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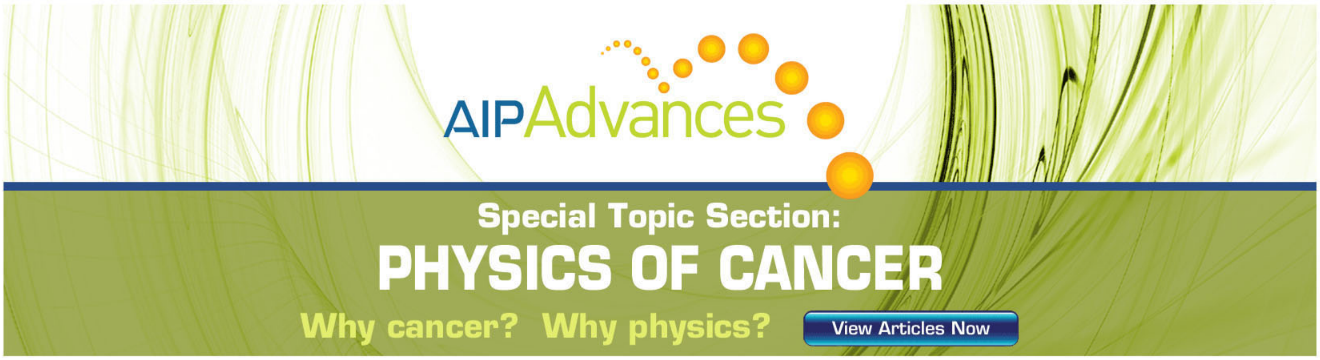

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Probing individual weakly-coupled π-conjugated molecules on semiconductor surfaces

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A weak perturbation of a single molecule by the supporting substrate is a key ingredient to molecular electronics. Here, we show that individual phthalocyanine molecules adsorbed on GaAs(110) and InAs(111)*A* surfaces represent prototypes for weakly coupled single-molecule/semiconductor hybrid systems. This is demonstrated by scanning tunneling spectroscopy and bias-dependent images that closely resemble orbital densities of the free molecule. This is in analogy to results for molecules decoupled from a metal substrate by an ultrathin insulating layer and proves a weak electronic molecule-substrate coupling. Therefore, such systems will allow single-molecule functionality to be combined with the versatility of semiconductor physics. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4742977]

I. INTRODUCTION

In the ultimate limit of downscaling electronic devices, the functional parts would be single molecules or even atoms. One promising route towards this goal is the combination of single-molecule functionality with semiconductor based nanoscale devices, which are the building blocks of today's electronics.[1–3] On this route, the coupling between the molecule and the substrate is of key importance. Here, one needs to discriminate between (i) the molecule-surface bond, which is required to be strong to achieve thermal stability of the device, and (ii) the electronic coupling of the molecule's frontier orbitals, which must be weak to retain a desired single-molecule functionality. At first glance, these two premises seem to be contradictory. However, the use of molecular anchoring groups, e. g., carboxylic acids,[4] allows to pin the molecule to the substrate. Such anchoring groups will not significantly contribute to the frontier orbitals and will therefore allow to ensure thermal stability independent of premise (ii). Here, we focus on the latter, by presenting a electronically weakly coupled molecule-substrate system.

A weak coupling between the molecules frontier orbitals and the substrate can be made impossible by the chemical reactivity of semiconductor substrates, leading to a rich variety of reactions like chemisorption with strong covalent bonding,[1,5] cycloaddition reactions,[6,7] or even molecular fragmentation.[8] This obstacle may be overcome by surface passivation[9] or by the use of a low-reactive molecule/semiconductor system. Single-molecule functionality has been demonstrated in the class of phthalocyanine (Pc) molecules, exhibiting molecular magnetism[10–12] and various types of conductance switching.[13–15] Interestingly, Pc molecules on some III–V semiconductor surfaces are believed to interact weakly with the substrate, as is mainly concluded from self-ordering in thin molecular films, as found by averaging techniques like low energy electron diffraction.[16–18] In addition, the appearance of these molecules in films in scanning tunneling microscopy (STM) imaging hinted at a weak coupling.[19] However, despite these promising indications, to date the electronic structure of an *individual* physisorbed molecule on a bare semiconducting substrate has not been resolved.

