The Physicochemical Origins of Coincident Epitaxy in Molecular Overlayers: Lattice Modeling vs Potential Energy Calculations

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The physicochemical basis for epitaxial stabilization of coincident molecular overlayers is illustrated by comparison of optimum overlayer—substrate configurations calculated with potential energy (PE) methods and a simple geometric lattice misfit modeling algorithm (EpiCalc) that neglects molecular orientations and intermolecular potentials. Using β-bis(ethylenedithio)tetrathiafulvalene triiodide (β-ET$_3$I$_3$), perylenetetracarboxylic diimide (PTCDI), and perylenetetracarboxylic dianhydride (PTCDA) overlayers on a graphite substrate as examples, both methods predict identical optimum azimuthal overlayer orientations for each overlayer that also agree with experimental observations. PE calculations for three hypothetical PTCDA overlayers, with identical lattice parameters but different molecular orientations, predict coincidence at the same azimuthal orientation for all overlayers. Identical results are achieved for PE calculations performed with this lattice when it is occupied by naphthalenetetracarboxylic dianhydride (NTCDA) molecules or argon atoms. These results demonstrate that the epitaxial orientation of coincident overlayers is governed more by geometric lattice matching than specific molecule—substrate interactions and that unambiguous determination of the optimum azimuthal orientation relies on establishing the phase relationship between several overlayer supercells and the substrate. In the case of PE methods, calculations with large overlayer sizes are computationally prohibitive and the energy differences between alternative orientations typically are smaller than the confidence limits of the method. In contrast, the calculation time required by EpiCalc is independent of overlayer size, providing a significant advantage over PE methods with respect to computational speed while enabling unambiguous assignment of the optimum coincident configuration. The reliability of EpiCalc in predicting observed epitaxial overlayer orientations indicates that geometric lattice misfit modeling can be used to screen efficiently for the most favorable epitaxial configuration (overlayer lattice parameters and azimuthal angle), which can then be used in subsequent PE calculations that allow for other degrees of freedom such as molecular orientation.

Introduction

Molecular films offer unique opportunities as components in electronic devices, sensors, displays, and logic elements because their optical and electronic properties can be systematically manipulated at the molecular level. Indeed, recent reports of light emitting diodes, field effect transistors, and photovoltaic devices with molecular films illustrate a growing interest in such materials. The properties of molecular films depend strongly upon their structure and their orientation with respect to the substrate upon which they are deposited. Therefore, their design and synthesis require careful attention to the interface between the primary molecular overlayer and the substrate. In the case of crystalline films grown on ordered substrates, elucidating the role of epitaxy at the overlayer—substrate interface is crucial for the fabrication of high quality films. While the influence of epitaxial interactions at the overlayer—substrate interface on film structure and orientation has been firmly established for inorganic and elemental systems, epitaxial principles for molecular films are just beginning to emerge.

Epitaxial principles for molecular overlayers merit special attention because overlayer structures depend on a delicate energetic balance of noncovalent interactions between the molecules comprising the overlayer and between the overlayer and substrate. The “soft” nature of these noncovalent interactions, which stems from shallow potential functions (i.e., small elastic constants), makes the structure of molecular films and the mode of epitaxy very sensitive to the competition between intralayer and overlayer—substrate interactions. Additionally, the size and symmetry of the unit cells of molecular overlayers typically differ from those of common substrates, arguing against commensurate lattices in the absence of severe distortions of a “native” close-packed overlayer structure. Consequently, native molecular overlayers will tend to be stabilized by coincidence, a condition in which the corners of a supercell, comprising several overlayer unit cells, coincide with substrate lattice points at periodic intervals, while overlayer lattice points within the supercell do not coincide with substrate lattice points.

In principle, the existence of an epitaxial relationship between a given overlayer and substrate can be predicted by potential energy (PE) calculations. However, PE calculations consider the interaction of every overlayer atom with every substrate atom and can be computationally intensive for the large overlayer...
Figure 1. (left) Schematic representation of a generic molecular overlayer on a rigid substrate. The substrate and overlayer lattices are defined by two-dimensional cells with lattice constants $a_1, a_2, \alpha$, and $b_1, b_2, \beta$, respectively. The angle $\theta$ between the vectors $a_1$ and $b_1$ defines the azimuthal orientation of the overlayer with respect to the substrate. (right) Schematic representations of specific commensurate and point-on-line coincident overlayer lattices (filled circles) on a hexagonal substrate lattice (open circles). In this example of coincidence, $b_1^* = 2a_2^*$ and the supercell has dimensions of $1 \times 2$ ($b_1 \times b_2$). For clarity we depicted coincidence with $\theta = 0^\circ$ and $b_1 = 3a_1$. However, it should be noted that this condition is not required for coincidence. Molecules at the corners of the supercells need not coincide precisely with substrate lattice atoms as coincidence only requires an integer periodicity in one direction of the lattices in direct space. However, the supercell is illustrated in this manner for conceptual simplicity.

Overview

A two-dimensional interface consisting of a substrate and an overlayer can be defined by seven independent parameters, the substrate by lattice constants $a_1, a_2$, and angle $\alpha$, the overlayer by $b_1, b_2$, and angle $\beta$, and the azimuthal orientation by the angle between $a_1$ and $b_1$ (Figure 1). Commensurism exists when the periodicities of the overlayer and substrate are related by integral multiples along two lattice vectors such that each overlayer molecule can be placed on equivalent substrate lattice points. The elastic constants are determined by the second derivative of the potential energy function, representing the curvature of the potential energy at the minimum energy position. If the in-plane overlayer–substrate elastic constants exceed the intralayer elastic constants of the overlayer, expansion or contraction of the overlayer to a commensurate structure will be preferred over a noncommensurate form in which some molecules do not sit on minimum energy substrate sites.

In contrast, intralayer elastic constants exceeding the in-plane overlayer–substrate elastic constants will tend to favor a given “native” overlayer structure and adopt a coincident epitaxial configuration if possible. The special case of point-on-line coincidence describes the condition in which rows of overlayer lattice points coincide with uniformly spaced rows of substrate lattice points corresponding to a specific lattice direction; that is, every lattice point of the overlayer coincides with a lattice vector of the primitive unit cell of the substrate. By definition, the direction of one of the overlayer reciprocal lattice vectors coincides with the direction of the reciprocal lattice vector defined by the substrate rows. The magnitudes of these reciprocal lattice vectors are related by an integral multiple.

