

Electron Lifetime in a Shockley-Type Metal-Organic Interface State

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The lifetimes of electrons at the interface between 3,4,9,10-perylene-tetracarboxylic acid dianhydride (PTCDA) and Ag(111) have been studied by means of time- and angle-resolved two-photon photoemission. We observe a dispersing unoccupied state 0.6 eV above the Fermi level with an effective electron mass of $0.39m_e$ at the $\bar{\Gamma}$ point. The short lifetime of 54 fs is indicative of a large penetration of the wave function into the metal. Supported by model calculations this interface state is interpreted as predominantly arising from an upshift of the occupied Shockley surface state of the clean metal due to the interaction with the PTCDA overlayer.

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The injection of charge carriers at molecule-metal interfaces plays a decisive role in the performance of organic semiconductor devices. The rate of charge injection depends on the energetic barriers that result from the alignment of the molecular levels in the semiconducting film with respect to the metallic Fermi level and on the wave function overlap at the interface. New electronic states that may develop due to the interaction of the adsorbed molecules with the metal substrate can thus drastically alter the injection mechanisms [1]. A promising system to study the microscopic mechanisms of such electron transfer processes is 3,4,9,10-perylene-tetracarboxylic acid dianhydride (PTCDA). One of the major advantages of this archetype molecular organic semiconductor is that it forms highly ordered films on a variety of substrates [2–5]. On Ag(111), PTCDA forms a long-range ordered commensurate monolayer with two flat lying chemisorbed molecules per unit cell in a herringbone arrangement [3]. Recently, Temirov *et al.* [6] observed a dispersing unoccupied state close to the Fermi level for monolayer islands by scanning tunneling spectroscopy (STS). However, the exact origin of the state and its role for charge transfer across the interface remained unclear. Originally it was attributed to the downshifted LUMO + 1 level of PTCDA in the monolayer [6], whereas its strong lateral dispersion points to a close relationship with the metallic Shockley surface state of Ag(111) [5]. Yang *et al.* [7], using two-photon photoemission (2PPE), showed that a similar state also exists for thicker layers. They reported that its effective mass depends on specific preparation conditions and interpreted this in terms of a varying overlap of the LUMO + 1 level of neighboring molecules [7].

In this Letter, we present experimental and theoretical evidence that the unoccupied state of the PTCDA/Ag(111) system, in fact, arises essentially from an upshift of the occupied Shockley surface state in the projected sp gap of the metal. Our angle-resolved 2PPE experiments display an effective electron mass at the $\bar{\Gamma}$ point identical to the latter state and independent of layer thickness. The data

clearly show that the state is located at the interface between the metal and the first PTCDA layer. Time-resolved 2PPE experiments reveal a simple exponential decay of electrons excited into the interface state with a lifetime of 54 fs. From the short lifetime we conclude that its wave function is predominantly located in the metal. This result is corroborated by model calculations which demonstrate that the basic properties of the interface state can be understood by simply considering the steepening of the metallic surface potential by the presence of a highly polarizable organic adsorbate layer. This interpretation is compatible with the expectation that the chemical interaction of the first monolayer with the metal must lead to an antibonding interface state with strong metal character in this energy range.

The experiments were carried out in a UHV chamber with a base pressure of 4×10^{-11} mbar. The Ag(111) surface was prepared by repeated sputter and annealing cycles and checked for cleanliness and structural order by x-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED), respectively. PTCDA films were prepared by vapor deposition with rates of ~ 0.5 Å/min at a substrate temperature of 270 K. From numerous careful investigations we know that under these conditions highly ordered monolayers and thin films are obtained with very large domains (~ 1 μm for the monolayer) [8]. The layer thickness was subsequently determined by XPS from the attenuation of the substrate signal. Monolayer (ML) films were prepared by thermal desorption of multilayer films at a temperature of 540 K. The 2PPE measurements were performed at room temperature with the p -polarized IR- and third harmonic UV pulses of a Ti:sapphire oscillator, which had a pulse duration of 54 and 65 fs, respectively. The photoelectrons emitted from the sample were recorded by a hemispherical analyzer with 25 meV energy and ± 0.015 Å⁻¹ angular resolution. The angle between the detected photoelectrons and the incident laser light was 75°. Angle-dependent spectra were recorded by rotating the sample.

