When the grafting of double deckers phthalocyanine on Si(100)-2×1 partly affects the molecular electronic structure.

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Abstract

A combined photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM) and density functional theory (DFT) study has been performed to characterize the adsorbate interaction of lutetium bi-phthalocyanine (LuPc₂) molecules on the Si(100)-2×1 surface. Large molecule-substrate adsorption energies are computed and are found to compete with the molecule-molecule interactions of the double-decker molecules. A

particularly good matching between STM images and computed ones confirms the deformation of the molecule upon the absorption process. The comparison between DFT calculations and XP spectra reveals that the electronic distribution in the two plateaus of the bi-phthalocyanine are not affected in the same manner upon the adsorption onto the silicon surface. This finding can be of particular importance in the implementation of organic molecules in hybrid devices.

Introduction

The Silicon (100) surface is one of the most widely studied surfaces due to its use in technologically advanced applications. There have been numerous studies, experimental as well as theoretical, carried out to characterize the surface^{1,2} and its interaction with different types of adsorbates.³⁻⁶ These studies are of interest due to the complex processes that happen at the interface between the substrate and the adsorbate. The adsorption can induce different phenomena like charge redistribution, in both substrate and adsorbate, changing the characteristic features of the adsorbates, substrates and the whole device in general.

In this article, we investigate the interaction between the Si(100):2×1 surface and lutetium bi-phthalocyanine (LuPc₂) molecules. LuPc₂ is one of the first identified intrinsic semiconductors within the phthalocyanine family.⁷ It is composed of two plateaus of phthalocyanine (Pc) that sandwich a Lu ion as depicted in Fig. 1, and it has been considered as an interesting material for use as an active medium in gas sensors based on organic field-effect transistors^{8,9} and resistors.^{10,11} As an active medium its role would be to react with specific gases and through the resulting charge transfer to provide quantitative information about the amount of target molecules present in the environment. An insight into the intra- and inter-molecular charge transfer processes as well as into the role of the substrate will lead to a better understanding of how the performance of molecular electronic devices in general could be improved.

The goal of the present study is to investigate the interaction of LuPc₂ on Si(100)-2 × 1

(pristine Si) and to identify the changes in the molecular features and electronic structure induced by the substrate. By means of a comprehensive and unique combination of experimental and computational techniques, namely X-Ray Photoelectron Spectroscopy, Scanning Tunneling Microscopy and Density Functional Theory, we will demonstrate the influence of the substrate on the electronic properties of the molecule, which affects mostly the lower Pc ring of the molecule, leaving the upper ring only weakly perturbed.

Experimental and Theoretical Methods

The photoelectron spectroscopy measurements were performed at MAX-lab, the Swedish national synchrotron facility, on beam line (BL) D1011.¹²

Core level XPS spectra were taken using VG Scienta SES-200 electron energy analyzer in normal emission of the photoelectrons. Photon energies of 330 eV and 470 eV were used for the C 1s and N 1s core levels, respectively. The overall resolution of the core level spectra was about 60 meV. A Shirley background was removed from all XPS spectra¹³ and all spectra have been normalized in intensity to unity for the main structure. The binding energy (BE) scale has been calibrated with respect to the silicon Si 2p peak at 99.16 eV.

STM measurements were performed at the Paris Institute of Nanosciences, with a commercial, variable temperature, STM system consisting of interconnected preparation and analysis chambers. A tungsten tip, etched *ex-situ* in NaOH solution and afterwards heated *in-situ* to remove the oxide layer, was used. All measurements were performed at room temperature at a base pressure in the low 10^{-11} mbar range. The STM images were treated using Gwyddion software.¹⁴

N-doped Si(100) surfaces, provided by Siltronix, were prepared using a standard procedure described in previous works¹⁵ and characterized by low energy electron diffraction or STM. The measurements were performed on clean Si(100)- 2×1 vicinal and nominal surfaces

and comparisons with passivated Si(100)- 2×1 surfaces were carried out.

