular, we explain the trend of the unusual increase of the IS lifetimes with rising temperature.

I. INTRODUCTION

Many well-defined interfaces between organic semiconductors and metals exhibit interface-specific electronic states that exist independently of the detailed molecule-substrate interaction.1–4 Like the surface states (SSs) of clean metals they are a consequence of the breaking of translational symmetry perpendicular to the interface. In the Shockley-type interface states (ISs) that have been identified at Ag(111) and Ag(100) interfaces the electrons are able to move almost freely parallel to the interface whereas the local charge density in the vicinity of the first molecular layer is strongly corrugated and resembles that of molecular orbitals. These general properties of the states have been revealed in recent experimental and theoretical works.5–16 For a few systems also the important factors that determine their electronic structure could be investigated.13,16

The dynamics of electronic decay and electron transfer processes at interfaces that involve these states, however, is not well understood. Previous two-photon photoemission (2PPE) experiments have measured lifetimes between 10 and 200 fs for electrons excited into normally unoccupied interface states above the Fermi level.6,10,13,15 From these short lifetimes a large overlap of the wave function with the metal has been concluded. These conclusions, although confirmed by density functional calculations,9,10,13–15 are based on very simplistic assumptions on the nature of electronic decay processes at such an interface. Many-body calculations, such that exist for surfaces states of clean metal surfaces, have not been performed so far.

In this publication, we make a first step in this direction. We perform a theoretical study of the decay of electrons in the interface states formed at the interfaces of silver with ordered monolayers of such organic molecules as perylene-3,4,9,10-tetracarboxylic acid dianhydride (PTCDA), naphthalene-1,4,5,8-tetracarboxylic acid dianhydride (NTCDA) and perfluoropentacene (PFP). First, on an equal footing we perform ab initio density functional calculations of the electronic structure of all the studied interfaces, of which the PFP/Ag(111) interface is published for the first time here. Our calculations show that the hybridization of molecular and metallic states is small in the region of the projected band gap of the metal. New elastic decay channels, which in principle could open up due to reduced translational symmetry of the organic overlayers, will thus only have a weak influence on the electron decay of the interface state. This allows us to focus on the inelastic decay of electrons excited to the IS. We calculate the corresponding lifetimes in the self-energy formalism of many-body theory using the GW approximation.18 In order to make the calculations feasible, we use one-dimensional model potentials for an approximate description of the electronic structure of the interfaces. The potentials are based on the so-called Chulkov potential19,20 of clean surfaces. They are modified in order to reproduce the experimentally observed energy upshift of the Shockley surface state in the presence of the organic overlayers. Comparison with the ab initio calculations allows us to judge how well the potentials reproduce the probability density of the states perpendicular to the interfaces. The results are in good overall agreement with the experimental data for PTCDA/Ag(111), NTCDA/Ag(111), PFP/Ag(111), and PTCDA/Ag(100). Calculated lifetimes are gen-
ally longer than experimental ones but agree well with experimental trends.

II. AB INITIO CALCULATION OF ELECTRONIC STRUCTURE OF INTERFACES

First, in order to have a detailed information about the electronic structure of the interfaces under study, we performed ab-initio calculations within the periodic slab geometry. We used the OPENMX (version 3.7) code, which is based on density functional theory and the linear combination of localized pseudoatomic orbital (LCPAO) method. We applied the generalized gradient approximation (GGA) of Ref. 25 for the exchange-correlation functional. Also we exploited norm-conserving pseudopotentials in order to replace deep core potentials by shallow ones. For silver atoms, we set basis functions to Ag7.0−s2p2d2f1, while for hydrogen, carbon, and oxygen atoms we use H6.0−s2p1, C6.0−s2p2d1 and O6.0−s2p2d1, respectively. On the example of silver, this notation means that two primitive orbitals for each s, p, and d orbital and one primitive orbital for the f orbital were used for representation of the basis functions with the cutoff radius of 7.0 Bohr.

