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Quasiepitaxial growth of the organic molecular semiconductor 3,4,9,10-perylenetetracarboxylic dianhydride

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Thin films of the organic molecular semiconductor 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) were grown by ultrahigh vacuum sublimation on graphite, and on As-saturated $c(4\times4)$, As-rich (2×4)-$c(2\times8)$, and Se-passivated (2×1) GaAs (100) surfaces. The Se-passivated GaAs and graphite surfaces resulted in PTCDA films with good crystallinity, whereas deposition under similar conditions on the (2×4)-$c(2\times8)$ GaAs surface produced films randomly oriented in the plane parallel to the surface. The films grown on the $c(4\times4)$ GaAs surface showed intermediate molecular ordering. These differences are analyzed in terms of interface bonding between the molecules and the substrate, specifically at defects and dangling bonds which pin the molecules at random sites. These interactions are considerably reduced on the inert surfaces of graphite and Se-passivated GaAs. The results presented here provide information on the conditions under which the quasiepitaxy of organic molecular crystals can be achieved on highly mismatched inorganic substrates.

I. INTRODUCTION

The deposition of high-quality organic semiconductor layers with good optoelectronic properties on a variety of substrates has made these materials interesting candidates for a number of novel device applications.[1,2] The deposition parameters and growth mechanisms leading to smooth, continuous and, in some cases crystalline, organic semiconductor layers have therefore received considerable attention over the past decade.

Early on it was recognized that films of van der Waals–(vdW-) bonded molecular solids such as 3,4,9,10 perylenetetracarboxylic dianhydride (PTCDA) (Fig. 1) and related compounds could be grown in vacuum with a high degree of orientation to the substrate in spite of a very large lattice mismatch.[3–6] This phenomenon, known as quasiepitaxy (QE), was associated with conditions that reduce the interface bonding strength and allow inter-molecular forces, rather than molecule-substrate bonds, to define the position of molecules at the interface.[7,8] A criterion leading to this situation has been described as $\Phi''(\text{inter}) \ll \Phi''(\text{intra})$ where the left-hand and right-hand terms are the second spatial derivative, or curvature, of the molecule-substrate and molecule-molecule interaction potentials, respectively.[7,8] Under these conditions, molecules can diffuse on the surface and assume near-bulk positions within the first few monolayers from the interface, leading to the growth of an ordered molecular crystal. Because of their highly ordered inert surfaces, two-dimensional solids like graphite [highly oriented pyrolytic graphite (HOPG)] and layered transition-metal dichalcogenides were found to be particularly well suited for QE of organic molecular solids.[9–11]

The extension of QE growth of organic vdW films on substrates of conventional semiconductors like Si and GaAs is of practical importance because of potential applications of hybrid organic/inorganic (OI) semiconductor structures.[12] It is also of fundamental interest given the opportunity that structurally ordered interfaces would offer in terms of studying band alignment and carrier transport at OI heterojunctions. However, the crystallinity of organic layers grown so far on conventional inorganic surfaces has been found to be inferior to that of layers grown on two-dimensional materials, and to be critically dependent on the inertness of the substrate surface. In that respect, Koma *et al.*[13] recently stressed the importance of terminating substrate dangling bonds (DB's) as a means of achieving inertness of conventional inorganic substrates. It was demonstrated that metal phthalocyanine layers deposited on hydrogen-terminated Si(111) (Ref. 14) and on Se-passivated GaAs(111) (Ref. 15) exhibited significantly improved molecular order as compared to layers grown on bare Si and GaAs surfaces. It should be pointed out that under the very slow (equilibrium) growth used in these experiments, only a few monolayers of a strained phthalocyanine film was achieved on GaAs(111) and Si(111) substrates.

Although the advantage of surface passivation as a general method for reducing interface interactions is clear, and is supported by the results presented below, questions remain concerning the relative impact, on the QE of molecular films, of the substrate surface defects and of the occupation of the substrate surface DB's. The interaction between the organic molecules and filled or empty DB's on nonpassivated surfaces is particularly important for understanding the general principle of QE on inorganic substrate.

To elucidate these points, we investigate molecular ordering of PTCDA layers grown on HOPG and GaAs(100) terminated with As-saturated $c(4\times4)$, As-rich (2×4)-$c(2\times8)$, and (2×1) Se-passivated surfaces. PTCDA and GaAs are two prototypical materials that

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have been extensively used in fundamental studies of organic and inorganic semiconductor growth, surfaces, interfaces, and device structures, and the PTCDA/GaAs system represents the archetype OI heterojunction that could serve as a basic reference in the expanding field of OI interfaces. In particular, the three GaAs surface terminations provide an ideal test of the impact of different DB energy and occupation in the molecule-substrate interaction.

In accord with previous results and prediction of QE on inert surfaces, we find that PTCDA grown on HOPG exhibits good crystallinity within the randomly oriented domains defined by the substrate. On the other hand, we find a significant gradation of the quality of PTCDA layers grown on the (2×4)-$c(2\times8)$, the $c(4\times4)$, and the (2×1) Se-passivated surfaces. The PTCDA films grown on the (2×4)-$c(2\times8)$ surface[16,17] exhibit long-range order only in the direction of the molecular stacking perpendicular to the substrate, whereas randomly oriented domains with typical dimensions of only a few tens of angstroms are obtained in the plane parallel to the substrate. The molecular disorder of the first few layers in contact with the substrate propagates throughout the film. On the other hand, the $c(4\times4)$ surface leads to a substantial improvement on the long-range two-dimensional orientation of the organic films. Although this improvement could be simply attributed to a smoother substrate morphology, we argue that it has more fundamental implications since the $c(4\times4)$ surface is not passivated and exhibits only filled DB's, instead of filled and empty DB's on the (2×4)-$c(2\times8)$ surface. Finally, we find a drastic improvement in the crystallinity of the PTCDA layers grown on the Se-passivated surface. A preferential orientation of the molecular unit cell with respect to the substrate is identified in this case. This improvement is attributed primarily to the Se-mediated passivation of the surface effect, which has been recently investigated by scanning tunneling microscopy (STM).[18,19]

