Reconstruction dependent growth of lead phthalocyanine layers on GaAs(001) surfaces

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We have investigated the adsorption of lead phthalocyanine (PbPc) layers on GaAs(001)-$c(4 \times 4)$ and (2×4) reconstructed surfaces. Samples with different PbPc coverages from submonolayers up to $\approx$20-nm-thick layers were prepared under ultra-high vacuum conditions and investigated by scanning tunneling microscopy (STM) and reflectance anisotropy spectroscopy (RAS). The STM measurements showed different adsorption geometries of the PbPc molecules on the different reconstructions. The RAS results revealed that these different adsorption geometries in the first monolayer induce different molecular arrangements within thicker adsorbed layers on the two different substrates. These results give strong evidence for an epitaxial-like growth mode of PbPc molecules on GaAs(001) surfaces driven by the atomic arrangement of the GaAs surface. We could also demonstrate RAS as a powerful tool to analyze the growth behavior of thin organic layers.

I. INTRODUCTION

Organic-inorganic semiconductor heterostructures involving metal phthalocyanine (MPc) layers have attracted a growing scientific and industrial interest because of their applications in electronic or optoelectronic devices[1] such as organic field-effect transistors (OFETs),[2] organic light-emitting diodes (OLEDs, displays),[3] organic solar cells,[4] or gas sensors.[5,6] In MPc layers, the electrical conductance of the organic layer depends crucially on the orientation of the molecules within the layer.[7] The control of the molecular ordering within organic layers is therefore an important aspect for the improvement of many electronic and optoelectronic devices that involve organic layers. Several parameters have already been considered to influence molecular layer growth on semiconductor surfaces, such as the substrate temperature, evaporation rate, and postevaporation annealing[8] or the atomic structure of the substrate surface.[9–13,37]

In this work, we present investigations on the influence of the atomic surface structure on the growth mode and molecular orientation of organic lead phthalocyanine (PbPc) layers. PbPc is an organic ringmolecule composed of four isoindole groups with a central Pb^{2+} ion standing out of the macrocycle (see Fig. 1).[9] The out-of-plane position of the Pb ion gives rise to an optical anisotropy and is leading to different possible adsorption geometries such as the Pb ion pointing either toward or away from the surface.[14]

In order to investigate the influence of the atomic surface structure on the adsorption geometry of PbPc molecules, different GaAs(001) reconstructions were used as substrates. The GaAs(001) surface offers various stable and well ordered reconstructions with different surface symmetries.[16–19] Adsorption experiments on these surfaces revealed that the atomic structure of the GaAs(001) surface can influence the adsorption process of smaller organic molecules significantly.[20–25] In this work, we concentrate on the two As-rich GaAs(001) reconstructions $c(4 \times 4)$ and (2×4).

II. EXPERIMENTAL

All experiments were carried out under ultra-high vacuum (UHV) conditions with a base pressure below 2×10^{-10} mbar. GaAs(001) epilayer substrates doped with Si ($n = 3.5 \times 10^{17}$ cm^{-3}) were grown by molecular beam epitaxy (MBE). A capping layer of amorphous arsenic protects the surface for a contamination-free transfer through air.[26,27] The clean GaAs(001)-$c(4 \times 4)$ surface reconstruction was obtained by thermal desorption of the amorphous protection layer at 350 °C ($\pm$20 °C) inside the UHV chamber.[27,28] The (2×4) reconstructed surfaces were prepared by further annealing up to 430 °C ($\pm$20 °C). The clean reconstructed substrates showed a well ordered $c(4 \times 4)$ and (2×4) low-energy electron diffraction (LEED) pattern, respectively, and were held at room temperature during growth and characterization.

PbPc molecules were obtained commercially (ABCR). For the sublimation of PbPc at about 350 °C ($\pm$20 °C), a well degassed water cooled Knudsen cell was used. The evaporation rate of 0.5 monolayer/min was calibrated by comparing the element concentration measured by Auger electron spectroscopy (AES) and was later on confirmed by scanning tunneling microscopy (STM) observations. For the submonolayer preparation, a deposition time of 30 s was followed by annealing at about 300 °C for 15 min. The preparation and adsorption processes were monitored by reflectance anisotropy spectroscopy (RAS). STM measurements on the PbPc submonolayers were performed at room temperature. The bias values refer to the sample voltage with respect to the STM tip.