To improve the description of the surface state (SS), we used the enlarged cutoff radius (9.0 Bohr) for silver atoms in the uppermost layers of the slab. The latter contains 10 silver layers together with the molecular monolayer (ML) attached on one side of the silver film. The vertical distances between the Ag(111) surface and the carbon atoms of NTCDA, PTCDCA, and PFP MLs are taken to be equal to its experimental values. The oxygen atoms of NTCDA and PTCDCA monolayers on Ag(111) are fixed at the same distance as carbon ones.

The optimized geometry of PTCDCA/Ag(100) found in Ref. 15 is used in our calculation. The real-space grid for numerical integration and solution of the Poisson equation was specified by the energy cutoff of 250 Ry. The total-energy convergence was better than 0.027 meV. The surface Brillouin zone (SBZ) of the supercell was sampled with a 3×3×1 mesh of k-points.

As seen in Fig. 1 due to the unit cell of the interfaces, which is larger than the (1×1) cell naturally used for the bare surfaces, the SBZ becomes smaller, and, consequently, the metal bands of the initial SBZ corresponding to the (1×1) unit cell get folded into the reduced SBZ, hybridizing at that with the orbitals of the molecular ML. This leads to a surface band structure that does not exhibit the projected band gap at the Γ point any more. To restore the (1×1) unit-cell representation of the interface electronic structure, we performed an unfolding procedure using the BandUP code based on the method by Popescu and Zunger. Upon the unfolding procedure each electronic state mK (where m is the band index and K is the wavevector in the SBZ of the interface) is projected onto a set of corresponding points k_i in the unfolded Brillouin zone (UBZ) of the (1×1) unit cell, resulting the weights W_{mK}(k_i). The BandUP code deals with wavefunctions, expressed in the plane-wave basis set. Thus we perform calculations with the VASP code based on the plane-wave basis, employing the projector-augmented wave (PAW) method. The exchange-correlation was calculated within the GGA, like in the LCPAO method. The energy cut-off was fixed at 350 eV and a 6×4×1 Monkhorst-Pack grid of k-points was used. These calculations are notably more time-consuming than the LCPAO-calculations, thus we restrict ourselves to the case of NTCDA@Ag(111).

The band-structure calculations indicate that the deposition of a ML on top of the silver surface influences the partly occupied SS in a qualitatively similar manner for different interfaces. In the cases of Ag(111) surface the SS is shifted to a higher energy and transformed into the interface state (IS). In the case of the Ag(100) surface, the unoccupied Shockley resonance (SR) is also upshifted in energy, which changes its character to a distinct electronic state. The magnitude of the upshift depends on the molecular type, coverage, surface orientation, and
adsorption geometry.\textsuperscript{6,9,10,13,15} (see Table I). Additionally, the bare-surface electronic structure is filled up by the molecular-derived weakly dispersive states, which are thought to have an effect on electron dynamics in higher lying states.

In the unfolded bandstructure (Fig 2b) one can see a clearer picture how the deposition of an NTCDA ML modifies the electronic structure of the Ag(111) surface. Below \(-3\) eV one can see a set of \(d\)-bands, which are not affected by the molecular ML. At higher energies the bulk-derived \(s - p\) bands forming the gap at the \(\Gamma\) point at \(-1.2\) eV \(< E < 3.6\) eV, also have practically the same energies for surfaces with and without NTCDA. The main effect of NTCDA ML consists in the transformation of the bonding and anti-bonding surface states into the SS of the clean side of the slab (at -0.06 eV) and (at -0.17 and +0.08 eV) of the bare 10-layer Ag(111) slab.

The main factors: (i) the phase space of the final states \((f_{q_f})\) will be discussed further in sections IV. (ii) the overlap between the wave functions of the initial and final states, and (iii) the magnitude of the imaginary part of the self-energy operator \(\Sigma\) onto this state:

\[
\Gamma_{ee} = -2\langle \Psi_{k_i} | \text{Im} \Sigma | \Psi_{k_i} \rangle \quad (1)
\]

\[
= -2 \sum_j \int d\mathbf{z} d\mathbf{z}' M_{ij}(z, z')
\]

\[
\times \int \frac{d\mathbf{q}}{(2\pi)^2} \left[ 1 - f_{q_f} \right] \theta(E_{k_i} - E_{q_f})
\]

\[
\times \text{Im} W(z, z'; \mathbf{k} - \mathbf{q}, E_{k_i} - E_{q_f}).
\]

