522 *Chem. Mater.* **2011,** *23,* 522–543
DOI:10.1021/cm102231b

CHEMISTRY OF
MATERIALS
Review

Application of Molecular Simulation Techniques to the Study of Factors Affecting the Thin-Film Morphology of Small-Molecule Organic Semiconductors[†]

Paulette Clancy*

School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, New York 14583, United States

Received August 5, 2010. Revised Manuscript Received December 3, 2010

We provide a short review of the status of using atomic- or molecular-scale simulations to look at the phenomena associated with growing thin films of small organic semiconductor materials, such as surface diffusion, thin film growth, Ehrlich−Schwoebel step-edge barrier, etc. We offer a summary of the advantages and limitations of existing computational tools (Molecular Dynamics, kinetic Monte Carlo, ab initio methods, etc.) and hint at method development that may help to deepen our understanding of "functional π"-materials. We provide a deeper focus on computational, as well as related experimental, studies of fundamental questions related to the thin-film growth of a representative member of this class of materials, pentacene, on a variety of substrates from insulating oxides to metals, and show results for some other organic semiconductor members of the class, wherever possible.

1. Introduction and Scope of the Review

1.1. Current State of the Art. As this special issue attests, there has been a growing interest, over the past few decades, in the study of "small molecule" organic semiconductors (defined, as is typical, to mean molecular weights MW < 1000), to differentiate from research into polymeric semiconductors. This is mainly due to the promise these materials offer in several commercial arenas, including large area, mechanically flexible electronic devices (field-effect transistors, sensors, light-emitting diodes, etc.) and in components of photovoltaic solar cells. Using small organic semiconducting molecules has several key advantages: They are compatible with flexible substrates and they offer the inherent manipulability of organic molecules to be synthesized to a custom structure or desired properties (for example, to favorably align ionization potential and electron affinity). As a result of this intense study, the electrical performance of such molecules in thin-film applications such as transistors[1−7] and LEDs[8−10] is sufficiently attractive to be in use in commercial flexible displays, and is under investigation as a component in photovoltaic cells.[11,12]

There are a large variety of small organic semiconducting molecules that could be considered as candidates for the thin films that drive these applications, and many of them are under current investigation. Typical candidates cover the acenes, thiophenes, phenyls, perylene derivatives, and many others. These molecules share an important structure-directing characteristic, namely a highly anisotropic intermolecular interaction: if two molecules are considered in isolation, the most energetically favored configuration occurs in a configuration that is essentially a cofacial arrangement with a small amount of lateral and horizontal offsets. The magnitude of acene−acene interactions, for instance, is relatively weak, on the order of a few tenths of an eV (i.e., ~1−2 kcals), while exhibiting almost no interactions in any other configuration. These weak interactions are often referred to by an "umbrella" term as "π-electron" overlap, but in fact involve contributions from a variety of interactions including interface dipoles, dispersion, and the term implied by van der Waals forces. See for example, electronic structure calculations by Sherrill and co-workers for acene *n*-mers that investigate such contributions.[13,14] This class of semiconducting molecules maximizes the net individual intermolecular interactions with their neighbors such that this generally results in the formation of a "herringbone" pattern in a variety of crystalline phases (polymorphs). Satisfying these anisotropic molecule−molecule interactions largely drives the self-assembly process during thin film construction. Control over the stacking can be driven further by appropriate and clever changes in the chemical constituency of the molecules to defeat the prevalence of the herringbone structure common to many of the molecules listed above, and create a so-called two-dimensional "π-stacked" material in which the semiconducting small organic molecules stack like bricks in a wall. John Anthony's creative ("ball and stick") organic chemistry synthesis of a family of silylethynyl-substituted acenes (that are more soluble and stable in solution than the

---

[†] Accepted as part of the "Special Issue on π-Functional Materials".

*Author to whom correspondence should be addressed. E-mail: Paulette.Clancy@cornell.edu.

parent acene) is an exemplar of what can be achieved in this regard (see refs 15 and 16 for reviews). We will consider some of the more well studied systems below, confining ourselves to reviewing organic thin film systems, and not considering blends with polymers (such as poly(3-hexylthiophene), better known as P3HT) to keep the scope of this short review to a manageable length.

The low-temperature processing dictated by the use of these temperature-sensitive materials has the effect of allowing a lot of different substrates to be considered as the supporting layer for these systems. Thus, the choice of substrate is an additional consideration to the choice of molecules for the semiconducting thin film itself. It became apparent quite early on that it was the balance of the interactions between the semiconducting thin film and the underlying substrate in comparison to the strength of the interaction between the thin-film molecules themselves that would play a crucial role in determining the structure of the adsorbed thin film. The thin-film structure is frequently characterized using the degree of order that can be achieved in the thin film. Indeed, structural order is widely used as the key measure for ascertaining the likely charge carrier mobility of the film; it is assumed that the higher the degree of crystalline order, the higher the mobility of the material. At room temperature, charge carriers are mainly localized on individual molecules, making "hopping" the predominant mechanism of charge transport. Charge carrier mobilities around $1-2\ \mathrm{cm}^2\ \mathrm{V}^{-1}\ \mathrm{s}^{-1}$ are considered a desirable benchmark target (being close to that for amorphous silicon) and this has been achieved for small organic molecules such as pentacene.

In fact, order is a good metric to use to correlate with mobility, although there have been assertions that crystalline order is not essential for high charge-carrier mobility. For instance, studies by Hanna and co-workers offer smectic liquid crystalline phases (of materials such as oligothiophenes and hexabenzocoronenes) as an alternative to thin films of organic semiconductors.[17,18] Their advantage is their self-assembling and self-annealing characteristics that give rise to larger domains without charge-trapping grain boundaries. Again, the more ordered the smectic phase, the higher the mobility; typical mobilities approach 1×10^{-2} cm/V s. Molecular Dynamics simulations coupled to Monte Carlo simulations of metal-free phthalocyanines[19-21] show the potential for molecular-scale simulation to model charge-transport properties of these liquid-crystalline systems and predict the nature of defects that can arise and modify the mobility.

It is clear from recent calculations[22] that the minimum requirement for high mobility is the presence of a percolating path by which electrons and holes can be transported through the material. Thermally induced disorder will certainly mean that the resultant mobility will be affected by the material's ability to find percolating paths for charge transport, as discussed for instance in ref 20. The ability to find optimal percolation paths is dependent on the field, as discussed in ref 21. The use of percolation theory to describe the mobility of relatively ordered small organic semiconducting molecules[22,23] is less common than for polymer blend semiconductor systems where crystallinity is frequently lower and amorphous polymers are not uncommon.[24-26] The interested reader is pointed toward other reviews that pursue this line of enquiry; see, for example, a review by Moliton and Hiornes[27] and a recent book on conducting polymers by Inzelt.[28]

Beyond the choice of organic semiconductor thin film and the underlying substrate, the processing method used to create the thin films, e.g., by deposition, introduces new variables (like substrate temperature, deposition rate/flux, angle of the incident beam, energy of the incident beam, etc.) that can be used to control the crystallinity of the thin film. Solution processing allows other variables to be considered and manipulated, from choice of solvent to temperature, concentration, etc.

The prevalent focus, especially from commercial endeavors, on using electrical performance as the, often singular, figure of merit for organic TFTs has not, in general, been matched by an equivalent activity to understand the fundamental "design rules" that govern the production of good quality thin films. Nor are we as a community at the point where we have established fundamentals-based links between processing variables (and/or approaches) and resultant thin-film morphology and properties. The situation has not been assisted by the fact that the large body of knowledge of the growth of inorganic thin films is not directly transferable to organics: The anisotropic intermolecular interactions that characterize small molecule organic semiconductors create a very different "phase space" to explore than we understand for inorganic semiconductors such as Si and Ge. And the almost infinite number of candidate molecules (achievable by modifying the chemical composition of organic molecules) offers a dauntingly large "playing field." These physicochemical differences are compounded by the fact that even small changes in deposition conditions, or postdeposition annealing, can have a very strong affect on the final morphology and topology of the deposited film, driven by the weak intermolecular driving forces.[29-35]

1.2. Role of Molecular Simulation Computational Studies. The nanometer scale of organic semiconductor devices and the computation tractability of many candidate organic molecules makes a computational investigation of thin-film growth and morphology highly attractive and, by and large, computationally viable. In principle, molecular simulation can provide unparalleled insight into the molecular mechanisms that govern these processes, often in ways that experiment cannot emulate. This is especially true for small and/or rare structural defects or unexpected molecular-scale mechanisms that cannot be imaged experimentally, and for investigations of buried interfaces that are difficult to even image experimentally. Although it is common for atomic-scale simulation to be used to explain experimentally observed phenomena, molecular simulation can play a potentially more important, and certainly more interesting, role to predict the outcome of processing at conditions as yet unexplored by experiments. For example, simulation can be used as a means to predict promising processing conditions and hence narrow the unmanageably large parameter space that experiments might otherwise have to explore. Second, simulation can be used to design, de novo, small organic molecules or self-assembled monolayer molecules that would provide better structural and electronic properties than the ones that are currently available. Finally, while simulation can be used to emulate the results of a chosen thin-film/substrate combination at routinely used experimental conditions, this is clearly not the best use of this still time-intensive approach. Thus a worthy ultimate goal of computational work in this area should be, we suggest, to understand the underlying design rules that relate molecular characteristics (shape, flexibility, chemical composition, binding energy to a given surface, energy levels, etc.) to predict the viability of a selected (but as yet unexplored) thin-film/substrate combination for a preselected morphology or electrical properties. The long-range goal of molecular simulation should be to lay the framework for understanding phenomena like thin-film growth in terms of readily available physicochemical properties to such an extent that further in-depth molecular simulation study is unnecessary; in essence, the goal of these simulation studies should be to do itself out of a job!

1.3. Scope of the Review. Any review of the computational efforts to understand and, in the future, control thin-film growth to achieve desired attributes of a material potentially covers a dauntingly large scope. A review can consider the broad range of candidate molecules under investigation, or confine itself to a study of selected properties, or of a particular computational approach. We have taken the tack not to confine this review solely to computational studies, partly because the context of what is known experimentally would thus be lost, and partly because computational efforts are dispersed and less prevalent. Hence the review below will attempt to highlight computational work but put it in the context of complementary experimental studies. To make the scope of this review more tractable, we choose to consider only the behavior of thin films of small organic semiconducting molecules (no polymer blends) on a variety of substrates, and restrict our consideration of thin-film technique to vapor deposition techniques, ignoring solution-based processing in order to keep the focus of the review within our limited expertise. The computational approaches that we are considering to fall within the purview of this review are limited to what might called "small-scale" simulation, meaning any computational approach that considers the thin-film system at the mesoscopic or molecular scale, or smaller. Thus we include computational studies using methods such as Molecular Dynamics, Kinetic Monte Carlo, and energy minimization techniques as well as electronic structure calculations. But we choose to largely ignore charge transport calculations, many of which rely on a foundation using Marcus theory, despite the centrality of needing a link between the calculation of charge mobilities once we know the molecular structure. This is done so that we may focus on understanding the largely unexplored linkage between thin-film structure and processing conditions. Readers can receive a good introduction to the theory of charge transport in organic semiconductor molecules in the review article by da Silva Filho et al.[36] the 2007 book *Organic Field-Effect Transistors* by Bao and Locklin[7] and in the article by Coropceanu et al.[27]

The goals of this review are thus, first, to provide a perhaps eclectic review of existing molecular simulation, and some related experimental studies, of the nature of thin films of some representative small organic semiconductor molecules. Second, we seek to offer readers, especially nonspecialists in the simulation field, a brief introduction to the range of molecular simulation techniques that might gainfully be employed for studies of organic semiconducting thin films, and outline their relative merits and limitations. We provide a fairly in-depth review of the state of computational, and related experimental studies, of thin-film deposition for the most well-studied representative molecular system, pentacene. Then, rather than provide a catalog of studies for different molecules, we will change to a more global view of properties and phenomena (e.g., surface diffusion, crystal structure, etc.) that are important in our understanding of the growth of organic thin films. Finally, we hope to step back at the conclusion of this paper and provide a "50 000 foot" view of the current state of computational studies of these fascinating systems and offer some suggestions for avenues of study at the intersection of computation and experimentation that could be beneficial to the community.

2. Molecular Simulation Methods for Thin-Film Growth and Surface Science

If we examine the molecular modeling "toolkit" that currently exists to simulate thin-film growth and, more generally, to study the nature of thin films on a dissimilar substrate, there are a variety of suitable methods at our fingertips. However, each is accompanied by strengths and limitations that, in practice, suggest to us that it is rarely the best choice to use one method to the exclusion of others. These methods are best used in conjunction with one another if a comprehensive understanding of the materials system is to be elucidated. "Small scale" computational approaches can be delineated in terms of their accessible length and time scales. They range from electronic structure calculations that take into account the positions of electrons within a small system that is modeled extremely accurately, to molecular simulations in which every atom in the molecule is explicitly modeled, and the system is allowed to evolve in time and space using Molecular Dynamics, to mesoscale, more coarse-grained, kinetic Monte Carlo methods where molecular detail is replaced by a representation that views the systems as a catalog of possible "events" (and associated rates) that describe the evolution of a larger system in time and space. As a rule of thumb, the more accurate the level of representation of the molecular system, the more intense the computational effort, leading to compromises in system size and the length and time scales that can be covered. We now provide some background for each of these approaches.

