Growth and Properties of Ultra-Thin PTCDI-C8 Films on GaN(0001)

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Abstract: Ultra-thin PTCDI-C8 films are vapor-deposited under ultra-high vacuum (UHV) conditions onto surfaces of p- or n-doped GaN(0001) samples. The X-ray photoelectron spectroscopy (XPS) results reveal a lack of strong chemical interaction between the PTCDI-C8 molecule and the substrate. Changes in the electronic structure of the substrate or the adsorbed molecules due to adsorption are not noticed at the XPS spectra. Work function changes have been measured as a function of the film thickness. The position of the HOMO level for films of thicknesses 3.2–5.5 nm has been determined. Energy diagrams of the interface between p- and n-type GaN(0001) substrates and the PTCDI-C8 films are proposed. The fundamental molecular building blocks of the PTCDI-C8 films on GaN(0001), assembled by self-organization, have been identified. They are rows of PTCDI-C8 molecules stacked in “stand-up” positions in reference to the substrate, supported by the π–π bonds which are formed between the molecular cores of the molecules and monomolecular layers constituted by rows which are tilted in reference to the layer plane. The layers are epitaxially oriented. The epitaxial relation between the rows and the crystallographic directions of the substrate are determined. A model of the PTCDI-C8 film’s growth on GaN(0001) substrate is proposed. The 3D islands of PTCDI-C8 molecules formed on the substrate surface during film deposition are thermodynamically unstable. The Volmer–Weber type of growth observed here is a kinetic effect. Rewetting processes are noticeable after film aging at room temperature or annealing at up to 100 °C.

Keywords: thin films; organic layers; PTCDI-C8; semiconductors; GaN(0001)

1. Introduction

There are two main factors determining the electric charge transport inside active layers of organic electronic devices: the molecular structure of the molecules constituting the layer and the supra-molecular organization of the layer. The first one depends on the current abilities of organic synthesis, which, until present, has achieved very high precision in adjusting the electronic properties of the molecules through their chemical modification [1–4]. The second one depends on interactions between the molecules and direct interactions between the substrate and the molecules. The charge transport in an organic semiconductor layer is directional. It prefers a characteristic direction. In the case of low-molecular-weight semiconductors, this is the direction of π stacking. Molecular disorder along this direction substantially lowers charge carrier mobility. It is therefore important from a practical point of view to produce optimally arranged organic films to minimize the negative effects of molecular disordering on the film’s conductivity. There is also still very little known about the substrate’s influence on the interactions responsible for the π stacking.

The N,N’-dioctyl-3,4:9,10-perylene tetracarboxylic diimide (PTCDI-C8) is one of the best n-type organic semiconductors currently available [5–8]. The electron mobility mea-
sured for organic thin-film transistors based on PTCDI-C8 equals up to ~1.7 cm²/Vs [5]. The molecule (C₄₀H₂₀O₄N₂) consists of a planar core and two alkyl chains on opposite sides. Its high molecular stability in air enables its operation in ambient conditions. The PTCDI-C8 molecules relatively easily organize themselves into supra-molecular architectures through hydrogen bonding, metal ion coordination and π stacking [9,10]. There are few studies on the properties of PTCDI-C8 thin films and they have been performed on various substrates such as SiO₂ and Al₂O₃; so far these molecules have not been studied on GaN(0001) [11,12].

GaN(0001) is the most frequently studied surface of gallium nitride (GaN). In combination with thin organic films, GaN surfaces offer several unique properties. The wide band gap of GaN allows optical access through the substrate and makes it easier to align the highest occupied and lowest unoccupied molecular orbitals of the organic film with the substrate band edges. It permits more flexibility in device design and, in the case of applications dependent on the charge transport across the interface, it increases the possibility for molecular control of the electronic properties of the hybrid organic–inorganic system [13–15]. Due to its high electron mobility, chemical stability under physiological conditions, nontoxicity and biocompatibility, GaN is a very attractive material for biosensors [16–19]. It has been shown that by using the GaN thin-film high-electron-mobility transistors one can electrically detect proteins, antibodies, glucose and strands of DNA selectively and with high sensitivity [17,18].