Here \(f_{q_f}\) is the Fermi factor and the wave-function product \(M_{ij}(z, z') = \varphi_i(z) \varphi_j(z') \varphi_j(z) \varphi_j(z')\) is determined by the real eigenfunction \(\varphi_i(z)\) being the solution of the one-dimensional Schrödinger equation

\[
-\frac{1}{2} \frac{d^2}{dz^2} + V(z) \varphi_i(z) = \epsilon_i \varphi_i(z)
\]

with the respective eigenvalue \(\epsilon_i\). In Eq. (2), the self-energy is represented by the first term of the expansion in terms of the screened Coulomb interaction \(W\), which is calculated within the random phase approximation. Thus, the many-body decay rate is determined by three main factors: (i) the phase space of the final states \((q_f)\), (ii) the overlap between the wave functions of the initial and final states, and (iii) the magnitude of the imaginary part of the screened Coulomb interaction \(\text{Im} W\). The latter is given in linear response theory by

\[
W(z, z', q, \omega) = v_c(z, z', q) + \int dz_2 dz_3 v_c(z_2, z_3; q) \chi(z_1, z_2; q, \omega) v_c(z_2, z_3; q),
\]

where \(v_c(z, z', q) = 2\pi e^{-\eta|z - z'|}/q\) is the 2D Fourier transform of the bare Coulomb interaction, and \(\chi\) is the density-density response function of interacting electrons, which is evaluated from the equation

\[
\chi(z, z', q, \omega) = \chi^0(z, z', q, \omega) + \int dz_2 dz_3 \chi^0(z_1, z_2; q, \omega) \chi(z_2, z_3; q, \omega).
\]

Here \(\chi^0(r_1, r_2; q)\) is the density-density response function of a non-interacting electron system:

\[
\chi^0(z, z', q, \omega) = \sum_{ij} \int \frac{dk}{(2\pi)^2} \left( f_{kj} - f_{k + q, ij} \right) M_{ij}(z, z') \frac{1}{\omega + E_{kj} - E_{k + q, ij} + i\eta}
\]
TABLE I: Experimental and theoretical values of the IS energy $E_{IS}$ (in eV) and lifetimes $\tau_{IS}$ (in fs). Theoretical values of $\tau_{IS}$ are given for the $E$-shifted / $V$-shifted scheme, accounting for inelastic electron-electron scattering only.

|                | PTCDA@Ag(111)       | PTCDA@Ag(100)       | NTCDA@Ag(111)       | PFP@Ag(111)       |
|----------------|---------------------|---------------------|---------------------|-------------------|
| $E_{IS}$       |                     |                     |                     |                   |
| Experiment     | 0.57 $\pm$ 0.02$^a$| 2.25 $\pm$ 0.03$^a$| 0.38 $\pm$ 0.02$^a$| 0.1-0.2$^a$       |
| Theory         | 0.55                | 2.26                | 0.40                | 0.17              |
| $\tau_{IS}$    |                     |                     |                     |                   |
| Experiment     | 53 $\pm$ 3$^a$      | 3 $\leq$ $\tau$ $\leq$ 18$^b$ | 115 $\pm$ 10$^a$   |                   |
| Theory         | 110 / 270           | $\sim$ / 24        | 250 / 500           | 1280 / 1850       |

$^a$From Ref. 13
$^b$From Ref. 15
$^c$From Ref. 38

with $\eta$ being an infinitesimally small positive constant.

IV. MODEL OF SHIFTED SURFACE STATE

As noted above, the one-dimensional (1D) potential model may be used for the description of the decay of IS electrons. We start with the pseudopotential, introduced in Refs. 13 and 20 and a set of parameters that ensure the proper description of the surface electronic structure of the bare Ag surfaces. Further we need to modify the model to reproduce the energy of the IS, which is presented by the SS, shifted to higher energies, together with the energy of the $n = 1$ IPS and the gap edges.