An important consequence of coincidence is the existence of an overlayer supercell with molecules on its corners that coincide periodically with substrate lattice points, but with molecules within the supercell that do not coincide with substrate lattice points. The existence of a real-space supercell has been largely unrecognized, yet it is highly instructive and facilitates an understanding of coincidence. Contrary to assertions in ref 18 that coincidence models lack a compelling physical foundation, the registry of the supercell corners with the substrate provides a physicochemical basis for coincidence that is conceptually identical to true commensurism. The two modes of epitaxy differ only with respect to their “degree of commensurability”. It should be noted that the molecules at the corners of the supercells need not coincide precisely with substrate lattice atoms as coincidence only requires an integer periodicity in one direction of the lattices in direct space. However, the supercell in Figure 1 is illustrated in this manner for conceptual simplicity.

If the coinciding lattice points at the supercell corners are the most energetically favorable, by inference the noncoinciding lattice positions are less favorable. However, small in-plane overlayer–substrate elastic constants, expected for van der Waals interfaces, diminish the energetic penalty and stress...
associated with the noncoinciding lattice positions of a coincident overlayer, reducing the driving force for the overlayer to adopt a true commensurate structure. The favorable interactions between the substrate and the molecules at the supercell corners can stabilize a specific coincident configuration. The existence of less favorable noncoinciding overlayer lattice points within the supercell implies that the overlayer stability of a given rigid overlayer will decrease with the fraction of noncoinciding sites, that is, with increasing size of the supercell, as demonstrated recently in our laboratory.\textsuperscript{20} As the number of noncoincident overlayer lattice points increases, the overlayer will tend to adopt a more stable alternative coincident configuration or a truly commensurate structure.

The general lack of awareness of coincident epitaxy probably can be attributed to the difficulty in predicting, and even visualizing, coincident lattices, particularly for organic overlayers with oblique symmetries. In fact, it has even been suggested that epitaxy cannot be important for organic films.\textsuperscript{21} Nonetheless, the observation of numerous molecular overlayers with azimuthal orientations and lattice parameters that reflect coincidence\textsuperscript{15} argues that this mode of epitaxy is governed by the thermodynamics, not kinetics,\textsuperscript{18} of the overlayer–substrate interface.

Advances in the design and fabrication of coincident (and commensurate) molecular overlayers hinge on the ability to predict (i) the optimum configuration with respect to the orientation of molecules within the overlayer, (ii) the size and symmetry of the overlayer, and (iii) the azimuthal orientation of the overlayer with respect to the substrate. The most direct approach for predicting epitaxial configurations involves total potential energy (PE) calculations, typically based on semiempirical Buckingham or Lennard–Jones 6–12 potential functions. However, PE methods tend to be computationally intensive, requiring \( r \times s \) calculations for each azimuthal orientation of a given overlayer, where \( r \) and \( s \) represent the number of overlayer and substrate atoms, respectively. Calculations that allow additional degrees of freedom, such as permitting molecules to translate and rotate within the unit cell, become computationally prohibitive, particularly for the large basis of a typical coincident supercell. This limitation is further exacerbated by the need to establish the phase relationship between a coincident overlayer and the substrate, which may require calculations based on numerous supercells (vide infra). Consequently, PE calculations of large coincident overlayers can be unreasonable unless the positions of the molecules and the lattice parameters are fixed, leaving the azimuthal orientation as the only degree of freedom. Furthermore, the accuracy of semiempirical PE calculations, which do not account for Coulomb, dipolar, and multipolar forces, may not be sufficient for unambiguous assignment of an optimum structure among polymeric alternatives.

In contrast, methods based solely on geometric lattice misfit models can predict optimum epitaxial configurations for a specific overlayer in a fraction of the time required for PE methods. Although lattice matching routines neglect intermolecular potentials and therefore cannot predict detailed overlaver structure, they can simplify subsequent PE calculations by first identifying the optimum coincident configuration (i.e., lattice parameters and azimuthal angle) for an overlayer. However, it first must be demonstrated that lattice matching routines predict epitaxial configurations that are identical to those predicted by PE calculations. Under these conditions, the surface potentials of the substrate and overlayer would correspond to their respective lattice periodicities. Such agreement would signal that overlayer configurations are influenced primarily by lattice matching rather than the detailed supramolecular organization within the overlayer.

A geometric lattice model adapted from Bollmann’s coincident-site lattice method for describing grain and phase boundaries has been used by Reeves and Evans to identify preferred epitaxial orientations\textsuperscript{22} based on the number density of coinciding lattice sites in the 2-D overlayer–substrate interface. The analytical function used in this method typically produces numerous orientations with similar coinciding site densities, thereby complicating assignment of a single optimum orientation. Another method based on numerical iteration has been used by Hoshino to surmise the best degree of fit between the overlayer and substrate,\textsuperscript{23} but this procedure is computationally intensive. EpiCalc, a program devised in our laboratory that relies on a direct analytical function, is computationally efficient. The time required for calculations with EpiCalc is independent of overlayer size, enabling analysis of systems with large bases (such as coincident lattice supercells) and examination of numerous different overlayer–substrate lattice combinations in a timely manner.

Methods

Potential energy calculations were performed on a Hewlett-Packard 710 workstation using universal force field\textsuperscript{24} parameters and the Lennard–Jones 6–12 potential function. These calculations were combined with a FORTRAN code that allowed approach, translation, and rotation of an overlayer with respect to a substrate. Calculations were performed with the chosen overlayer lattice plane parallel to the HOPG substrate surface (vide infra). The minimum energy overlayer–substrate separation was determined by positioning the origin of the overlayer unit cell (taken as the origin of its crystallographic analog) over the crystallographic origin of the HOPG substrate and calculating energy as a function of distance. The overlayer was then fixed at this separation and the energy calculated at 1° increments of azimuthal angle \( \theta \). All PE calculations considered only overlayer–substrate interatomic potentials such that intermolecular interactions within an overlayer were neglected.