The aim of the study reported herein is to characterize substrates’ influence on the morphological, structural and electronic properties of PTCDI-C8 adsorption films on GaN(0001). The decisive factor for undertaking these experiments has been a willingness to identify substrate properties that have an influence on both the type of direct chemical bond between the molecules and the substrate and on the nature of the intermolecular bonds between the molecules inside the adsorption layer as well.

2. Experimental Details

The substrates used were 10 µm thick, (0001)-oriented, p-GaN (Mg-doped, 10¹⁸ cm⁻³) and n-GaN (Si-doped, 10¹⁸ cm⁻³) epitaxial layers deposited on Al₂O₃ (Technologies and Devices International, An Oxford Instruments Company, Oxford, UK). Typical size of the sample was about 4 × 8 mm². The samples were ex situ degreased in isopropanol, and then washed in distilled water and dried in air. Before organic film evaporation, the substrate was in situ annealed at about 800 °C to remove any residual gases. This procedure allowed for the reduction of oxygen and carbon contaminations; however, they were not completely eliminated.

The samples were characterized in two separate UHV setups at room temperature (RT), using scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and low-energy electron diffraction (LEED) techniques. The first setup included a VT STM/AFM microscope (Omicron,). The imaging was accomplished in the constant current mode using a tungsten tip. WSxM software (version number 5.0) was applied to analyze the STM results [20]. The XPS/UPS measurements were performed in the second UHV setup, equipped with Mg and Al anodes (Mg Kα (1253.6 eV) and Al Kα (1486.6 eV) lines) and a He I line (21.2 eV) radiation source. Due to the signals overlapping the Mg anode was used for the substrates N 1s and Ga 3d’s lines measurements; the adsorbates C 1s and O 1s’ lines were measured using the Al anode. Emitted photoelectrons were collected by a hemispherical electron energy analyzer (Phoibos 100-5, SPECS, Germany) with a pass energy of 10 or 2 eV and step size of 0.1 or 0.025 eV for core-level lines or a valance band, respectively. Optical axis of the analyzer entrance was normal to the substrate surface. The Fermi level position (E_F) was found by UPS measurement on a clean Au sample. The threshold of photoemission, which corresponds to the vacuum level of the sample, was also measured with a voltage (~5 V) applied to the samples to clear the detector’s work function. The XPS spectra were analyzed using KolXPD (Kolibrik.net, Prague, Czech Republic) and/or CasaXPS software (version
number 2.3.19 PR1.0). Deconvolution of the XPS peaks was modeled using Gaussian and Lorentzian line shapes and a Shirley-type background subtracting. LEED measurements were carried out in the energy range 0–300 eV with a step of 0.5 eV; diffraction patterns were recorded using a CCD camera.

Organic films of PTCDI–C8 molecules (98% purity, Sigma-Aldrich, MilliporeSigma, Burlington, MA, USA) were deposited by physical vapor deposition (PVD) on the substrates kept at room temperature (RT) under UHV, with a base pressure of ~10^{-10} Torr. The temperature of the quartz crucible used as the evaporator was about 300 °C. The evaporation rate at this temperature did not exceed 0.6 nm/min. The efficiency of the evaporator was calibrated by means of a quartz crystal resonator. The organic film growth and its characterization were performed step by step. In the case of XPS/UPS measurements, the average thickness of PTCDI-C8 films was additionally controlled on the bases of the Ga 3d substrate’s line intensity decay (measured with the Mg anode) following the progress of adsorption layer growth, assuming a mean free path of electrons λ in PTCDI-C8 layer equal to 2.84 nm [21]. In the case of STM observations, the amount of deposited adsorbate was counted directly from the STM topographies.

3. Results

3.1. Samples Characterization Prior to Deposition

Prior to PTCDI-C8 deposition, the surface quality of the samples was evaluated by means of STM, LEED, XPS and UPS. Extended-area STM topographies of the p- and n-type GaN(0001) showed regularly stepped surfaces with a very small number of defects (Figure 1a,b). Their long-range atomic order was revealed by LEED (Figure 1c). Satisfactory STM imaging required relatively high bias voltages of around +5 V for p-type samples and about −5 V for n-type ones. The surfaces of the p- and n-GaN samples, subjected to the same cleaning procedures, did not differ in surface topography. The presence of terraces, which were tens of nanometers wide and a half or single GaN bi-layer high, were typical for both types of samples.