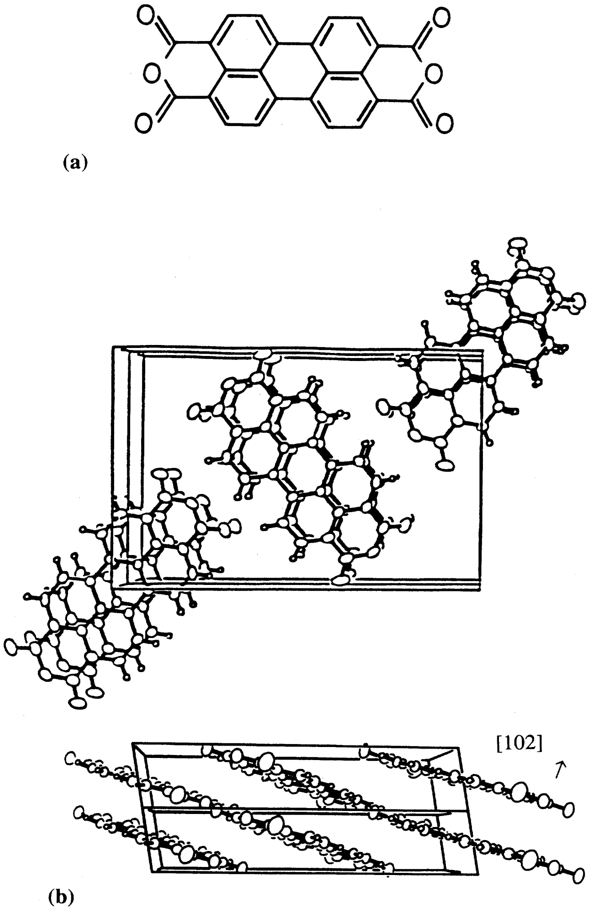


FIG. 1. (a) Chemical structure of the PTCDA molecule; (b) perspective views of the monoclinic bulk crystal structure of PTCDA. The [102] direction is perpendicular to the plane of the molecules.

Considering these differences, we address for the first time the role that DB's with different electronic occupations might play in perturbing the QE process. We provide a qualitative model of the PTCDA-GaAs(100) interactions based on the ionization energies of PTCDA and GaAs(100), on the density and energy position of the substrate surface states obtained from previous STM and photoemission spectroscopy studies,[20,21] and on the relative energies of the PTCDA and substrate energy levels. An important result is that the interaction between molecules and the nonpassivated substrate appears to be dominated by coupling between the PTCDA highest-occupied molecular orbital (HOMO) and empty or partially filled GaAs DB's. We argue that interface disorder, which leads to disorder in the molecular film, results predominantly from the pinning of molecules at these empty or partially filled DB "defect" sites. The larger density of empty and partially filled sites on the (2×4)-$c(2\times8)$ surface explains the poorer quality of the PTCDA films as compared to that of the films grown on the $c(4\times4)$ surface. The passivation of the surface leaves each surface atom with a closed electronic shell structure consisting of a fully occupied bonding and dangling orbitals, giving a minimal interaction with the molecules and allowing QE of the organic film.

The next section of this paper describes the experimental procedure. The results are presented in Sec. III and the discussion is presented in Sec. IV.

II. EXPERIMENTAL PROCEDURE

The experiments were carried out in a dual-chamber UHV system consisting of a molecular beam epitaxy chamber equipped with Ga, As, and Se effusion cells, and a surface analysis chamber equipped with low-energy electron diffraction (LEED), Auger electron spectroscopy, and a PTCDA effusion cell. The base pressure was $\sim 5\times10^{-11}$ Torr in both chambers.

The deposition of PTCDA on HOPG was performed on surfaces freshly peeled *ex situ* and introduced into the analysis chamber via a load lock. For the PTCDA/GaAs experiments, 2000-Å-thick layers of undoped GaAs were first grown on (100) GaAs substrates (*n*-doped, $\sim 10^{18}$ cm^{-3}) at $\sim 550\,^{\circ}$C. Following growth, the substrate was kept under As flux, first at the growth temperature for a few minutes to improve the surface morphology, then during cooling to 350 °C. The surface exhibited a (1×1) reflection high-energy electron diffraction (RHEED) pattern indicative of an As coverage superior to that corresponding to the $c(4\times4)$ surface. After recovery from As residual pressure, the $c(4\times4)$ and (2×4)-$c(2\times8)$ reconstructions were obtained by annealing up to 250 °C and 450 °C, respectively.

Se passivation was achieved by *in situ* deposition on the GaAs surface. The bare sample was first annealed at 450 °C to obtain the (2×4)-$c(2\times8)$ reconstruction, then placed under Se flux for 2 min followed by a 5–10-min anneal at ~510 °C. This cycle was repeated several times to improve the uniformity of the Se coverage,[18] as identified by the sharpness of the (2×1) RHEED pattern. During the deposition of Se, the pressure remained below 1×10^{-9} Torr.

PTCDA was sublimated from an effusion cell heated to about 250–300 °C, giving deposition rates of 4–5 Å/min (one monolayer of PTCDA corresponds to a nominal thickness of 3 Å). The film thickness ranged between 3 and 150 Å. All the substrates were kept at room temperature during deposition. These conditions of relatively rapid deposition rates on room temperature or cooled substrates have been shown previously to result in highly oriented, although slightly strained, incommensurate PTCDA overlayers.[22] As already mentioned, this growth mode is termed "quasiepitaxial" due to the ability of the substrate to provide an orientational template to the incommensurate overlayer.[6,7,22]