A way to achieve the shift of the SS, is to change the corresponding energies $\epsilon_i$, entering Eqs. 2, 3, 4 and 5 "by hand", while leaving the wavefunctions $\varphi_i(z)$ unchanged. Hereafter, we refer to such a scheme as to the one of the $E$-shifted surface state. In this case we do not change the overlap between the IS and the bulk states, while the phase space and to a certain extent the screened interaction are modified. Another way is to tune the parameters of the 1D potential in the near-surface region in a way, which provides a shift of the surface-state energy towards higher values at the $\bar{\Gamma}$ point (see Fig. 2b,c). This scheme will be referred to as the one of the $V$-shifted surface state. Here, all the aforementioned factors that determine the inelastic decay are affected. In both schemes the energy of the IPS ($n = 1$) and the surface barrier are held unchanged.

In Fig. 3, the starting-point 1D potential and the corresponding wave functions, as well as their counterparts at the largest energies considered, are shown. As seen in the figure, the shifted-SS penetration into the bulk becomes smaller upon modifying the potential, leading to a redistribution of the SS charge density into the vacuum side. This redistribution to a certain extent reflects the situation observed in ab initio calculations, where in the case of the interface the charge outside the metal is larger than in the case of the bare surface (see Fig. 4).

On the one hand, the $V$-shifted scheme looks more consistent, because the energies $\epsilon_i$ and wavefunctions $\varphi_i(z)$ are the solutions of the same Schrödinger equation 2. However, Fig. 4(top) shows the ab initio calculated wave function of the IS in comparison with the SS of the bare silver surface, where along with the aforementioned redistribution to the vacuum side the penetration, and, consequently, overlapping with the bulk states, remains to be similar to the case of the bare surface. This means that the $E$-shifted SS scheme is valid and can be more suitable in the lifetime description.

As an advantage, both schemes developed allow us to get $\Gamma_{e-e}$ as a function of the IS energy, instead of specific calculations for a given IS energy. The decay rate of the
FIG. 3: One-dimensional potential and respective wave functions for the surface (interface) states and bulk states in the case of the Ag(111) and Ag(100) surfaces at different energies of the shifted surface state ($E_{SS/IS}$). The bulk charge density was normalised to fit the same scale as SS/IS.

$V$-shifted SS electrons at $\Gamma$ as a function of the SS(IS) energy is shown in Fig. 3 (top) for the Ag(111) surface. For example, for the experimental values of the IS energy observed at 300 K for NTCDA and PTCDA monolayers on Ag(111) (see Table I) the decay rate $\Gamma_{\text{e-e}} = 1.3$ meV ($\tau \sim 0.5$ ps) and 2.4 meV ($\tau \sim 0.3$ ps), respectively. Such a difference between the indicated values of $\Gamma_{\text{e-e}}$ is caused by the fact that for the bigger IS energy there is a larger decay phase space formed by the bulk states. However, the difference could be bigger, if the aforementioned overlap between the SS(IS) and the bulk states did not decrease with the increasing SS(IS) energy. Calculations performed with the unmodified bare-surface 1D potential but with changed SS(IS) energies ($E$-shifted surface state) clearly show how the decreasing overlap reduces the gain in the decay phase space (see dashed line in Fig. 3 (top)). In this case, for NTCDA and PTCDA monolayers on Ag(111) the decay rates are $\Gamma = 2.6$ meV ($\tau \sim 0.3$ ps) and 6.0 meV ($\tau \sim 0.1$ ps), respectively. The absolute values of the lifetimes found within both schemes for the interfaces are substantially longer than those experimentally observed: $\tau_{\text{NTCDADAG}(111)}^{\text{IS}} = 115 \pm 10$ fs and $\tau_{\text{PTCDADAG}(111)}^{\text{IS}} = 53 \pm 3$ fs at 300 K and $\tau_{\text{NTCDADAG}(111)}^{\text{IS}} = 43$ fs and $\tau_{\text{PTCDADAG}(111)}^{\text{IS}} = 26$ fs at 90 K as reported in Ref. 13. However, their ratio is very close to its experimental counterpart. Moreover, the presented results allow us to nicely reproduce the trend of the unusual increase of the lifetimes with rising temperature (see Fig. 3 (top)). Actually, at higher temperature the absorption distance becomes larger and, as a consequence, due to the weakened interaction between the molecular ML and metal substrate, the IS energy gets smaller, providing by this the smaller decay rate.