Determination of the mode of epitaxy and optimum overlayer orientation was accomplished using EpiCalc, a program developed in our laboratory that has been designed for operation in the Windows 95 environment. EpiCalc relies on an analytical function devised in our laboratory that enables calculation of \( V/V_o \), which we termed a “dimensionless potential” (eq 1).\textsuperscript{15}

\[
\frac{V}{V_o} = \left\{ 2MN - \frac{\sin(M\pi p_x\sin(N\pi q_x))}{\sin(\pi p_x)\sin(\pi q_x)} - \frac{\sin(M\pi q_x\sin(N\pi p_x))}{\sin(\pi q_x)\sin(\pi p_x)}\right\} \left(\frac{1}{2MN}\right)
\]

where \( 1/(MN) \) is a normalization constant and \( M \) and \( N \) define the size of the overlayer. The values of \( p_x, q_x, p_y, \) and \( q_y \) are defined by a transformation matrix that relates the overlayer lattice vectors to the lattice vectors of the substrate (eqs 2–6).

\[
\begin{bmatrix} b_1 \\ b_2 \end{bmatrix} = [C][a_1 \ a_2] = [p_x \ q_x, \ q_y \ p_y][a_1 \ a_2]
\]

and
layer of bulk PTCDI so that the PTCDI planes were confined to the lattice plane. The lattice parameters were then expanded to the values reported in ref 16e and the molecules repositioned within the expanded unit cell to the original fractional coordinates. The overlayer was verified as coincident with EpiCalc.

The PTCDA overlayers examined here were modified forms of the bulk (100) and (102) layers. PTCDA overlayers 1–IV were based on the overlayer structure reported in ref 17. PTCDA-I (Figure 2c) was generated by flattening the (102) layer of the bulk crystal so that the PTCDA planes were confined to the lattice plane, expanding the lattice parameters to the coincident values determined by EpiCalc, and repositioning the molecules to the original fractional coordinates. The PTCDA molecules were then rotated in-plane so that the in-plane orientations of the molecules at 0,0 and 1/2,1/2,1/2 are +49.3° (clockwise) and −68.2° (counterclockwise) from \( b \), respectively, generating the structure that was previously reported as the minimum energy configuration. PTCDA-II (Figure 2d) was generated by flattening the (102) layer so that the PTCDA planes were confined to the lattice plane, expanding the lattice parameters to the coincident values determined by EpiCalc, and repositioning the molecules to the original fractional coordinates. The in-plane orientations of the molecules at 0,0 and 1/2,1/2,1/2 are +48.8° (clockwise) and −48.8° from \( b \), respectively.

PTCDA-III (Figure 2e) was generated by expanding the unflattened (102) layer to the coincident values determined by EpiCalc and repositioning the molecules to the original fractional coordinates. PTCDA-IV (Figure 2f) was generated by expanding the unflattened bulk (100) layer to the coincident lattice parameters and repositioning the PTCDA molecules within the unit cell to the original fractional coordinates. Both PTCDA-III and PTCDA-IV were not flattened. A hypothetical overlayer, constructed by replacing PTCDA molecules in a flattened (102) layer with naphthalenetetracarboxylic dianhydride (NTCD-DA), was also examined.

A PTCDA overlayer (on HOPG) with lattice parameters nearer those of the bulk (102) plane than the PTCDA overlayers above has also been reported. This overlayer structure, PTCDA-V (Figure 8), was generated by adjusting the unflattened (102) layer to the coincident values found by EpiSearch, nearest the reported values. The molecules were repositioned to their respective original fractional coordinates after the unit cell was adjusted.

Results

\( \beta-(ET)_2I_3 \) Overlayer. Using in situ atomic force microscopy, we previously observed the formation of a 15.5 Å thick ET\(_2\)I\(_3\) overlayer on HOPG at an azimuthal orientation of \( \theta = 18^\circ \) with lattice parameters \( b_1 = 6.2 \pm 0.5 \) Å, \( b_2 = 9.4 \pm 0.8 \) Å, and \( \beta_2 = 107 \pm 4^\circ \).19 These lattice parameters were nominally identical to the values for the (001) plane of bulk \( \beta-(ET)_2I_3 \) (\( a = 6.6 \) Å, \( b = 9.1 \) Å, \( \gamma = 110^\circ \) and (001) layer thickness = 15.5 Å). The ET molecules in the (001) orientation are tilted 38° from a normal to the HOPG surface. The value of \( \theta \) in this case (and in all following examples) is based on the angle between \( b_1 \) and \( a_1 \), the latter assigned to the conventionally accepted lattice vector for HOPG (this is emphasized here as some reports have used a lattice vector rotated 30° from \( a_1 \) to measure \( \theta \)).

EpiCalc produced \( V/\nu = 0.5 \) at \( \theta = 19.8^\circ \) for a 51 × 51 overlayer, verifying the existence of coincidence for these lattice parameters (Figure 3a). This azimuthal angle is identical, within experimental error, to the observed value.

A comparison of PE calculations with EpiCalc for the (001) \( \beta-(ET)_2I_3 \) overlayer reveals the importance of overlayer size when
attempting to determine the optimum azimuthal angle (Figure 4). PE calculations performed with a $3 \times 3$ overlayer produces multiple, broad minima. A $10 \times 10$ overlayer affords five minima at $\theta = 18^\circ$, $\theta = 21^\circ$, $\theta = 24^\circ$, $\theta = 38^\circ$, and $\theta = 60^\circ$ (Figure 4). The two minima at $\theta = 18^\circ$ and $\theta = 21^\circ$ converge with increasing overlayer size to $\theta = 20^\circ$ for a $15 \times 15$ overlayer.

The azimuthal angle predicted by PE methods is nominally identical to the coincident value of $\theta = 19.8^\circ$ determined by EpiCalc and observed experimentally (the slight difference is simply a consequence of the $1^\circ$ increments used in the PE calculation). The minima at $\theta = 38^\circ$ and $\theta = 60^\circ$ remain for the $15 \times 15$ overlayer, although these orientations were never observed experimentally. We note that at small overlayer sizes the energy at and near the coincident orientation of $\theta = 20^\circ$ is less negative than the energy for other, noncoincident orientations. This is due to the contribution of local interactions that predominate at small overlayer sizes, wherein the energy is sensitive to molecular structures and orientations within the unit cell as well as overlayer translational positioning on the substrate. A similar trend with overlayer size was observed with EpiCalc. Small overlayer sizes exhibited multiple and broader minima, but the single coincident value of $\theta = 19.8^\circ$ is clearly evident for overlayer dimensions exceeding $15 \times 15$.