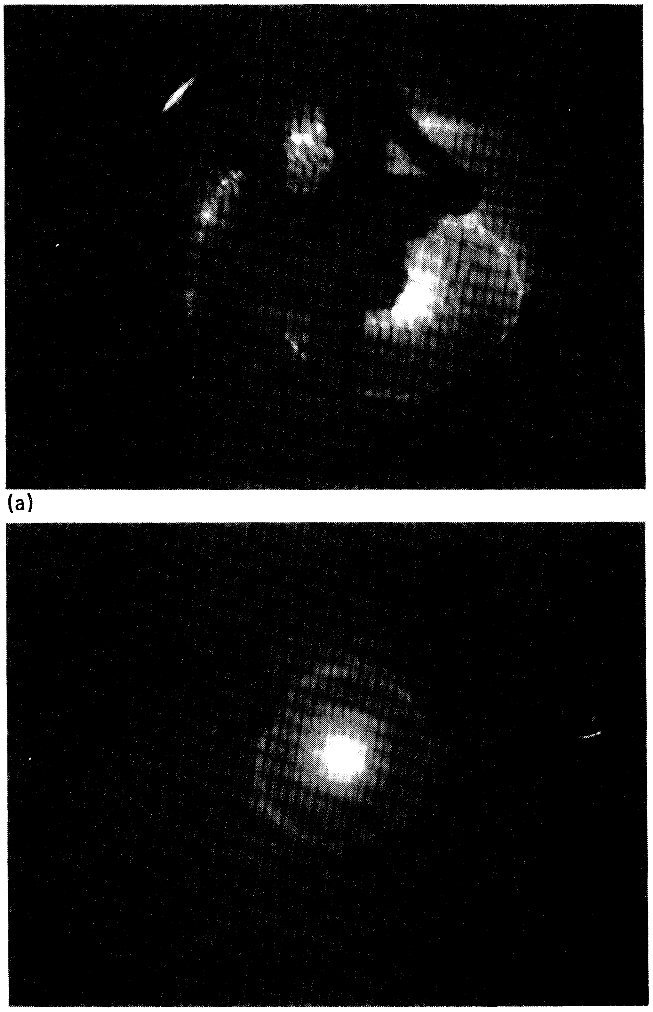
The evolution of the surface structure was monitored by LEED after each deposition. During diffraction experiments on PTCDA, the LEED electron energy (E_p) and current were kept below ~20 eV and 100 nA, respectively, in order to limit electron-beam-induced damage to the film. No degradation of the PTCDA LEED pattern was noticed for cumulative exposures to the electron beam of up to 10–15 min. Given previous experience of rapid degradation of PTCDA diffraction patterns during RHEED observations,[10] it was decided not to expose the organic surfaces to the high-energy RHEED electron beam.

III. RESULTS

Figures 2(a) and 2(b) show the LEED patterns obtained from HOPG ($E_p = 100$ eV) and from a 50 Å PTCDA layer ($E_p = 13$ eV) grown on HOPG, respectively. Both exhibit a ringlike structure characteristic of multiply rotated, single-crystal domains distributed on a flat surface. In Fig. 2(a), the radius of the inner ring corresponds to a real-space dimension of 2.46 Å, which is very close to the known HOPG lattice constant. The HOPG domain size is on the order of a few microns, roughly two orders of magnitude larger than the LEED coherence length (100–200 Å) and two orders of magnitude smaller than the size of the electron beam spot size. Thus the pattern results from a superposition of multiple hexagonal patterns slightly rotated with respect to each other. Spots remain visible in the ringlike structure of Fig. 2(a).

The PTCDA diffraction rings [Fig. 2(b)] are continuous and indicate the presence of multiply rotated PTCDA domains distributed inside the HOPG domains. Nevertheless, the characteristic dimensions of the PTCDA single-crystal domains remain larger than the LEED coherence length, as evidenced by the thinness of the diffraction rings. As will be shown below, this pattern can be obtained by continuous rotation of the pattern observed from PTCDA/Se-passivated GaAs(100) and is therefore characteristic of a similar PTCDA unit cell.

The LEED patterns in Figs. 3(a) and 3(b) were obtained from the (2×4)-$c(2\times8)$ GaAs(100) surface and from a 50-Å PTCDA overlayer grown on that substrate, respectively. The (2×4)-$c(2\times8)$ pattern exhibits streaks in the [011] (×4) direction, indicative of a perturbation of the As dimer structure on the length scale of the LEED coherence length. It is assumed that the origin of this disorder lies with various types of point defects, steps, and displacement of the missing As dimer row leading to kinks in the As dimer row structure. The LEED pattern


(a)

(b)

FIG. 2. LEED pattern from (a) a HOPG surface (100 eV) and (b) a 50-Å PTCDA film grown on the HOPG surface taken (13 eV).

from the PTCDA layer grown on this surface [Fig. 3(b)] indicates that the two-dimensional order is very poor in the plane parallel to the (100) GaAs surface. The highly diffuse ring, which has a diameter comparable to that of Fig. 2(b), indicates that molecular order exists only on a length scale short with respect to the LEED coherence length. However, the presence of the sharp specular spot is consistent with previous x-ray diffraction (XRD) data that showed regular stacking of the molecules in the direction perpendicular to the GaAs surface.[16] These XRD data also indicated that the intermolecular distance was 3.21 Å, in excellent agreement with the value characteristic of the molecular stacking perpendicular to the (102) plane of bulk PTCDA.[7,23] The molecular planes are believed to lie parallel to the GaAs substrate.

The LEED patterns from the Se-passivated GaAs(100) surface and from a 50-Å PTCDA layer grown on this surface are shown in Figs. 4(a) and 4(b), respectively. The LEED pattern in Fig. 4(a) displays the (2×1) symmetry of the passivated surface. The structural model based on STM (Ref. 18) and transmission electron microscopy[24] studies includes a full monolayer of Se dimers bound to second-layer Ga atoms, a layer of Se atoms replacing As atoms in the third layer, and a half monolayer of Ga vacancies in the fourth layer.[19] Electron counting at this surface indicates that the Se DB's are filled. STM investigations have shown that the surface is morphologically smoother than the (2×4)-$c(2\times8)$ surface and exhibits very long-range order.[18] Scanning tunneling spectroscopy has also shown that the density of gap states is very low, and that the Fermi level is not pinned in the band gap at the substrate surface. The surface is considered as passivated. Note that passivation involves, in this case, the modification of several atomic layers and should not be ascribed merely to the termination of the substrate DB's.