For the PFP@Ag(111) interface no experimental data is available on the IS lifetime. Our calculations yield a very small inelastic decay rate $\sim 0.5$ meV, corresponding to the lifetime of 1-2 ps due to the low energy of the IS, and hence small phase space for the inelastic decay. However, this value should be sufficiently shortened by elastic decay channels, e.g. electron-defect scattering.

In the case of the Ag(100) surface, the decay rate of the surface resonance (SR) cannot be calculated within the present framework. However, when the SR is pushed into the band gap, it becomes the IS. The decay rate of the latter decreases with its energy (see Fig. 3 (bottom)) in spite of the growing decay phase space. Such a decrease is caused by the rapid reduction of the IS–bulk states overlap (see Fig. 3). For the IS energy that corresponds to the PTCDA/Ag(100) interface, the decay rate is of 27 meV. The corresponding lifetime $\tau = 24$ fs is surprisingly close to the upper limit of 18 fs found experimentally in Ref. 15. Note that we consider here the $V$-shifted SS scheme only, since we cannot extrapolate
FIG. 5: Calculated decay rate $\Gamma$ of the shifted surface state as a function of its energy. Solid (dashed) lines correspond to the $V$-(E)-shifted scheme, respectively. Light-gray stripes cover the energy intervals, which correspond to the experimental values of the IS energy, including its variations with temperature. In the case of Ag(111), red points show the decay as obtained within the $E$-shifted scheme with taking into account the contribution of the former LUMO. Error bars here are caused by changing the former LUMO energy (see Fig. 1) within the $\pm 50$ meV interval.

FIG. 6: Calculated decay rate $\Gamma$ as a function of the energy of the shifted surface state. For Ag(100) and Ag(111), the resonance-like wavefunction of the bare Ag(100) surface to the projected band gap energy region.

V. MONOLAYER PSEUDOPOTENTIAL

In an attempt to take into account a possible contribution coming from the molecular-derived states presented in Fig. 1 by the fat bands (or red circles in Fig. 2a), the localization of these states lying energetically below the IS (the former LUMO in the Ag(111) interfaces) should be reproduced. (See Fig. 4(top)) For this purpose we develop a pseudopotential that models the molecular ML as a quantum well and contains a barrier, separating the ML from the bulk Ag(111). We refer to this model as the ML potential. This model allows us to get the shifted SS and the former LUMO with quite close energies (reproducing the ab initio values) and localized in the interface region and at the molecular layer, respectively, with the overlapping $\int |\varphi_{\text{IS}}(z)|^2|\varphi_{\text{LUMO}}(z)|^2 \, dz$ as obtained from the ab initio calculations.

In Fig. 4(bottom), we plot the obtained model wave functions. Note, that in the calculation of lifetimes we have replaced the wavefunction of LUMO $\varphi_{\text{LUMO}}(z)$ by $\varphi_{\text{LUMO}}(z)/\sqrt{N}$ in order to take into account the unfolding onto the $(1 \times 1)$ Ag(111) BZ. Here $N$ is the number of atoms in the Ag(111) surface layer unit cell of the interface: $N = 33$ and 24 for PTCDA and NTCDA, respectively. The resulting contribution accounting for transitions from the SS(IS) to the LUMO was estimated to be of $\sim 0.3 - 0.7$ meV. Fig. 5(top) shows the quite moderate effect of this contribution being added to the decay rate of the $E$-shifted SS scheme by red dots. By error bars, we demonstrate how variations in the former LUMO energy ($\pm 50$ meV) can affect the resulting $\Gamma$.