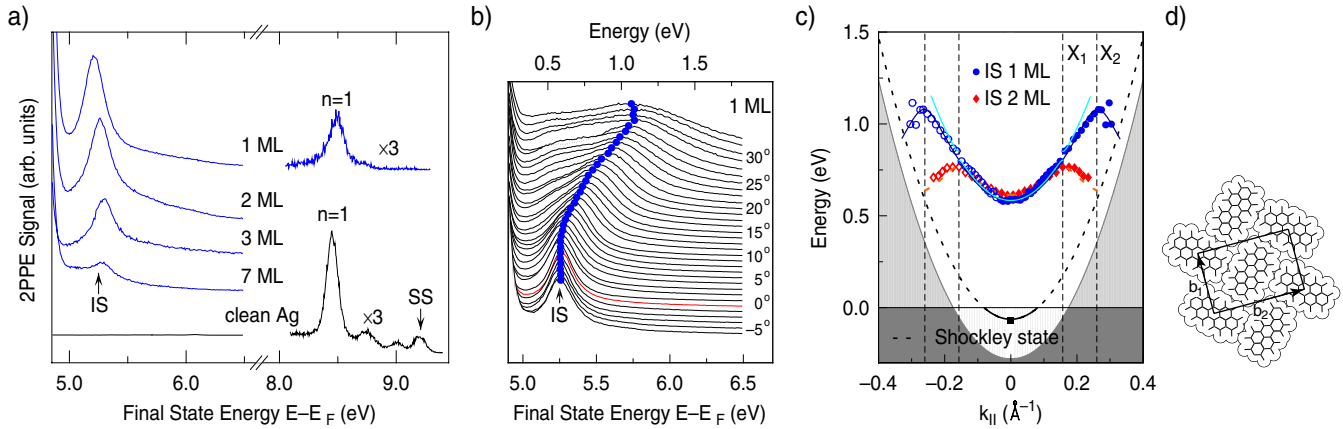


FIG. 1 (color online). (a) Normal emission (0°) single-color 2PPE spectra of PTCDA/Ag(111) for different coverages (top) and the clean surface (bottom). The energy of the unoccupied states (IS), ($n = 1$) and ($n = 2$) with respect to the Fermi level is obtained by subtracting the UV photon energy of 4.68 eV from the final-state energy. (b) 2PPE spectra of one ML PTCDA/Ag(111) for different emission angles. (c) Map of the measured dispersion of the interface state (IS) for 1 ML (circles) and 2 ML (diamonds) of PTCDA together with the projected Ag(111) bulk bands (gray shaded area) and the Shockley state of the clean surface (dotted line). The borders of the PTCDA Brillouin zone for the two unit cell vectors are indicated by X_1 and X_2 . (d) Real-space structure for PTCDA molecules adsorbed on Ag(111) including the rectangular unit cell after Ref. [3].

Figure 1(a) displays 2PPE spectra of clean Ag(111) and for different coverages of PTCDA/Ag(111), recorded at normal emission. UV pulses with a photon energy of 4.68 eV served as pump and probe pulses. At high energies the spectrum of the clean surface shows clearly visible peaks due to the normally unoccupied ($n = 1$) and ($n = 2$) image-potential states and the occupied Shockley surface state (SS). The latter is located 0.06 eV below the Fermi level and appears at a final-state energy of 9.2 eV as a result of a direct 2-photon transition. Upon adsorption of 1 ML of PTCDA, the image-potential peaks shift slightly and get weaker. The peak (SS), however, vanishes completely. Instead, an intense new peak, denoted (IS), appears at a final-state energy of 5.27 eV [Fig. 1(a)].