To this end, we performed low-temperature STM of iron-II-phthalocyanine (FePc) adsorbed on bare GaAs(110), deposited at a substrate temperature below 20 K. We probe the electronic properties of individual molecules using scanning tunneling spectroscopy and bias-dependent imaging. These images closely resemble the orbital densities of the free molecule. In analogy to molecules electronically decoupled by an insulating layer from a metal substrate, this finding proves a weak electronic coupling.[20] This is further corroborated by the possibility of current-induced lateral movement by inelastic excitation. The findings are applicable also to other systems as is confirmed by probing naphthalocyanine (NPc) molecules on the InAs(111)*A* surface, also revealing a weak perturbation of the electronic structure of the molecules by the semiconductor substrate.

II. EXPERIMENTAL

The experiments were carried out with two separate low-temperature STMs operated below 10 K. The GaAs sample was grown by molecular beam epitaxy (MBE) and consists of a 250 nm thick slab of intrinsic GaAs grown atop of a degenerate n-doped GaAs-based heterostructure,[21] capped by a 200 nm thick degenerate p-doped layer. It was cleaved in ultrahigh vacuum to expose the (110) surface. The InAs(111)*A* surfaces used were prepared by MBE growth and As capping/decapping as described in Ref. 22. Molecules were adsorbed at a sample temperature $T < 20\,\mathrm{K}$, with

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the sample inside the STM. All voltages refer to the sample bias with respect to the tip. Spectra were acquired with lock-in technique (50 mV modulation amplitude at 160 Hz). All images of the GaAs(110) surface are acquired within the intrinsic region or the n-doped part next to the intrinsic region.[23] The finite conductance within the undoped part at low temperatures is attributed to tip-induced band bending (TIBB),[24] spatially extended across the intrinsic region. We assume that for negative (positive) bias voltages exceeding a certain magnitude, the conduction (valence) band is dragged across the Fermi-level, resulting in an accumulation or depletion layer at the surface. As imaging of the complete heterostructure for both bias polarities was already possible prior to the adsorption of molecules, we can rule out that doping by FePc is responsible for the finite conductance.

III. RESULTS AND DISCUSSION

A. FePc on GaAs(110)

Figure 1(a) shows a constant current STM image of two FePc molecules adsorbed on the (110) surface of intrinsic GaAs. The molecules are found in two inequivalent adsorption geometries, one aligned with the $[\bar{1}10]$ and [001] directions [labeled P in Fig. 1(a)], the other one rotated by an angle of $\pm(25 \pm 3)^\circ$ (labeled R). The lattice directions indicated are the same for Figures 1–3. The adsorption geometry of both species has been determined by bias-dependent imaging as is described in the supplemental material[25] and is shown in Figure 1(b). To probe the electronic properties of adsorbed FePc, we record differential conductance (dI/dV) spectra and acquire corresponding bias-dependent images for FePc in P geometry (data for FePc in R geometry do not qualitatively differ from those). dI/dV spectra of individual FePc molecules exhibit distinct features on the positive and negative bias side, separated by a broad gap of low conductance [Fig. 2(a)]. To resolve metal-centered as well as ligand-centered molecular resonances, spectra were acquired at the center and at the periphery of the molecule. dI/dV spectroscopy of bare GaAs acquired with the same tip apex in the direct vicinity of the molecule shows an apparent band gap of about 2 eV but is featureless where molecular resonances are observed. We attribute this large apparent band gap to TIBB.[26,27] To achieve a high dynamic range in dI/dV spectroscopy, the tip-sample distance is decreased while the bias voltage is ramped [$\Delta z(V)$-curve in Fig. 2(a)]. Spectra acquired with the tip-sample distance kept constant do not qualitatively differ from those, as is clarified by the inset of Fig. 2(a), in which data for a different molecule acquired with a different tip apex are shown (dI/dV data points are averaged over 53 mV). Bias-dependent images at voltages corresponding to different spectroscopic features [Figs. 2(b), 2(c), 2(e), 2(f)] qualitatively differ from each other: When imaging with relatively low absolute bias voltage, exceeding the apparent band gap of GaAs [Fig. 2(e)], the molecule appears as a featureless cross closely resembling the molecules cross-shaped geometry. In contrast, for voltages corresponding to the peak positions, the molecule shows pronounced internal structure. The image of the ligand-centered resonance at a negative bias of −1.7 V [Fig. 2(c)] shows the well-resolved orbital structure of the a_{1u}-orbital, which is the highest occupied ligand-centered orbital.[28,29] In particular, we find that the nodal plane structure revealed in our images corresponds exactly to the structure of the free molecule as calculated by density functional theory (DFT) [cf. Figs. 2(c) and 2(d)].[29–31] The image at a more negative bias voltage, beyond the metal-centered peak in dI/dV spectroscopy at −1.8 V [Fig. 2(b)], shows, in addition to the structure observed at −1.7 V, a pronounced protrusion at the metal center. Consequently, the peak in dI/dV spectroscopy