The Se passivation of the GaAs surface leads to a remarkable improvement of the two-dimensional order in the PTCDA overlayer as compared to the two previous cases. The pattern of Fig. 4(b) exhibits sharp spots indicative of long-range order at the PTCDA surface, and a twofold symmetry that defines a preferential orientation

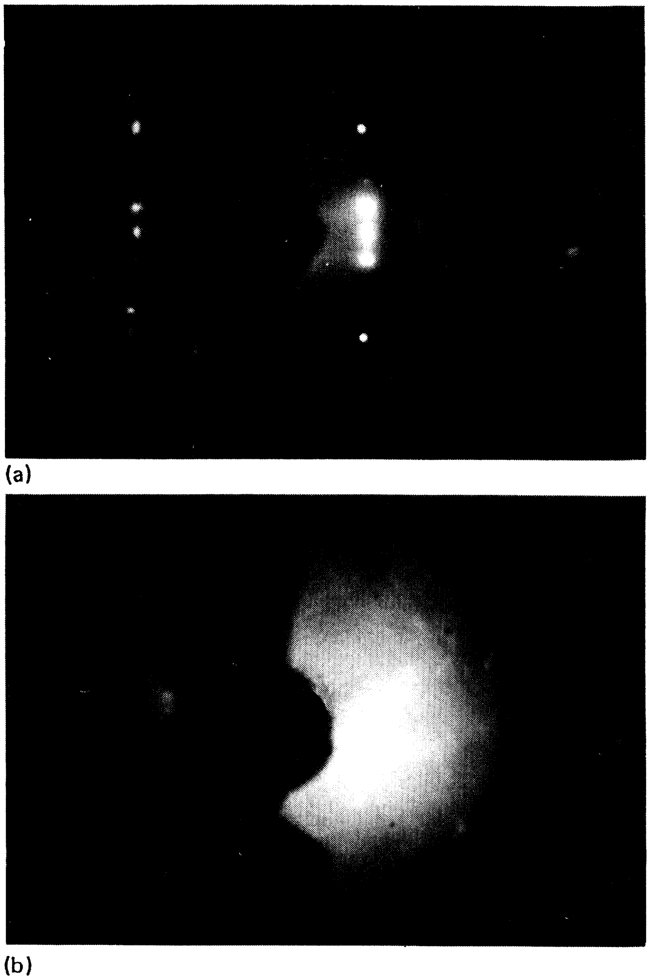


FIG. 3. LEED pattern from (a) a (2×4)-$c(2\times8)$ GaAs(100) surface (65 eV) and (b) a 50-Å PTCDA film grown on top of that surface (13 eV).

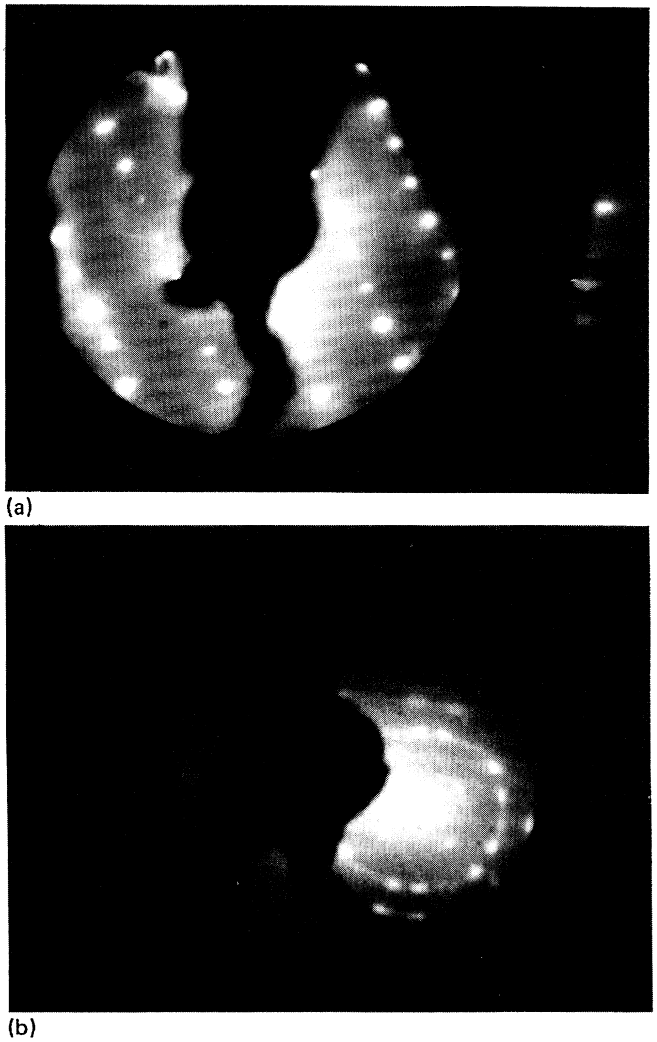


FIG. 4. LEED pattern from (a) a (2×1) Se-passivated GaAs(100) surface (83 eV) and (b) a 50-Å PTCDA film grown on top of that surface (13 eV).

of the organic unit cells with respect to the substrate. Furthermore, the symmetry of the PTCDA pattern is found to be identical for monolayer films (3–10 Å), thin films (30–200 Å), and thick films (~500 Å), suggesting that the PTCDA film grows from the onset in its bulk structure. Considering the large lattice mismatch between the two solids, this structural continuity points out that the interface interaction is sufficiently weak to allow molecules to settle in low-energy positions imposed principally by the intermolecular forces, a necessary condition for QE.[7]

An interpretation of the PTCDA/Se-GaAs diffraction pattern based on a two-dimensional close-packing configuration of the molecules on the passivated surface was recently proposed.[17] The absolute dimensions of the real-space unit cell are calculated with an error bar of ±5% using the calibration provided by the substrate LEED pattern. The proposed structure is based on a 12 Å×19.4 Å rectangular unit cell, dimensions that are very close to that of the (102) plane of the bulk crystal.[7] The c axis of the cell is rotated by ~40° with respect to the direction of the Se dimers (Fig. 5). Other orientations of the cell are obtained by mirror symmetry with respect to the $[0\bar{1}1]$ and [011] axes of the substrate. The interface appears to be incommensurate.