III. RESULTS

A. PbPc on GaAs(001)-$c(4 \times 4)$

During the deposition of thicker PbPc layers on the surface, the adsorption process was monitored online by RAS. Figure 2(a) shows the RAS spectra in the range from 1.45 to
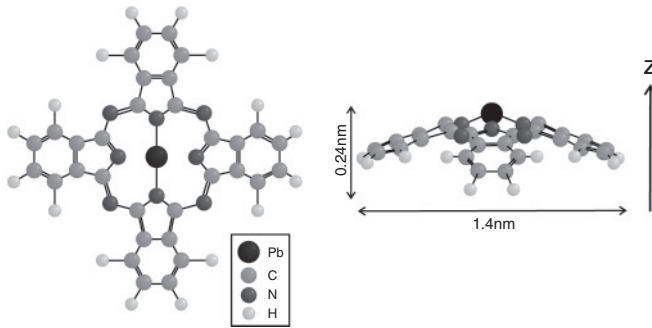
FIG. 1. Structure model (top and side views) of PbPc according to Papageorgiou *et al.*[15]

5.0 eV with increasing coverage up to about 20 nm PbPc on the $c(4 \times 4)$ reconstruction as determined from atomic force microscopy (AFM) and AES measurements. With increasing PbPc coverage, the characteristic RAS signature of the clean $c(4 \times 4)$ reconstructed surface disappears. At the same time, new negative anisotropies arise at 1.5, 2.0, 2.6, 3.45, and 4.5 eV, which increase steadily with increasing PbPc layer thickness. Up to this thickness, no saturation of the RAS intensity at these energies is observed. For a better visualization of the changes in the RAS signature upon adsorption, Fig. 2(b) shows the difference between the spectrum of the clean surface and the thick PbPc layer on the GaAs(001)-$c(4 \times 4)$ substrate.

In order to elucidate the origin of these new anisotropies, the features of the spectrum in Fig. 2(b) were compared to the optical transition energies of PbPc molecules. Edwards *et al.*[29] identified the optical transitions of PbPc in vapor phase at 1.78 (Q), 1.94 (Q), 3.73 (B), and 4.43 eV (N band). These transition energies are indicated by solid grey lines in Fig. 2(b). For PbPc molecules evaporated onto quartz substrates, Seoudi *et al.*[30] determined the optical absorption bands at 1.69 (Q), 1.85 (Q), 2.79 (Q), and 3.53 eV (B band). These transition
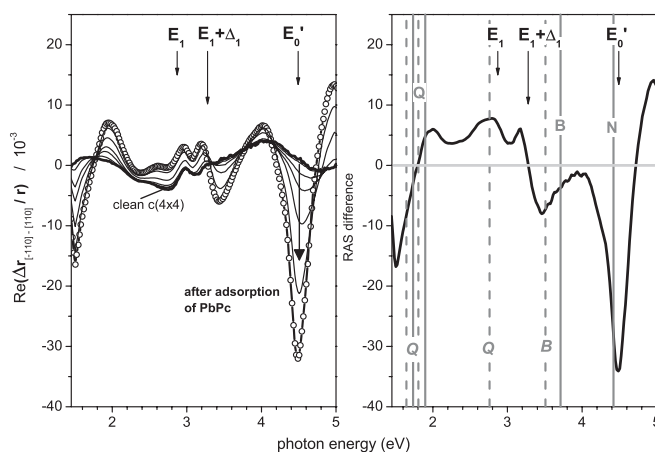

FIG. 2. (a) RAS spectra of clean GaAs(001)-$c(4 \times 4)$ (black line) and after deposition of 20 nm of PbPc (open circles). (b) Difference spectra between the RAS after adsorption of the 20-nm PbPc and the clean $c(4 \times 4)$. Positions of molecular absorption bands of PbPc in vapor phase (solid grey lines) and on quartz glass (dashed grey lines). The new anisotropies after PbPc can be attributed to intramolecular transitions.

energies are indicated by dashed grey lines in Fig. 2(b) and are not equal to the transition energies of PbPc in vapor phase.