2.1. Electronic Structure Calculations. In an ideal world in which computing resources were infinite in extent, speed, and availability, we would almost certainly choose to model thin-film growth of small organic semiconducting molecules using "electronic structure" calculations, as they provide accurate structural information, access to electronic properties, and information about reaction pathways that we might most want to elucidate. Unfortunately, this is not the situation we face and electronic structure calculations are still limited to some degree by the computational intensity that they entail. The term "electronic structure" code covers many different methods, each with their own protagonists and developers. We take no stance on the relative merit of these methods except to make "broad brush" delineations between methods that might be helpful to the inexperienced reader. Readers are directed to some recent reviews[37-39] for more details on electronic structure methods.

In cases where the highest accuracy is needed, or for which electronic properties are sought, it is inevitable to recommend use of ab initio, or "electronic structure," methods such as Hartree–Fock (HF)-based or Density Functional Theory (DFT) methods; these methods are introduced briefly below. However, despite advances in computer processor speed, fully ab initio computations remain sufficiently onerous that it is typical to consider only a small number of atoms (or electrons in the system). This is typically on the order of 100 to perhaps several hundred atoms on a serial multicore processor. Early versions of plane wave-based electronic structure codes involved the diagonalization of large Hermitian matrices that scaled poorly, often with the cube (or worse) of the number of basis functions. However, in recent times, parallel versions of commonly used codes like the "Vienna code" (VASP)[40] and Gaussian,[41] and the many other electronic structure codes, have made studies of perhaps 1000 or so electrons accessible; see ref 42 for a recent review.

Ab initio methods offer the important advantage that they require little or no empirical data and involve far less parametrization than semiempirical models (isolated largely to the parametrization of some functionals, like the commonly used B3LYP as just one example). Indeed, the use of approximate ab initio methods such as orthogonal tight-binding in which the eigenstates are expanded in orthogonal basis set of localized atomic-like wave functions, is less common because the speed of modern computing processors has increased sufficiently to allow full ab initio calculations of electronic properties of large enough system sizes for which tight-binding used to offer the only practical solution. Such tight-binding calculations involved fitting a large number of parameters each time a new species was considered (often close to a hundred for transition metals). The parameters were typically fitted to ab initio calculations. In addition, the way that tight-binding methods handle charged species is rather opaque. There are, however, many variations on the theme of "tight-binding" and the more recent concept of "self-consistent charge density-functional tight-binding" (SCC-DFTB)[43] is gaining popularity for their faster computations than DFT in applications like biomolecules[44] or other systems whose size strains the ability of DFT to represent (see, for example, ref 45 for studies of nanorods and ref 46 for charge transport in organic molecules). In DFTB, a self-consistent redistribution of charges is implemented within a two-center nonorthogonal tight binding theory, using the approach of a second-order expansion of the Kohn–Sham total energy (DFT) functional.

All of the calculations involve a certain degree of approximation in solving the Schrödinger equation, $H\Psi = E\Psi$. Electronic structure calculations can, roughly speaking, be divided into wave function-based methods that relate the ground-state wave function to the ground-state total energy, and those that rely on Density Functionals to relate the electron density to the total energy. Traditionally, independent electron Hartree–Fock-based methods approximate the solution to the Schrödinger equation by a Slater determinant of molecular orbitals. This "mean-field" method includes so-called "statistical" electron correlations and ignores "dynamic" correlations. In contrast to DFT functionals, wave function-based methods such as the so-called "Moller–-Plesset" perturbation theory methods[47] (of which MP2 is perhaps the best known) include electron correlations to the Hartree–Fock method to second or higher order. These corrections are primarily responsible for the large computational time as the Hartree–Fock calculation itself is relatively simple.

Density functional theory (DFT) is the most prevalent approach to calculating the ground state electronic properties of materials. Its basis rests on the Kohn–Hohenberg theorem that the ground-state energy from the Schrödinger equation is an exact functional of the electron density and a second theorem that the electron density that minimizes the energy of the overall functional is a true descriptor of the density resulting from the solution of the Schrödinger equation. DFT uses the Kohn–Sham equation[48] to describe the Schrödinger equation for a set of noninteracting particles (usually electrons) that generates the same density as the true system of interacting particles. However, the exact form of the energy density functional is unknown and has to be approximated. This can be accomplished in many ways, of which the local density approximation (LDA) is a common strategy. In DFT, an initial density is guessed (usually by a superposition of the free-atom densities), the total energy of the system is calculated from the respective density functionals and the Kohn–Sham Hamiltonian is set up. Diagonalization of this Hamiltonian provides a set of molecular orbitals (and orbital energies). A new density is then derived from the lowest energy occupied orbitals and the process is repeated until self-consistency is achieved.

The explosion in choices of electronic structure, quantum chemical techniques over the past two decades has created a large number of wave function approximations as well as functionals to describe the electron correlation and exchange part of the Kohn–Sham equations.[49] An example of the former (wave function approximations) is the MP2 approach[50–53] (mentioned above), well-used examples of the latter (exchange-correlation functionals) include the hybrid functional "Becke, three-parameter, Lee–Yang–Parr," more commonly known as B3LYP,[54–57] the Perdew, Burke, and Ernzerhof pure functionals PBE[58] and PBE0,[59] and many others. It is difficult to know a priori which functional to use to calculate a chosen property for a given molecule and in a given environment (proximity to a surface, say). In practice, it is best to repeat the calculations using several functionals to determine the sensitivity of the results to such a change in mode. All three of these factors (property, molecule, environment) can affect this sensitivity. If the results show considerable differences, then a more careful analysis of the results has to be undertaken. If experimental data are available for comparison, it is tempting to choose the functional that most closely matches experiment, but this is both unsatisfying and can be misleading if the match is coincidental. It is worth taking the time to understand the origin of the functional and the set of experimental data to which its parameters were fitted.

Thus, ab initio methods give us, in principle, a very high accuracy in terms of predicting many key structural and energetic properties of materials. However, there are some limitations of these methods, e.g., the well-established fact that DFT methods (using a local density approximation or generalized gradient approximation approaches) invariably underestimate the band gap for both inorganic and organic materials. For example, see the recent work by Tsetseris and Pantelides[60] showing the band gap of pentacene to be around 1 eV, whereas the experimental value is 2.2 eV.[61] Thus, DFT-derived band gaps are best used to show trends rather than provide a reliable estimate, or readers might consider using a more accurate approach such as the GW perturbative method, cognizant of the fact that such methods impose an additional considerable computational effort over DFT methods; see review in ref 62.

For organic semiconductors, the most important limitation of the approximate functionals used in DFT and some other electronic structure methods is the neglect of, or inability to accurately represent, weak van der Waals (or London dispersive) forces that are important for this class of materials. These forces are not typically well handled by conventional hybrid functionals. Indeed, neglect of van der Waals forces can affect the prediction of the geometry of small organic semiconducting molecules,[63] a phenomenon we have also observed in published work on the geometry optimizations of some members of the metal-phthalocyanine family. Although there are many choices of ways to rectify this situation, reviewed briefly in ref 63, there is a respect for the ability of semi-empirical methods that include kinetic energy spin density terms in the "semi-local" component of the Generalized Gradient Approximation (GGA) approach. Promising approaches can be found in the studies of nonlocal van der Waals forces described in the literature.[64–66] They explain the compromises of attempting to optimize both geometric and electronic properties for some small-molecule organic semiconductors that will help the reader to make thoughtful choices of functionals. However, adding a more extended use of nonlocal exchange comes with a performance detriment: our calculations of some metal-phthalocyanine systems, for instance, show that using M06 over B3LYP, for instance, takes approximately 1.2–1.3 times as long. Similarly, adding a van der Waals correction to the PBE functional resulted in a roughly 15–35% slowdown in execution speed compared to B3LYP. Note that fair comparisons of different functionals can be difficult since execution speed depends on a number of implementation variables (e.g., processors used, clock speeds, use of threading/parallel algorithms, etc.) as discussed a little more below.

There is also the enduring issue of computational efficiency and scalability that limits the scope of the system that can be considered using ab initio approaches. In addition, both the level of theory used and the basis sets chosen need to be investigated carefully to ensure that the system is being properly described. A critical review of the advantages and shortcomings of the treatment of van der Waals forces in density functional theory methods was given recently by Tkatchenko et al.,[67] and by Riley et al. for small molecule motifs of the type likely to be found in proteins.[68] Riley et al. compared the ability of many basis sets for DFT and GGA (generalized gradient approximation) to predict properties such as the geometries, vibrational frequencies, ionization potentials, etc., for a variety of small molecules.

All these standard electronic structure calculations refer to the estimation of ground-state energies. The modeling of excited states in conjugated systems is, however, of considerable interest because low-lying excited states of π-conjugated molecules play an important role in the performance of TFTs, LEDs, and photovoltaic cells. Unfortunately, standard (implicitly ground state) DFT techniques show significant deviations from experiment when excited states are considered. In the past, it has been difficult to perform accurate calculations of excited states. Simple approaches such as configuration interaction singles (CIS)[69] used to have well-documented pitfalls that compromised their accuracy (e.g., 1–2 eV overestimation of excitation energies). Very accurate computations of excited states using Quantum Monte Carlo (QMC)[70] are prohibitively expensive. The use of time-dependent DFT (TDDFT) offers an alternative approach that is more accurate than CIS and more computationally efficient than QMC.[71] Excitonic spectra can be obtained by solving the Bethe–Salpeter equation for the two-body Green's function for the electron–hole pair; see for example a paper by van der Horst et al.[72] that uses such an approach to study the excited states of conjugated polymers. It should be noted that the accuracy of the TDDFT approach depends on the exchange-correlation functional that is used[73] and appears to be most accurate when the valence excited states are relatively low-lying. Some newer approaches to fill this need have come from the Brédas[74] and Chan[75] groups, whose use of ab initio density matrix renormalization group (DMRG) theory is capable of accurately reproducing the electronic properties of low-lying excited states of small π-conjugated oligomers. A later modification of this approach, known as Harmonic Davidson DMRG theory, allows the extension to higher-lying excited states as demonstrated for the acenes.[76]

2.2. Molecular Dynamics Simulations. Molecular Dynamics (MD) is a deterministic solution of the classical equations of motion of a system of atoms or molecules, essentially solving Newton's equation: $F = ma$, where F is the force between particles, m is the mass of the particles, and a is the acceleration.[77] MD provides an evolution of the system forward in time, advancing in a linear manner one time-step at a time. For systems like the organic molecules considered here, the time step is typically 1 fs or less, a compromise between wanting the time step to be large (to cover as long a time trajectory as possible) without negatively affecting the convergence of the algorithm solving the equations of motion. Algorithms that accurately solve the equations of motion (e.g., the widely used Verlet algorithm,[78] or the more accurate Beeman algorithm,[79] etc.) have been established for some time. Though the algorithms are well-developed, care still has to be taken in a number of user-controlled directions. First, and perhaps most importantly, the configuration of the system has to be set up with some forethought, ranging from a consideration of how to manage the periodic boundary conditions appropriately, especially in multiphase, multicomponent, or strained systems, to how the substrate is configured in terms of numbers of fixed layers versus "dynamic" layers (free to move under the influence of the intermolecular forces). Other user-controlled variables include deciding on the largest time step that can reasonably be used, the length of time for the simulation, system size, and the choice of an appropriate ensemble (e.g., the microcanonical "constant energy" ensemble NVE, the canonical isothermal ensemble, NVT, and the isothermal−isobaric ensemble, NPT, etc.). There are several good introductory books for readers to learn more about the foundations of Molecular Dynamics.[80−82]

A cautionary tale regarding setting up the system configuration should suffice to explain the care that needs to be given to produce well-designed MD simulations. We recently conducted an MD study of the diffusion of C_{60} buckyballs over a few monolayers of pentacene that are lying essentially face down on a fixed layer of metal or Si atoms with the intent to look at any tendency to form buckyball nanowires. The same system (a submonolayer of C_{60} on one or two layers of pentacene on a solid silver substrate) had been studied experimentally and shown to produce nanowires at low coverage.[83] Consideration of even a small number of buckyballs diffusing over a sufficiently large pentacene surface area (with additional subsurface layers of pentacene and Si in some cases) is a large system to simulate, involving close to 10 000 atoms. To save considerable computational effort, we initially fixed the x, y, z coordinates of two subsurface monolayers of pentacene molecules at positions found by equilibrating them in a constant-temperature MD simulation. Molecules in the topmost pentacene layer were allowed to move under the influence of the intermolecular forces. Superficially, this would seem to be a reasonable compromise, since the structure of sublayers is assumed to be flat. However, fixing the sublayers of pentacene (at effectively 0 K) significantly disordered the structure of the topmost pentacene layer (see Figure 1a) in a manner we felt was unphysical. But if these fixed subsurface layers of pentacene are replaced by a silicon or metal layer (i.e., the substrate more closely matches the experiment), the topmost pentacene layer remains ordered with the pentacene lying flat as expected (Figure 1b). If multiple C_{60} molecules are present, the topmost pentacene layer again becomes highly disorganized (driven, in this situation, by an imbalance between stronger $C_{60}-C_{60}$ and the weaker pentacene−pentacene interactions); see Figure 1c.