Finally, Figs. 6(a) and 6(b) show LEED patterns from the As-saturated $c(4\times4)$ GaAs surface and from a 50-Å PTCDA overlayer grown on top of that substrate, respectively. The high structural quality of the $c(4\times4)$ surface is evident from the sharpness of the diffraction spots and the low incoherent scattering intensity in Fig. 6(a). The model for this reconstruction is that of three As dimers and one missing dimer row per unit cell on top of a complete As layer.[25] Rows of unit cells are shifted with respect to each other in a $c(4\times4)$ pattern. The simple method of electron counting shows that all As DB's are filled on this surface.[21,26]

The two-dimensional order in the corresponding PTCDA layer [Fig. 6(b)] is considerably better than that of the layer grown on the (2×4)-$c(2\times8)$ surface. The symmetry of the diffraction pattern is similar to that of the layer grown on the Se-passivated surface, indicating that the structure of the unit cell is at least similar to that of PTCDA/Se-passivated GaAs. The diffraction spots are elongated and somewhat diffuse, pointing out the reduced averaged size of single-crystal domains. Yet, the fact that sizable single-crystal domains can be grown on such "nonpassivated" surfaces is surprising and calls for a reevaluation of the notion of substrate inertness with respect to organic molecules like PTCDA.

Note that in the cases of the $c(4\times4)$ and Se-passivated surfaces, the substrate reconstruction remains observable by LEED following the initial deposition of PTCDA. This is an additional indication that the interface interaction is weak with respect to common chemical interactions at interfaces between GaAs and inorganic solids. Changes in the energy of interaction, and the varying degrees of substrate perfection in the various examples presented above, are therefore bound to have a substantial impact on the structure of the organic overlayer, as confirmed by the experimental results.

IV. DISCUSSION

The initial stages of molecular adsorption define the interface molecular arrangement and the ultimate crystallinity of a molecular film. During that phase, the interaction between the molecule and the substrate is dominated by coupling between molecular energy levels and the substrate surface states. Thus some understanding of the strength of the molecule-substrate coupling should in principle be gained from a consideration of the relative energies of the electronic levels involved in the interaction.

In the present case, the relevant energy levels are deduced from previous photoemission spectroscopy measurements of PTCDA and GaAs ionization energies and of the PTCDA/GaAs valence-band offset.[27] These levels are represented in Fig. 7. The ionization energy of the condensed phase of PTCDA is 6.4±0.15 eV vs 5.5±0.1 eV for GaAs. The large PTCDA ionization energy is compared, for example, to that of pure perylene [5.2±0.15 eV (Ref. 28)]. Assuming that the charge transfer at the PTCDA/GaAs interface is small enough that no significant interface dipole shifts one band structure with respect to the other, the ionization energy difference puts the PTCDA HOMO below the GaAs valence-band maximum. This relative position is confirmed by direct photoemission measurement of the PTCDA/GaAs valence-band offset, which shows the PTCDA HOMO at 0.7±0.1 eV below the GaAs

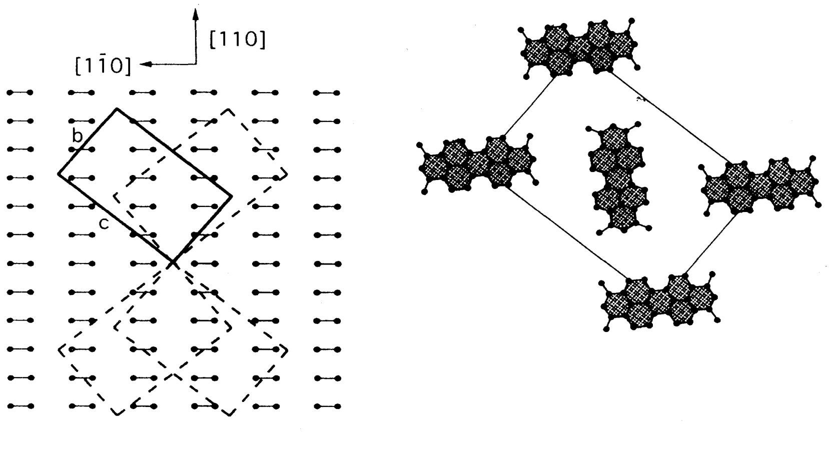


FIG. 5. Schematic of the PTCDA unit cell and orientation with respect to the Se dimers. A possible close-packing arrangement corresponds to one PTCDA molecule at each corner and one at the center of the cell.

valence-band maximum.[21]

A diagram of possible interactions in the case of PTCDA/Se-passivated GaAs is given in Fig. 7(a). The passivated substrate surface has no significant density of states in the band gap.[19] Intrinsic surface states associated with DB's of the Se dimers overlap completely with the valence band. Furthermore, the high structural quality of the surface means that the density of extrinsic, defect-induced, gap states is very small. Thus the molecule-substrate coupling must occur via states that overlap with the valence or conduction bands. However, coupling between the PTCDA HOMO and the filled DB (interaction 2) should be small since both levels are doubly occupied. Furthermore, coupling between the HOMO and empty states in the conduction band should also be weak (interaction 1) given the large energy difference between these levels. As on H-terminated Si(111) (Ref. 14) and Se-terminated GaAs(111),[15] the high degree of structural perfection of the substrate surface added to a weak interaction of the molecules with the inert surface produces the necessary conditions for QE. The passivation of the substrate eliminates the chemically active sites derived from unsaturated dangling bonds and associated with large curvature in the adsorbate-surface interaction potential and pinning of the molecules on the substrate. The elimination of these sites weakens the molecule-surface interaction and leads to a situation where $\Phi''(\text{inter}) \ll \Phi''(\text{intra})$, compatible with QE. The vdW intermolecular forces dominate the molecular arrangement at the interface and lead to the packing of the molecules according to the bulk PTCDA structure. A well-defined orientation of the unit cells with respect to the substrate is observed, as illustrated in Fig. 5, and corresponds to a minimum in the interface interaction energy. This minimum, however, remains to be calculated.