![Figure 1. STM images of (a) p-GaN(0001) surface (imaged area equals to 1 × 1 µm², V_s = 5.1 V, I_t = 43.5 pA) and (b) n-GaN(0001) surface (1 × 1 µm², V_s = −5.1 V, I_t = 55.4 pA). Dark points correspond to the ends of screw dislocations. (c) Characteristic for both samples, the diffraction pattern exhibits hexagonal 1 × 1 structure with lattice constant of 0.319 nm (in this case the pattern is taken from an n-type sample by applying primary electron beam of energy equal to 150 eV). The arrow corresponds to <2110> direction in the real space.](image)

XPS analysis of the samples revealed a surface oxygen concentration of approximately 20%. Unfortunately, carbon impurities could not be eliminated from the surfaces. The n-GaN surface exhibits a higher concentration of carbon contaminants compared to the p-GaN substrate. For both samples, the main N 1s and Ga 3d lines consisted of the same components. An example of the result of the deconvolution of these lines for p-GaN is presented in Figure 2. The Ga 3d line has four components (Figure 2a). The dominating one corresponds to Ga–N bonds. The component located at a higher binding energy relates to the presence of residual oxygen. The component denoted as Ga–Ga correlates to a metallic bond between gallium atoms [22]. Three components of the N 1s line are demonstrated in Figure 2b. The first one originates from Ga–N bonds, constituting the bulk of the line
Ga correlates to a metallic bond between gallium atoms [22]. Three components of the N 1s line are demonstrated in Figure 2b. The first one originates from Ga–N bonds, the second one comes from the surface Ga–N bonds; and the third one relates to nitrogen–hydrogen bonds (N–Hx) [23].

![Figure 2. Components of (a) Ga 3d and (b) N 1s lines from p-GaN surface. See text for details.](image)

The XPS analysis performed for n-GaN looks similar; however, the Ga 3d and N 1s lines are shifted by about 0.5 eV towards a higher binding energy. This comes from the different Fermi level locations on both p- and n-type surfaces [24].

The UPS spectra of the substrates, measured before PTCDI-C8 deposition, revealed the typical spectra for semiconductors. The position of the valence band maximum (VBM) can be determined by extrapolating the inclinations of the spectral curve in the region of the lowest binding energies (directly below the \( E_F \)). A predictable shift of the valence band edges between p- and n-type samples was observed. The VBM is at 1.7 eV and 3.1 eV for p- and n-type GaN, respectively. An example of the UPS spectrum for p-GaN is presented in Figure 3. The electron affinity of the GaN(0001) surface amounts to 4.0 eV and 3.3 eV, respectively, for p-GaN and n-GaN, as calculated from the relationship

\[
\chi = \hbar \nu - W - E_g,
\]

where \( \hbar \nu = 21.2 \text{ eV} \) is the energy of photons; \( W \) is the width of the recorded spectrum, measured as the energy difference between the VBM and the cut-off threshold of the spectrum; and \( E_g = 3.4 \text{ eV} \) is the GaN band gap width. The obtained results of the VBM’s position and electron affinity are in line with other studies [22, 25].

![Figure 3. The UPS spectra measured for p-GaN(0001) samples prior to PTCDI-C8 deposition. Inserts depict the position of VBM.](image)

### 3.2. The PTCDI-C8 Thin Films’ Growth

The HOMO level signal becomes clearly visible in the UPS spectra when the thickness of the PTCDI-C8 film reaches 3.2 nm. An example of the UPS spectrum for the molecules on p-GaN is presented in Figure 4. The UPS results showed that the HOMO levels are located 1.9 eV and 2.2 eV below the \( E_F \) for the p- and n-GaN substrates, respectively.