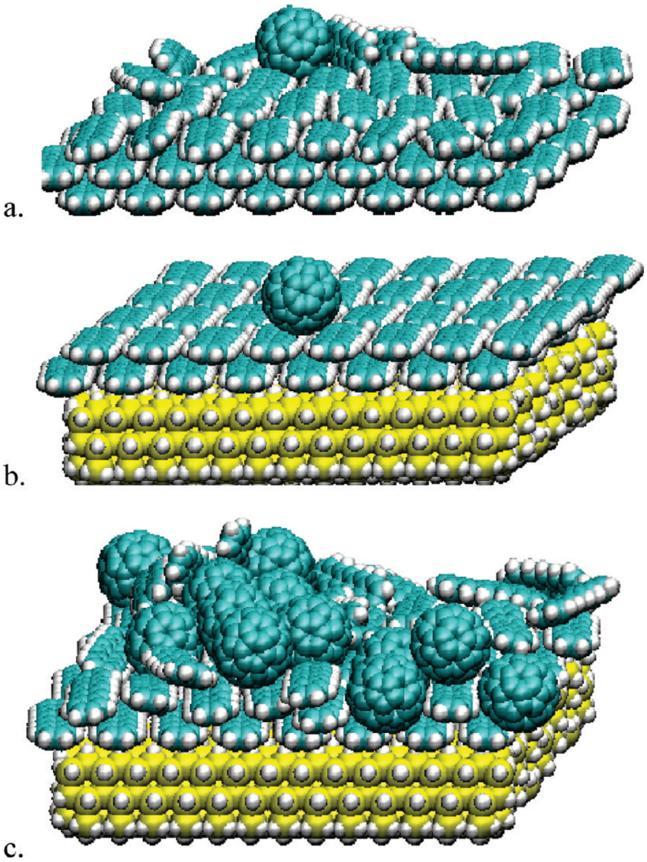

Figure 1. Snapshots from Molecular Dynamics simulations of C_{60} molecules on pentacene showing the effect of substrate interactions. (a) Single C_{60} molecule sitting on top of a monolayer of pentacene molecules that are free to move, supported beneath by two further monolayers of pentacene that are fixed in place (effectively at 0 K). Disorder is apparent in the topmost surface pentacene molecules, especially in the vicinity of the C_{60} molecule. (b) Situation is the same as in part a, except that the bottom pentacene layer in part a is replaced by a silicon substrate (shown in gold) whose atoms are fixed in place. The strong Si-pentacene interactions promote an ordered surface. (c) Situation is as in part b except that many more C_{60} molecules have been deposited. The stronger $C_{60}-C_{60}$ interactions in comparison to C_{60}-pentacene again creates disorder on the surface.

Amateur practitioners of MD simulations also need to beware of any tendency to consider the results of an MD simulation as indicating a "global energy minimum" or a "stable" system. The small time steps used in MD (1 fs, typically) and finite computing resources typically restrict MD simulations of small organic semiconducting molecules to system evolutions on the order of a few nanoseconds, though it is certainly possible for MD simulations to be run for 100 ns if necessary. This typically precludes studying the growth of very few monolayers for a reasonably sized substrate. There are ways to finesse this restriction, usually in the form of an accelerated MD algorithm. Voter has been the driving force for accelerated MD schema, from the "parallel replica," to "temperature-accelerated dynamics" and "hyperdynamics".[84,85] The general theme is to provide a "boost" to allow particles to overcome energy barriers that would not be possible using traditional MD schemes, but, importantly, without moving the relative positions in phase space of the energy barriers. Choosing the "boost" has to be done with care. More recently, Fichthorn et al. used the "bond-boost" method to accelerate an MD scheme and apply this to thin-film growth.[86] They used the "state-bridging bond-boost" method to investigate the dynamics of systems in which there is a relatively flat region in the potential energy surface ringed by higher barriers, i.e., consisting of a collection of small energy barriers and separated from the rest of phase space by large barriers.

Molecular simulation techniques such as Molecular Dynamics and Monte Carlo rely on the availability of a relatively simple description of the intermolecular forces that effectively coarse-grains the system so that the electronic structure of the atoms is captured in a semiempirical manner that does not attempt to describe molecular orbitals. A common strategy involves constructing a mathematical model for the potential energy function (energy as a function of intermolecular separation) between two or more molecules that phenomenologically describes, and is often fitted to, experimental and/or electronic structure calculations. The main advantage of this approach is that the resultant intermolecular potential models offer the mathematical simplicity and computational efficiency to allow the study of system sizes containing up to 10 000−50 000 atoms relatively easily, or to perform smaller-sized systems over longer time scales, allowing more detailed searches or dynamic simulations to be undertaken.

The study of small organic semiconducting molecules (and the constituents of self-assembled monolayers that are often employed in the growth of quality thin films) largely involves aromatic and alkyl chains of electrically neutral species all of which are quite tractable and well described by a number of existing intermolecular potential energy functions. Although it is straightforward to write your own Molecular Dynamics code, the availability in MD freeware codes (of which DLPOLY[87] and TINKER[88] are just two of many choices) of many optional intermolecular potential functions is perhaps the most compelling reason to use these packages. Choosing which of the available potential energy functions to use for a given material is not straightforward and there is no "prescription" to guide users in this choice. Using potential parameters from a paper or the Web site of a freeware code should be approached with caution. First, the origin of the parameters (invariably from a published paper) must be established; this reference is usually given on the freeware code's Web site. In particular, it is important to learn to which properties the parameters were fitted, because most semiempirical potentials cannot be relied upon to predict properties not used in the fitting process, nor to predict accurately even the same properties outside the range (of temperatures or pressures, say) that they were fitted. Once the parameterization has been established, it is advisible to use the model to predict some properties of the material for which experimental data are usually readily available and preferably ones that were not used in the parameter fitting process. Good choices are the prediction of the experimentally known lowest-energy crystal structure, the cohesive energy and lattice parameters, and the stress coefficients. The next step should normally be to test the semiempirical predictions against known experimental and/or ab initio calculations of the kind of properties that the study is likely to be addressed. Only once this somewhat lengthy testing phase is complete, can the semiempirical model be used for original studies outside the range for which the model has been used before. Skipping these steps is akin to building a house on sand; having a solid foundation and confidence in the suitability of the model to represent the chosen system is essential.

Given these caveats on using intermolecular potential models, it is perhaps not surprising that many authors tend to keep to a particular class or classes of models with which they build some expertise and some assessment of the model's strengths and weaknesses. For instance, our own studies of molecules in the acene series have found that the MM3 model, one of the "Molecular Mechanics" class of intermolecular potential functions, has worked well in describing the growth of thin films. The Molecular Mechanics class of models was devised by Allinger in the early 1970s and has since evolved through a series of reparameterizations and modifications into its present form.[56−59] We (and others) have found MM3 to provide an excellent representation of aliphatic and aromatic organic molecules in comparison to ab initio and experimental data, invariably without reoptimizing the parameters given by Allinger and co-workers.[89−92] We have tested the MM3 potential for the linear fused acenes (naphthalene, anthracene, and pentacene), phenyls, and C_{60},[93−97] and for molecules that form self-assembled monolayers (OTS, ODTS, and FOTS),[98] and found that the model performs very well in comparison to reference experimental data or those from electronic structure calculations. Other studies have observed the same high quality of the MM class of models for aromatic molecules.[99−101] On the other hand, there are few optimized MM3 models that represent interactions with inorganic species, e.g., the noble metals. Nor can bond-breaking events be handled.

If faced by a situation for a new material in which the best choice of model is unclear, there is little recourse for the simulator but to investigate the sensitivity of the predictions of growth processes (or whatever is the focus of the simulation study) to different choices of models. For example, we recently became interested in the behavior of the sexiphenyl molecule, whose flexibility to twist and bend around its C−C bonds might render it less well represented by an MM class model than a rigid molecule like the acenes. Thus, it was necessary to compare the ability of four different density functional theory models and four different semiempirical models to represent the equilibrium conformation of sexiphenyl.[93] In this case, we found remarkably good correspondence among all eight models, but this may not always be the case.

In addition to consideration of the intermolecular potential energy function, discussed above, the study of molecules with their associated rotational and vibrational degrees of freedom involves additional intramolecular terms to the total energy of the system, E_{tot}. The total energy is thus described by adding together contributions arising from inter- and intramolecular interactions

$$E_{\text{tot}} = E_{\text{intra}} + E_{\text{inter}} \tag{1}$$

The intramolecular energy of molecules is generally calculated by summing a number of contributions from bending and stretching bonds and from bond vibrations. The resultant, so-called, force field is typically composed of terms such as these given in items a−f below in which $U(r)$ is the potential energy as a function of the distance r; k (k', k'', etc.) are force constants, r_0 is the ideal (equilibrium) position; θ is the included angle between three atoms; ϕ is the dihedral angle between the planes forming the angle. Thus, these terms treat molecules essentially as being defined by their separation, their characteristics as a set of interacting springs, and their relative orientations.

(a) Bond Stretching Potentials

$$U(r) = \frac{k}{2}(r-r_0)^2 + \frac{k'}{3}(r-r_0)^3 + \frac{k''}{4}(r-r_0)^4$$

(b) Angle Bending Potentials

$$U(\theta) = \frac{k}{2}(\theta-\theta_0)^2 + \frac{k'}{3}(\theta-\theta_0)^3 + \frac{k''}{4}(\theta-\theta_0)^4 + \frac{k'''}{5}(\theta-\theta_0)^5 + \frac{k''''}{6}(\theta-\theta_0)^6$$

(c) Torsion

$$U(\phi) = \frac{k}{2}(1+\cos(\phi)) + \frac{k'}{2}(1+\cos(2\phi)) + \frac{k''}{2}(1+\cos(3\phi))$$

(d) Stretch−Bend Interaction

$$U(r,\theta) = k(\theta-\theta_0)(r-r_0+r'-r'_0)$$

(e) Torsion−Stretch Interaction

$$U(r,\phi) = \frac{k}{2}(r-r_0) + (1+\cos(3\phi))$$

(f) Bend−Bend Interactions

$$U(\theta,\theta') = k(\theta-\theta_0)(\theta'-\theta'_0)$$

The intermolecular energy is composed of the following terms:

(1) van der Waals interactions

$$U(r) = A\exp\left(-\frac{r}{\rho}\right) - \frac{C}{r^6}$$

where in this example model, the Buckingham potential, A, C, and ρ are constants.

(2) Electrostatic and dipole−dipole interactions are also included. Although these terms are not considered to be important for saturated hydrocarbons, they do play a role with aromatic structures.

(3) Another important inclusion for some aromatic molecules is the role played by electron correlation in the delocalization of the π electrons.[59] The MM3(2000) release contained a "π system" correction,[102] which includes a correction for electron correlation at the level of the Moller−Plesset second-order theory MP2 method.[47] Because the method relies on an iterative process to generate self- consistency, it is much more computationally expensive (typically a factor of 20−100 slower for a system of about 1000 small organic molecules) and this expense increases rapidly with the number of atoms present. As a rule of thumb, this limits MM3-π simulations to studies of only about 100 or so atoms. Use of MM3-π, despite its cost, is warranted in some cases such as those with significant torsional contributions, such as we found for sexiphenyl.[93]

2.3. Transition Path Sampling Methods. To elucidate the mechanism and/or quantify the kinetics of key steps during processes such as surface diffusion or crystal nucleation and growth, it is often necessary to produce an ensemble of transition paths (as opposed to just one, or a handful, of dynamic trajectories). This can be inaccessible via traditional MD techniques, or even KMC, because of the long waiting time at dynamic bottlenecks. As an alternative to using "accelerated" methods to estimate rates (like those based on transition state theory), several "exact" methods have been developed that are often referred to as "transition path sampling" techniques.[103,104] One such technique that combines simplicity, efficiency, and the ability to work under equilibrium and non-equilibrium conditions is the "forward flux sampling" (FFS) method.[105−107] FFS uses a "divide-and-conquer" strategy to create complete paths from partial, shorter paths between successive "interfaces" between initial and final states along a chosen order parameter. FFS has been successfully used to study many processes,[106,107] including crystal nucleation[108] and crystallization on a porous

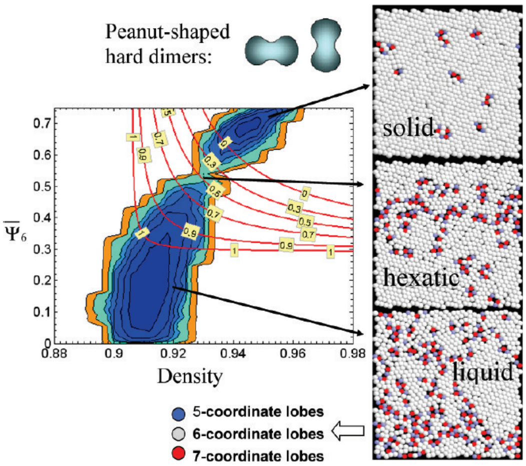

Figure 2. Order parameter, ψ_6, versus density for dimer particles in 2D at solid−liquid coexistence, showing iso-lines of the optimized order parameter (in red) for different probabilities to commit to the isotropic phase found by Forward Flux Sampling.

substrate.[109] Figure 2 shows a simple application of FFS to the 2D melting of a monolayer of dimer particles, showing the presence of a hexatic-like phase at the transition state (the order parameter, Ψ_6, measures hexagonal symmetry in the bond orientation of nearest neighbor lobes). It is expected that ongoing methodological improvements will allow FFS to tackle increasingly complex processes and molecules.[110−113] So far, there has been very little use of transition path sampling to study organic semiconductor systems, despite the promise of the method to produce a more realistic approximation to the true global minimum of the system.