A similar situation occurs in the case of PTCDA on HOPG. The graphite π orbitals interact weakly with the π orbitals of the PTCDA molecule. Furthermore, the

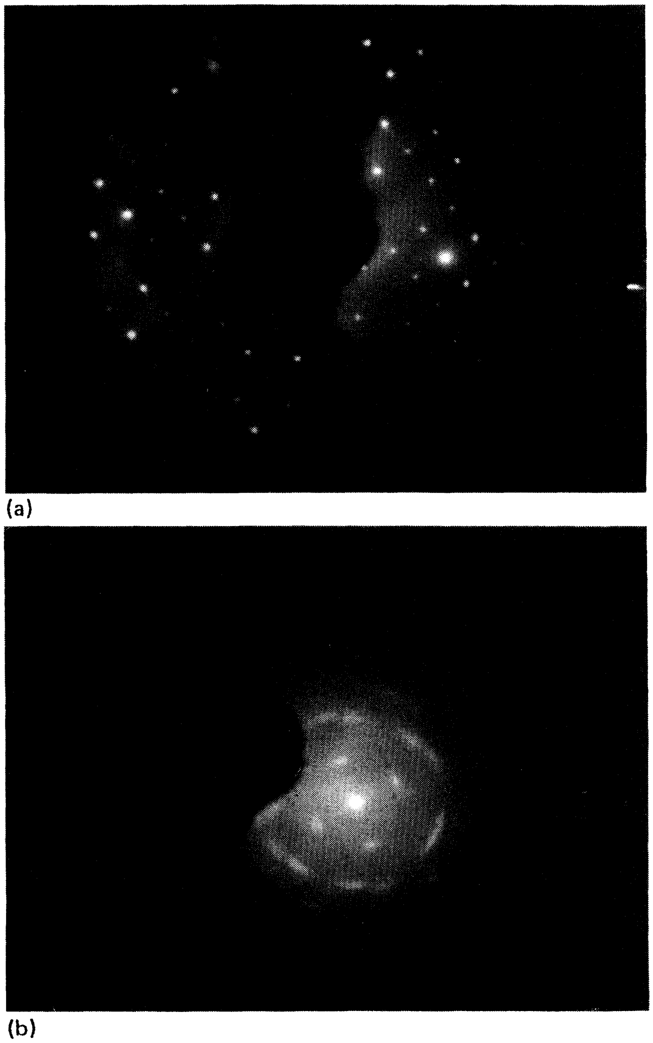


FIG. 6. LEED pattern from (a) a $c(4\times4)$ GaAs(100) surface (83 eV) and (b) a 50-Å PTCDA film grown on top of that surface (13 eV).

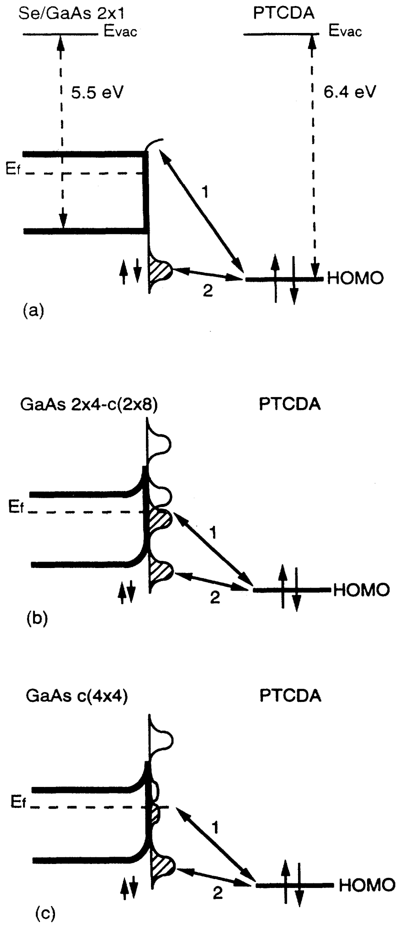


FIG. 7. Schematics of interactions between PTCDA molecules and (a) the (2×1) Se passivated, (b) the (2×4)-$c(2\times8)$, and (c) the $c(4\times4)$ GaAs(100) surface. The PTCDA HOMO is fully occupied. The GaAs surfaces are represented with various densities of filled and empty surface states. The ionization energies of both materials are represented in (a).

HOPG surface is flat and defect free within each domain. The conditions for QE are therefore fulfilled and lead to highly ordered organic layers in which long-range order is affected mostly by the multidomain nature and higher symmetry of the substrate.[17] STM images of monolayer films of PTCDA/HOPG show a highly regular two-dimensional structure with an orientation defined by the sixfold coincidence of the hexagonal benzene and graphite rings.[5,10]

According to experiments[29,30] and theory,[31] the (2×4)-$c(2\times8)$ and $c(4\times4)$ reconstructed GaAs surfaces are semiconducting and do not have intrinsic surface states deep in the gap. In the case of the (2×4)-$c(2\times8)$ GaAs substrate, however, the density of extrinsic surface defects appears to be large. These defects produce gap states that pin the Fermi level near midgap, as inferred from numerous photoemission measurements.[32] The strong interaction between PTCDA molecules and this surface, which results in a disruption of QE, can therefore be attributed in part to coupling between the HOMO and empty and partially filled gap states [interaction 1 Fig. 7(b)]. QE ordering is further disrupted by the presence of Ga dangling bonds exposed to vacuum. In the (2×4)-$c(2\times8)$ unit cell, the top atomic layer consists of a fractional monolayer of As dimers bound to a second layer of Ga atoms.[25] According to the electron counting rule,[26] the As DB's are doubly occupied whereas the Ga DB's are empty. The former are in resonance with the valence band and the latter have an energy close to the bottom of the conduction band. This situation may lead to increased coupling between the filled HOMO and the empty Ga DB, resulting in additional interface bonding. Thus we attributed the lack of two-dimensional order in the PTCDA layer with the combined interactions of the molecule energy levels with these extrinsic and intrinsic states associated with large Φ''(inter).

The results obtained for PTCDA grown on the $c(4\times4)$ GaAs surface indicate a weaker interaction than with the (2×4)-$c(2\times8)$ surface. The origin of this difference is twofold. First, the structural quality of the $c(4\times4)$ surface is higher, as revealed by the well-defined LEED pattern in Fig. 6(a). The density of corresponding defect-induced gap states is reduced with respect to the (2×4)-$c(2\times8)$ surface, even though it clearly remains sufficient to pin the Fermi level near midgap.[21] Note however, that only $\sim10^{12}$ cm^{-2} states are necessary to induce a significant band bending at the surface of GaAs doped in the $10^{17}-10^{18}$-cm^{-3} range, and that the mere occurrence of band bending is not a good criterion for evaluating the potential impact of surface defects on these molecular films. Second, and more significant, all intrinsic states on the $c(4\times4)$ surface are derived from doubly occupied As DB's in resonance with the valence-band states. The top As dimers are bound to a second layer of As atoms that completely covers the next layer of Ga atoms. Thus, the HOMO-Ga DB interaction illustrated in Fig. 7(b) is eliminated. The PTCDA interaction with the $c(4\times4)$ surface is therefore expected to be weaker than that with the (2×4)-$c(2\times8)$ surface, leading to the observed improved QE ordering.