Following the film’s growth, changes in the work function \( \phi \), calculated from the expression

\[
\phi = \hbar \nu - E_{\text{cut-off}},
\]

where \( E_{\text{cut-off}} \) is the cut-off threshold of the spectrum, follow different paths for p- and n-samples, as is seen in Figure 5. For p-GaN, \( \phi \) keeps the value of 5.7 eV characteristic for the bare substrate up to an average film thickness \( d = 3.0 \text{ nm} \).
d = 3.2 nm onwards, the work function $\phi$ drops, reaching a value of 4.2 eV at an average thickness of 5.5 nm. In the case of n-GaN, the film growth brings about a work function increase after the first deposited dose of PCTDI-C8. The work function reaches 4.2 eV at an average thickness $d = 1.8$ nm.

**Figure 4.** The UPS spectra taken for the 3.2 nm thick PCTDI-C8 film on p-GaN(0001). Inserts show the position of the leading edge of the HOMO level.

**Figure 5.** Work function changes as a function of the average thickness of the PCTDI-C8 layer on n- and p-GaN surfaces.

From the XPS spectra it is seen that PCTDI-C8 adsorption on a GaN(0001) surface does not alter the position of the dipper atomic levels of the atoms of both the surface and the molecule. Following the PCTDI-C8 film’s growth, the main substrate lines Ga 3d and N 1s only lose their intensity, and do not undergo any shift. In Figure 6a, the C 1s lines of a bare p-GaN surface (spectrum (1)) and a surface covered with a 5.5 nm thick PCTDI-C8 film (spectrum (2)) are compared. For the bare substrate, the line contains only one peak (maximum at 284.6 eV) which originated from the remnants of carbon left on the surface after rapid annealing at the end of the cleaning procedure. In the case of the surface covered by the film, the line contains two components coming from the imide group (maximum at 285.0 eV), which are clearly identifiable. Both components increase their intensity following the film’s growth. The N 1s line measured for the p-type sample before and after the 5.5 nm thick PCTDI-C8 film’s deposition is shown in Figure 6b. For the bare substrate (spectrum (1)), the line consists of only one component associated with the Ga–N bonds (maximum at 397.3 eV). The height of the signal is scaled down ten times to fit the figure. After PCTDI-C8 deposition (spectrum (2)), in addition to this peak, attenuated by the deposited film substrate signal coming from the Ga–N bonds, another component appears in the spectrum of this line (with its peak at 400.2 eV) which originates from the imide group. These two species differ by 2.9 eV. The same energy difference between these two signals is also measured for the n-type sample. When the
Ga–N bond signal decreases following film growth, the signal originating from the imide group increases.

![Figure 6](image_url)

**Figure 6.** The XPS spectra of (a) the C 1s line, taken using Al anode, and (b) the N 1s line, taken using Mg anode. Spectra from bare p-GaN samples are denoted by (1). Spectra collected after deposition of the 5.5 nm thick PTCDI-C8 film are denoted by (2). See text for details.

Below a certain coverage of the substrate surface by PTCDI-C8 molecules, the STM images were of very low quality. In the case of p-GaN substantial improvement was reached when the average thickness of the deposited film exceeded 0.4 nm and formation of islands of adsorbate began. The STM topography of the substrate surface at this stage is shown in Figure 7a. The average height of the islands is about 1.5 nm (Figure 7b). The STM topography of part of the PTCDI-C8 island in Figure 7c reveals details of the shape of its edges. The magnified pattern of the area denoted by the dotted square in Figure 7c is in view in Figure 7d, revealing rows of molecules constituting an island. The distance between the two closest rows is equal to 1 nm and the rows are parallel to the [210] direction of the substrate.

![Figure 7](image_url)