2.4. Kinetic Monte Carlo Methods. Kinetic Monte Carlo (KMC) belongs to the larger class of Monte Carlo simulation methods whose development began in the 1940s and 50s. Unlike the Monte Carlo method developed by Metropolis et al.,[114] which samples configurations of an atomic or molecular system of particles governed by an appropriate thermodynamic ensemble, kinetic Monte Carlo is a method that facilitates an evolution of the system from state to state by choosing "events" singly or multiply from a library of user-supplied events (e.g., diffusion from point A to point B, rotation, deposition, annihilation, reaction, etc.) each of which is associated with a user-determined rate. Time is associated with the rate of events and hence the simulation clock advances nonlinearly depending on the event completed. Because the moves are related to the random choice of event (and associated rate), it is possible (given some rare events) for the system to simulate seconds, hours, or geologic time (in principle) if all the rates are known. As stated in Voter's review article,[115] unlike Molecular Dynamics, which captures atomic motion resolved to the vibrational level, KMC is usually practiced by assuming that atoms or molecules reside in energy wells separated by energy barriers that have to be overcome if the event (or transition) is to occur. Good reviews of the KMC method can be found in the literature.[115−117] Even in the earliest days of kinetic Monte Carlo, its suitability for following surface diffusion and growth processes (like chemical vapor deposition, atomic layer deposition, and molecular beam epitaxy) was recognized and many papers exist in the literature related to molecules not covered in the scope of this review. It has the advantage that, in principle, it provides an exact dynamical evolution of a system of particles, though this is rarely if ever explored.

Kinetic Monte Carlo is an attractive emulation of experiments, which we might also think of as corresponding to a series of activated events. Indeed, the primary incentive to perform KMC simulations is generally to explore the final morphology of a system over length, and especially, time frames that come close to those of experiments and/or far exceed those accessible from MD or ab initio calculations. On the other hand, KMC has some significant "activation energy" barriers of its own for potential users to overcome: First, a set of rates for all of the events that are considered important in the process being simulated is a prerequisite. These rates often come from MD or ab initio calculations and/or experiments. This is usually the "rate-determining step" for users. Determining these rates is invariably the most time-consuming part of a KMC study. If rates are unknown and are guessed by the user, the information content of the KMC results is significantly degraded, because the results only show how high the rate has to be in order to affect the outcome, or drive the simulation to an experimental observation. This is compounded by the fact that the library of events considered by the user depends on the intuition or experience of the user to anticipate which events might be important. This means that the compilation of the events list often has to be made with insight obtained from preceding MD or ab initio calculations (or the user's imagination). For example, the dissociation of a C_{60} trimer into a dimer and a single (mobile) C_{60} molecule is an event that cannot be seen during an MD simulation of even several nanoseconds. Energy minimizations of this situation can, however, readily be undertaken to determine the rates involved. Another limitation of KMC is that it inherently assumes Arrhenian behavior for the events, which is not always followed.

On a more practical note, there is no widely adopted commercial or freeware KMC code; nothing, for instance, to compare to the popularity of Gaussian or VASP, say, in the electronic structure world, or TINKER, DLPOLY, NAMD, LAMMPS, or many others, in the arena of Molecular Dynamics codes. Part of the reason for this is that most KMC codes have to be hand-coded to capture a specific solid-state process within the constraints of the lattice-based framework underlying the vast majority of KMC codes. Few KMC codes offer the ability to transition from one lattice to another during a simulated growth process. For example, depositing 1−2 monolayers of C_{60} on pentacene would involve a KMC code that could gracefully transition from pentacene's herringbone (triclinic) lattice to C_{60}'s face-centered cubic lattice.[118]

Rather than try to merge dissimilar lattices on a case-by-case basis, it is perhaps more profitable to develop off-lattice KMC algorithms that, as their name implies, removes the restriction to predefine the lattice

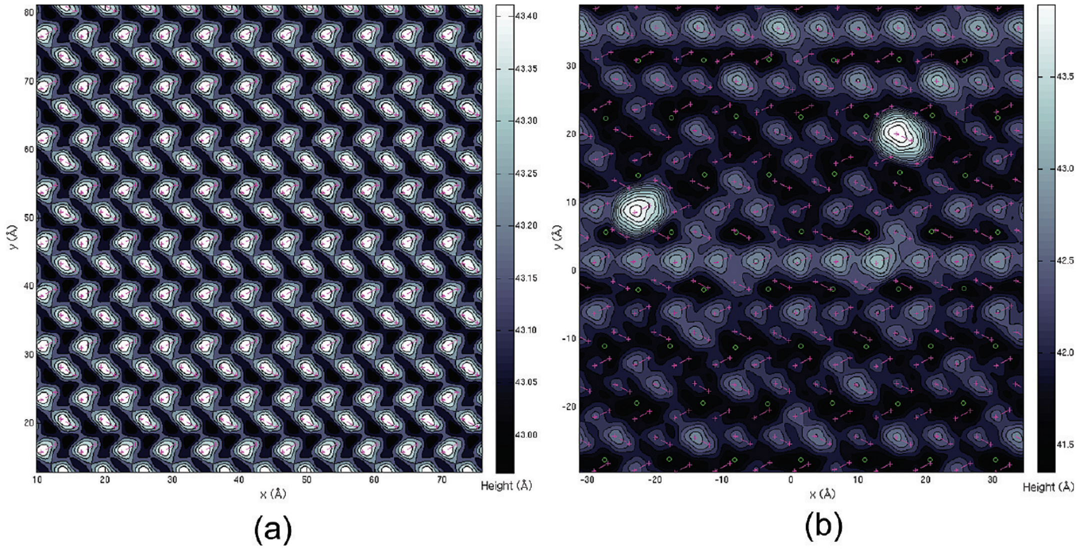

Figure 3. Potential energy surfaces for C_{60} on pentacene. (a) Height map representing perfectly crystalline pentacene in the thin-film phase underneath a layer of FCC arranged C_{60}. Heights were computed by removing the C_{60} layer and tracing a single C_{60} molecule over the pentacene film and determining the height at which the total potential energy is at its lowest. In each map, the violet symbols represent the location of the top two hydrogen atoms in each pentacene molecule. (b) Same pentacene-C_{60} system, after energy minimization of a C_{60}/pentacene heterojunction in Molecular Dynamics with MM3 potentials for both components followed by energy minimization of a single C60 molecule rastered over the resulting positions of the pentacene molecules. The green circles represent the location of each C_{60} in the over layer. The effect of minimization is an uneven broadening of the distribution of heights, from a standard deviation of 0.13 Å on the left to 0.37 Å on the right. The disorder can be traced back to the location of each pentacene relative to the C_{60} in the over layer: molecules in between bulky spheres have more translational freedom than molecules directly underneath bulky spheres.

(often called "solid-on-solid" techniques) and allow the representation of strain and mismatch between substrate and adsorbant molecules. Off-lattice KMC methods are reasonably uncommon.[119,120] One approach is to represent particles, not as being fixed on lattice sites, but as being connected by "springs";[121] other approaches have used an off-lattice KMC to study strained heteroepitaxial growth in Lennard-Jones alloys,[122] or a so-called "self-learning" off-lattice KMC to study the heteroepitaxy of dissimilar metals[123] and island coarsening on fcc (111) surfaces.[124] Exploiting off-lattice KMC approaches could be a fertile direction for future computational activity.

2.5. Energy Minimization Techniques. Computation of the (implicitly zero-Kelvin) potential energy surface providing the energy minimum structure of a surface or thin film (especially for submonolayer coverage, or the first two or three monolayers of a thin film or a buried interface) is a useful and informative part of the arsenal of modeling techniques at the disposal of computational materials science. Unlike techniques like Molecular Dynamics or Monte Carlo, energy minimization methods seek points of zero gradient in the energies between molecules in the system. Its strength is its simplicity; its inherent weakness is that the mathematical techniques (conjugate gradient, steepest descent, etc.) used to find such points of zero-force invariably find the locations of local minima and not the elusive "global minimum."

Although this is true of all systems, the weak binding between small organic semiconducting molecules and insulating substrates makes the system particularly sensitive to the method used to determine the energy minimum configuration of molecule−substrate interactions. Indeed, we showed recently[93] that not allowing the system to fully explore configuration space can lead methods like the nudged elastic band method, which determines the minimum energy reaction pathway between a given initial and final state, to find reaction paths incommensurate with the global minimum. This was found in connection with calculations of the Ehrlich−Schwoebel barrier,[125] the energy required for an atom or molecule to descend a monolayer step-edge beyond that of the conventional surface diffusion barrier, a phenomenon that is described in more detail in section 3.4 below. Even perturbations of 0.1 eV, which are small on an absolute scale, can be structure-directing in systems, like those of small organic semiconducting molecules, in which weak forces (on the order of a few tenths of an electron-volt) dominate and the cohesive energy is on the order of 1−2 eV.[126,127]

As an example of the usefulness of creating potential energy surfaces in relation to organic semiconductor systems consider the planar interface between C_{60} and pentacene molecules, which is under consideration as an all-organic p−n semiconducting junction. If a C_{60} molecule is "rastered" (translated) across a perfect crystalline interface of pentacene (whose molecules are not allowed to move) and the height of the C_{60} molecule is allowed to vary to find the potential minimum between the C_{60} and the pentacene surface, this gives rise to Figure 3a. The range of heights adopted by the C_{60} molecule is, not surprisingly, very small: 0.4 Å, with a standard deviation of 0.3 Å, reflecting the frozen nature of the pentacene surface. If, however, the positions of the pentacene molecules are obtained from a Molecular Dynamics simulation of a C_{60}/pentacene heterojunction and then a C_{60} molecule is rastered over the surface performing an energy minimization at each position on the surface, the height variation of the C_{60} molecule is much larger, 2.8 Å,

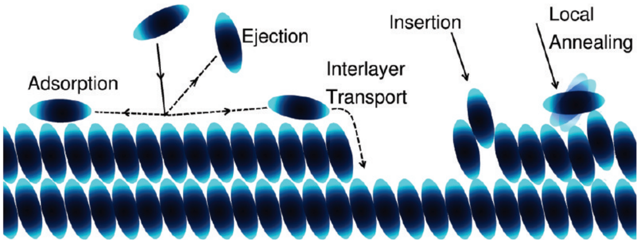

Figure 4. Schematic of the major molecular mechanisms at play during thin-film deposition and growth.

with a standard deviation of 0.37 Å, as shown in Figure 3b.

3. Pentacene: The "Poster Child" of Small Organic Semiconducting Molecules

In this section, we will look at applications of the simulation methods described above to studies of phenomena like crystal habit, surface diffusion, crystal nucleation, and growth processes (particularly thin films involving only a few monolayers), limiting this review to papers that involve small organic semiconducting molecules on a variety of substrates. Thin-film growth involves a variety of molecular mechanisms, from the initial deposition on the surface, to adsorption, insertion, step-edge repulsion, and scattering; see Figure 4. We will refer to these molecular mechanisms throughout the rest of this paper.

