

# Evidence for strong interaction of PTCDA molecules with defects on sulphur-passivated GaAs(100)

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## Abstract

Raman spectroscopy was employed to investigate the initial stage of interface formation between 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) molecules and sulphur passivated GaAs(100) surfaces. Monitoring the Raman spectra for submonolayer coverage as well as after annealing above the desorption temperature of PTCDA reveals the presence of a C-H mode which is shifted by  $13\text{ cm}^{-1}$  towards lower frequency compared to its value in bulk PTCDA. The molecules remaining at the surface after annealing are proposed to interact with surface defects predominantly induced by the dopant atoms. This proposal is supported by density functional theory calculations considering the interaction of dopant atoms with single molecules.

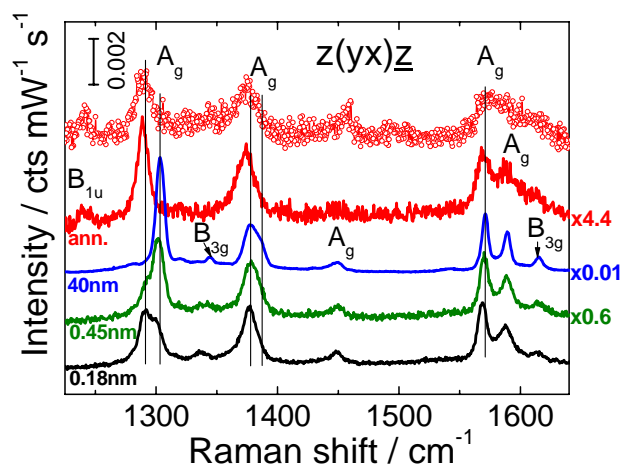
The use of thin organic interlayers in metal/inorganic semiconductor junctions is a promising direction for applications in high-frequency and microwave technology [1]. For instance, the usage of the perylene derivative 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) in hybrid Ag/PTCDA/GaAs junctions results in a lowering of the operating voltage [1]. Furthermore, the current-voltage characteristics can be systematically varied by the PTCDA layer thickness [1]. The complex interplay between chemistry, structure and electronic band alignment at the metal/semiconductor interface also strongly affects the device performance. The structural properties of PTCDA films deposited by organic molecular beam deposition (OMBD) onto Se-passivated GaAs(100) interfaces were assessed by means of low energy electron diffraction (LEED) and scanning tunnelling microscopy (STM)[2-4], while the electronic properties of the same interfaces were investigated by X-ray and ultraviolet photoemission spectroscopies (PES) [5]. Both STM and PES results indicate that the first PTCDA molecules arriving on the surface are pinned at chemically active defect sites. After saturation of defects the subsequently arriving molecules experience a weaker interaction with the chalcogen modified surface due to the passivation of surface dangling bonds. The preferential adsorption of molecules at defect sites reduces the inhomogeneous Fermi level pinning while hardly changing the band bending in the GaAs substrate [5]. Raman spectroscopy probes the light scattering by internal vibrational modes stemming from the movement of various groups of atoms in the molecule and hence it is very sensitive to the nature of the molecule-substrate and molecule-molecule interaction [6,7]. The region of the most intense vibrational modes with C-H bending character was monitored during PTCDA growth onto Se-GaAs(100) [6]. For PTCDA thicknesses above 1.8 nm the spectra resembled those in a single crystal, hence the interaction between the PTCDA molecules and the Se-passivated GaAs substrate was proposed to be weak and comparable with intermolecular interaction.

In this letter the Raman spectra of sub-monolayer coverages of PTCDA on S-passivated GaAs(100) are analysed and compared with theoretical frequency calculations in order to explore the initial interface formation. The detection of the Raman signal for such low coverages was achieved using an excitation energy in resonance with the  $S_0$ - $S_1$  absorption band of PTCDA.