**Figure 7.** (a) The STM topography of two-dimentional molecular islands of PTCDI-C8 grown on p-GaN(0001) surface. The average thickness of the PTCDI-C8 film, estimated from the topography, is 0.4 nm. The islands are formed directly on the 1 × 1 μm² area of the substrate (imaging conditions: \(V_s = 4.7 \text{ V}, I_t = 107 \text{ pA}\)). (b) Profile of the black line in (a). (c) Fragment of one of the islands and its surroundings, covering a 150 × 150 nm² area (\(V_s = 4.7 \text{ V}, I_t = 182 \text{ pA}\)); (d) Magnified part of the PTCDI-C8 island surface marked by a dotted square in (c) (18 × 18 nm², \(V_s = 4.7 \text{ V}, I_t = 103 \text{ pA}\), revealing the rows of molecules constituting the island. Distance between the rows is equal to 1 nm and the rows are parallel to the [210] direction of the substrate.
The results of using 2D fast Fourier transform (FFT) on the STM pattern of the ordered monomolecular layer of PTCDI-C8 on the p-GaN(0001) surface are shown in Figure 8. The FFT of the unfiltered STM pattern from Figure 8a is displayed in Figure 8b. The inverse Fourier transform obtained after noise filtering is seen in Figure 8c, exhibiting a long-range order along the rows as well. The distance between the two closest molecules in the row is equal to 0.6 nm. The islands of the first monomolecular layer deposited directly on the substrate surface are epitaxially oriented in relation to the substrate, with molecular rows mostly parallel to the densely packed <11̅20> or less frequently to the <10̅10> substrate directions.

![Figure 8](image)

The STM pattern of ordered monomolecular layer of PTCDI-C8 on p-GaN(0001) surface (10 × 10 nm², V_s = 4.7 V, I_t = 51 pA), (b) 2D FFT of the pattern. (c) Inverse FTT after noise filtering.

Under the deposition conditions applied here, the second monomolecular layer begins to grow before the first one is complete. An example of a PTCDI-C8 film composed of two monomolecular layers is shown in Figure 9. The total amount of deposited adsorbate corresponds to an average film thickness d = 1.8 nm. The first monomolecular layer of the topography in Figure 9a covers about 75% of the substrate surface. The second monomolecular layer covers about 17% of the surface of the first one. The profile of the superimposed layers is shown in Figure 9b. The height of each layer is equal to 2.0 nm. The edge of the upper layer is seen in the bottom right-hand corner of the topography in Figure 9c. The molecular rows of each layer are parallel, retaining the same distance between the rows of 1.2 nm. Due to coalescence, the islands of different rows’ orientations form domains. The bottom PTCDI-C8 layer, visible on the right side of the topography in Figure 9d, consists of two domains A and B, whose rows are perpendicular. In this case, the rows of the upper layer are parallel to the rows of domain A. Nucleation of the third layer is noticed when the first layer covers 96% of the substrate and the second covers 70% of the first one. At this stage of the film growth, the heights of the layers amount to 2 nm in the case of the first layer and 1.7 nm in the case the second and the third layers.

The bilayer or three-layered PTCDI-C8 islands deposited on the substrate at RT under the conditions of our experiment are not thermally stable. After aging at RT (one hour or more), under UHV or short annealing (a few seconds) at up to 100 °C, the molecules from the upper layers diffuse down, completing the first layer and causing the growth and coalescence of islands in the first layer. As a result, the first layer, which has direct contact with the substrate, completes itself to the extent allowed for by the amount of deposited adsorbate. The STM topography of 3D islands constituting a PTCDI-C8 film of about 4.0 nm average thickness, just after deposition, is shown in Figure 10a. Some of the islands consist of three monomolecular layers, forming terraces that are very well distinguished from the terraces of the substrate (see Figure 1a,b). The topography in Figure 10b exhibits a PTCDI-C8 film of an average thickness of 1.0 nm after one hour of aging at RT. The film, which just after deposition was a bilayer film with a topography like that shown in Figure 9a, after aging, has been transformed into a monolayer film. The islands constituting the film are rounded and mostly merged, forming meandering chains. The same effect can be achieved after a few seconds of annealing. The topography in Figure 10c demonstrates a film of an average thickness of 1.5 nm. About 85% of the substrate surface is covered with the monolayer film, which, before the annealing, was a bilayer one. Similar behavior was also observed for films up to 5.5 nm thick.
Figure 9. Morphology of the PTCDI-C8 film grown on a p-GaN(0001) surface at the stage of growth where the first layer of the molecules is not fully completed and the second layer is already growing. (a) Topography of a 1 × 1 µm² area of the sample. A profile of two superimposed layers measured along the white segment is shown in (b). (c) Topography of a 30 × 30 nm² area, revealing parallel molecular rows of the upper layer and the bottom layer, which are visible in the bottom right-hand corner of the pattern. Molecular rows of each layer retain the same distance of 1.2 nm. (d) Topography of a 25 × 25 nm² area in which the domain morphology of the bottom layer is visible. Dotted line divides domains A and B, who’s rows are perpendicular.