LuPc₂ molecules (see Fig.1) were synthesized following literature methods.¹⁶ A Knudsen cell type evaporator from Ferrovac was used to evaporate LuPc₂ molecules, which were outgassed for a few hours at 250°C until recovering the base pressure (low 10^{-10} mbar range). During the molecular deposition, the crucible was heated resistively to around 300°C, while keeping the vapor pressure in the 10^{-9} mbar range.

The thicknesses of the organic films were estimated from photoelectron spectroscopy data using a so-called overlayer method,¹⁷ monitoring the change in intensity of the Si 2p peak upon absorption of LuPc₂.

Density Functional Theory (DFT) calculations were performed with the plane wave based code VASP.¹⁸⁻²¹ In all calculations, the Brillouin zone was sampled at the Γ -point and the electronic states were described in the projector augmented wave (PAW) method^{22,23} with a kinetic energy cutoff of 400 eV. The many-body effects between the electrons manifesting in correlation and exchange energy, were accounted with the semi-local generalized gradient approximation in the flavour of PBE²⁴ in the single particle picture drawn by DFT. This set up was used to compute adsorption energies and structures, as well as XPS spectra of the C and N atoms in LuPc₂ and STM images.

In detail, starting points of the geometry optimizations were several initial geometries distributed over the simple Si(100) 2×1 surface lattice with a spacing of 0.5 Å in x and y directions. The optimized gas-phase LuPc₂ molecule was deposited at a minimal distance of 3.3 Å perpendicular to the substrate. The reconstructed Si(100) 2×1 was built with the experimental lattice constant (a_0) of 5.431 Å in three layers where the lowest layer was passivated with hydrogen atoms being optimized in a separate calculation. The structural optimizations, performed until all Hellman-Feynman forces were less than 0.02 eV/Å, included van der Waals (vdW) forces described by the Tkatchenko-Scheffler method.²⁵ The adsorption energies were calculated as total energy difference between the adsorbed system, e.g. LuPc₂/Si(100), the energy of the single molecule and the bare surface.

Employing the optimized structure with the largest adsorption energy, final state calculations in the framework of DFT were performed with the VASP code.^{18–21} The binding energies E_b of the core-level electrons of the N and the C atoms were the focus of our investigations. The PAW method^{22,23} modified by Köhler²⁶ was used to account for the core ionization. For each of the 16 N atoms and the 64 C atoms in the LuPc₂ molecule, the relative binding energies were obtained by comparing the energy difference between the core ionized system with a $1s^1$ configuration and the system in its ground state for each of the N and C atoms separately. Relaxation effects of the electronic density are included in the final state approach via the relaxation of the remaining electrons in the presence of the core-hole.

Here we distinguish between two types of core-level shifts. The first one labeled as Δ_{BE} is the shift due to the different chemical environment within the molecule, e.g. binding energy of atom C_i is compared to the one of C_j . The other shift is δ_{BE} , which compares the binding energy of the same atom before and after adsorption. The Δ_{BE} and δ_{BE} are averaged over the same kind of atoms (pyrrole and benzene like carbon atoms for C 1s and pyrrole and aza-bridge like nitrogen atoms for N 1s). They provide information about the strength of the chemical change induced via adsorption in an averaged way (Δ_{BE} and δ_{BE}) and about the largest changes ($\max\{BE\}-\min\{BE\}$). Also the distribution width, computed as standard deviation σ_{BE} , helps to reveal convolution effect in the experimental spectra.