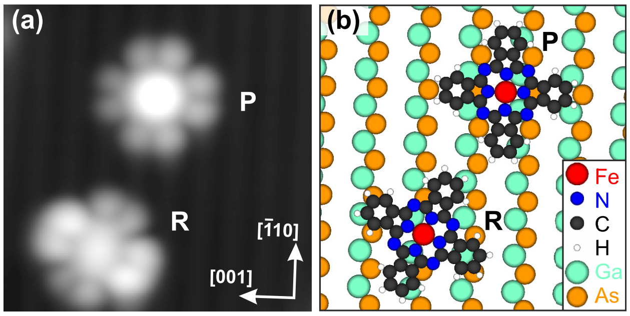

FIG. 1. STM image and geometric model for FePc on GaAs. (a) Two iron-II-phthalocyanine molecules on the (110) surface of intrinsic GaAs in two inequivalent adsorption geometries, labeled P and R. $55 \times 55\,\text{Å}^2$, STM image acquired at −2 V, 3 pA. (b) Model for FePc on the top-layer of relaxed GaAs(110). Images and distances between molecules in (a) and (b) are not to scale.

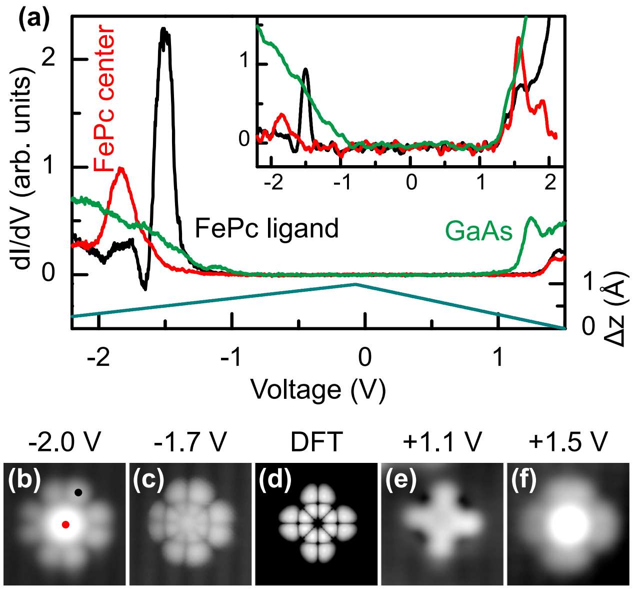

FIG. 2. Tunneling spectroscopy and bias-dependent images of FePc on GaAs. (a) dI/dV spectroscopy at the molecules metal-center (red line) and at the ligand (black line), as indicated by the colored dots in (b). For comparison, a spectrum acquired on bare GaAs (green line) is shown. Whereas the tip-sample distance was varied for the spectra in the main figure (cyan curve, Δz is the change in vertical tip position), it was kept constant for the spectra in the inset. For both bias polarities, distinct peaks are observed and attributed to molecular resonances. (b, c, e, f) While images at absolute bias voltages below molecular resonances show a featureless cross, pronounced intra-molecular contrast is observed for higher absolute values of the bias voltage. $30 \times 30\,\text{Å}^2$, STM images acquired at (from left to right): 3 pA, 1 pA, 2 pA, 1 pA, and bias voltages as indicated. (d) Shows the a_{1u} orbital-density of the free molecule calculated by DFT.