Figure 10. (a) The STM topography of 3D islands constituting a PTCDI-C8 film of about 4.0 nm average thickness, just after deposition. Some of the islands consist of three monomolecular layers. (b,c) The STM topographies of single-layer PTCDI-C8 films obtained from bilayer ones through rewetting mechanisms: (b) a bilayer film of an average thickness of 1.0 nm after aging for 1 h at RT, and (c) a bilayer film of an average thickness of 1.5 nm after annealing at up to 100 °C for a few seconds.

The initial growth stages of PTCDI-C8 films on n-GaN follow the same path as those for p-GaN. The only difference is the quality of the STM imaging. The STM patterns of the films growing on n-GaN are blurred up to a film thickness of about 1.8 nm, which corresponds to the stage at which the first PTCDI-C8 monolayer covers 70% of the substrate and the second layer start to grow, in opposition to p-GaN; where, for films with an average thickness exceeding 0.4 nm, imaging become substantially improved, allowing the detection of the morphological details of the growing film. The STM studies of thicker films on n-type substrates have been given up on at this stage.

4. Discussion

The STM topographies clearly show that carbon and oxygen residues, detected by XPS after applying the same cleaning procedures, were not uniformly distributed over the
substrate surface. Instead, they were concentrated in groups, leaving an extended area of the substrate clean, with a characteristic terrace topography.

It is obvious that n- and p-type samples essentially differ in their electron structure. p-GaN(0001) has a work function $\phi = 5.7 \text{ eV}$ and electron affinity $\chi = 4.0 \text{ eV}$. The n-type sample has lower values for its work function and electron affinity, respectively, 3.6 eV and 3.3 eV. The important features of the electron band structure of the PTCDI-C8/GaN(0001) interfaces are collected in the diagrams in Figure 11a,b. The $E_f$, in bulk, is located 3.3 eV and 0.1 eV above the valence band maximum ($E_V$) for the n- and the p-type samples, respectively [23]. The surface band bending at the vacuum/GaN(0001) interface for bare substrates, as calculated from the equation $V_C = (E_F - E_V)_{\text{bulk}} - (E_F - E_V)_{\text{surface}}$ is equal to 0.2 eV for the n-type and 1.6 eV for the p-type sample. The bending comes from electrostatic surface charging. Solving Poisson’s equation, the space-charge region width $x_d = \left(\frac{2\epsilon_0 V_C}{qN_d}\right)^{-\frac{1}{2}}$ can be obtained, where $\epsilon = 8.9$ [25] is the dielectric constant of GaN, $\epsilon_0$ represents the permittivity of free space, and $q$ is the elementary charge of an electron. The depletion layer width amounts to about 14 nm for n-GaN and about 40 nm in the case of p-GaN. Corrections connected to surface photovoltage (SPV) effects are not considered in the above estimations. It is known that, in the case of GaN, the SPV due to UPS or XPS radiation is determined to be ~0.5 V in magnitude [24]. In contrary to n-GaN, the band bending of p-GaN is strong due to the considerable depletion of holes in the near-surface region, caused by surface states which originate from Ga dangling bonds [26,27], thus, the Fermi level is pinned to these states, situating itself in the middle of the energy band gap [28–30].

![Figure 11](image_url)

**Figure 11.** Energy band diagrams of the PTCDI-C8/GaN(0001) interface formed by a 5.5 nm thick film on: (a) n-doped and (b) p-doped GaN substrates. The left sides of each diagram correspond to the bulk band structure and show bending in the region near the interface. The right sides schematically illustrate the position of the vacuum level $E_V$ as a function of the PTCDI-C8 layer thickness and the position of the HOMO level of the film in reference to its Fermi level.

From the XPS measurements it is seen that the interaction between the substrate and PTCDI-C8 film is very weak, and rather of a Van der Walls character. A stronger chemical interaction can be excluded because the Ga 3d and N 1s lines of the substrate do not change their positions or shapes following the first and successive doses of PTCDI-C8 deposition. Also, the C 1s lines originating from the imide group or from the core of the PTCDI-C8 molecule (Figure 6a), as well as the N 1s line from the imide group (Figure 6b), do not change their positions or shapes following the film growth. Taking these into account, it can be safely assumed that the influence of the PTCDI-C8 film on the band bending of the substrate can be neglected.