STM images were simulated based on the Tersoff-Hamann²⁷ approximation, e.g. the band decomposed charge density from DFT calculations is interpreted as being proportional to the conductance measured in the experimental STM images. This approach has been able to obtain good agreement for similar systems^{28,29}

The charge redistribution and transfer were computed based on the charge density difference driven by the interaction between the molecule and the surface. The charge transfer can be obtained by employing the charge transfer curve $\Delta\rho_{xy}(z)$. The latter one is the curve of the in-plane charge differences plotted over the adsorption direction z . If this curve is integrated from quasi-infinity to the neutral charge plane between the molecule and the

substrate, the charge transfer between molecule and surface can be estimated.²⁸

Results and discussion

XPS and DFT

DFT calculations were performed to gain a detailed understanding of the physical mechanisms occurring during the adsorption. The computed adsorption energies are found between 2.99 eV and 4.63 eV and the corresponding geometries of the adsorbed molecules become deformed through the strong chemical interaction with the substrate. The lowest energy structure with an adsorption energy of 4.63 eV, which was used to calculate the binding energies for all non-equivalent carbon and nitrogen atoms, is shown in Figure 2a. In this structure, the molecule has three of the isoindole rings, belonging to the lower Pc ring, bent towards the substrate, while the remaining one is lifted away from it. In the upper part of figure 2b, the non-equivalent nitrogen atoms are indicated in the top ring while in the lower part, the C atoms that are chemically bond to the surface, are highlighted. Figure 2c shows the changes in the charge density due to the adsorption of the molecule on the substrate. The DFT calculation demonstrates that a charge accumulation, shown in dark red colour, is observed between the C and Si atoms, indicating the formation of bonds between the molecule and the substrate. Meanwhile, charge depletion regions, shown in light blue colour, are observed around the pi orbitals of the molecule, resulting in the conservation of charge. The observed changes are mostly dominant at the interface, while the upper Pc ring does not undergo major changes of the charge density. The total charge redistribution between the Si surface and the LuPc₂ molecule, resulted in 0.28e/molecule being transferred from the Si surface to the LuPc₂ molecule. This is illustrated in Fig. 2d, which shows the charge transfer curve along adsorption direction. The formation of dipoles within the molecule, between upper and lower Pc ring, and between the lower Pc ring and the Si surface can

be noticed. A further indication for the chemical interaction of the six C atoms (C_{ben}^{Si}) of the lower ring with the surface are their computed short distance of less than 2.1 Å with Si atoms of the surface, which is similar to the distance of 1.8 Å already calculated for C_2H_4 on Si(100) surfaces.³⁰

Figure 3 shows a comparison between the experimentally obtained N 1s (a) and C 1s (b) core level spectra for a thick layer of LuPc₂ on a hydrogenated Si surface³¹ and a thin layer of LuPc₂ on a pristine Si substrate together with the calculated Δ_{BE} for the respective core level atoms. The Δ_{BE} s have been calculated for a D_{4h} symmetric molecule (gas-phase) and for an adsorbed molecule on the pristine Si surface, and their relative positions have been aligned to the maximum intensity of the experimental results for easier comparison. The C 1s spectrum of the thick film is formed by an intense peak at 284.1 eV, attributed to the electrons coming from the benzene-like atoms (C_{ben}), a lower peak at 285.2 eV, attributed to pyrrole carbon atoms (C_{pyr}) and a broad, low intensity feature observed around 286.8 eV due to shake-up structure. The N 1s spectra on the thick layer is formed by one main peak at 398 eV coming from two non-equivalent N atoms - one in the pyrrole ring that is directly bound to the lutetium atom (N_{pyr}) and the aza-bridge, which is connecting the isoindole groups (N_{aza}). The shoulder on the higher binding energy side at 398.9 eV is ascribed to shake-up features from both N species.