We begin by looking at pentacene, one of the first, and subsequently the most widely studied, small p-type organic semiconducting molecule both from an experimental and a computational viewpoint. This simple polyaromatic hydrocarbon (PAH) exemplifies many of qualities typical of these molecules. In particular, pentacene has demonstrated one of the best electrical properties in its class, *e.g.*, with hole mobilities up to 1 $\mathrm{cm^2\ V^{-1}\ s^{-1}}$, comparable to amorphous silicon. Pentacene acquired a certain distinction in 2009 as the first individual molecule to be imaged in 3D by researchers at IBM Zurich using an atomic force microscope.[128]

3.1. Polymorphism. For computational studies of any of the class of small organic semiconducting molecules, an appropriate place to start is a calculation of the preferred crystal habit. This offers an early, and usually accessible, way to compare the results of the modeling to experiment. Pentacene, like many small organic molecules, exhibits polymorphism (many crystalline phases differing by only a few tenths of an eV in free energy),[129−132] of which the so-called "thin-film" and bulk phases are the most common. The crystal cohesive energy for these relatively large molecules (in comparison to the dominant inorganic semiconducting molecules, like Si and Ge) is on the order of a few electron-volts,[126,133] with the intermolecular forces being dominated by weak long-range van der Waals type interactions. Early studies by Northrup et al.[126] showed that the weak interaction between pentacene molecules within the layer was, nonetheless, stronger than the interlayer forces that give rise to, or drive, many characteristic aspects of growth processes. During growth processes, pentacene, like many small organic semiconducting molecules, preferentially adopts a herringbone arrangement, with the long-axis of the pentacene molecule making a small angle with the surface normal (9° for the thin-film phase and 23° for the bulk phase). This "upright" morphology can be altered to one in which the pentacene lies down on the surface if the surface is reactive, typically Si[33] or a metal (see section below). Della Valle et al.[134] have provided a careful study of the thermodynamic stability of several polymorphs of rigidly constrained pentacene (whose geometry was obtained from ab initio calculations) on a rigid model (due to van Beest et al.[135]) of amorphous silica where they confirm the stability of the low-temperature ("bulk) phase and the metastability of the other "thin-film"-like phases.[134] The consequences of using rigid models of pentacene and holding fixed the molecules in the glassy silica were not addressed.

3.2. Pentacene Thin-Film Growth on Silicon Oxide. Taken as a group, the existing computational studies of pentacene are emblematic of those of the class of small organic semiconducting molecules in that they tend to cover properties of most significance to their major application, the growth of thin films. Hence it is typical to see calculations of surface diffusion, of molecule−substrate binding (and the associated tendency to wet, or more commonly, dewet the substrate), critical cluster sizes, island nucleation, and ultimately, the thin-film growth of pentacene on a given substrate. Calculations of the charge carrier mobility of the film supply the final piece of critical information.

Ruiz et al.[136] reviewed the experimental and computational studies of pentacene growth on silicon oxide up to 2004. They described the difficulties of growing pentacene in a preferred two-dimensional layer-by-layer thin film beyond a few monolayers.[137,29] In classic Stranski−Krastanov fashion, nucleation of the second monolayer begins when the first layer is about 75% complete, and the third layer begins to grow before the second is complete, leading to a three-dimensional (3D) ziggurat-like growth, as seen experimentally in Figure 5.[136] 3D growth is also inferred in MD and energy minimization simulations, where the Schwoebel barrier (~0.2 eV, which is about two-thirds the value of the maximum cofacial interaction) is substantial enough to preclude 2D growth.[93] Unhelpfully, both the thin-film and bulk phase polymorphs nucleate simultaneously on oxide and grow independently of each other.[138] The sole presence of either phase alone would be preferable for a higher quality, more ordered, growth. Rapid nanosecond laser processing of bimodal pentacene[139] has shown to produce a single polymorph, albeit at the expense of creating an extremely rough surface postlaser annealing, facilitated by a previously unseen liquid phase. Several researchers have shown growth to proceed in a manner consistent with diffusion-limited aggregation,[140] which Zorba et al.[137] attributed to the influence of the Ehrlich−Schwoebel barrier, discussed in more detailsin the next section. The effect of temperature of the oxide substrate on the charge carrier mobility of the pentacene thin films has been confusing: the oldest work[141] suggested, unexpectedly,

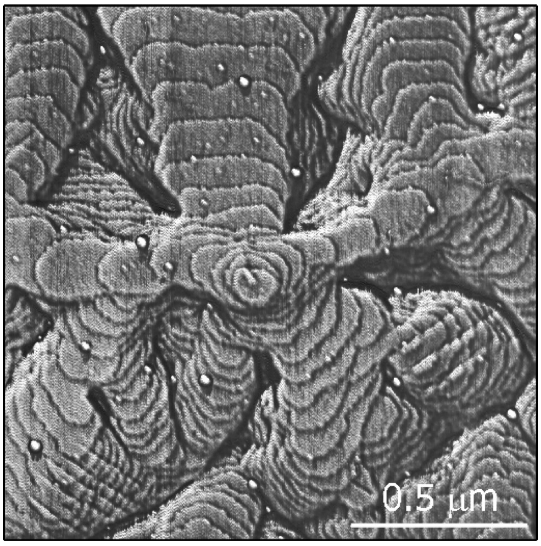

Figure 5. Image of the three-dimensional growth habit of pentacene. Reprinted with permission from ref 99. Copyright American Chemical Society 1999.

that charge carrier mobility decreases with substrate temperature, whereas newer work suggests that it increases[142] or stays the same.[143] Very recently, work by Guo et al.[144] suggest that the growth mechanism of pentacene on oxide gradually transforms from Stranski−Krastanov to Vollmer−-Weber growth mode with a decreasing charge carrier mobility, validating the early results by Dimitrakopolis.[141]

3.3. Critical Cluster Size of Pentacene. One informative property that lends itself to insight from computation is the concept of the critical nucleus size, R_c, which indicates the minimum number of pentacene molecules needed to form a stable crystal nucleus. Experimentally, this is a difficult property to determine, even indirectly. R_c depends strongly on the rate of deposition, the surface diffusion constant and the Ehrlich−Schwoebel barrier at the island's step edge.[125] The critical cluster size of pentacene on SiO_2 at room temperature was first calculated by Ruiz et al.[29] to be in the range 4−6 molecules, using scaling relationships from Amar and Family.[145] Tejima et al.[146] showed the temperature dependence of the critical cluster size to be small and certainly within the experimental uncertainty (2 at temperatures around 223−248 K; 3 at 304 or 342 K). Our own work to use KMC to determine the critical cluster size for a very simple "dimer" model of pentacene (i.e., assuming a 2:1 aspect ratio and all the limited set of events this model implies) found a value of the critical cluster size to be 6−16 molecules.[147] Using a "trimer" model of pentacene (3:1 aspect ratio, with concomitant additional possible events), the results shown in Figure 6 lowered the prediction of the critical cluster size to 3−12 molecules. Potential KMC practitioners may be interested to learn that, in our experience, these results are susceptible to changes of around 0.1 eV in the energies associated with key events. However, we are usually able to predict such energies with a precision of less than 0.02 eV and hence these results for the critical cluster size should be reasonably accurate within the confines of the simple model used. The increased critical cluster size at higher temperatures was credited to poorer sticking coefficients,[147] reflecting a change in competition between surface adsorption and scattering.

In hindsight, KMC may not be an ideal route to estimate the critical cluster size, because it relies on a purely energetic approach, without any consideration of entropic events beyond the intrinsic stochasticity of choosing events at random. Molecular Dynamics simulations or, preferably, forward flux sampling Monte Carlo simulations of the tendency of pentacene clusters or islands of a chosen size to remain lying down as a group, versus standing up on the substrate, would be a more accurate route to this quantity, albeit far slower than a KMC simulation (assuming all the energy barriers for the KMC simulation are already known). It would also be helpful if the pre-exponential factor for pentacene attachment to the surface was known. Such information can be indirectly obtained from experiments, but is generally unreported.

3.4. Effect of the Underlying Substrate on the Structure of Pentacene Films. It has been well-established by now that the balance between the binding energy of pentacene to an underlying substrate, in comparison with the energy gained by aligning with another pentacene molecule is the key to understanding growth on pentacene on any given substrate X. We showed, using a simple dimer model for pentacene and a KMC approach, that varying this

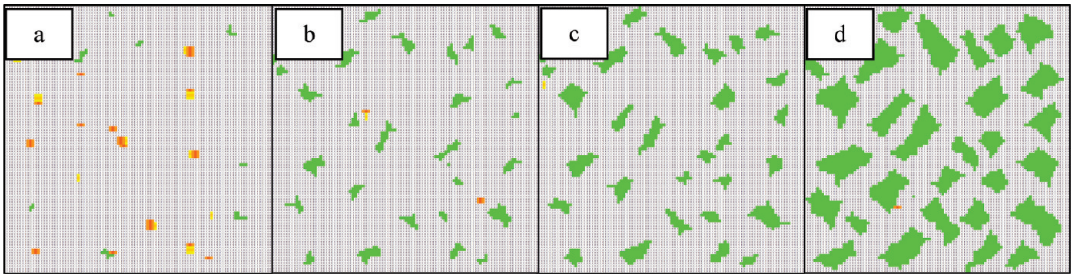

Figure 6. Results of KMC simulations of a simple "trimer" model of pentacene using Kawasaki dynamics of the submonolayer growth of pentacene on silicon oxide at room temperature using energy barriers from ab initio calculations and a pre-exponential factor of around 1 × 10^4 Hz [Goose, unpublished data (2006)]. The panels above show the time progression of simulations after the deposition of a number of deposited molecules (a) 100, (b) 500, (c) 1000, and (d) 3000 molecules. Color code: Yellow and red dots denote pentacene lying down on the surface with different orientations; green denotes molecules standing up. Islands can be seen to nucleate and grow, and show spontaneous "flipping" of clusters from lying down to standing up as time proceeds from a−d.

balance of forces arbitrarily, that is, without being constrained to the interaction of pentacene with a real (explicitly modeled) substrate "X", can give rise to a rich tapestry of potential morphologies that could be obtained in experiments by skillfully translating this energy balance into the blueprint for a designer substrate.[147] Motifs can be found that blend pentacene molecules standing up or lying down in different patterns; and growth could occur as either fractal or compact structures. Several of these predictions have now been observed experimentally. KMC is the perfect tool for such a study; it allows the user to ask "what if" questions, which range ahead of what is known and suggests what could be. These predictions also provide a target of possible structures for experimentalists to make tangible.

The recent activity in studying pentacene growth has concentrated on two major classes of substrates: (1) coatings and self-assembled monolayers (SAMs), and (2) metals. In the case of coatings, the motivation is largely to thwart the tendency for pentacene to dewet the surface and encourage layer-by-layer 2D growth. In the case of metals, the interaction between the pentacene and metal is strong, invariably forming an initial monolayer of pentacene that lies flat on the metal (or Si) and a second monolayer of pentacene that tilts up from its prone orientation to exhibit a tilt of its short-axis with the substrate. The motivation for this situation is again to promote ordering of the adsorbed thin film and there are indications that the work function of the metal can be used to manipulate the tilt of the pentacene surface to form nanowires.[148] We now discuss each of these two classes (coatings and SAMs, and metals) in more detail.

Early studies by Heringdorf et al.[149] showed that coating bare silicon surfaces with cyclohexene produced large grains of pentacene with high mobility. Complementary ab initio simulations by Choudhary confirmed the transition from the strong covalent binding to Si compared to the weak van der Waals binding to coatings such as cyclohexene.[150]

Interest in using self-assembled monolayers (SAMs) for the deposition of pentacene range from creating buffer layers on dielectric gate material, use in pentacene thin-film transistor fabrication, and their ability to improve mobility (by increasing intralayer order) and reduce or eliminate dewetting on surfaces.[151] As early as 2002, Shtein et al.[5] used a common alkyl-chain SAM, octadecyltrichlorosilane (ODTS), on SiO_2 to improve the charge carrier mobility of the resulting OTFT (organic thin-film transistor) to around 1.6 $cm^2/(V\ s)$. By 2008, progress in improving the mobility of the system was shown by Ito et al.[152] to produce and characterize alkyl chain SAMs, octadecyltrimethoxysilane (OTMS) and ODTS as well-ordered smooth surfaces that improved the mobility of the resulting OFET to about 3 $cm^2/(V\ s)$ for pentacene (and higher for C_{60}). Käfer et al.[151] showed that modifying gold surfaces with a SAM suppressed dewetting and produced relatively smooth films that were reasonably independent of the terminal functionality of the alkylthiol SAM or the roughness of the gold (111) surface. Recent books by Bao[7] and by Wöll[153] review other studies of pentacene on SiO_2 and on metals, especially gold. These studies make it quite clear that the structural characteristics of the first monolayer of pentacene on the SAM play a key role in determining its electrical performance.[154] A review of the fundamentals of organic molecular beam deposition (notably for pentacene, diindenoperylene and PTCDA) is also available that emphasizes the role of weak binding forces on morphology during deposition and growth.[155]

There is an opportunity for molecular simulation to provide arbitration among contradicting experimental data and this is certainly present in this case: Two papers published in 2008 offer diametrically opposed results for the link between SAM ordering and mobility: Lee et al.[156] demonstrated the somewhat more intuitive result that increased ordering within an ODTS SAM interlayer on SiO_2 led to improved ordering and mobility in the pentacene. In contrast, in Kim et al.'s study[157] of C_8-C_{18} alkyl chain SAMs on SiO_2, the shorter-length, more disordered SAMs gave rise to higher mobility, which they attribute to higher surface diffusion and "fewer nucleation sites" of pentacene on the shorter SAMs. A third result from Hill et al.[158] suggests that for n-alkyl phosphonic acid-based SAMs on SiO_2, the best electrical performance occurs with a chain length of 8−10 carbon atoms.