The 5.5 nm thick films have the same work function value, 4.2 eV, independent of the substrate type (n- or p-) onto which the film was deposited. The only difference in the electronic structure of the PTCDI-C8 films concerns their HOMO level position. In the case of the film on p-GaN, its level is situated 0.3 eV closer to the Fermi level than for the film.
on n-GaN. This shift of the HOMO level of the PTCDI-C8 film on p-GaN is caused, most probably, by the same surface states which are responsible for strong band bending at the subsurface region of p-GaN.

There were no positive results of our STM studies regarding the adsorption of single PTCDI-C8 molecules on the GaN(0001) surface. STM topographies of the surface after the first dose of deposition are blurred, indicating that the adsorbate is weakly bounded and the molecules are mobile. In the case of p-GaN, the situation improves when the self-organization of the adsorbate begins and the two-dimensional islands start to grow. In the case of n-GaN, the poor quality of the STM images made STM observations more difficult at least up to the 1.8 nm thick films; the thickest PTCDI-C8 films on n-GaN studied herein using STM. It seems that at the first stages of the growth interaction between PTCDI-C8 molecules and the substrate are weaker on the n-type substrate. This could be caused by stronger rewetting mechanisms, which compete with the 3D growth mechanisms. Rewetting could be strengthened by the larger amount of carbon residue left on the n-type surface after cleaning procedures. The presence of carbon on the surface is the only factor which chemically differentiates the n- and p-GaN substrates.

The self-organization of the PTCDI-C8 molecules deposited on p-GaN(0001) begins when the film reaches an average thickness of 0.4 nm, at which the first 2D islands are observed. The islands have an ordered row structure. The analysis of the STM patterns of the films, for this range of thickness, reveals that the molecules in the row are in stand-up positions, as evidenced by the island’s height of 1.5 nm (the thinnest observed), with a linear molecule packing density of $1.7 \times 10^{17}$ molecules/cm. This corresponds well with the arrangement of PTCDI-C8 molecules shown in Figure 12a. Although the dominant factor in self-organization is the interaction between molecules, the substrate structure influences the growth condition used in this study during deposition, as well as the distribution of the deposited molecules or substrate temperature during deposition, as well as those at which the organic films could grow layer-by-layer, according to the Frank van der Merve growth mode.

The height of the layer depends on the tilting angle of the rows. For the layer depicted in Figure 12, the tilting angle is equal to ~30°, which makes the layer 1.5 nm high, with the distances between the alkyl tiles of the molecules forming a row equal to 1.0 nm, just like for the PTCDI-C8 layer shown in Figure 9.

![Figure 12](image_url)

**Figure 12.** Schematic sketch of the first monomolecular layer of PTCDI-C8 film grown on a p-GaN(0001) surface: (a) view from the side of the row, positioned along the [2\(\overline{2}\)T0] direction of the substrate, (b) view along the tilted rows which constitute the layer (or along the GaN [2\(\overline{2}\)T0] direction).

The growth of 2D islands transforms into 3D growth when the average thickness of the film exceeds 1.2 nm. PTCDI-C8 molecules do not form a wetting layer. The substrate is not fully covered by the first layer when the second starts to grow. The increase in the average thickness $d$ of the film results in the growth of consecutive layers of adsorbate on top of the bilayer. Three-layered islands bordering with uncovered by the adsorbate areas of the substrate are observed even for the 5.5 nm thick films. The molecular structure of the second and consecutive monomolecular layers is like the one sketched in Figure 12. It seems that height of the monomolecular layer increases following the increase in the quantity of the molecules composing the layer. Usually, the bottom layers of the island are...
thicker than the top one. This may be caused by a change in the tilting angle of the rows or the angle between the core and the alkyl tiles of the molecule. Similar mechanisms of growth and similar results concerning the morphology of the growing films of PTCDDI-C8 and PTCDDI-C13 were observed on SiO$_2$ surfaces [11,31].