Si-doped ( $N_d=2.7 \cdot 10^{18} \text{ cm}^{-3}$ ) GaAs(100) wafers provided by Freiberger Compound Materials were used as substrates. In order to clean and passivate the surface, the GaAs substrates were wet-chemically treated under atmospheric conditions. They were first degreased of organic contaminants by successively dipping into acetone, ethanol and de-ionised water in an ultrasonic bath, for 5 min each. The etching in  $\text{S}_2\text{Cl}_2+\text{CCl}_4$  solution (1:3) removes the oxides and chemically passivates the surface dangling bonds with sulphur atoms. The substrates are then rinsed in acetone, ethanol and de-ionised water to stop the etching process. The sulphur atoms in excess and residual alcohol molecules sticking to the surface are removed by annealing at 620 K in the OMBD chamber with a base pressure below  $2 \times 10^{-8}$  Pa. The resulting surface has a  $2 \times 1$  reconstruction reflected in the sharp low energy electron diffraction (LEED) diffraction pattern. By analogy to a recent model proposed for Se-passivated GaAs(100): $2 \times 1$  surfaces [8] the treatment results in gallium-sulphur layers terminated by single S atoms [9]. The bulk structure starts only with the fifth layer from the surface. The band bending is reduced compared to the epi-ready substrate [9]. However, for the Se-passivated GaAs(100): $2 \times 1$  system, it was shown that defects related to doping atoms cannot completely be removed [8,9].

PTCDA molecules purchased from Lancaster Synthesis were thermally evaporated in ultra-high vacuum (UHV) onto the freshly prepared  $2 \times 1$  reconstructed S-GaAs(100) substrates maintained at room temperature. The evaporation rate was 0.3 nm/min as determined by a quartz microbalance and an external calibration by means of atomic force microscopy. The thickness of one monolayer (ML) is defined as the amount of PTCDA molecules ( $7.6 \cdot 10^{15} \text{ cm}^{-2}$ ) that cover the entire surface assuming flat-lying PTCDA molecules:  $1 \text{ ML} \cong 0.32 \text{ nm}$ . The UHV chamber is optically aligned with a Raman spectrometer, allowing *in situ* measurements to be performed. The Raman spectra were excited with the 2.54 eV line of an  $\text{Ar}^+$  laser. The scattered light is collected by a Dilor XY 800 triple monochromator with a multichannel charge coupled device detector. The spectral resolution was  $\sim 3 \text{ cm}^{-1}$  and  $\sim 3.5 \text{ cm}^{-1}$  for the thicker and thinner films, respectively, as determined from the full width at half maximum (FWHM) of the laser line spectrum. Typical values of the incident laser power were in the range from 50 mW to 100 mW below the damage threshold of the absorbing PTCDA films ( $\sim 100 \text{ kW/cm}^2$ ).

Theoretical calculations were performed with the B3LYP functional and the 3-21G basis set using the Gaussian'98 package [10]. A mode assignment is made according to ref. [11].



**Figure 1.** Raman spectra in the region of C-C and C-H modes for several thicknesses of PTCDA films on S-GaAs(100) and after annealing a 14 nm thick film for 30 min at 623 K (top), taken in crossed polarization. The top-most spectrum was recorded after annealing a 20 nm thick film grown on H-Si(100) substrate at 683 K for 15 min.

The evolution of PTCDA modes with contributions from C-C and C-H vibrations as a function of film thickness was recorded in  $z(y,x)$ - $z$  polarization configuration (with  $x = [001]$ ,  $y = [010]$ ,  $z = [100]$  defined by the GaAs substrate) and is presented in fig. 1. All spectra are normalized to the height of the  $\nu_{C-C} + \delta_{C-H}$  mode at  $1572 \text{ cm}^{-1}$ . The thicknesses of the as-deposited films were calculated from the deposition time and frequency shift of the quartz microbalance. The Raman spectrum of a 40 nm thick PTCDA/S-GaAs(100) layer is considered as reference, since it resembles in terms of line-shape and frequency positions that of PTCDA single crystal.