As Fig. 2(b) shows, the new anisotropies observed in the RAS spectra after PbPc deposition lie approximately at the same energetic positions as the optical transitions determined by Seoudi *et al.*[30] and Edwards *et al.*[29] Because of this agreement and since the new anisotropies increase steadily with increasing layer thickness, we can explain the new anisotropies occuring upon PbPc deposition to result from intramolecular absorption bands of the PbPc molecules but not from transitions at the bulk critical points of GaAs.

The comparison shows that the new anisotropies do not agree exactly with the transition energies determined by Edwards *et al.* and Seoudi *et al.*[29,30] but experience a slight shift to smaller energies, which is also found to increase with increasing layer thickness. This energetic shift can be explained to result from intermolecular interactions, which are not present in the reference data taken in vapor phase. The shift to lower energies observed in our spectra is slightly larger than the shift of the transitions energies at PbPc deposited on quartz glass.[30] Within a PbPc layer deposited on an amorphous substrate, we expect randomly oriented molecules and hence less intermolecular interaction than in a well ordered molecular layer. A nearly linear shift to smaller photon energies as observed for the new anisotropies in Fig. 2 could likewise originate from increasing intermolecular interactions with increasing layer thickness. We therefore expect the intermolecular interactions to be stronger in the layer deposited on the GaAs(001) substrate than on the quartz glass, which results in a slightly larger shift of the transition energies to lower photon energies.

Since the optical transition moment lies in the plane of the Pc ring,[36] the PbPc is in-plane optically isotropic but exhibits an optical anisotropy in z direction. The observed molecule-induced anisotropies in the RAS spectra can thus only result from a tilting of the molecules within the layer with respect to the surface normal.

Since the intensities of the observed anisotropies increase with increasing coverage, we suggest that the molecules in all layers are tilted following the first monolayer. In order to check for this assumption, we performed STM measurements for a submonolayer deposition of PbPc. Figure 3 shows an STM image of a PbPc submonolayer on GaAs(001)-$c(4 \times 4)$ recorded at a voltage of -2.94 V and current of 0.52 nA. The image shows the typical brickstone-like structure of the As-As dimer triplets of the $c(4 \times 4)$ surface.[31,32] Besides the structures of the GaAs surface, several objects can be observed in the STM image and each object consists of four smaller protrusions giving rise to a four-leaf clover shape. These bright protrusions are typical for the four isoindole groups of the PbPc molecule and have also been observed on several other substrates.[14,33–35] Therefore each four-leaf-clover object relates to one PbPc molecule. In the STM image, all adsorbed PbPc molecules show a dark center in the middle between the four isoindole groups. In several other investigations of PbPc adsorption on different substrates,[14,33,35] this dark center was interpreted to result from a molecular adsorption geometry with the Pb atom pointing toward the surface substrate. In case of PbPc on MoS_2,[14] molecules with dark and bright centers were found, meaning that both configurations of the
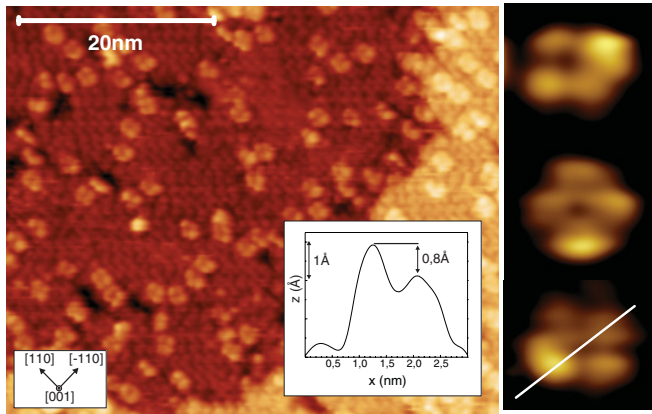
FIG. 3. (Color online) STM images of single PbPc molecules adsorbed on GaAs(001)-$c(4 \times 4)$ ($U_G = -2.94$ V). All molecules show a dark center indicating an adsorption geometry with the Pb atom pointing toward the surface. Also, one isoindole group always appears brighter than the others, revealing a tilting angle of approximately 6°.
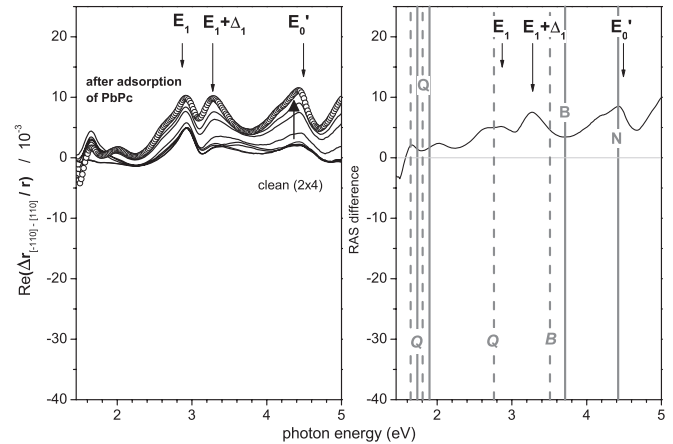