**PTCDI Overlayer.** The lattice parameters of epitaxial PTCDI overlayers on HOPG, as determined by scanning tunneling microscopy,\textsuperscript{16e} are $b_1 = 14.5$ Å, $b_2 = 16.9$ Å, and $\beta_0 = 83.6^\circ$, with an azimuthal orientation of $\theta = 12.7^\circ$. EpiCalc for a $51 \times 51$ overlayer indicates that an overlayer with these lattice parameters is coincident at $\theta = 47.3^\circ$ (Figure 3b). This is identical to the reported value of $12.7^\circ$ (the convention used for lattice parameter assignment in ref 16e differs from that used here; $47.3^\circ$ is simply the $60^\circ$ complement of $12.7^\circ$).\textsuperscript{27} PE calculations for this overlayer were performed on a PTCDI layer structure (Figure 2b) generated by flattening the bulk (1 0 2) layer so that the PTCDI planes would lay flat on the HOPG
The results agree with EpiCalc, which produces prominent and the sharp minimum at the PE minimum at deep minimum at overlayer size is increased several others emerge, including a 18). reported by Forrest et al. indicated a of 14.2 EpiCalc. The PE calculation for a 3 values reported in ref 16e, which was verified as coincident by surface, followed by expanding the lattice parameters to the Figure 3. Calculated dependence of \( V/V_0 \) on azimuthal angle \( \theta \) and schematic representations of the optimum overlayer orientations for the coincident overlayer—substrate systems: (a) \( \beta \)-ET\(_4\)/HOPG \((b_1 = 6.6 \text{ Å}, b_2 = 9.1 \text{ Å}, \beta_0 = 109.8^\circ)\); (b) PTCDI/HOPG \((b_1 = 14.5 \text{ Å}, b_2 = 16.9 \text{ Å}, \beta_0 = 83.6^\circ)\); and (c) PTCDA/HOPG \((b_1 = 20.43 \text{ Å}, b_2 = 15.7 \text{ Å}, \beta_0 = 90^\circ)\). The calculations were performed with 51 \( \times \) 51 overlayers.

### PTCDI Overlayers

Several groups have reported PTCDI overlayers on HOPG, with Forrest et al. describing overlayer growth as “quasiepitaxial”.\(^{17,18}\) However, the experimental data reported by Forrest et al. indicated a single azimuthal orientation of \( \theta = 21.6 \pm 4^\circ \) with lattice parameters \( b_1 = 20.5 \pm 1.2 \text{ Å}, b_2 = 14.2 \pm 1.5 \text{ Å}, \) and \( \beta_0 = 90^\circ \) (Table 1).\(^{17,18,28}\) A second structure, reported by two other groups as epitaxial, is described below. Previous PE calculations\(^{17,18}\) for the “quasiepitaxial” structure, with the PTCDI molecular planes parallel to the HOPG substrate, predicted a minimum energy unit cell structure with lattice constants \( b_1 = 20.0 \pm 0.5 \text{ Å}, b_2 = 15.7 \pm 0.5 \text{ Å}, \) and \( \beta_0 = 90^\circ \). These calculations were performed with a Buckingham potential and a single PTCDI unit cell on HOPG. The energy minimization resulted in PTCDI molecules adopting specific in-plane orientations, with the long axes of the two independent molecules in the unit cell rotated by \(+49.3^\circ\) and \(-68.2^\circ\) from \( b_1 \). Subsequent PE calculations performed for a \( 10 \times 10 \) PTCDI overlayer constructed from this unit cell, with the molecules in fixed positions, predicted an optimum azimuthal angle of \( 19^\circ \).\(^{17,18}\)

The availability of structural data and PE calculations for this overlayer prompted us to examine its epitaxial relationship with HOPG using EpiCalc and compare these results with PE calculations. EpiCalc returns \( V/V_0 = 1 \) for all values of \( \theta \) with these lattice parameters, indicating that this overlayer is incommensurate. However, EpiSearch finds \( V/V_0 = 0.5 \) for a \( 51 \times 51 \) overlayer on HOPG at \( \theta = 18.2^\circ \) for \( b_1 = 20.43 \text{ Å}, b_2 = 15.70 \text{ Å}, \) and \( \beta_0 = 90^\circ \) (Figure 3c). Notably, these values are within the errors for the experimental data and PE computations in ref 17. PE calculations performed in our laboratory (not

**TABLE 1: Comparison of Bulk, Experimental, and Calculated Lattice Parameters and Azimuthal Orientations for Coincident Overlayers on a HOPG Substrate**