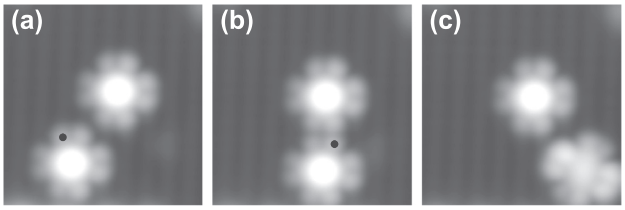

FIG. 3. Series of images showing two FePc molecules, the bottom one is moved and switched into R geometry by current-induced inelastic excitation. The dot indicates the position where current was injected. 50×50 Å^2 STM images acquired at: (a), (b) 3 pA, −2 V and (c) 3 pA, −2.2 V.

at −1.8 V can be attributed to a metal-centered molecular resonance. This fits well to an a_{1g} metal-centered resonance which is expected at an energy close to the highest occupied molecular orbital (HOMO).[29] At positive bias, we observe one peak in dI/dV spectroscopy at about +1.5 V both on the ligand and on the metal center. Correspondingly, the resonance image shows strong intensity distributed across the entire molecule [Fig. 2(f)]. This image shows no pronounced nodal planes, and its appearance would be consistent with an incoherent superposition of two orthogonal e_g orbitals. An incoherent superposition of orbitals in STM imaging is expected if the orbitals in question all contribute to the current. The free molecule has indeed two degenerate e_g frontier orbitals.

The above described observations of well-resolved peaks in dI/dV spectroscopy and the corresponding orbital structures in bias-dependent images are very reminiscent to studies of molecules on ultrathin insulating films.[13,15,20] This proves that the electronic structure of the free molecule is preserved to a large extent upon adsorption. We note that the absolute energies of the FePc's resonances are not straightforward to extract from dI/dV spectra due to TIBB. As the apparent substrate surface corrugation is unperturbed in the direct vicinity of the molecules for both bias polarities, we conclude that the molecule is uncharged at all tunneling conditions used.[32,33] Qualitatively, spectroscopic data and corresponding images for FePc adsorbed on intrinsic and on n-doped GaAs do not differ from each other, except for the positions of molecular resonances in energy, the latter might be due to different TIBB and a change of potential within our heterostructure.

The comparison of the appearance of the molecules in P and R configuration in Fig. 1(a) reveals that the nodal plane structure is the same for both orientations, underpinning the small influence of the substrate. Only differences in the relative height of the different lobes can be observed. Similar differences are also observed for opposite lobes within individual P-type molecules with respect to the [001] direction. We note that this effect was present for all investigated molecules in the P geometry (24 in total). The observed slight differences in lobe intensities are attributed to the different local environment, caused by the polar nature of the GaAs substrate.

FePc can be moved laterally by current-induced inelastic excitation, as shown in Figures 3(a)–3(c).[34] The current required for an inelastic excitation that results in a lateral motion within a few seconds, is in the low pA regime and similar to those for current-induced manipulation processes of molecules on ultrathin insulating films.[35,36] In the case of insulating films, such a high yield was attributed to a strongly increased lifetime of electrons in the molecules due to the electronic decoupling.[13] Similarly, FePc molecules adsorbed in P geometry can be switched into the R geometry (Figs. 3(b) and 3(c)) and vice versa (not shown here). After these current-induced processes, spectra and images are the same as before, confirming that the molecule and the substrate are not damaged, providing further evidence that the bonding to the substrate is weak.

B. NPc on InAs(111)*A*

The broader validity of our findings was verified by STM imaging of NPc molecules on InAs(111)*A*. The InAs(111)*A* surface exhibits features significantly different from those of GaAs(110): a reduced bandgap of 0.42 eV and Fermi-level pinning in the conduction band due to the presence of surface-accumulated electrons,[37,38] preventing TIBB. On the other hand, a feature in common is that InAs(111)*A* is characterized by completely saturated dangling bonds due to its intrinsic (2×2) In-vacancy reconstruction,[39] rendering the surface chemically nonreactive. The Laplace-filtered STM image in Fig. 4(c) shows a NPc molecule adsorbed on a phase boundary separating coherent domains of the (2×2) surface reconstruction. NPc molecules adsorbed on phase boundary lines turn out to be more stable in STM imaging compared to those adsorbed on free terraces, indicating a weaker surface bonding in the latter case. Empty-state imaging at 0.4 V [Fig. 4(d)] reveals an appearance very similar to the lowest unoccupied molecular