For normal emission, the energetic position of peak (IS) changes very little to 5.32 eV when two or more monolayers of PTCDA are adsorbed. Its intensity, however, decreases by a factor of 2 per three monolayers [Fig. 1(a)]. This indicates that the state is located at the interface between the metal and the PTCDA layers. Upon change of the photon energy of the UV pulses the position of peak (IS) shifts linearly with a slope close to 1, a behavior characteristic for an unoccupied electronic state which is populated by the incident UV light and then probed by one UV photon. At $k_{||} = 0$, the state is located 0.6 eV above the Fermi level.

With increasing emission angle peak (IS) broadens and shifts to higher energy [Fig. 1(b)]. The dispersion $E(k_{||})$ along the Ag(111) $\bar{\Gamma}$ - \bar{X} direction determined from Fig. 1(b) and from similar data with a PTCDA coverage of 2 ML is depicted in Fig. 1(c). Because there are six rotational domains in PTCDA monolayers on Ag(111) [3], the measurement averages over different orientations and the direction cannot be specified with respect to the unit cell of

the PTCDA adlayer. In Fig. 1(c), the borders of the PTCDA Brillouin zone for the two unit cell vectors are indicated by X_1 and X_2 . The monolayer data reveal a small gap at X_1 and the backfolding of the peak maxima clearly coincides with the zone boundary X_2 . For 2 ML the backfolding is clearly pronounced at the X_1 boundary [Fig. 1(c)].

The almost parabolic dispersion of the band at $k_{||} = 0$ corresponds to an effective electron mass of $m^* = 0.39 \pm 0.03m_e$. This effective mass is almost exactly the same as that of the Shockley surface state of clean Ag(111) ($m^* = 0.397m_e$, [9]) and only slightly smaller than the value deduced by Temirov *et al.* [6] from STS measurements of PTCDA islands of different sizes ($0.47m_e$). Yang *et al.* [7] reported higher effective masses between $0.52m_e$ and $0.96m_e$ depending on preparation conditions and coverage, an observation from which we conclude that the value of $0.39m_e$ corresponds to well ordered homogenous layers [8].

To gain information about the dynamics of the electron transfer process between the metal and the interface state (IS) we use the 1.56 eV IR pulses to populate it and probe it with time-delayed UV pulses (Fig. 2). For spectroscopic measurements, this excitation scheme has the disadvantage that the image-potential state ($n = 1$), pumped with UV and probed by IR, appears almost at the same final-state energy as the interface state. With increasing delay of the UV pulse, however, the ($n = 1$) state can no longer become populated before the arrival of the IR pulse and the 2PPE spectrum is dominated by the interface state (Fig. 2). Figure 3 displays the 2PPE intensity from the peak (IS) as a function of time delay between the IR and the UV pulse on a semilogarithmic scale. The exponential decay of the signal can be followed over 3 orders of magnitude. It corresponds to a lifetime of the state (IS) of

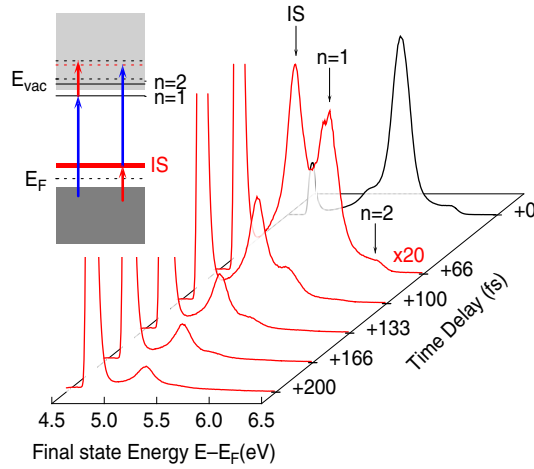


FIG. 2 (color online). Time-resolved two-color 2PPE-spectra for 2 ML PTCDA/Ag(111) and excitation schemes for the image-potential states ($n = 1, 2$) and the interface state (IS). Positive delays denote UV pulses ($\hbar\omega = 4.68$ eV, long arrow) arriving after IR pulses ($\hbar\omega = 1.56$ eV, short arrow). The sharp intensity rise at 4.73 eV indicates the sample work function.

$\tau_{IS} = 54 \pm 5$ fs. A systematic study as a function of PTCDA coverage (Fig. 3, inset) shows that τ_{IS} changes very little between 1 and 4 ML. For higher PTCDA coverages we observe a small increase.