<table>
<thead>
<tr>
<th>Overlayer</th>
<th>( b_1 (\text{Å}) )</th>
<th>( b_2 (\text{Å}) )</th>
<th>( \beta_0 )</th>
<th>( \theta )</th>
<th>( \theta ) (PE)(^{a} )</th>
<th>Supercell size(^{b} (b_1 \times b_2) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta )-ET(_4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bulk (001)(^{26})</td>
<td>6.61</td>
<td>9.10</td>
<td>109.8(^{\circ} )</td>
<td>—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>experimental(^{24})</td>
<td>6.2 ± 0.5</td>
<td>9.4 ± 0.8</td>
<td>107 ± 4(^{\circ} )</td>
<td>18(^{\circ} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>coincident(^{d} )</td>
<td>6.6</td>
<td>9.1</td>
<td>110(^{\circ} )</td>
<td>19.8(^{\circ} )</td>
<td>20(^{\circ} )</td>
<td>1 ( \times ) 3</td>
</tr>
<tr>
<td>PTCDI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bulk (102)(^{f} )</td>
<td>14.42</td>
<td>14.73</td>
<td>90(^{\circ} )</td>
<td>—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>experimental(^{16e} )</td>
<td>14.5</td>
<td>16.9</td>
<td>83.6(^{\circ} )</td>
<td>12.7(^{\circ} )</td>
<td>47.3(^{\circ} )</td>
<td>2 ( \times ) 1</td>
</tr>
<tr>
<td>coincident(^{d} )</td>
<td>14.5</td>
<td>16.9</td>
<td>83.6(^{\circ} )</td>
<td>47.3(^{\circ} )</td>
<td>18(^{\circ} )</td>
<td>1 ( \times ) 3</td>
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<td>PTCDI</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>bulk (100)(^{f} )</td>
<td>17.34</td>
<td>11.96</td>
<td>90(^{\circ} )</td>
<td>—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bulk (102)(^{f} )</td>
<td>19.89</td>
<td>11.96</td>
<td>90(^{\circ} )</td>
<td>—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>experimental(^{e,17,18} )</td>
<td>20.5 ± 1.2</td>
<td>14.2 ± 1.5</td>
<td>90(^{\circ} )</td>
<td>21.6 ± 4(^{\circ} )</td>
<td>incommensurate</td>
<td></td>
</tr>
<tr>
<td>PE(^{e,17,18} )</td>
<td>20.0 ± 0.5</td>
<td>15.7 ± 0.5</td>
<td>90(^{\circ} )</td>
<td>19(^{\circ} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>coincident(^{d} )</td>
<td>20.43</td>
<td>15.7</td>
<td>90(^{\circ} )</td>
<td>18.2(^{\circ} )</td>
<td>18(^{\circ} )</td>
<td>1 ( \times ) 3</td>
</tr>
<tr>
<td>bulk (102)(^{f} )</td>
<td>11.96</td>
<td>19.89</td>
<td>90(^{\circ} )</td>
<td>—</td>
<td></td>
<td></td>
</tr>
<tr>
<td>experimental(^{16e} )</td>
<td>12.7</td>
<td>19.22</td>
<td>89.5(^{\circ} )</td>
<td>3.2(^{\circ} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>experimental(^{12} )</td>
<td>12.69</td>
<td>19.22</td>
<td>89.5(^{\circ} )</td>
<td>3.1(^{\circ} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>coincident(^{d} )</td>
<td>12.72</td>
<td>19.20</td>
<td>89.5(^{\circ} )</td>
<td>56.8(^{\circ} )</td>
<td>57(^{\circ} )</td>
<td>3 ( \times ) 1</td>
</tr>
<tr>
<td>NTCDAc</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>coincident(^{d} )</td>
<td>20.43</td>
<td>15.7</td>
<td>90(^{\circ} )</td>
<td>18.2(^{\circ} )</td>
<td>18(^{\circ} )</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) This work. \(^{b}\) Determined by EpiCalc from the matrix coefficients that define the coincident configuration. \(^{c}\) Lattice parameters determined by in situ atomic force microscopy. \(^{d}\) Coincident lattice parameters were determined with EpiCalc. \(^{e}\) Cambridge Structural Database entry LENPEZ, G. Klebe, private communication, 1994. \(^{f}\) Private communication, R. Pascal. \(^{g}\) Lattice parameters determined by scanning tunneling microscopy. \(^{h}\) PE calculations were used to determine the minimum energy structure and lattice parameters for a single unit cell on the HOPG substrate. The optimum value of \( \theta \) was subsequently determined by PE methods for a \( 10 \times 10 \) overlayer with the structure and lattice parameters locked (refs 17, 18). \(^{i}\) Hypothetical structure.
Each plot. Overlayer sizes for the Vı and lattice parameters calculated in ref 17, produce minima at shown here) on a 10 × 10 overlayer, having the same structure and lattice parameters calculated in ref 17, produce minima at \( \theta = 14^\circ \) and \( \theta = 17^\circ \). We observe that even at large (15 × 15) overlayer sizes these minima are shallow and not well defined. To further explore the importance of using coincident lattice parameters when performing PE calculations, we examined the overlayer identified as PTCDA-I (Figure 2c), which is identical to the overlayer described in ref 17 but has lattice parameters expanded to the exact coincident values determined by EpiCalc. Three minima at \( \theta = 14^\circ, 18^\circ, \) and \( 23^\circ \) are observed for a 3 × 3 overlayer, but as the overlayer size is increased the minimum at \( \theta = 23^\circ \) vanishes, the minimum at \( 14^\circ \) shifts to \( 13^\circ \), and the peak at \( 18^\circ \) remains (Figure 6). Calculations performed for a 15 × 15 overlayer reveal that the energy minimum at \( \theta = 18^\circ \) is approximately 0.1 kcal/mol less than that at \( \theta = 13^\circ \).

In contrast, EpiCalc produces six minima at \( \theta = 3.2^\circ, 13.0^\circ, 18.2^\circ, 41.8^\circ, 47.0^\circ, \) and \( 56.8^\circ \) for a 15 × 15 PTCDA-I overlayer. The first three values are simply the complements of the last three owing to symmetry considerations associated with the rectangular overlayer unit cell and the hexagonal symmetry of the HOPG substrate (Figure 6, minima at complementary angles are denoted by the symbols *, †, or ‡). This symmetry equivalence is absent in the PE calculations because the asymmetric orientation of the two PTCDA molecules in PTCDA-I reduces the overlayer symmetry. The minima at \( \theta = 3.2^\circ, 13.0^\circ, 47.0^\circ, \) and \( 56.8^\circ \) become less prominent with increasing overlayer size until only the single coincident orientation at \( \theta = 18.2^\circ \) (and its complementary angle of \( \theta = 41.8^\circ \)) was observed for the 51 × 51 overlayer (Figure 3c). The coincident lattice parameters agree with the measured values, arguing that the observed PTCDA overlayer is coincident rather than incommensurate. The convergence toward a clearly identifiable and unambiguous minimum in both EpiCalc and PE calculations with increasing overlayer size illustrates the importance of using large overlayers in calculations.

The observation of the same minimum at \( \theta = 18^\circ \) for EpiCalc and PE calculations for the PTCDA-I overlayer argues convincingly that the lattice registry associated with coincidence is primarily responsible for the observed epitaxial configuration. This prompted us to examine if the arrangement of molecules in the overlayer, for a given set of lattice parameters, affected the optimum \( \theta \) value produced by PE calculations. PE calculations were performed on various PTCDA lattices derived from bulk (102) and (100) layers (Figures 2d–2f), with lattice

Figure 4. Dependence of the total PE (---) and \( VV_o (- - -) \) on overlayer size for the (001) \( \beta \)-ET-I overlayer in Figure 2a with \( b_1 = 6.6 \) Å, \( b_2 = 9.1 \) Å, \( \beta_1 = 109.8^\circ \) and a HOPG substrate with \( a_1 = 2.46 \) Å, \( a_2 = 2.46 \) Å, \( \alpha_0 = 120^\circ \). Overlayer sizes are indicated on each plot. However, for (c) the overlayer size for the \( VV_o \) calculation is 11 × 11 (even \( M \) and \( N \) values cannot be used as inputs for EpiCalc). The PE calculations were performed with the ET layer in contact with the HOPG substrate; the triiodide layer was not included in the calculations.