Two major changes affect the nitrogen and carbon XP spectra in the case of the thin layer adsorbed on the pristine silicon : a general shift to higher binding energy and a broadening of the overall spectra. The systematic shift to higher BE for both carbon and nitrogen core levels is in apparent contradiction with the prediction of 0.28e/molecule being transferred from the substrate to the molecule, that should result in a decrease of the BE for the thin layer as evidenced on metal systems.³² In our case, two phenomena contribute to the energy shifts: the change in the valence cloud (i.e. charge redistribution and transfer between substrate and molecule as calculated in DFT) and the screening from the surrounding atoms, molecules and silicon substrate. Both effects typically differ in sign and can result in a small core-level

shift to either higher or lower binding energy. Moreover, no BE shift is observed on the Si 2p core level that could also be an indication of the charge transfer suggesting that in the case of Pc adsorbed on silicon, screening effects are dominant due to the strong interaction between the molecule and the substrate. The latter fact is reflected in the large adsorption energies found in DFT.

In the case of the D_{4h} molecule,³³ the XPS energies have the typical splitting of 0.18 eV due to the chemically different nitrogen species (N_p and N_a) in the molecule (Fig. 3a). For the adsorbed molecule, the core-level calculations reveal that the additional spread of the experimental XPS spectra arise from the deformation and adsorption of the molecule on the Si surface. When disentangling the BE positions for each of the Pc rings, we observe that the binding energies of N 1s core level are perturbed for both Pc rings. We note that the BEs of N atoms of both Pc rings, that are directly bound to the metal center are more affected than the aza-bridge N atoms. Due to the complex electronic interaction between surface and molecule as well as the distortion of the Pc molecule, the maximum spread of the BE is much larger for the lower Pc ring, having a maximum spread of 0.58 and 0.53 eV for pyrrole and aza-bridge N atoms, respectively. The Δ_{BE} and δ_{BE} can be found in Tab. 1 together with the maximum spread in BE positions is given.

Similarly, Fig. 3b shows a comparison between the experimental C 1s spectra and the calculated Δ_{BE} for all C atoms. In order to compare the calculated Δ_{BE} with the experimental results, we align the average BE of C_{ben} to the maximum peak position of the experimental data. The interaction with the pristine Si substrate, as in the case of N 1s, leads to a wider spread of the BE of the C atoms with chemically different surroundings. The analysis of the Δ_{BE} reveals that even though only six benzene carbons (C_{ben}^{Si}) form chemical bonds with the Si substrate, the BE positions of the rest of the carbons, notably the non-bonded carbon atoms of the bottom Pc, are also strongly affected. The average Δ_{BE} between benzene type carbons (C_{ben}) and pyrrole type carbons (C_{pyr}) is 1.2 eV for a single molecule and 1.1 eV for C atoms of the top Pc ring of the adsorbed molecule, which is consistent with previous

studies of similar systems.³⁴ For the bottom Pc of the adsorbed molecule, the BE positions are rather different, having a maximum spread in the BE of 0.48 eV for the C_{pyr} and 0.78 eV for the C_{ben} atoms. Even though the Δ_{BE} between the C_{ben} and C_{pyr} is 1.4 eV in the case of non-bonded C atoms and 0.95 eV for chemically bonded C atoms, the average Δ_{BE} remains similar to the “gas-phase” single molecule calculations with Δ_{BE} of 1.2 eV between the C_{ben} and C_{pyr} contributions. This provides an explanation of why no major changes upon adsorption, except the broadening of the peak width, can be observed. Interestingly, the (C_{ben}^{Si}) atoms have very small σ_{BE} and Δ_{BE} , which points towards chemical equivalence and indicating as well the formation of bonds.

From the comparison between experimental XPS core level spectra and DFT calculations, we have evidenced that the adsorption process mainly affects the lower ring of the molecule for the C atoms, whereas both rings are affected for the N contribution although to a smaller extent.

STM and DFT

The sub-monolayer of LuPc₂ on pristine Si was imaged using STM at room temperature and can be seen in Figure 4. One can observe single molecules as well as clusters of molecules on the surface appearing as light grey and white protusions. On the Si surface, white small spots are also present that are most likely caused by water molecules on the surface, whereas dark spots are rather missing silicon atoms or dimers and both defects occupy less than 2% of the surface. We did not observe any preferential adsorption sites (e.g. steps or step edges, defects, missing Si dimers) nor a dimer oriented adsorption. But in most of the cases (70 %), the molecules seem to adsorb with the molecular plane parallel to the Si surface. However, one can observe that the molecules start forming clusters already from sub-monolayer coverages.