Interestingly, there have been only a few molecular simulation papers on the effect of adsorption on SAMs,[159−166] most of which describe the behavior of the inert gases on SAMs, and none that describe the structure of a layer of small organic semiconducting molecules on a SAM interlayer. We have investigated the deposition of diindenoperylene, a small organic semiconducting molecule, on OTS, ODTS and FOTS SAMs[98,167] and highlighted the role of a largely overlooked variable, the density of the SAM, to affect the propensity of the SAM to allow insertion of DIP molecules between the SAM molecules.[98] It is not immediately obvious if significant insertion is a beneficial outcome for either the structural or electrical properties and this molecular mechanism deserves more attention to resolve this, because it could provide unexpected leverage in creating smoother films. The dynamics of the SAM molecules are very important: At low densities, the long alkyl chains (like the 8-carbon chain, OTS; and the 18-carbon chain, ODTS) frequently employed as SAMs wave around like grass in the wind. At high densities, steric hindrance inhibits this motion.

There have been quite a few papers studying the deposition of small organic semiconducting molecules on metals. Studies of pentacene on the noble metals (copper,[168−170] silver[171,172] and gold[173−177] are the most prevalent, but studies also exist for other molecules: PTCDA,[178] perylene,[179,180] alpha−sexithiophene[181] and the oligomer poly(3,4-ethylenedioxythiophene) (PEDOT)[182] on metal surfaces and on C_{60},[183,83] which, although not a metal, offers an interesting comparison, especially for theorists and computationalists looking for the importance of shape and intermolecular forces on resultant structure.

Given the stronger bonding between acenes and metals, compared to insulating surfaces, say, this situation lends itself to study using ab initio calculations, and such studies have been made for pentacene on Al 100,[184] on gold (001),[185,186] on copper[185,187−190] and on iron 100.[191] Recent work by Toyoda et al.[192] has provided ab initio derived computational confirmation of earlier experimental studies using photoemission spectroscopy (PES) that the interface between metals, like Au, Ag, and Ca, with pentacene creates an interface dipole that scales linearly with work function.[193] Note that the decision whether to deposit acene on metal, versus metal on acene, does not necessarily lead to the same interface formation. For instance, Au and Ag diffuse through the pentacene substrate, whereas pentacene does not diffuse through these metals as substrates. Ca, on the other hand, forms symmetric interfaces with pentacene whether Ca is the substrate or the top layer.[193]

The motivation for this kind of study is usually the opportunity to study the situation where the organic molecule is more strongly bonded to the surface than on oxide, SAM or insulating materials, and hence is perhaps more likely to form ordered thin films, given the stronger influence of the underlying substrate. In almost all these cases referenced above,[168−182] the first monolayer of pentacene (or other small organic semiconducting molecule) lies down on a metallic surface (as compared to its behavior on insulating surfaces in which pentacene molecules adopt a nearly vertical orientation of their long axis in pentacene's thin film and bulk phases). An exception to this general rule is that of PEDOT on Cu[182] for which both STM characterization and DFT calculations of the well-ordered growth of nanowires confirm that the sulfur atom in the thiophene ring binds strongly to the flat Cu (110) surface, causing the remainder of the EDOT to stand proud of the surface, rather than lying flat.

Many groups have been fascinated by what happens to the orientation of the second and subsequent monolayers on metals. In virtually all cases, the second layer of pentacene also lies reasonably flat, but with its short axis angled somewhat more vertical. The angle of this second and third layer is typically about 60−90° off the surface-normal (or 0−30° from lying flat).[168−182] Among the dozen papers on such systems, it is not uncommon for both experimental studies and ab initio studies to be used to describe the system with a typically strong confluence of results from both approaches.

An interesting contrast to the behavior of pentacene on the noble metals described above can be found in the case of pentacene adsorption on a semi-metal like bismuth. If thin films of bismuth are deposited on surfaces such as reconstructed Si (111) and then pentacene is deposited on top of the bismuth, the pentacene molecules stand up with their long-axis in a bulk-like polymorph,[194−196] akin to the behavior of pentacene on thermal oxide. The weak interaction of the pentacene and bismuth, caused presumably by a small density of states near the Fermi level of the bismuth, is the driving force for this observation. For instance, Tromp and co-workers[194] showed that depositing a thin film of bismuth (001) on silicon reduced the step density and allowed pentacene to grow exclusively as the bulk phase in an ordered crystalline manner.

In the same spirit, the ability to use STM analysis to study organic thin films has been extended by Zheng et al.[197] who used O_2 plasma to "lightly oxidize" a gold surface (to form a polycrystalline O_x-Au surface) at room temperature so as to reduce the strong gold−pentacene interaction enough to allow STM to study the thin film phase morphology of multiple layers of pentacene, even on rough surfaces. They also provide a "control" study of growth on bare gold, which produced the expected flat-lying pentacene phase. This study effectively shows that as you "dial back" the strength of the initially strong bare metal−acene interaction to the lightly oxidized surface, the morphology of acene growth changes from molecules lying down on the surface to one in which they are standing up.

3.5. Ehrlich-Schwoebel Barriers. *3.5.1. Schwoebel Barriers for Atomic Systems.* The Ehrlich−Schwoebel barrier[125] (which we will call the Schwoebel barrier hereafter) is the energy required for an atom or molecule to descend a monolayer step-edge beyond that of the conventional surface diffusion barrier, as illustrated in Figure 7. As such, it is a clear "suspect" as a mechanism that promotes three-dimensional growth if the barrier is sufficiently high. The Schwöebel barrier will suppress the downward flux of particles between crystalline layers, inhibiting the favored 2D layer-by-layer growth. It is therefore of considerable interest to quantify these barriers in order to understand the inherent limitations of thin film growth for a given system.

The existence of the Schwoebel barrier was first observed for tungsten ad-atoms on various tungsten surfaces[125b] and it has been estimated for some inorganic substances: Computationally, this barrier has been observed and quantified for monatomic crystals such as copper and silicon where the atom's coordination number decreases as it negotiates the step-edge, resulting in an increase in potential energy. Unfortunately, experimental determination of the Schwoebel barrier can only be deduced indirectly. The complex morphology of the surface with many different step edges, grain boundaries, etc., will give rise to a range of different barriers. Thus whatever value is deduced from experimental data is, by necessity, an ensemble average of these many different step-edge barriers that exist in the system, whether they are classifiable as identifiable step-edges or exist simply as a collection of defective edges. Experimental routes to the Schwoebel barrier for organic molecules typically involve scaling models fitted to experimental data such as atomic force microscopy or in situ X-ray diffraction. Though more accurate experimental determinations are being sought,[125c,198] the real promise for understanding these barriers will come from molecular simulation techniques, which are capable of determining the Schwoebel barrier for a particular step. In a sense, simulation suffers from its own opposite constraint: It can predict the barrier for a given specific step, but there is no

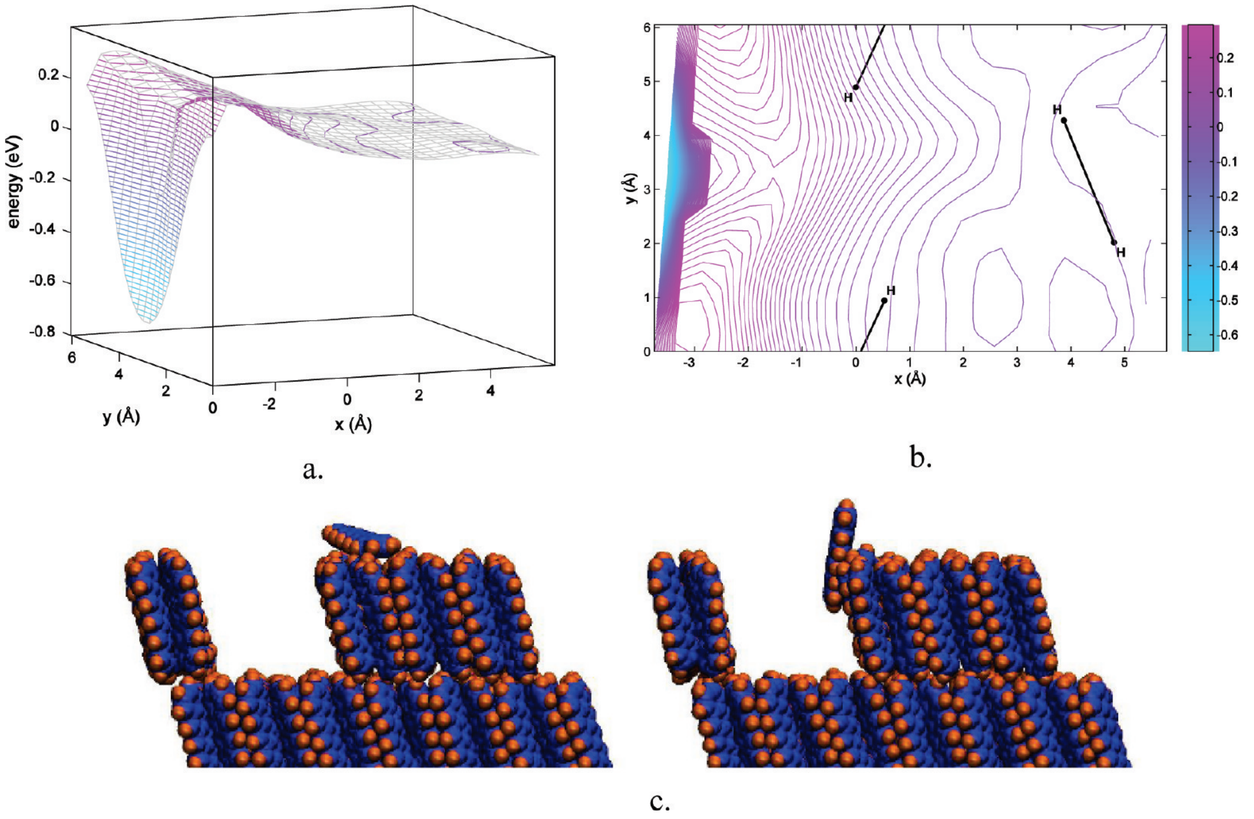

Figure 7. Various representations of the Schwoebel barrier. (a) Total energy shows the pronounced uphill energy barrier that a molecule experiences as it traverses a step-edge on a pentacene surface. (b) Plan view of panel a where the energy contours can be clearly seen to rise as the step edge is approached. (c) Molecular-scale representation of a successful step-edge descent is provided showing a pentacene molecule reorienting itself as it falls over the step-edge.

way to know accurately which step edges are present and in what populations in an experimental sample. For atoms, the step edges in the system are far less complex, and hence it is not surprising that Schwoebel barriers for atomic systems are quite well researched. For instance, the self-diffusion barriers of Al ad-atoms have been calculated using ab initio techniques for kinks, steps, and corners,[199,200] including some novel atomic exchange mechanisms. Xiang et al.[201] have extended this to ab initio calculations of 3D step-edge barriers of the Cu$\{111\}$ system which increase when the adatom diffuses down more than one layer of steps.

3.5.2. Schwoebel Barrier for Organic Molecules. The situation for organic molecules is far more complicated. As noted above, the Schwoebel barrier is the additional energy required for a particle to diffuse down a step-edge beyond the 2D surface diffusional energy. Unfortunately, even the 2D diffusion pathway on the surface is not easily defined for organic molecules since they often do not occupy single sites at any given time.[96] The diffusion cannot be characterized as being either "site−site" jumping or continuum random walks and there can be considerable bias in the direction of diffusion (as in the case of C_{60} on pentacene[95]). The behavior of small organic semiconducting molecules is also complicated by factors such as (i) the conformational freedom provided by the nature of their chemical bonds, (ii) the anisotropic interactions associated with "π-stacking," (iii) their molecular shape (or aspect ratio), and (iv) their flexibility.