Figure 5. Dependence of the total PE (---) and \( VV_o (- - -) \) on overlayer size for the PTCDI overlayer in Figure 3b with \( b_1 = 14.5 \) Å, \( b_2 = 16.9 \) Å, \( \beta_1 = 83.6^\circ \) and a HOPG substrate with \( a_1 = 2.46 \) Å, \( a_2 = 2.46 \) Å, \( \alpha_0 = 120^\circ \). Overlayer sizes for the PE calculations are indicated on each plot. Overlayer sizes for the \( VV_o \) calculations of a–d are 3 × 3, \( 9 \times 9, 11 \times 11, \) and \( 15 \times 15 \), respectively (even \( M \) and \( N \) values cannot be used as inputs for EpiCalc).

Figure 6. Dependence of the total PE (---) and \( VV_o (- - -) \) on overlayer size for the PTCDA-I overlayer with \( b_1 = 20.43 \) Å, \( b_2 = 15.7 \) Å, \( \beta_1 = 90^\circ \) and an HOPG substrate with \( a_1 = 2.46 \) Å, \( a_2 = 2.46 \) Å, \( \alpha_0 = 120^\circ \). Overlayer sizes are indicated on each plot. However, the \( VV_o \) calculation for (c) was performed with an 11 × 11 overlayer (even \( M \) and \( N \) values cannot be used as inputs for EpiCalc).
for PTCDA-III. This can be attributed to the nominally parallel orientation of the molecules in contact with the HOPG substrate.

The energies of the PE minima are evident for the other three overlayers: (a) PTCDA-I, (b) PTCDA-II, (c) PTCDA-III, and (d) PTCDA-IV. The overlayer size was 10 x 10 for each PE calculation and 11 x 11 for each VVv calculation.

Overlayer PTCDA-II is a (102) layer, flattened and expanded, with the PTCDA molecules retained in their bulk in-plane orientations (the long molecular axes of the two independent molecules are oriented 48.8° and 48.8° with respect to b1). PE calculations and EpiCalc produce two minima at θ = 13° and θ = 18° for a 10 x 10 overlayer of PTCDA-II (Figure 7). These angles are identical to those obtained for PTCDA-I, although the actual energy values from the PE calculations differ slightly (≈ 1 kcal/mol, < 1% of total energy). Two peaks were also observed at the complementary angles of θ = 42° and θ = 47°. The observation of an energy maximum at θ = 47°, instead of a minimum, has been noted previously for other systems. The observation of this maximum, which also is a consequence of the phase coherence of the substrate and overlayers, is due to the sensitivity of the energy to overlay translations on the substrate.

The remaining two overlayers, PTCDA-III and PTCDA-IV, correspond to unflattened versions of the (102) and (100) planes, respectively, expanded to the coincident parameters. The out-of-plane tilts of the PTCDA molecules are 3° and 20° for PTCDA-III and PTCDA-IV, respectively. Even though the arrangements of PTCDA molecules in these overlayers differ substantially, PE calculations for both produce the same azimuthal orientations predicted for PTCDA-I and PTCDA-II at θ = 13° and θ = 18° (and two minima at the complementary angles of θ = 42° and θ = 47°). The energies of the PE minima for PTCDA-III are approximately four times that of PTCDA-IV. This can be attributed to the nominally parallel orientation of the molecules in PTCDA-III, which has more atoms in contact with the HOPG substrate.

In contrast to the other three overlayers, PTCDA-IV exhibits the deeper minimum at θ = 13°. However, the energy difference between the two minima for PTCDA-IV is only 0.1 kcal/mol, less than 0.4% of the total energy. Small differences in the energy of the two minima are evident for the other three overlayers as well. The data in Figure 7 indicate that [E(θ = 18°) - E(θ = 13°)] for PTCDA-I is only −0.2 kcal/mol (< 0.2% of total energy), while for PTCDA-II and PTCDA-III this quantity is < 0.05% of the total energy. These same two minima are also evident in the EpiCalc results, their VVv values indicating near coincidence at θ = 13° and coincidence at θ = 18°. The peak at θ = 13° vanishes completely for overlayer sizes exceeding 31 x 31 when using EpiCalc, while the peak at θ = 18° remains.

A PTCDA overlayer with a structure differing from PTCDA-I, II, III, and IV, but having lattice parameters nearer those of the (102) layer of the bulk crystal structure, has also been reported (Table 1). Using the reported lattice parameters as a starting point for EpiSearch, we found a precisely coincident lattice with lattice parameters b1 = 12.72 Å, b2 = 19.7 Å, β0 = 89.5° and a HOPG substrate with a1 = 2.46 Å, a2 = 2.46 Å, α = 120°. The overlayer size was 10 x 10 for the PE calculations and 71 x 71 for VVv.

Discussion

The observed trends described above demonstrate that the determination of the optimum azimuthal angle by either method is ambiguous for overlayers with dimensions of 15 x 15 or less. However, the lattice modeling calculations with large overlayers return a single optimum azimuthal angle that reflects a coincident overlayer. In all cases, the orientations determined with EpiCalc agree with the corresponding experimentally observed values and one of the minima predicted by PE methods. This agreement argues that the overriding factor governing epitaxy for these van der Waals interfaces is phase coherence between the overlayer and substrate.

The observation of multiple and false minima has been attributed to “edge effects” that are only eliminated upon
increased. Consequently, the energy of the false minimum error for the coincident minimum as the overlayer size is the exact coincident configuration, accumulates faster than the minima, which represent greater misfit than the minimum for as the overlayer size increases. The total error for the false error in the calculations due to these inexact parameters increases different number of substrate atoms within this cutoff. The total overlayer molecules in different unit cells can encounter a many unit cells would reside on identical substrate positions lographically equivalent overlayer lattice points separated by the overlayer (to at least several decimal places), two crystal-lographically equivalent overlayer lattice points separated by many unit cells would reside on identical substrate positions and would encounter the same number of substrate atoms within the 15 Å cutoff. However, if the lattice parameters are inexact, overlayer molecules in different unit cells can encounter a different number of substrate atoms within this cutoff. The total error in the calculations due to these inexact parameters increases as the overlayer size increases. The total error for the false minima, which represent greater misfit than the minimum for the exact coincident configuration, accumulates faster than the error for the coincident minimum as the overlayer size is increased. Consequently, the energy of the false minimum increases faster than the optimum minimum, eventually disappearing while the optimum minimum only decreases slightly. The same principle applies to the energy values in the immediate vicinity of the optimum minimum, resulting in a narrowing of this peak.