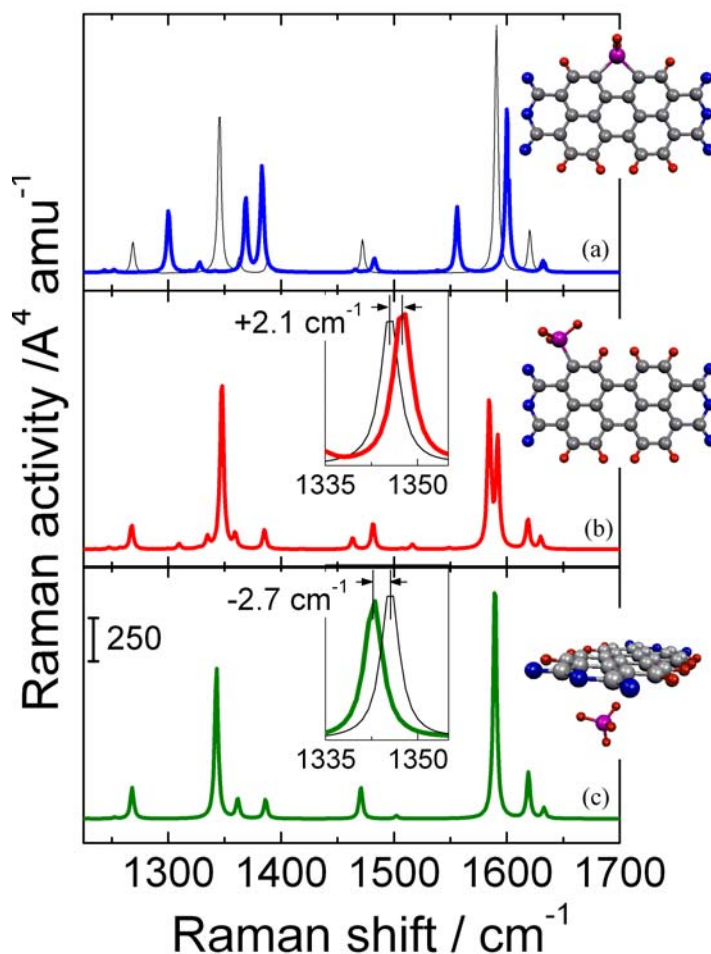
Several differences can be noticed when comparing the spectra of the 0.18 nm with that of the 40 nm thick PTCDA film. A novel mode is observed with high intensity at  $1290 \text{ cm}^{-1}$ . The other modes are shifted towards lower frequencies, *e.g.* with  $\sim 2.4 \text{ cm}^{-1}$  for the C-C stretching mode at  $1572 \text{ cm}^{-1}$ . The amount of shift is reduced for the modes at  $1303 \text{ cm}^{-1}$  (C-H bending) and  $1572 \text{ cm}^{-1}$  upon increasing thickness to 0.45 nm. The intensities of these modes increase, while that of the  $1290 \text{ cm}^{-1}$  band remains almost constant. Obviously, there are molecules experiencing a different type of interaction in the initial phase of adsorption compared to the inter-molecular interaction specific to thicker films and single crystal PTCDA. The spectral contribution and hence the number of such molecules remains almost constant upon increasing the coverage above 0.18 nm.

Further insight in the molecule - substrate interaction and the origin of the new band at  $1290 \text{ cm}^{-1}$  is obtained by annealing a 14 nm thick PTCDA film at 623 K for 30 min. This temperature is higher than the desorption temperature for PTCDA multilayers determined to be 598 K for PTCDA on glass substrates [12]. Thus only molecules experiencing a bonding to the substrate stronger than the inter-molecular interaction should remain on the GaAs surface. The spectrum after annealing is shown in the upper part of fig. 1. By comparing the height of the C-C mode at  $1572 \text{ cm}^{-1}$  for the annealed and the as-deposited 0.18 nm film a number of molecules corresponding to  $\sim 0.04 \text{ nm}$  nominal coverage is evaluated as remaining on the surface, *i.e.* approximately 1/8 of a ML. However, it must be noted that a precise determination of the absolute number of molecules from the Raman peak intensities may be limited by a number of parameters, *e.g.* the growth mode or the resonance conditions. Recent photoemission measurements have shown from the attenuation of the substrate core levels that the PTCDA growth mode at room temperature on Se- as well as on S-passivated GaAs(100) [13,14] surfaces is layer plus island - like. Thus the first monolayer (ML) should be complete before the second one starts to form and hence the signal from a 0.18 nm film most probably originates only from molecules in direct contact with the substrate. In the following it will be shown that the interaction between the molecules and the surface after annealing does not involve the disruption of the molecule and hence should not modify significantly the resonance conditions. Therefore the relative change in the intensity of the C-C mode when comparing the spectra of the as-deposited 0.18 nm and the annealed film is expected to give a reasonable estimate on the number of the molecules remaining on the surface after annealing.