There are very few computational studies in the literature that provide values for the self-Schwoebel barrier for small organic semiconducting molecules using molecular simulation techniques. Studies of PTCDA (3,4,9,10-perylene-tetracarboxylic-3,4,9,10-dianhydride)[202] and sexiphenyl[203] report barriers of 80 and 60 kJ/mol, respectively; for reference, our value of the minimum barrier for sexiphenyl is 32.5~kJ/mol.[93] Goose et al.[93] showed that simply stating a single value for the Schwoebel barrier of molecular systems is not a suitable metric to use; instead, molecular systems exhibit a range of barriers depending, stochastically, on their angle of approach to the step edge. We calculated the Schwoebel barrier not only for molecules on a surface of like molecules (the self-Schwoebel barrier) but also, for the first time in the literature, the barriers for the chosen set of test molecules on surfaces of other molecules in the set ("hetero-Schwoebel barriers"). The molecules chosen were three small acenes, C_{60}, rubrene, diindenoperylene, and sexiphenyl. All of them form herringbone crystal structures (except C_{60}, which is fcc), but they differ in shape, aspect ratio, flexibility, etc. We found a pervasive preference for these molecules to "log-roll" over the step-edge and began to uncover the effect of even subtle changes in the nature of the step on the Schwoebel barrier. Perhaps of most practical use for experimentalists, we found that a roughly linear correlation exists between the binding energy of a given molecule to the surface and the resultant Schwoebel barrier, enabling researchers to readily estimate the Schwoebel barrier for either self- or heterointerface situations without the need to perform the time-consuming molecular simulations we had done. For molecules with many internal rotational degrees of freedom, like rubrene, it was clear that the concept of a Schwoebel barrier is less meaningful because as it navigates surfaces and steps, rubrene experiences roughly similar-sized barriers whether at the step-edge or traversing the surface.

4. Studies of Surface Adsorption and Diffusion of "Small" (and "Large") Organic Semiconducting Molecules on a Substrate

Having information about the surface kinetics (diffusion, binding, etc.) is extremely important in terms of understanding molecular ordering and, ultimately, film morphology. And indeed, much is known about these properties for atomic or quasi-spherical molecular systems. However, systems/materials involving "larger" molecules that possess flexibility, rotational freedom, a well-defined shape, or anisotropic interaction with a substrate, i.e., the quintessential characteristics of small organic semiconducting molecules, are surprisingly poorly studied. Experimentally, the study of surface diffusion of pi-electron-rich organic molecules on a metal surface only began roughly a decade ago with Weckesser et al.'s STM study of 4-trans-2-(pyrid-4-yl-vinyl) benzoic acid (PVBA) on Pd(110),[204] although interestingly they called this a "large" molecule (in comparison to atomic systems). At the time, this was the first use of STM to image the "dog-bone"-shaped molecular structure, and to determine that PVBA molecules (like all subsequently imaged π-electron-rich small organic semiconducting molecules) lie flat on the metal surface. They also report an additional quantity, the angles that the long- (or short-) axis makes with the substrate, which we believe play a role in determining the tendency to template the growth of small organic semiconducting molecules, for example to form nanowires. In this case, the submonolayer coverage showed that PVBA molecules prefer to lie across the Pd rows at an angle of about 35° with the $[1, \bar{1}, 0]$ Pd rows and at 90° to the surface normal (i.e., lying flat on the metal). The well-cited later STM study by Tromp and co-workers of pentacene on bare silicon showed that pentacene likes to lie either parallel or perpendicular to the Si (001) rows with roughly equal probability and rarely diagonally across the rows (unlike PVBA on Pd).[33] Arrhenius plots of surface diffusion can (with sufficient patience to observe site-hopping) be constructed to provide estimates for the activation energy barrier and attempt frequency. In the example case of PVBA on Pd, a large activation barrier of about 0.8 eV was found for the migration energy (emblematic of the strong binding to the surface) and a relatively small attempt frequency of about 1×10^{10}/s (about 2 orders of magnitude smaller than benzene on the same surface). These data, in turn, can be used to determine an intrinsic diffusion coefficient of around 7×10^{-6} cm^2/s, assuming a single site-hopping model.

This assumption of single site, nearest neighbor, hopping is difficult to prove in many cases since the uncertainty in experimentally determined prefactors is large and the Arrhenius data notoriously difficult to determine accurately. And indeed, there is evidence for a different mode of diffusion, one that involves multiple lattice site hopping, so-called "long jumps" that can dominate in the behavior of "large" molecules (large by atomic standards, but relevant to 'small' organic semiconducting molecules). Schunack et al.[205] studied the adsorption of decacyclene (DC) and hexa-*tert*-butyldecacyclene (HtBDC) on the Cu(110) surface. These two structurally related molecules offer an interesting comparison: They both have a similar pi-system that adsorbs parallel to the Cu surface, but the tertiary butyl groups in HtBDC hold the molecule away from the surface (like stilts). This comparison clearly shows the ability of adsorbent binding to influence diffusion; the t-butyl groups on HtBDC bind much more weakly to the Cu surface than DC, resulting in a factor of 10 000 times higher surface diffusion coefficient. For these molecules, "long jumps" are the dominant mechanism for diffusion, with rms jump lengths in the range 4−7 nearest neighbor sites (for DC and HtBDC, respectively). Like the earlier work on PVBA, the activation energies were high, 0.6−0.75 eV, but with higher prefactors ($\sim 1 \times 10^{14}$/s), which lead to fast diffusion coefficients on the order of 1×10^{-3} cm^2/s. The authors checked the precision of their experimental results for jump lengths against Kinetic Monte Carlo (KMC) simulations of a simple one-dimensional random walk description of the system. The KMC determined the probability of a jump length of a given distance and, finally, found a value of a hopping rate and an rms jump length. The authors showed that the simple 1D KMC model provided a consistent underestimate of the hopping rate and explained this in terms of the neglect of the model to capture multiple jumps between observations. This was an interesting idea that could be revisited with a more complex KMC model.

In a related study, Otero et al.[206] used STM images to show that changing the orientation of an organic molecule known as Violet Lander, $C_{108}H_{104}$, on the surface of a metal (Cu (110)) by gently pushing it with an STM tip can alter the diffusion coefficient by 2 orders of magnitude, albeit very low values, from about 1×10^{-17} to about 1×10^{-19} cm^2/s as the molecule is rotated 70° from its normal orientation parallel to the Cu (110) rows. Using standard semiempirical force field Molecular Dynamics simulations of a model of a single Violet Lander (VL) molecule on a surface containing about 1600 Cu atoms, they found that the two lowest energy orientations of the VL molecule on the metal were parallel to the Cu $[1, \bar{1}, 0]$ direction and 70° away from this orientation, in excellent agreement with experiment. They also imparted a small amount of momentum to the VL molecule to emulate a surface phonon and found that the $[1, \bar{1}, 0]$-aligned molecule needed more momentum to be displaced from its position on the surface, which the authors designated as being "locked" into the surface.[207]

These two papers and others highlight a common theme: the Schunack et al. paper[205] suggested a way to design molecules to significantly alter the surface binding and diffusion, a theme carried on by Otero et al.[206] and by subsequent papers. For example, a paper by Trevethan and Shluger[208] reiterated the idea that an organic molecule's structure and flexibility can "profoundly" affect diffusion rate and mechanism, even on insulating surfaces like TiO_2 (110) (in contrast to the other studies mentioned[205,206]). They used molecular simulation computational routes to find energy barriers for polar groups binding to the surface and then used these barriers in a KMC simulation to look for links between the design of the polar functional groups and the diffusivity of the organic molecule. These authors recently extended this idea as a means to "designing molecules, predicting their adsorption and diffusion at surfaces, simulating atomic force microscopy imaging and manipulation of atoms and molecules at insulating surfaces and studying electron conduction in prototype molecular devices" in a recent review article.[209]

5. Growth of Thin Films of Other Small Organic Semiconducting Molecules

The growth of thin films of pentacene was reviewed in section 3 above. Experimental studies of the growth of other small organic semiconducting molecules are also underway in the search for a successor to pentacene in terms of improved charge mobility. Given no a priori direction from theoretical or computational sources, this has led to the study of many different thin film materials and substrate combinations in a wide-ranging search guided by experimental experience and intuition. Reviewing all the molecule/substrate candidates currently under consideration is beyond this review, but a 2007 review by Murphy and Fréchet[210] categorized existing results for both vacuum-deposited and solution-processed p-type and n-type oligomers. A 2010 review by Lehnherr and Tykwinski[211] extends this by focusing on substituted pentacene building blocks that allow better "π-stacking" to occur. Other reviews exist with different foci: An older review focuses on the charge transport performance of different classes of small organic molecules was given by Horowitz,[212] whereas those of Witte and Wöll[213] and Ruiz et al.[136] in 2004 focus more on the growth morphologies of different molecules.

From a computational standpoint, simulation of thin film growth in these systems is a challenge. System sizes are inevitably large given a number of factors: (1) the number of atoms in an individual organic molecule under consideration is getting larger as we study increasingly more complex systems (e.g., 32 atoms in pentacene, 60 in the fullerene, C_{60}), (2) the number of organic molecules that must be deposited in order to create a reasonable semblance of even a monolayer of thin film (without undue influence of any periodic boundaries present), (3) an adequately sized and deep underlying substrate, and (4) the need to allow sufficient time between deposition events for individual molecules to strike the surface and equilibrate on the surface (or to scatter away) before the next particle arrives; this typically takes on the order of 20−100 ps per event (i.e., $2-10 \times 10^4$ iterations of the equations of motion given a 1 fs time step). The combination of large system sizes and long time evolutions precludes ab initio studies at this point and challenges even accelerated MD schemes. For instance, the deposition (and subsequent equilibration) of C_{60} molecules on a pentacene surface (three monolayers deep) is sufficiently resource-intensive that MD simulations become essentially intractable in a reasonable elapsed time after about 4 or 5 C_{60} molecules have been deposited (in essence, probing the practical limit of studying thousands of atoms for nanoseconds). This situation makes Kinetic Monte Carlo studies look appealing, but they involve extensive Molecular Dynamics or DFT calculations to already be in hand, providing an adequate database (or "library") of energy barriers that define the rates of individual events that could occur. Not surprisingly then, KMC studies of thin film growth have tended so far to cover deposition of like-on-like, e.g., C_{60}-on-C_{60}[214] or pentacene on pentacene.[150] In studies we have underway in our group, a KMC study of C_{60} growth on pentacene has to contend with minimizing strain at the periodic boundaries, and has to provide a scheme to gracefully transition from the lattice constant and preferred morphology of the substrate to that of the growing film, with all the inherent rates that these considerations imply. This constitutes quite a challenge for an on-lattice KMC approach.

Some of these issues can be circumvented by other approaches. For instance, we have deconstructed the simulation of thin film growth to look at the propensity of various events to occur during deposition. In energetic deposition processes, for instance, a study of the propensity to insert into layers of the surface can elicit the importance of individual molecular mechanisms than can occur during thin film growth. We have studied the likelihood of pentacene to deposit on pentacene[95,97] and, most recently, the tendency for diindenoperylene to deposit on a self-assembled monolayer via competing adsorption and insertion processes on the surface;[98] see Figure 8. Calculating the potential energy surface for a potential adsorbate molecule like C_{60} over a pentacene surface shows a rough interface (see Figure 9) with asymmetric low-energy pathways whose existence was later borne out by Molecular Dynamics simulations.

In general, there has been relatively little examination of fundamental growth processes themselves, particularly at a molecular level, with the result that speculation into the causes of experimentally observed variations in final morphologies of grown films often remains just that. Processes such as surface diffusion have until relatively recently have not been investigated, although this is changing. Our own results for systems like C_{60} on pentacene illustrate the fact that diffusion cannot be assumed to be characterizable within an established diffusion regime, e.g., Arrhenian diffusion; indeed, we have observed Lévy flightlike behavior for C_{60} on pentacene. And growth processes are complicated in the case of π-electron-containing small organic molecules by the tendency of individual molecules to diffuse face down over the surface,

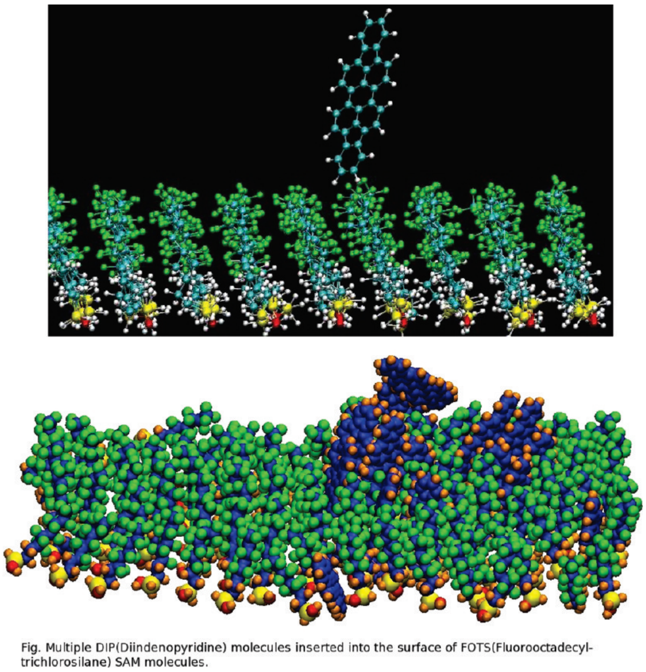

Figure 8. (a) Moment of deposition of a single DIP molecule on an FOTS self-assembled monolayer surface. (b) MD simulation of the deposition of multiple DIP molecules onto an FOTS SAM surface. As can be seen readily, the DIP molecules tend to insert between the SAM molecules rather than adsorb on top of the SAM surface.

whereas clusters of such molecules (or islands above a critical size) spontaneously stand up to take advantage of the stronger face-to-face interactions among themselves. The net result is that there is a considerable difference between the modes of diffusion of an organic molecule over a surface compared to inorganic semiconductors, say.