PE calculations and EpiCalc also produce different values of θ at small overlayer sizes. This difference can be attributed to local, nonperiodic molecule—substrate interactions that appear in PE calculations and contribute more at small overlayer sizes. Such effects are not germane to EpiCalc, which relies solely on lattice registry. However, the agreement between these methods (with respect to θ) when large overlayer sizes are used, and the agreement of these values with experimentally observed values of θ, corroborates the existence of coincidence and its importance in determining epitaxial configurations.

The reliability of EpiCalc with respect to predicting the correct azimuthal orientation for a coincident overlayer is fortunate in two respects. The precision of semiempirical PE calculations is not sufficient for confident assignment of a global thermodynamic minimum when multiple minima are observed. Additionally, the computational time required for EpiCalc is significantly less than for PE methods so that EpiCalc can be reasonably performed with large overlayer sizes at which a single optimum azimuthal orientation can be observed. PE calculations rely on calculating the interaction of every atom of the overlayer with every atom of the substrate. Consequently, the computational time increases exponentially with increasing overlayer area, quickly becoming prohibitive. This is exacerbated by the numerous atoms per lattice site in molecular films and the need to perform calculations with large overlayer sizes to establish the phase coherence that is necessary for accurate calculations. In contrast, computational time for EpiCalc is independent of overlayer size and, for a single set of user-defined lattice parameters, requires less than one second per calculation at each azimuthal angle.

An illustrative comparison of computation times for the two methods is depicted in Figure 9. Calculation of the total PE over the range 0° ≤ θ ≤ 60° for a 10 × 10 overlayer with a fixed set of lattice parameters and 48 atoms per unit cell (the hypothetical NTCDA overlayer) requires approximately 12.5 h, while the corresponding calculation with EpiCalc requires only seconds. This time for PE calculations is actually a conservative estimate as molecular overlayers typically contain more than 48 atoms per unit cell, for example, 55 and 76 atoms in the unit cells of β-ET₃J and PTCDA, respectively.

Conclusions

The results described above demonstrate that geometric lattice matching routines such as EpiCalc can be used reliably to detect the existence of coincidence and predict the optimum azimuthal orientation for a given set of overlayer and substrate lattice parameters. EpiCalc is unique among geometric models with respect to its capacity to search for lattice parameters that are coincident with a chosen substrate. Because of the analytical nature of the EpiCalc algorithm, searching for coincident configurations is rapid even though the calculations involve four degrees of freedom (b₁, b₂, b₃, and θ). Such calculations with PE methods are computationally prohibitive, particularly for large overlayer sizes that are required for unambiguous assignment of optimum configurations.

The agreement of experimental data and PE calculations with the configurations predicted by EpiCalc demonstrates the validity of using this geometric lattice misfit model to predict and visualize epitaxial configurations, particularly coincident overlayers that are difficult to predict and visualize owing to their oblique symmetry, large size, and reduced commensurability with the substrate. EpiCalc is a convenient method for rapid screening of optimum coincident configurations (b₁, b₂, b₃, and θ) that can be used in subsequent PE calculations that allow relaxation of the molecular orientation to a minimum energy structure within the overlayer. The ability to reduce the degrees
of freedom in the PE calculation by first determining the coincident lattice parameters and \( \theta \) makes the calculation of overlayer structures more feasible for large overlayers. Furthermore, the agreement between experiment, semiempirical calculations, and a modeling routine based solely on lattice geometry demonstrates that molecular overlayer orientations are commonly governed by coincident epitaxy. More important, these results confirm that coincidence has a fundamental physicochemical foundation that is identical to that used to explain the occurrence of strictly commensurate lattices.

Interestingly, the results of these simulations have been advanced to explain the orientation of strictly commensurate lattices. More important, geometries demonstrate that molecular overlayer orientations are commonly governed by coincident epitaxy. Further calculation, and a modeling routine based solely on lattice parameters and \( \theta \) makes the calculation of overlayer structures more feasible for large overlayers. Further calculations, and a modeling routine based solely on lattice geometry demonstrates that molecular overlayer orientations are commonly governed by coincident epitaxy. More important, these results confirm that coincidence has a fundamental physicochemical foundation that is identical to that used to explain the occurrence of strictly commensurate lattices.

We note that phenomenological arguments based on Moiré patterns have been advanced to explain the orientation of apparently noncommensurate, simple inorganic lattices, which also were shown to be energetically favorable by numerical simulations. Interestingly, the results of these simulations do not depend strongly on the form of the potential function used in the calculation. Other analyses have demonstrated that these systems are actually coincident and have concluded that the phase coherence resulting from coincidence is responsible for overlayer stabilization. Notably, the minima observed for PE calculations of the PTCDA-I overlayer are reproduced when the PTCDA molecules are replaced with smaller NTCDA molecules or argon atoms. This further substantiates that the phase coherence between the substrate and overlayer lattices governs the optimum azimuthal angle, not the specific arrangements or structures of the molecules within the unit cell. We anticipate that the recognition of the importance of coincidence to molecular overlayers and the use of convenient methods such as EpiCalc will significantly facilitate the design and fabrication of complex functional molecular films.