As one can see, the calculated lifetimes are generally longer, than the experimental ones. On the one hand, this is a typical picture, because there are usually some other decay channels, which are not taken into account in the model. On the other hand, the difference between theoretical and experimental results may be caused by inaccurate description of the charge density distribution. As follows from ab-initio calculations, in the interfaces under study the presence of the molecular ML causes a redistribution of not only the SS charge density in the vicinity of the ML plane, as we show above, but also the bulk-states charge density. This simultaneous redistribution can produce an additional overlap between the IS and the bulk states, making the IS lifetime shorter. In order to take it into account, one should modify the 1D pseudo-potential in a way to properly describe its behavior within the ML region. Since it involves the bulk states and affects the image-potential tail of the 1D pseudo-potential, it should be done consistently with a study of energies and lifetimes of image-potential states, which, in turn, need to be experimentally analyzed first. On the other side further experimental studies of IS lifetimes for the organic monolayers on top of the Ag(111) surface might shed light on peculiarities of this surface, that provide a distinct decay process as compared to the Ag(110) surface.

VI. CONCLUSIONS

We have presented a theoretical study of lifetimes of interface states (IS) on metal-organic interfaces within one-dimensional pseudopotentials. The presented results allowed us to address the question about the description and explanation of recent experimental data. We have demonstrated, that the folding of the BZ of the Ag sur-
face due to substantial enlarging of the surface unit cell upon the deposition of organic molecules does not have a drastic effect on the phase space of final states for electron decay.

By means of the unfolding procedure we demonstrated, that the BZ folding upon organic monolayer deposition plays a minor role in the phase space for electron decay. Actually, it introduces only a weak background to the bandstructure of the $(1 \times 1)$ unit cell, and hence weakly affects the lifetimes. The presence of the unoccupied molecular state below the IS gives a small contribution to the decay rate of the IS, while the lifetime is mostly determined by the change of the phase space of final states upon the energy shift of the IS.

In the case of PTCDA@Ag(100), the IS lifetime obtained in the $E$-shifted SS scheme agrees well with the experimental data, while for PTCDA and NTCD at Ag(111) these model strongly overestimates the corresponding lifetimes of the IS. Being applied to these Ag(111) interfaces, the $E$-shifted SS scheme, which is based on the phase-space description, yields shorter lifetimes, but still quite long as compared with the experiment. However, our calculations provide the ratio $\tau^{IS}_{\text{NTCD} \oplus \text{Ag}(111)}/\tau^{IS}_{\text{PTCD} \oplus \text{Ag}(111)}$, in agreement with the experiments, and explain the trend of the unusual increase of of the IS lifetimes with rising temperature.

**Acknowledgments**

This work is a project of the SFB 1083 "Structure and Dynamics of Internal Interfaces" funded by the Deutsche Forschungsgemeinschaft (DFG). We acknowledge partial support from the University of Basque Country UPV/EHU (IT-756-13), the Departamento de Educación del Gobierno Vasco, The Tomsk State University Academic D.I. Mendeleev Fund Program (Grant No. 8.1.05.2015), the Spanish Ministry of Economy and Competitiveness MINECO (Grant No. FIS2013-48286-C2-1-P), and Saint Petersburg State University (Project No. 11.50.202.2015).