From the experimental STM images one can conclude that the molecule-molecule interaction is strong, and that the surface-molecule interaction is also strong. This gives two competing interactions acting on the LuPc_2 . It appears unlikely that the molecules possess a high mobility after adsorption, since there is no experimental observation of a uniform reordering or redistribution of the molecules on the surface. The calculations of vdW energy, performed for the first time to our knowledge on LuPc_2 molecules staggered in the vacuum, confirm these observations, giving a large value of 2.7 eV. For this calculation, we estimate the attractive interaction distance to be more than 1 nm., which is very close to the range of adsorption energies obtained for some possible adsorption geometries, and analog to adsorption energies of other phthalocyanines^{28,29} These results hint at a possible deposition/adsorption mechanism for this case. The long-ranged vdW interaction attracts the free molecules which are about to hit the surface to the ones that are already adsorbed in random positions. The scarce mobility on the Si surface crystallises these adsorption configurations. We argue that in general, the complex interplay between the double decker structure and different kinds of competing interactions might, in the case of LuPc_2 on pristine Si, result in a complex adsorption process and structure, and specifically a van der Waals guided clustering of the molecules on the surface.

In Fig.4 (1-2-3-4-5), selected molecules from the large scale STM image of Figure 4 (top), with different adsorption sites, are displayed. The majority of the molecules have the typical four lobes structure (Fig.4 (1-2-3)) observed for LuPc_2 ,³⁵ the direction between the lobes corresponding to the benzene ligand axis of the lower ring. Other molecules present a structure having instead two brighter lobes, denoting a large number of adsorption geometries of the molecules (Fig.4 (4-5)). In order to elucidate the interaction with the pristine Si substrate, we calculated STM images using DFT calculations for the single molecules adsorbed on the $\text{Si}(100) - 2 \times 1$ surface that have the largest energy adsorption. The simulated STM images in Fig.4 (A-B-C), match very well with the experimentally observed molecular shape in Fig.4 (3-4-5). When adjusting carefully the contrast, one can note that the four lobes do

not show the same height as it was seen on the large scale image (Fig.4 top) with a grey scale. This behavior reflects the small tilt of the upper Pc ring with respect to the substrate, which is caused by the deformed lower Pc ring, resulting in a height difference of the outer parts of these isoindole rings of about 0.1 Å, as shown in the DFT calculation. The lower Pc ring being rotated by 45° with respect to the upper Pc ring, the non-bonded isoindole ring of the lower Pc causes a lifting of two Pc rings of the upper plane due to repulsion of the electron clouds, leading to a non flat lying molecule as observed on the Fig.4 (3-4-5). The adsorption of the LuPc₂ molecules does not induce a large variation of the shape of the upper Pc ring, while the calculations reveal a strong perturbation of the lower Pc ring. Due to the relatively close distance of the Pc rings to the substrate of about 3.2 Å, the deformed lower Pc ring still affects the upper ring, although to a smaller extent, resulting in small conjugations and then in a small change in the overall height of the molecule as observed on the experimental image.

The comparison of the experimental and computed STM images confirms the deformation of the lower ring of the LuPc₂ when adsorbed in a flat lying geometry on the pristine silicon surface and DFT calculation reveals a large molecular-molecular interaction.