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Appendix

Determination of the mode of epitaxy and optimum overlayer orientation can be accomplished using EpiCalc, a geometric lattice misfit algorithm developed in our laboratory. EpiCalc relies on an analytical function devised in our laboratory that enables calculation of \( \frac{V}{V_o} \) which we termed a “dimensionless potential” (eq A1).

\[
\frac{V}{V_o} = \left\{ 2MN - \frac{\sin(M\pi p_s)\sin(N\pi q_s)}{\sin(\pi p_s)\sin(\pi q_s)} + \frac{\sin(M\pi q_s)\sin(N\pi p_s)}{\sin(\pi q_s)\sin(\pi p_s)} \right\} \left( \frac{1}{2MN} \right) \quad (A1)
\]

term A: \( 2MN \)

\[
\frac{\sin(M\pi p_s)\sin(N\pi q_s)}{\sin(\pi p_s)\sin(\pi q_s)}
\]

term B: \( \frac{\sin(M\pi p_s)\sin(N\pi q_s)}{\sin(\pi p_s)\sin(\pi q_s)} \)

term C: \( \frac{\sin(M\pi q_s)\sin(N\pi p_s)}{\sin(\pi q_s)\sin(\pi p_s)} \)

term D: \( 1/(2MN) \)

Note: \( M = 2m + 1 \) and \( N = 2n + 1 \); \( m \) and \( n \) are the values input into EpiCalc, resulting in \( M \) and \( N \) always being odd. This is required to achieve nonzero values for numerators in terms B and C in (A1) so that the discrete values of \( \frac{V}{V_o} \) \( (1, 0.5, \) and \( 0) \), which are necessary to distinguish the different modes of epitaxy, can be realized. The function in (A1) behaves as follows for the different modes of epitaxy.

1. Commensurism. Every matrix element is an integer. In this case, terms B and C are both equal to 0/0 \( (\text{sin}(\text{integer}\cdot\pi) = 0) \). Therefore, L’Hopital’s rule (eq A2) must be invoked.

\[
\lim_{x \to 0} \frac{f(x)}{g(x)} = \frac{f'(a)}{g'(a)} \quad (A2)
\]

Then, the numerator of term B becomes

\[
\frac{d}{dq_s dp_s} = M\pi \cos(M\pi p_s)N\pi \cos(N\pi q_s)
\]

and the denominator becomes

\[
\frac{d}{dq_s dp_s} = \pi \cos(\pi p_s)\pi \cos(\pi q_s)
\]

Therefore,

\[
\text{term B} = \frac{M\pi \cos(M\pi p_s)N\pi \cos(N\pi q_s)}{\pi \cos(\pi p_s)\pi \cos(\pi q_s)}
\]

Similarly,

\[
\text{term C} = \frac{M\pi \cos(M\pi q_s)N\pi \cos(N\pi p_s)}{\pi \cos(\pi q_s)\pi \cos(\pi p_s)}
\]

For the case of two identical, square lattices, \( p_s = p_t = 1 \) and \( q_s = q_t = 0 \). Then,

\[
\frac{V}{V_o} = \frac{2MN - MN - MN}{2MN} = 0
\]

2. Coincidence. Here, \( p_s \) and \( q_s \) or \( p_t \) and \( q_t \) must be integers. This will result in either term A or term B being indeterminate with a value of 0/0. Therefore, L’Hopital’s rule must be used to solve the indeterminate term. For example, if only \( p_s \) and \( q_s \) are integers,

\[
\text{term C} = \frac{M\pi \cos(M\pi q_s)N\pi \cos(N\pi p_s)}{\pi \cos(\pi q_s)\pi \cos(\pi p_s)} = MN
\]

However,

\[
\text{term B} = \frac{\sin(M\pi p_s)\sin(N\pi q_s)}{\sin(\pi p_s)\sin(\pi q_s)}
\]

A property of coincidence is that \( p_s \) and \( q_s \) are fractions with values such that the products \( M p_s \) and \( N q_s \) will be integers if \( M \) and \( N \) are integer multiples of the supercell dimensions. If \( M \) and \( N \) are not integer multiples of the supercell, \( M p_s \) and \( N q_s \) are not integers and term B = \( \pm 1 \). Therefore,

\[
\frac{V}{V_o} = \frac{2MN \pm 1 - MN}{2MN}
\]

As \( MN \) becomes large compared to 1, the \( \pm 1 \) term becomes negligible and \( \frac{V}{V_o} \to 0.5 \). Therefore, large values of \( M \) and \( N \) will enable convergence toward an unambiguous minimum for coincidence. Conversely, if \( M \) and \( N \) are integer multiples of the supercell, \( M p_s \) and \( N q_s \) will be integers and term B = 0. However, this condition requires that the lattice parameters be exactly the coincident values so that the matrix elements assume values that ensure that \( M p_s \) and \( N q_s \) are integers. It is improbable that the user will select lattice parameters for the calculation

Last et al.
that are the exact values required for coincidence. Consequently, in most calculations $M_P$ and $N_Q$ can be slightly nonintegral and term B (or term C if $p_i$ and $q_i$ are the pair of integral matrix coefficients) will be slightly nonzero. Therefore, EpiCalc is most reliable when $M$ and $N$ are large values.

3. Incommensurism. Here $p_B$, $q_B$, $p_C$, and $q_C$ are not integers. Therefore, $M_B$, $N_B$, $M_C$, and $N_C$ will not be integers and terms B and C will be equal to $\pm 1$. Then,

$$\frac{V}{V_0} = \frac{2MN \pm 1 \pm 1}{2MN}$$

As $MN$ becomes large, the $\pm 1$ terms become negligible and $V/V_0 \to 1$.

References and Notes


27. If $\beta_0$ is assigned a value of 94.6°, the 180° complement of 83.6°, EpiCalc produces a value of $V/V_0 = 0.5$ at $\theta = 12.7°$. Alternatively, a $V/V_0$ value of 0.5 at 12.7° with $\beta = 83.6°$ can be produced by altering the EpiCalc algorithm so that the overlayer is rotated clockwise ($b_1$ clockwise from $a_1$) instead of counterclockwise.

28. The angle of azimuth in refs 17 and 18 actually was reported to be $\theta = 8.4°$. However, this value was based on the angle between $b_1$ and a vector rotated 30° from $a_1$.


30. This concept can be understood by considering (i) a single unit cell, exhibiting a minimum at angle $\theta_1$ that has lattice parameters differing from exact coincident values by 0.1% and (ii) a different unit cell, exhibiting a minimum at angle $\theta_2$ that has lattice parameters differing from exact coincident values by 1%. If the overlayer comprises 10 unit cells, the PE calculations for the overlay at $\theta_1$ will have a total error of 5.5% (= 0.1 + 0.2 + ... + 0.9 + 1) at angle, whereas the total error for the other overlayer at angle $\theta_2$ will be 55% (= 1 + 2 + ... + 9 + 10).