The short measured lifetimes of 54 fs clearly indicate that the excited (IS) electrons relax by interaction with metallic silver states. Since the interface state is located in the projected bulk band gap of Ag(111) the electrons cannot escape into the metal elastically but only due to

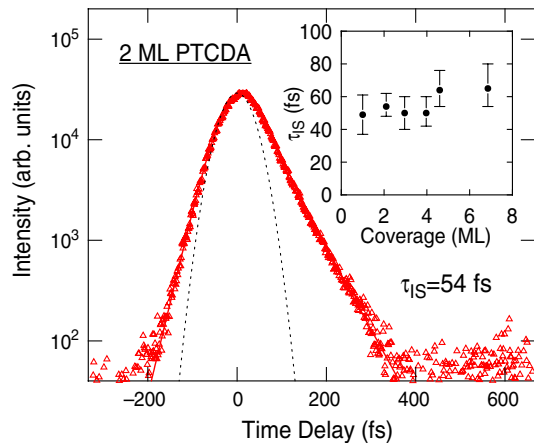


FIG. 3 (color online). Two-color 2PPE signal recorded at the peak maximum of the interface state (IS) for a 2-ML PTCDA film. The lifetime τ_{IS} is determined from the exponential decay observed for UV pulses arriving after IR pulses (positive delays). The signal at negative delays is dominated by the shoulder of the image state ($n = 1$), which has a lifetime of 22 fs at this PTCDA coverage. The dotted line represents the cross correlation between UV and IR pulses. Inset: Lifetimes of the state (IS) determined for different PTCDA coverages.

inelastic electron-hole-pair decay. Such decay processes have been studied intensively at metal surfaces for image-potential states [10]. In general, these are complicated many-body processes depending on details of the wave function, available phase space for e - h creation and screening of the Coulomb interaction. For states on the same surface which are not too close to E_F , however, it has often been observed that the lifetime scales nearly linearly with bulk penetration $p = \int_{-\infty}^0 |\Psi(z)|^2 dz$ of the wave function and with the energy difference $E - E_F$ [11,12].

The image-potential state ($n = 1$) on clean Ag(111) is located at $E_{n=1} - E_F = 3.8$ eV (Fig. 2). The wave function is located mainly in the vacuum, the bulk penetration is $p_{n=1} = 23\%$ [13]. For this state we measure a lifetime at the Γ point of $\tau_{n=1} = 25$ fs, in agreement with previous results [14,15]. The PTCDA-induced state (IS) at 0.6 eV is located more than 6 times closer to the Fermi level. Therefore, the phase space for electron-hole-pair decay will be reduced considerably for this state. We would expect it to have a lifetime of more than 150 fs if it had a similar bulk penetration as the image-potential state; i.e., it was located mainly in the PTCDA layer. However, its lifetime of $\tau_{IS} = 54$ fs is only 2 times larger than that of the ($n = 1$) state. Therefore, our measurements indicate a larger bulk penetration of $p_{IS} \sim 75\%$, comparable to that of the Shockley state. We arrive at a similar conclusion if we consider the linewidth of the Shockley state itself [12]. Furthermore, we note that τ_{IS} is comparable to the lifetime of adsorbate-induced states of Cs/Cu(111) [16–18] and C_6F_6 /Cu(111) [19]. Since these states are located ~ 3 eV above E_F and their phase space for e - h decay is thus considerably larger than that of the state (IS) also this comparison is indicative of a very good overlap of the wave function of the state (IS) with the metal.

The results discussed above showed that the interface state (IS) of PTCDA/Ag(111) has very similar properties as the Shockley state (SS) of the clean surface. This suggests that adsorption of PTCDA basically causes an upshift of the latter state by 0.66 eV. Such an effect is well known for the adsorption of weakly chemisorbed molecules and physisorbed rare gases, although the magnitude of the corresponding shift is much smaller (≤ 200 meV) [20–22]. In the case of PTCDA/Ag, the chemisorptive bond strongly changes the electronic properties of the interface [23]. Although this suggests that all valence electrons of the interface are somehow involved we first assume in the following a weakly coupled PTCDA overlayer and discuss its influence on the Shockley state. We then come back to the chemisorption aspect.