---

1. P. Szymanski, S. Garrett-Roe, and C. B. Harris, Prog. Surf. Sci. **78**, 1 (2005).
2. M. Marks, A. Schöll, and U. Höfer, J. Electron. Spectrosc. Relat. Phenom. **195**, 263 (2014).
3. J. Zhao, M. Feng, D. B. Dougherty, H. Sun, and H. Petek, ACS Nano **8**, 10988 (2014).
4. N. Ilyas and O. L. A. Monti, Phys. Rev. B **90**, 125435 (2014).
5. R. Temirov, S. Soubatch, A. Luican, and F. S. Tautz, Nature **444**, 350 (2006).
6. C. H. Schwalb, S. Sachs, M. Marks, A. Schöll, F. Reinert, E. Umbach, and U. Höfer, Phys. Rev. Lett. **101**, 146801 (2008).
7. A. Yang, S. T. Shipman, S. Garrett-Roe, J. Johns, M. Strader, P. Szymanski, E. Muller, and C. Harris, J. Phys. Chem. C **112**, 2506 (2008).
8. A. Scheybal, K. Miller, R. Bertschinger, M. Wahl, A. Bendouman, P. Aebi, and T. A. Jung, Phys. Rev. B **79**, 115406 (2009).
9. M. S. Dyer and M. Persson, New J. Phys. **12**, 063014 (2010).
10. N. L. Zaitsev, I. A. Nechaev, and E. V. Chulkov, J. Exp. Theor. Phys. **110**, 114 (2010).
11. S. Sachs, C. H. Schwalb, M. Marks, A. Schöll, F. Reinert, E. Umbach, and U. Höfer, J. Chem. Phys. **131**, 144701 (2009).
12. C. H. Schwalb, M. Marks, S. Sachs, A. Schöll, F. Reinert, E. Umbach, and U. Höfer, Eur. J. Phys. **75**, 23 (2010).
13. M. Marks, N. L. Zaitsev, B. Schmidt, C. H. Schwalb, A. Schöll, I. A. Nechaev, P. M. Echenique, E. V. Chulkov, and U. Höfer, Phys. Rev. B **84**, 081301(R) (2011).
14. N. L. Zaitsev, I. A. Nechaev, P. M. Echenique, and E. V. Chulkov, Phys. Rev. B **85**, 115301 (2012).
15. M. C. E. Galbraith, M. Marks, R. Tonner, and U. Höfer, J. Phys. Chem. Lett. **5**, 50 (2014).
16. B. W. Caplins, D. E. Suich, A. J. Shearer, and C. B. Harris, J. Phys. Chem. Lett. **5**, 1679 (2014).
17. P. M. Echenique, R. Berndt, E. V. Chulkov, T. H. Fauster, A. Goldmann, and U. Höfer, Surf. Sci. Rep. **52**, 219 (2004).
18. L. Hedin, Phys. Rev. **139**, A796 (1965).
19. E. V. Chulkov, V. M. Silkin, P. M. Echenique, Surf. Sci. **391**, L1217 (1997).
20. E. V. Chulkov, V. M. Silkin, P. M. Echenique, Surf. Sci. **437**, 330 (1999).
21. openmx-square.org.
22. T. Ozaki, Phys. Rev. B **67**, 155108 (2003).
23. T. Ozaki and H. Kino, Phys. Rev. B **69**, 195113 (2004).
24. T. Ozaki and H. Kino, Phys. Rev. B **72**, 045121 (2005).
25. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
26. N. Troullier, J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
27. C. Stadler, S. Hansen, A. Schöll, T.-L. Lee, J. Zegenhagen, C. Kumpf, and E. Umbach, New Journal of Physics **9**, 50 (2007).
28. A. Hauschild, R. Temirov, S. Soubatch, O. Bauer, A. Schöll, B. C. C. Cowie, T.-L. Lee, F. S. Tautz, and M. Sokolowski, Phys. Rev. B **81**, 125432 (2010).
29. S. Duhm, S. Hosouomi, I. Salzmann, A. Gerlach, M. Oehzelt, B. Weil, T.-L. Lee, F. Schreiber, N. Koch, N. Ueno, and S. Kera, Phys. Rev. B **81**, 045418 (2010).
30. BandUP: Band unfolding code for plane-wave based calculations, [www.ifm.liu.se/themod/compphys/band-unfolding](http://www.ifm.liu.se/themod/compphys/band-unfolding).
31. P.V.C. Medeiros, S. Staafström and J. Björk, Phys. Rev. B **89**, 041407(R) (2014).
32. P.V.C. Medeiros, S.S. Tsirkin, S. Staafström and J. Björk, Phys. Rev. B **91**, 041116(R) (2015).
33. V. Popescu and A. Zunger, Phys. Rev. B **85**, 085201 (2012).
34. G. Kresse and J. Hafner, Phys. Rev. B **48**, 13115 (1993).
35. G. Kresse and J. Furthmüller, Comput. Mater. Sci. **6**, 15 (1996).
36. P.E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
37. G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
38 M.C.E. Galbraith, M.Sc. thesis, Philipps-Universität Marburg, 2012.

39 J. Kliewer, R. Berndt, E. V. Chulkov, V. M. Silkin, P. M. Echenique, S. Crampin, Science 288, 1399 (2000).

40 L. Vitali, P. Wahl, M. A. Schneider, K. Kern, V. M. Silkin, E. V. Chulkov, P. M. Echenique, Surf. Sci. Lett. 523, L47 (2003).