FIG. 4. (a) RAS spectra of clean GaAs(001)-(2 × 4) (black line) and after deposition of 20 nm of PbPc (open circles). (b) Difference spectra between the RAS after adsorption of 20 nm of PbPc and the clean (2 × 4). Positions of molecular absorption bands of PbPc in vapor phase (solid grey lines) and on quartz glass (dashed grey lines) are shown. After PbPc adsorption, there are no new anisotropies that relate to intramolecular transitions of the adsorbed PbPc.

position of the Pb ion could be observed simultaneously. Since we observed dark centers for the PbPc molecules only, we conclude that all molecules are adsorbed with the Pb atom pointing toward the $c(4 \times 4)$ surface.

In Fig. 3, the three detail images of single adsorbed molecules show that within one molecule, one isoindole group always appears brighter than the other three isoindole groups. A line scan across such brighter isoindole groups reveals a height difference of approximately 0.08 nm, as depicted in Fig. 3. The observed contrast difference could result from two different effects. If the PbPc molecules form a chemical bond to the topmost surface layer with one of the isoindole groups, this group could appear brighter due to a charge transfer to the molecule caused by the bond formation. On the other hand, in this case, the optical anisotropy would not increase with the deposition, since only the first molecular layer could form such bonds. However, as such an increase is observed in Fig. 3 only a geometric tilting of the single molecules can explain that one of the isoindole groups appear brighter as a result of a true height difference. A quantitative evaluation of 50 molecules observed in a large scale STM measurement shows that the molecular plane experiences an average tilting angle of 6°(±1.5°) with respect to the surface. A statistical analysis of the azimuthal molecular orientation in the STM image shows that the diagonally opposite isoindole groups of the molecules do not align along the [110] and [$\bar{1}$10] crystalline axes of the GaAs substrate but more likely 45° rotated to them. This observation gives evidence for a preferential orientation within the molecular layer which explains the observed anisotropies in the RAS spectrum.

B. PbPc on GaAs(001)-(2 × 4)

Similar to the PbPc deposition on the $c(4 \times 4)$ surface, thicker PbPc molecular layers were prepared by subsequent PbPc deposition on the clean GaAs(001)-(2 × 4) surface. The adsorption process was monitored by RAS. Figure 4 shows the RAS spectra recorded for increasing PbPc coverages on a (2 × 4) reconstructed GaAs(001) surface up to a layer