V. SUMMARY

We investigated the QE growth of PTCDA by ultrahigh vacuum sublimation on graphite and on GaAs(100) surfaces terminated with several different atomic reconstructions. Although the analysis of the interface bonding at the PTCDA/GaAs heterojunction relies on arguments that, at this point, remain speculative, we attempted to *systematically* vary the strength of the substrate/organic molecule interaction and we qualitatively confirmed the primary requirement for QE growth. That is, the molecule-substrate shear stress [Φ''(inter)] must be smaller than the intramolecular elasticity [Φ''(intra)] within a PTCDA layer.

In the graphite experiment, the inert, flat, and defect-free substrate surface presents good conditions for the QE ordering of PTCDA and lead to films with good crystallinity within each substrate domains. In the GaAs experiment, we investigated the effects of different substrate terminations on the QE ordering of the organic solid. One of the main results is the demonstration that the passivation of the GaAs surface with Se leads to excellent conditions for ordering in this highly mismatched system. This result confirms those of previous investigations of organic molecular films deposited on graphite and on passivated (111) surfaces of Si and GaAs (Refs. 14 and 15) and provides an extension of the passivation technique to an interface where the substrate unit-cell symmetry does not match the hexagonal symmetry of the PTCDA benzene rings. The removal, by passivation, of chemically active defects from the substrate surface is viewed as the principal reason for the weak molecule-substrate interaction leading to molecular surface mobility during growth and molecular order in these archetype vdW-bonded organic thin films. The situation is opposite in the case of the (2×4)-$c(2\times8)$ GaAs surface, which exhibits more structural defects and chemically active sites. The empty Ga dangling bonds play a significant role in increasing the pinning of the interface molecules and the subsequent disorder in the PTCDA film. An intermediate situation is found for the $c(4\times4)$ surface, which, although not passivated, is structurally superior to the (2×4)-$c(2\times8)$ surface, and exhibits only As-derived doubly occupied dangling bonds that do not form bonds with the PTCDA molecules. This latter point is a highly significant result that provides additional insight into the conditions leading to improved growth of this important class of molecular solid on a variety of inorganic substrates.

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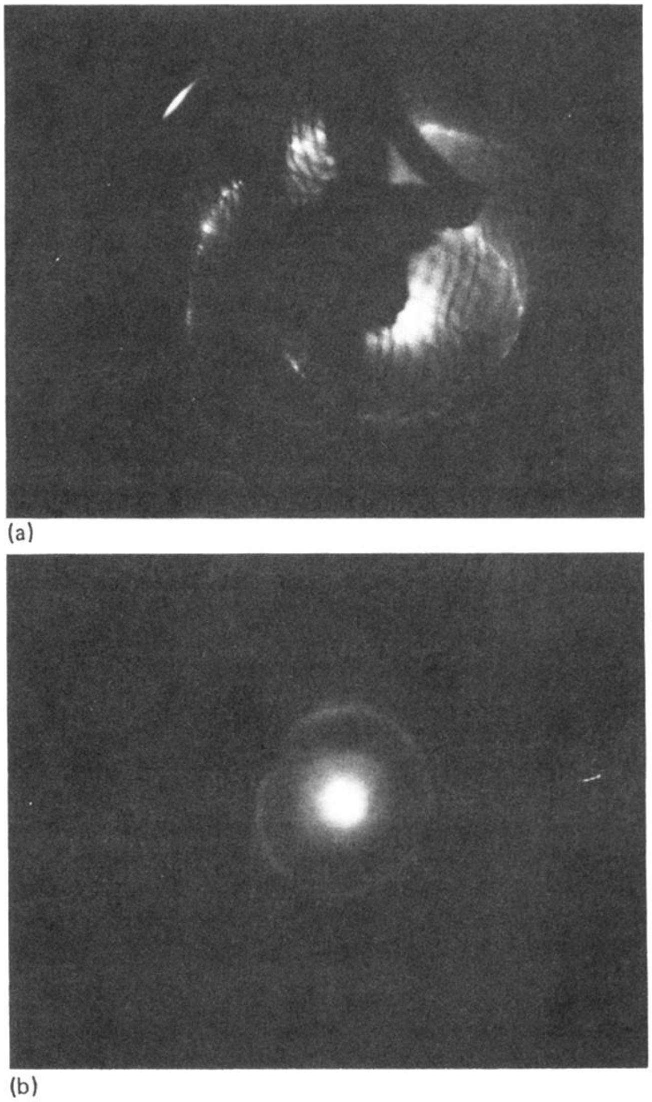

FIG. 2. LEED pattern from (a) a HOPG surface (100 eV) and (b) a 50-Å PTCDA film grown on the HOPG surface taken (13 eV).