The combined investigation by XPS, STM and DFT revealed that in the more stable configurations, the molecules adsorb rather flat on the silicon (100)-2 × 1 surface but in deformed geometries. Indeed, a bonding through the carbon atoms in the lower ring lead to a distorted geometry of the molecules for which a calculated charge transfer of 0.28e/molecule is found. The large adsorption energies between 3 eV and 4.6 eV indicates a great molecule-substrate interaction entering in competition with the large molecule-molecule interaction of 2.7 eV computed for the first time on double-decker phthalocyanines. This competition leads to the formation of clusters even at very initial coverage as evidenced by STM. A more important finding concerns the redistribution of the electronic cloud due to the adsorption onto silicon. The nitrogen atoms from both plateaus are weakly affected by the bonding with silicon,

whereas for carbon atoms the electronic contribution in the lower plateau of the double decker is much more modified, leaving the upper plateau unaffected by the bonding. This particular result can be of great interest for possible future implementations in electronic devices, where the molecule’s electronic characteristics would be preserved even on highly reactive substrate like pristine Si.

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Figure 1: LuPc₂ molecule optimized by DFT (B3LPY).

Figure 2: (Colour online) Results of the DFT calculations. The obtained structure of the adsorbed molecule is shown in (a). In (b) the upper and lower Pc rings are shown separately, indicating the different N species on the top ring and the chemically bonded C atoms (C_B^{Si}) on bottom ring. In part (c) the charge density difference due to the formation of chemical bonds is shown in blue indicating the gain in charge density and in red indicating the loss in charge density. This difference is mainly located at the lower Pc ring at the C_B^{Si} atoms. The same charge density difference $\Delta\rho_{xy}(z)$ is plotted in (d) related to the distance Z above the Si surface.

Figure 3: (Color online) Comparison between the experimental XP spectra of the N 1s (a) and C 1s (b) and binding energies for a thin layers of LuPc₂ on pristine Si and thick layers of LuPc₂ on a hydrogenated Si substrate. The thicknesses of the adlayers are indicated in the figures. The calculated BEs for “gas phase” single molecule (D_{4h}) and adsorbed molecule are summarized at the bottom of the N 1s and C 1s spectra. The calculated BE shifts are aligned to the intensity maxima of the experimental results.

Figure 4: $32 \times 40 \text{ nm}^2$ STM image of LuPc₂ on the pristine Si surface taken with a bias voltage of -2 V (top) and several different adsorption geometries from 1-5 as well as several calculated STM images with different adsorption geometries indicated letters A-C in (bottom).

Table 1: Upper table: The calculated Δ_{BE} 's for the “gas phase” single molecule (D_{4h}) are calculated relative to the C_P and N_P BE's, respectively. Lower table: The calculated Δ_{BE} 's for an adsorbed molecule on the pristine Si surfaces are calculated relative to the BE's of C_P and N_P in the D_{4H} molecule. The averaged Δ_{BE} 's over similar atoms of either the top or bottom Pc ring are indicated together with a maximum spread between the corresponding atoms. All values are given in eV.

LuPc ₂ (D _{4h})		Δ_{BE}	max{BE}-min{BE}
	C_{py}	0	0.00
	C_{ben}	-1.15	0.20 ¹
	N_p	0.0	0.00
	N_a	-0.18	0.00

LuPc ₂ /Si		Δ_{BE}	max{BE}-min{BE}	δ_{BE}	σ_{BE}
top Pc	C_{pyr}	-0.03	0.09	0.03	0.03
	C_{ben}	-1.11	0.25	0.04	0.09
	$C_{ben,i}$		0.05		0.07
	$C_{ben,m}$		0.08		0.02
	$C_{ben,o}$		0.06		0.02
	N_p	-0.46	0.07	0.46	0.03
	N_a	-0.37	0.06	0.20	0.03
bottom Pc	C_{pyr}	0.24	0.47	0.3	0.15
	C_{ben}	-1.13	0.78	0.04	0.22
	$C_{ben,i}$		0.61		0.28
	$C_{ben,m}$		0.46		0.20
	$C_{ben,o}$		0.43		0.17
	C_{ben}^{Si}	-0.71	0.18		0.07
	N_p	-0.34	0.58	0.34	0.28
	N_a	-0.31	0.53	0.23	0.23