thickness of about 20 nm ($\approx$80 monolayers). The development of the RAS spectra shows a behavior that is significantly different from the spectra recorded at the $c(4 \times 4)$ surface. The spectra in Fig. 4(a) show a small increase of the anisotropies related to the bulk critical transitions E_1 (2.9 eV), $E_1 + \Delta_1$ (3.3 eV), E_0' (4.5 eV), and E_2 (5.4 eV). However, any new anisotropies at the molecular transition energies between 2.1 and 5.0 eV are not observed. Only small new anisotropies show up below 2.0 eV that could correlate to Q band transitions of gas-phase PbPc, which lie at 1.78 eV.[29] This is explained by an interaction between the transition moments of adjacent molecules, since the Q band is assigned to a $\pi - \pi^*$ transition.[36] All higher energetic molecular transitions do not give rise to any anisotropies. Since the molecule is optically isotropic in the molecular plane but anisotropic in z direction, the RAS spectra in Fig. 4 therefore indicate that the adsorbed molecules are oriented with their plane parallel to the substrate surface. Another explanation for the observed optical isotropy of the PbPc layer on GaAs(001)-(2 × 4) could be domains where the respective anisotropies cancel out each other. However, on a homogenous substrate surface as in the case of GaAs (2 × 4), the evolution of such domains seems rather unlikely. Also, an arrangement of differently oriented molecular domains is not known for PbPc. Thus we conclude that the observed optical isotropy results from a molecular layer consisting of PbPc molecules with the molecular plane parallel to the surface.

Figure 5 shows a typical STM image of a submonolayer of PbPc adsorbed on the GaAs(001)-(2 × 4) surface. The image was taken at a bias voltage of -4.81 V and a current of 0.07 nA and shows the typical dimer rows of the (2 × 4) surface. Additionally, bright protrusions can be observed on top of the rows. These protrusions have an average height of 0.27 nm and an average diameter of 1.7 nm. Considering the theoretical height of 0.24 nm and width of 1.4 nm[15] of the domed molecule, these dimensions allow the bright protrusions to be identified as single adsorbed PbPc molecules lying on the
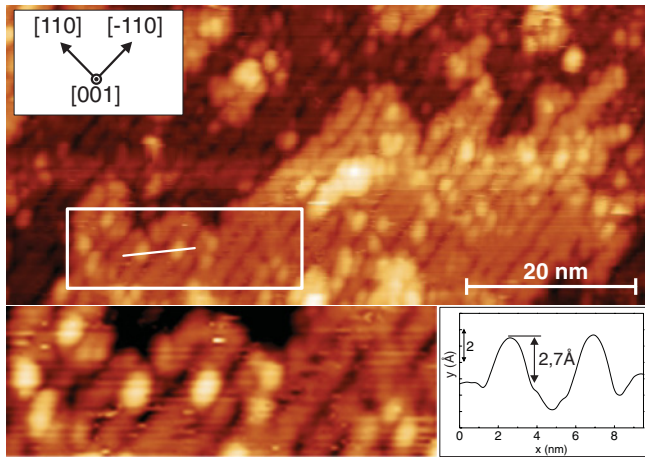
FIG. 5. (Color online) STM images of PbPc adsorbed on GaAs(001)-(2 × 4) ($U_G = -4.81$ V). All molecules show a bright center indicating an adsorption geometry with the Pb atom pointing away from the surface.

FIG. 6. Adsorption model for the epitaxial-like growth of thicker PbPc layers on the GaAs(001)-$c(4 \times 4)$ (a) and (2 × 4) (b) reconstruction with tilted and flat lying molecules, respectively. In (a) a higher angle than the experimentally determined 6° was chosen for demonstrative reason.

surface with their normal perpendicular to the surface. All of the adsorbed PbPc molecules appear with a bright center and no visible substructure of the molecule. The molecular center is the highest point of the molecule as shown in the respective line scan in Fig. 5. These observations differ significantly from the STM measurements at the $c(4 \times 4)$ surface and suggest an adsorption geometry with the Pb^{+2} ion above the molecular plane.

IV. INTERPRETATION AND DISCUSSION

The measurements presented above reveal remarkable differences between the adsorption behavior of PbPc on the two different reconstructions of GaAs(001). STM measurements indicate a planar adsorption geometry of PbPc on the (2 × 4) reconstruction with the Pb ion above the molecular plane. The RAS spectra furthermore indicate an optically isotropic and thus planar arrangement of the PbPc molecules in the PbPc layer unchanged upon increasing molecular layer thickness.