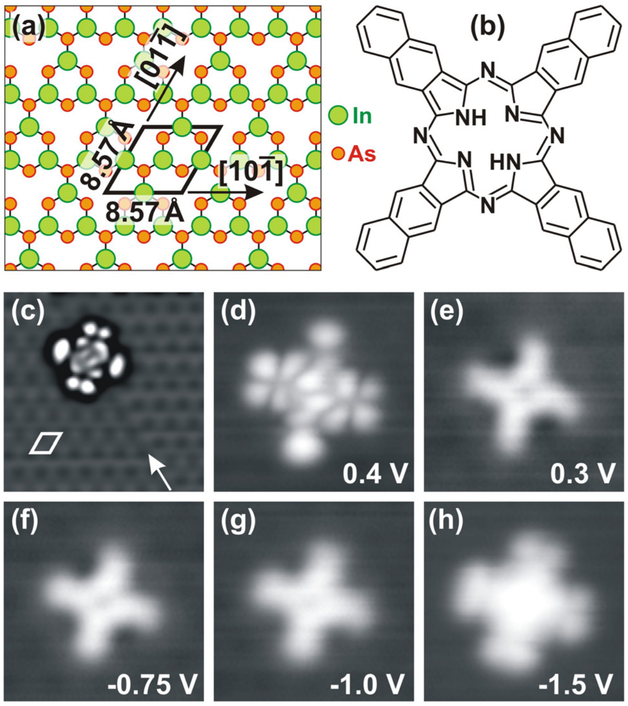

FIG. 4. Geometric model and STM images of NPc on InAs. (a) Stick-and-ball model of InAs(111)*A*-(2×2) characterized by a rhombic unit cell, In surface atoms are shown in green and As atoms in orange. (b) Molecular structure of naphthalocyanine. (c) Laplace-filtered STM image 75×75 Å^2, 0.5 V, 50 pA, showing a NPc molecule adsorbed on a phase boundary (arrow) separating coherent (2×2) domains, the In surface vacancies of the (2×2) reconstruction are imaged as depressions. (d)–(h) Constant-current STM images of NPc, 36×36 Å^2, 50 pA and bias voltages as indicated.

orbital (LUMO) density of free NPc as derived from DFT calculations.[13] For bias voltages between 0.3 V and −1.0 V, Figs. 4(e)–4(g) show the characteristic appearance of cross-shaped in-gap states as observed for NPc on insulating NaCl spacer layers within the HOMO-LUMO gap. Finally, at a bias of −1.5 V [Fig. 4(h)] we find an overall appearance that resembles the calculated HOMO density of free NPc.[13] Our findings prove that the molecular orbitals of adsorbed NPc are only weakly perturbed by the InAs(111)*A* substrate.

Note that the GaAs(110) and the InAs(111)*A* surfaces carry only fully occupied and empty dangling bonds, which apparently is of importance for the weak electronic interaction observed here. This behavior is in contrast to Si surfaces with partially occupied dangling bonds, showing strong reactivity.

IV. CONCLUSION

In conclusion, we studied the electronic properties of individual physisorbed molecules on bare semiconductor substrates in detail. The findings demonstrate that the electronic structure of Pcs is preserved to a large degree upon low-temperature adsorption onto the GaAs(110) and InAs(111)*A* surfaces. This results in molecular resonances well separated in energy allowing for molecular orbitals to be imaged. The energetic alignment of molecular and semiconductor states in such systems may be tailored by doping and material composition of the III–V semiconductor substrate.[40] In addition, the large screening length allows for an electrostatic interaction[41,42] between molecules, which may be used to implement supra-molecular functionality. Thus, our findings offer the prospect of implementing single-molecule functionality on semiconductor substrates, such that versatile inorganic-semiconductor and single-molecule electronics can be combined.

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