At the doping level used in this experiment ( $N_d = 2.7 \cdot 10^{18} \text{ cm}^{-3}$ ), the number of Si dopant atoms on the GaAs (100) surface should be at least  $10^{12} \text{ cm}^{-2}$  among  $6 \cdot 10^{14} \text{ cm}^{-2}$  surface atoms. Furthermore, previous investigations of ZnSe films grown on GaAs(100) have shown that already upon annealing at 553 K for 40 min Si dopant impurities diffuse towards the GaAs surface leading to the occurrence of silicon clusters [15]. Considering PTCDA molecules lying flat on the substrate at a nominal coverage of 0.04 nm would correspond to  $\sim 10^{13} \text{ cm}^{-2}$ , *i.e.* sufficient to cover all surface defect sites induced by Si dopant atoms. Further evidence for the interaction of molecules mainly with the Si dopant atoms is provided by the similarities between the spectra recorded after annealing the 14 nm PTCDA film grown on S-GaAs(100) and after annealing of a 20 nm PTCDA film grown on H-passivated substrate (top-most spectrum in fig. 1). Additional defect sites such as missing S atoms, substrate domain boundaries and step edges [3] may also be present and can probably explain the large value of  $10^{13} \text{ molecules/cm}^2$ . Recalling the STM [3] and PES [5] studies showing that the PTCDA molecules arriving first on the Se-GaAs surface interact with defects, it appears from the present experiment that the molecules remaining on the surface after annealing are the same entities as those first arriving at the surface.

In the spectrum after annealing the band at  $1303 \text{ cm}^{-1}$  is entirely replaced by the novel mode at  $1290 \text{ cm}^{-1}$ . This is a clear hint to the origin of the band at  $1290 \text{ cm}^{-1}$  as being a shifted

variant of the  $1303\text{ cm}^{-1}$  mode in agreement with the argument used for molecules adsorbed at Ag(111) substrates [16]. The band at  $1290\text{ cm}^{-1}$  is thus proposed to be characteristic for molecules having direct contact to the surface defects, while the band at  $1303\text{ cm}^{-1}$  is characteristic for molecules in a molecular crystalline-like environment.



**Figure 2.** Calculated Raman spectra (thick lines) for a PTCDA molecule bonded to one Si atom via two  $\sigma$ - bonds (a), one  $\sigma$ - bond (b) and for a PTCDA molecule with a passivated Si atom below the molecular plane (c). The calculated spectrum of a neutral molecule is shown for comparison in the graph (a) and in the insets (b) and (c) by the thin continuous lines. The Raman bands were modelled with Lorentz oscillators having a FWHM of  $3.5\text{ cm}^{-1}$ .

The  $0.18\text{ nm}$  coverage PTCDA corresponds to a number of molecules that is about four times larger than the number of molecules remaining on the surface after annealing. Thus the corresponding Raman spectrum should contain three types of contributions: from molecules in contact with defects, from molecules in contact with the passivated surface and from molecules interacting also with other molecules. The experimental spectrum, however, appears as a combination of the spectra of molecules interacting with defects and of the spectra of thick films. The intensity of the  $1290\text{ cm}^{-1}$  mode is approximately equal to that of the  $1303\text{ cm}^{-1}$  mode. The

intensity ratio of these modes reflects that at least half of the molecules at the surface are not interacting exclusively with the surface defects. Consequently, the molecules interacting with the passivated surface must contribute to the spectrum in a similar way as the molecules involved in inter-molecular agglomerations, hence the strength of the interaction between the molecules and the passivated GaAs surface is likely to be comparable to that of the inter-molecular interaction. This conclusion is similar to previous results obtained for PTCDA/Se-GaAs(100) interfaces by means of STM [3] and PES [5].

Considering the adsorption of the PTCDA molecules at surface Si dopant atoms (or other defects) at the GaAs surface, several mechanisms may be involved.