For clean surfaces, the so-called Chulkov potential [13], a one-dimensional parameterized analytical potential $V(z)$, is known to provide a very accurate description of surface states of many metals. It consists of a cosine pseudo-potential, which correctly describes the sp band of the metal, the image potential, and an intermediate part which smoothly connects both regions. Numerical solution of the

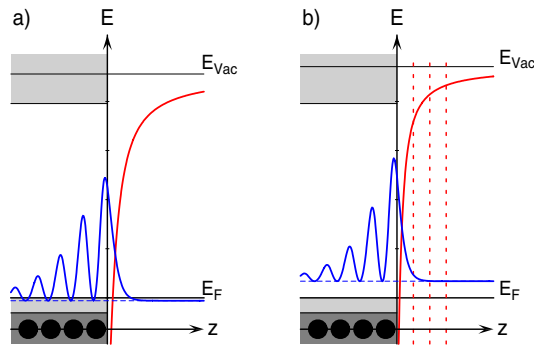


FIG. 4 (color online). Potential and wave function of the resulting Shockley state for (a) the clean Ag(111) surface and (b) the interface between Ag(111) and a dielectric layer with $\epsilon = 1.9$. Dashed lines represent molecular planes of PTCDA.

Schrödinger equation yields an energetic position of the Shockley surface state $E_{SS} = -0.06$ eV, in perfect agreement with experiment. According to the calculation, the bulk penetration of the wave function for this state is 75% [Fig. 4(a)]. We now simply treat the PTCDA overlayer as a homogenous polarizable medium characterized by a dielectric constant ϵ . The consequence is a screening of the image potential due to the polarizability of the overlayer. Already this basic effect is able to explain the upshift of the Shockley state. For $\epsilon = 1.9$, the value of bulk PTCDA along the stacking direction [24], the calculations yield a shift of the state by more than 0.4 eV to $E = 0.35$ eV [Fig. 4(b)]. Since the molecules in the first monolayer interact with the metal their polarizability is presumably higher than in the bulk. The measured value of $E_{IS} = 0.6$ eV can be reproduced by $\epsilon = 4.1$. A comparison of the potentials of Figs. 4(a) and 4(b) shows that the decisive effect of ϵ on the potential $V(z)$ is a steeper rise in the vicinity of the surface. As a consequence, the barrier for electrons near the Fermi level gets closer to the metal and the Shockley state shifts to a higher energy, without significantly changing the bulk penetration ($p = 79\%$).

We now come back to the aspect of chemisorption. It is well established that the LUMO orbital of the PTCDA monolayer is strongly involved in the bonding [5,23]. It disappears from the x-ray absorption and inverse photoemission spectrum, and a new state appears which is cut by the Fermi level and hence is only partially filled. This new state has some Ag $4s$ and strong PTCDA LUMO contributions. It has bonding character with respect to the PTCDA-Ag bond. Its antibonding analogue should be found at higher energy and hence must be unoccupied. Since this state should have predominant metal character it is hardly visible in x-ray absorption experiments using molecular $1s$ levels, but should be detected by 2PPE. In the chemisorption picture we hence expect a two-dimensional interface state with strong metal character showing an s -band-like dispersion parallel to the surface around $k_{\parallel} \sim 0$. Thus the chemical bonding picture for the state (IS) and the

physical picture of a Shockley-like interface state coincide in the present case. Finally we note that the presence of such a state modifies the density of states at the interface. For that reasons it is important to include it in theories of level alignment and barrier formation at metal-organic interfaces [25].

In conclusion, our results indicate that the unoccupied state (IS) of PTCDA/Ag(111) is a genuine interface state. It is located between the Fermi level of the metal and the LUMO of the PTCDA multilayers. Its wave function extends beyond the first chemisorbed PTCDA monolayer while the short lifetime of 54 fs indicates a large penetration into the metal. Similar interface states are likely to exist at other interfaces between metals and organic semiconductors.

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