The PTCDDI-C8 films on GaN(0001) grow following the Volmer–Weber growth mode. The rewetting mechanisms observed in the PTCDDI-C8/GaN(0001) system relax the thermodynamic instabilities in the morphology of the growing or already-grown films. The formation of instabilities is a kinetic effect that depends on growth parameters such as the flux of the deposited molecules or substrate temperature during deposition, as well as the intra- and interlayer surface diffusion controlled by Ehrlich–Schwöbel barriers (ESB). All these factors significantly influence the islands’ nucleation and morphology evolution under conditions far from thermodynamic equilibrium [32]. The fundamental molecular building blocks of the PTCDDI-C8 films on GaN(0001), produced by self-organization, are molecular rows formed by π–π bonds between the cores of the molecules and the layers assembled into rows by Van der Waals forces. Interactions between the layers constituting the 3D islands is also of a Van der Waals type. Under the growth condition used in this study during film deposition, the supersaturation of the 2D gas of the organic molecules adsorbed on the surface favors the formation of the critical nuclei of monomolecular layers on top of the already existing PTCDDI-C8 layers, and as a consequence of the growth of the 3D terraced mounds. The terraces of the PTCDDI-C8 mounds are clearly distinguishable from the terraces of the substrate (compare Figure 1a or Figure 1b with Figure 10a). The rewetting observed during the aging at RT or annealing at 100 °C results from the decay of the top-most layers, which are smaller, in favor of the lower ones, which are larger; this is the so-called “Ostwald ripening” [33]. The rewetting also shows that the ESB is lower for the diffusion of the organic molecule down-step of the terraces of the grown organic mounds than for the diffusion up-step. As observed here, Volmer–Weber growth is a kinetic effect; it seems possible to find such growth conditions as those at which the organic films could grow layer-by-layer, according to the Frank van der Merve growth mode.

5. Conclusions

The chemical composition and electronic structure of the surface and subsurface region, as well as the atomic structure and morphology of the bare n- and p-type GaN(0001) samples were characterized prior to PTCDDI-C8 film deposition using XPS, UPS, LEED and STM—the differences between both types of the surfaces used as substrates have been discussed. We did not notice at the measured XPS spectra, any variations in the electronic structure of the substrate or adsorbed molecules due to PTCDDI-C8 film growth; therefore, it has been assumed that the film–substrate interaction is of a Van der Waals character. Work function changes have been measured using UPS as a function of the average film thickness. The UPS measurements have allowed us to determine the position of the HOMO level for thicker films with an average thickness 3.2–5.5 nm. Energy diagrams of the interface between the n- and p-type GaN(0001) substrates and the PTCDDI-C8 films have been proposed. On the basis of STM observations, the fundamental molecular building blocks of the PTCDDI-C8 films on GaN(0001), assembled by self-organization, have been identified. The first type of such blocks are rows of PTCDDI-C8 molecules stacked in a “stand-up” position in reference to the substrate, supported by the π–π bonds which are formed between the molecular cores of the molecules. The second type are monomolecular layers constituted by rows which are tilted in reference to the layer plane. The layers are epitaxially oriented. The epitaxial relationship between the rows and the crystallographic directions of the substrate has been determined. Assuming that the interaction between the rows and between the layers is also of a Van der Waals forces origin, a model of the PTCDDI-C8 film’s growth on the GaN(0001) substrate is presented. The 3D islands of PTCDDI-C8 molecules formed on the substrate surface during film deposition are thermodynamically unstable. The Volmer–Weber type of growth observed here is a kinetic effect. Rewetting processes are noticeable after film aging at room temperature or annealing at up to 100 °C.
Anisotropy and the complexity of the interactions inside the PTCDI-C8/GaN(0001) system produce a wide spectrum of basic phenomena, which are of great importance for understanding the growth of organic films on the surfaces of inorganic semiconductors. But there are also practical aspects to such studies. Elements of the organic film’s morphology, such as the structure of the molecular building blocks of the film, its texture, its epitaxial relationship toward the substrate, etc., are key factors that determine its performance in various applications. A proper tuning of the growth parameters allows us to control all these elements; therefore, they may be used as tools for the engineering of hybrid organic–inorganic electronic devices.

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