The prediction of the Raman spectra corresponding to the PTCDA molecules interacting with Si defects requires the knowledge of the adsorption geometry as well as theoretical tools capable to handle systems with a large number of atoms comprising the PTCDA molecule and the first five layers of the S-GaAs substrate (see experimental section). To our knowledge there exists neither experimental evidence regarding the location of the Si defects with respect to the surface sites nor regarding the adsorption geometry of the PTCDA molecules on the defects. The calculation of the Raman spectra within the Gaussian package is possible only under coarse approximations of the molecule - defect interaction. Therefore the calculated Raman spectra can be only qualitatively compared to the experimental ones.

Charge transfer between a molecule and one defect was first considered and approximated by charging an isolated PTCDA molecule with one positive or negative elementary charge. Frequency calculations with the B3LYP:3-21G functional predict dramatic shifts for the C-C stretching Raman modes [17], that are not detected in the spectra after annealing.

In a second approach complexes consisting of a PTCDA molecule and one Si atom are considered and the corresponding Raman spectra are calculated with the same functional. The high affinity of Si atoms having dangling bonds to form  $\sigma$ -bonds with C atoms was experimentally proven by the chemisorption of maleic anhydride onto clean non-passivated Si(100):2x1 surfaces accompanied by the rehybridization of the C atoms from  $sp^3$  to  $sp^2$  [18]. Therefore complexes having  $\sigma$ -bonds between one Si atom and carbon atoms of the perylene core of PTCDA were considered. As can be seen in the calculated Raman spectra in fig. 2 (fig. 2 (a) and (b)), the formation of two  $\sigma$ -bonds between Si and PTCDA also leads to dramatic shifts of all modes, whereas the C-H Raman modes of the complex with a single  $\sigma$ -bond are slightly shifted towards higher frequencies. Thus none of the two complexes can explain the spectral changes observed upon annealing.

Finally calculations for a single Si atom with all valence electrons saturated with H atoms situated below the molecular plane of PTCDA were performed. Most of the modes in the spectral region of interest shift to lower frequencies by at most  $1.5\text{ cm}^{-1}$ , while the mode at  $1346\text{ cm}^{-1}$  (calculated for isolated molecule,  $1303\text{ cm}^{-1}$  in experiment) experiences the largest amount of shift ( $2.7\text{ cm}^{-1}$ ) to lower frequencies (fig. 2 (c)). This situation provides the best qualitative match to the experimentally observed shift, but the amount of shift is still lower than the experimentally observed one. The amount of accompanying static charge transfer from the PTCDA molecule is only 0.007 of an elementary charge. Besides strengthening the assignment of the mode at  $1290\text{ cm}^{-1}$  as being a shifted variant of the  $1303\text{ cm}^{-1}$  these calculations also show that small changes in the molecular environment can lead to significant frequency shifts for modes with pure C-H deformation character.

Here, an additional feature of the Raman spectra after annealing should be noted. A normally infrared active band ( $B_{1u}(y)$ ,  $\delta_{C-H}$ ) occurs at  $1243\text{ cm}^{-1}$ . Its presence can either be explained by a symmetry lowering to  $C_v$  for the molecules adsorbed at defect sites (by analogy with the case of  $D_{6h}$  molecules [19]), or by a dynamical charge transfer [20]. Therefore the molecules are proposed to interact with surface defects due to Si dopant atoms via a dynamic charge transfer modulated by molecular vibrations and/or accompanied by a molecular deformation.

In summary, the combination of Raman spectroscopy and frequency calculations of internal molecular modes with B3LYP:3-21G functional was employed to assess the initial stage of

PTCDA/S-passivated GaAs(100) interface formation. The molecules with a different spectral signature compared to those in a molecular crystalline environment are proposed to be adsorbed at defects mainly due to Si dopant atoms at the GaAs surface. The interaction involved is sufficiently strong to retain these molecules at the surface upon annealing above the desorption temperature of PTCDA. A comparison of the experimentally observed characteristic features and the calculated spectra excludes static transfer of an elementary charge or the formation of  $\sigma$ -bonds between the Si atom and the molecule as being responsible for this interaction. However, the observed break-down of selection rules points to an interaction mediated by dynamical charge transfer. From the similarity between the spectral response of molecules arriving at the surface after the defects are saturated and that of molecules in a crystalline environment, the interaction between PTCDA molecules and the S-passivated surface is estimated to be comparable to the inter-molecular one.

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