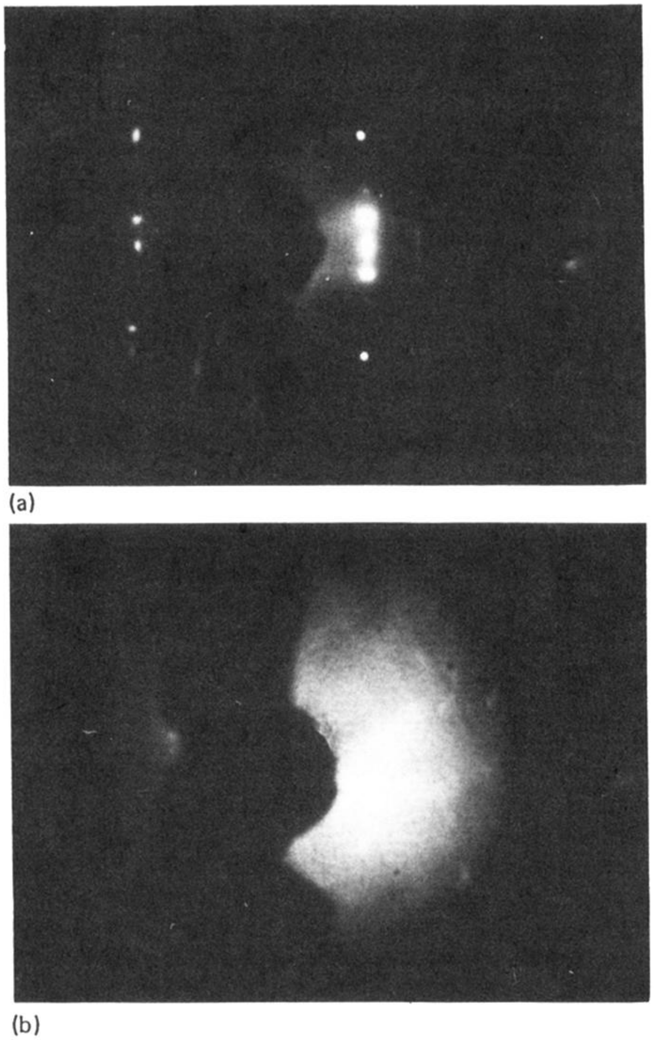

FIG. 3. LEED pattern from (a) a (2×4)-$c(2\times8)$ GaAs(100) surface (65 eV) and (b) a 50-Å PTCDA film grown on top of that surface (13 eV).

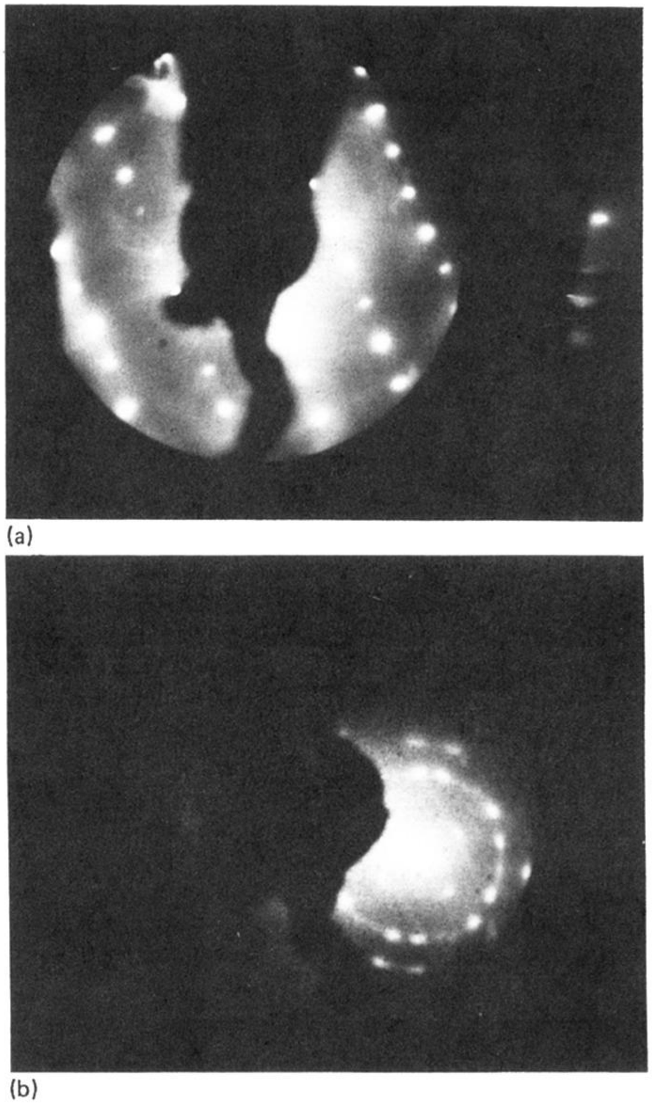

FIG. 4. LEED pattern from (a) a (2×1) Se-passivated GaAs(100) surface (83 eV) and (b) a 50-Å PTCDA film grown on top of that surface (13 eV).

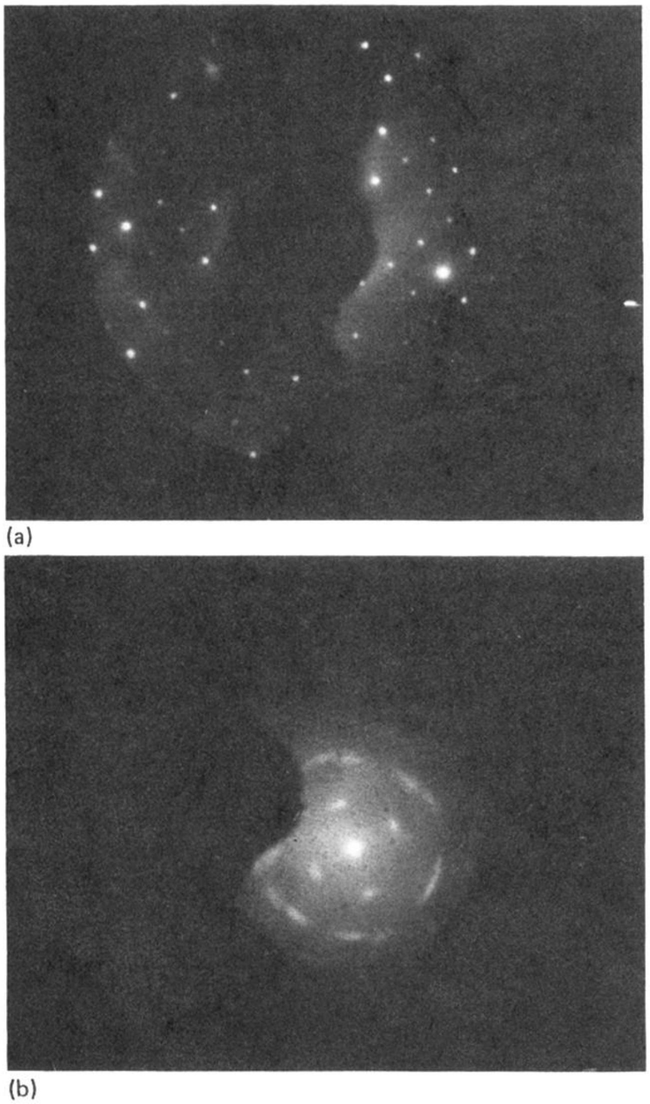

FIG. 6. LEED pattern from (a) a $c(4\times4)$ GaAs(100) surface (83 eV) and (b) a 50-Å PTCDA film grown on top of that surface (13 eV).