On the $c(4 \times 4)$ reconstruction, on the contrary, the molecules in the first adsorbed monolayer experience an adsorption geometry with their Pb ion pointing toward the GaAs surface and a tilting angle between the molecular plane and the surface. The RAS measurements reveal new anisotropies resulting from intramolecular absorption that increase with increasing layer thickness. This suggests an optically anisotropic and thus nonplanar arrangement of the molecules in the PbPc layer originating in the first monolayer. The intensity of the observed anisotropies increases with increasing deposition for the adsorption on the $c(4 \times 4)$, whereas on the (2 × 4), the RAS signature remains essentially the same. This indicates that the orientation of the PbPc molecules remains approximately the same for the different deposition steps, following the orientation in the first monolayer.

The results show that the PbPc orientation within the molecular layers is crucially depending on the atomic structure of the GaAs surface. STM measurements indicate that these different growth modes are indeed induced by different adsorption geometries of the PbPc molecules in the first
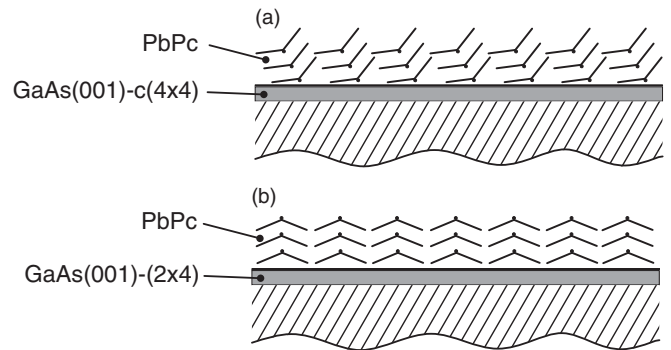
monolayer. A schematic illustration of the two different growth modes is depicted in Fig. 6.

In conclusion, we can state that the growth of PbPc very likely does not take place with a one-to-one relationship between adsorbent and substrate because of their very different lattice parameters. The increasing stress during the growth usually causes a relaxation into its organic bulk structure within 1–5 monolayers leading to a rough columnar surface morphology.[36,37] In the case of PbPc on GaAs(001)-(2 × 4) and $c(4 \times 4)$ surface reconstructions, the unequal RAS signatures of thicker layers prove the different morphological properties induced by the first monolayer. So even in case of a relaxation, the structural properties are conserved. Strictly speaking, this growth process is different from the common form of epitaxy of group IV and III-V semiconductors,[38] but because the variation of the atomic ordering of the substrate surface induces different adsorption geometries of the PbPc molecules in the first monolayer, these results evidence an epitaxial-like growth of PbPc layers on GaAs. This finding allows a controlled preparation of differently ordered molecular layers, which opens up perspectives for the controlled preparation of molecular layers.

V. SUMMARY

We have investigated the adsorption and layer growth of PbPc on the GaAs(001)-(2 × 4) and $c(4 \times 4)$ surface reconstructions from a submonolayer up to a 20-nm-thick layer by RAS and STM. On the $c(4 \times 4)$ reconstruction, the PbPc molecules are adsorbed with the Pb ion pointing toward the surface and a tilting angle between the molecular plane and the surface. This adsorption geometry induces an anisotropically ordered layer growth of PbPc on the $c(4 \times 4)$ surface. At the (2 × 4) surface, PbPc is adsorbed with the Pb ion pointing away from the surface. This adsorption geometry results in the growth of an optically isotropic layer with a planar arrangement of the PbPc molecules.

It could be shown that the orientation of the molecules in the first monolayer is followed by the next layers with increasing deposition, indicating an epitaxial-like growth mode of the PbPc layers. The results also show that the adsorption geometry of the first adsorbed monolayer depends

on the atomic ordering of the substrate and induces different epitaxial-like growth modes of PbPc layers on GaAs(001). We could also demonstrated that RAS is a powerful tool to monitor thin organic layer growth.

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