6. Summary and Future Outlook

It is clear that the field of all-organic semiconductors, as well as its organic−inorganic semiconductor "sister" field, is an exciting playground for computationalists and theorists. Several computationally focused reviews echo this excitement.[104,215−217] The "draw" is the opportunity to offer insights into the choice of materials, molecule choices and designs, and optimized processing conditions for a desired structural/electronic performance outcome that cannot be achieved by experiment alone, and some, especially molecular scale, insights that only computation can provide. There are sufficiently efficient computational tools to begin to tackle far more adventurous systems, for example polymeric semiconductors and polymer-small molecule interfaces, whose characteristic length and time scales offer a system that is tantalizingly on the edge of tractability using modern computational techniques. The field is also poised to tackle the simulation of monolayers of thin film growth of candidate small organic semiconducting molecules that is conspicuously absent in the current literature. And there are new and developing computational tools that will offer much better computational accuracy and reach in the search for the link between structure and electrical performance. Some examples of promising techniques include (1) quantum Monte Carlo, which is known to produce accurate band gaps,[218] reaction barriers,[219] and weak dispersive forces;[220,221] (2) developments in the treatment of excited states (building on[71−76]); (3) electronic structure methods that provide efficient treatment of condensed phases[222] (e.g., for solution processing); and (4) better routes to the elusive concept of finding a structural "global minimum" through transition path sampling techniques.[103−113] On the other hand, it has to be said that there remains a need for large computational resources to study thin film growth, which is still in the domain of semiempirical modeling techniques.

There is a growing consensus of some general principles of surface adsorption of simple small molecules organic semiconductors, for instance, the underlying balance of forces that determines their tendency to stand up or lie down on insulating or metallic substrates, respectively, say. This force balance clearly also allows isolated molecules to explore bent or twisted molecular orientations, but to exploit force anisotropies to maximize their interactions when these isolated molecules come together to form a crystal. And there is a better understanding of the

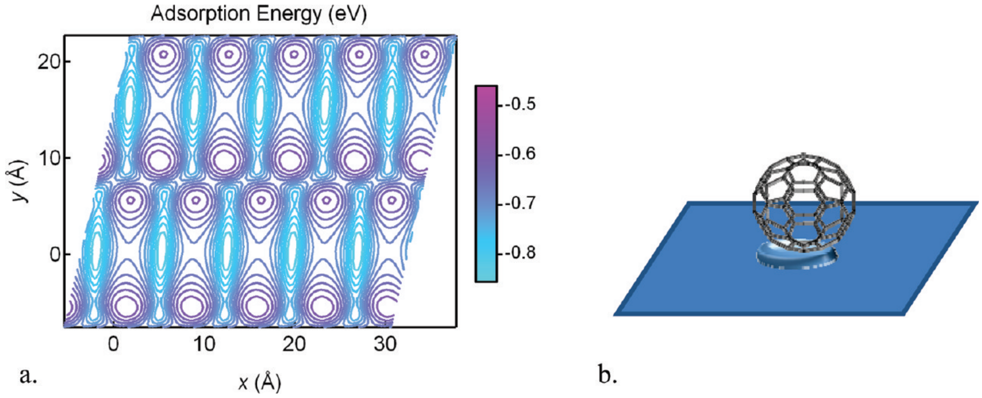

Figure 9. (a) Typical potential energy surface (PES) obtaining by "rastering" the $x-y$ position of a single C_{60} molecule over a pentacene surface in which the short axis is tilted up from a flat, horizontal position and computing the potential energy. Areas of higher potential energy are shown in pink, lower energies are shown in blue, and aqua represent the lowest energy, as referenced by the energy scale in electron-volts shown to the right of the figure. (b) The schematic of a C_{60} molecule sitting in a depression on the surface is intended to evoke the physical situation corresponding to the PES in part a where preferred spots for C_{60} to sit on the surface are visible between the pentacene rows but especially within the rows themselves (regions shown in aqua).

major molecular-scale mechanisms at play during vapor-phase deposition processes, especially a growing appreciation for the relative roles of film smoothening processes such as insertion and film roughening processes such as the existence of appreciable Ehrlich–Schwoebel barriers. However, the field of computational studies of these organic semiconductor materials has not matured to the point at which we can predict the thin film growth morphology of a given molecule on a chosen substrate.

There are also conspicuously understudied areas in thin film growth from a computational point of view. Most notably, this includes the modeling and simulation of heterojunctions, the identification and characterization of intrinsic and processing-induced defects, and computational studies of solution processing. Much of this is a reflection of the current newness of computational attention in this area; there is, in principle, no barrier to studying these issues computationally. On a higher-level, there are very few existing examples of places where computation has provided a "design rule" that allows computation to jump ahead of experimental studies and/or provide information that experimentalists can readily apply without the need to perform computationally intense simulations. But the outlook for this is promising: for example, we have provided a simple relationship between the binding energy of adsorbate organic molecule and the underlying substrate and the resulting Schwoebel step-edge barrier that appears to work for many different small organic molecules and is consistent with other careful work. The existence of this particular rule will, for instance, allow experimentalists to readily insert the relevant parameter for the Schwoebel barrier in theoretical models of film growth to fit to X-ray data, say.

The set of molecules themselves are also a fitting challenge for computational study: On one hand, their similarity of crystal packing offers a good chance to provide an overarching design rule that should cover many candidate materials, with hopefully small perturbations due to molecular flexibility (e.g., sexiphenyl versus pentacene), aspect ratio (acene series), shape (perylenes versus pentacene for 2D shape, or C_{60} versus acenes for spherical/nonspherical comparison), access to vibrational modes (rubrene versus pentacene). Our suggestion is that the guiding rule is dominated by the role of the binding energy to largely override these other considerations mentioned. On the other hand, the weak binding among this class of materials and the many choices of substrate under consideration has the concomitant effect of allowing subtleties to be manifested that can have ramifications for computational studies. As an example, for reasons of computational efficiency, given the size of the systems that typically have to be considered for surface properties and thin film growth, it is tempting to "freeze" layers of molecules or to make assumptions of rigidity of the molecules that can lead to artifactual results (as we have seen in studying C_{60} nanowires growing on flat-lying pentacene surfaces). Even a few tenths of an electron-volt difference in orientational preference can lead to profound changes in mechanistic effect (as we have documented for the Schwoebel barrier). Thus we recommend that computationalists take particular care to study the impact of such assumptions on the results. This could allow us to learn as a community where we can safely take computational short cuts and where we cannot.

As a computationalist, I think it would also be very helpful to have some more targeted, systematic, experimental studies of a given phenomenon. As a case in point, in reviewing our understanding of the effect on the critical first few monolayers of a small organic semiconductor, like pentacene, on a strongly binding surface like a noble metal, the results were typically given for just one system and invariably with little contextual information to compare or relate the results to other molecule/noble metal combinations. It would be very helpful to have experimental results for the morphology of the first 2–3 monolayers of pentacene, say, on a variety of different substrates tailored in terms of work function to range from the most strongly binding to the least. Alternatively, in the spirit of this review, perhaps computational predictions of this effect will offer a target for experimentalists to confirm or refute.

There is a great need for computationalists and experimentalists alike to make a more concerted effort to more systematically study the fundamentals of organic semiconductor binding to self and unlike surfaces for which many open questions still exist and resist the temptation to use electrical performance as the defining metric. With the growing interest in the field of organic semiconducting materials, it will be imperative to underpin this area with a knowledge and understanding of fundamental structure–property relations.

Acknowledgment. The author is indebted to her colleagues Fernando Escobedo, for providing information about Transition Path Sampling methods, and Garnet Chan, for information on the status of calculations of excited states, and to Tomas Arias and Garnet Chan and to the reviewers for reviewing the electronic structure section of the text. She is also very grateful to her graduate students, Matthew Windt, Rebecca Cantrell, and Ananth Kaushik, for assistance in compiling the references and reading the manuscript carefully. Funding was provided by the National Science Foundation through the CEMRI award to the Cornell Center for Materials Research and through IGERT Graduate Fellowships in the Nanoscale Control of Interfaces and Surfaces program. Computing resources were supplied in part by gifts of equipment from Intel.

References

(1) Dimitrakopoulos, C.; Malenfant, P. *Adv. Mater.* **2002**, *14*, 99.
(2) Dimitrakopoulos, C.; Mascaro, D. *IBM J. Res. Dev.* **2001**, *45*, 11.
(3) Lee, J. H.; Kim, S. H.; Kim, G. H.; Lim, S. C.; Lee, H.; Jang, J.; Zyung, T. *Synth. Met.* **2003**, *139*, 445.
(4) Torsi, L.; Cioffi, N.; Franco, C. D.; Sabbatini, L.; Zambonin, P. G.; Bleve-Zacheo, T. *Solid-State Electron.* **2001**, *45*, 1479.
(5) Shtein, M.; Mapel, J.; Benziger, J. B.; Forrest, S. R. *Appl. Phys. Lett.* **2002**, *81*, 268.
(6) Hsu, C. H.; Deng, J.; Staddon, C. R.; Beton, P. H. *Appl. Phys. Lett.* **2007**, *91*, 193505.
(7) Bao, Z. ; Locklin, J. J., Eds. *Organic Field-Effect Transistors*; Optical Science and Engineering Series; CRC Press: Boca Raton, FL, 2007.
(8) Yanagi, H.; Morikawa, T. *Appl. Phys. Lett.* **1999**, *75*, 187.
(9) Piaggi, A.; Lanzani, G.; Bongiovanni, G.; Mura, A.; Graupner, W.; Meghdadi, F.; Leising, G.; Nisoli, M. *Phys. Rev. B* **1997**, *56*, 10133.
(10) Grem, G.; Martin, V.; Meghdadi, F.; Paar, C.; Stampfl, J.; Sturm, J.; Tasch, S.; Leising, G. *Synth. Met.* **1995**, *71*, 2193.

(11) Brabec, C. J. *Sol. Energy Mater. Sol. Cells* **2004**, *83*, 273.

(12) Lloyd, M. T.; Mayer, A. C.; Tayi, A. S.; Bowen, A. M.; Kasen, T. G.; Herman, D. J.; Mourey, D. A.; Anthony, J. E.; Malliaras, G. G. *Org. Electron.* **2006**, 243.

(13) Sinnokrot, M. O.; Sherrill, C. D. *J. Phys. Chem. A* **2006**, *110*, 10656.

(14) Sinnokrot, M. O.; Valeev, E. F.; Sherrill, C. D. *J. Am. Chem. Soc.* **2002**, *124*, 10887.

(15) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452.

(16) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028.

(17) Funahashi, M.; Hanna, J.-I. *Appl. Phys. Lett.* **1986**, *73*, 3733. Funahashi, M.; Hanna, J.-I. *Mol. Cryst. Liq. Cryst.* **2001**, *368*, 303.

(18) Funahashi, M. *Polym. J.* **2009**, *41*, 459.

(19) Olivier, Y.; Muccioli, L.; Lemaur, V.; Geerts, Y. H.; Zannoni, C.; Cornil, J. *J. Phys. Chem. B* **2009**, *113*, 14102.

(20) Marcon, V.; Vehoff, T.; Kirkpatrick, J.; Jeong, C.; Yoon, Do Y.; Kremer, K.; Andrienko, D. *J. Chem. Phys.* **2008**, *129*, 094505.

(21) Nelson, J.; Kwiatkowski, J. J.; Kirkpatrick, J.; Frost, J. M. *Acc. Chem. Res.* **2009**, *42*, 1768.

(22) Vehoff, T.; Baumeier, B.; Troisi, A.; Andrienko, D. *J. Am. Chem. Soc.* **2010**, *132*, 11702.

(23) Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Bredas, J.-L. *Chem. Rev.* **2007**, *107*, 926.

(24) Vehoff, T.; Chung, Y. S.; Johnston, K.; Troisi, A.; Yoon, D. Y.; Andrienko, D. *J. Phys. Chem. C* **2010**, *114*, 10592.

(25) Meller, G.; Kosina, H. *Microelectron. J.* **2006**, *38*, 47.

(26) Russell, D. M.; Newsome, C. J.; Li, S. P.; Kugler, T.; Ishida, M.; Shimoda, T. *Appl. Phys. Lett.* **2005**, *87*, 222109.

(27) Moliton, A.; Hiorns, R. C. *Polym. Int.* **2004**, *53*, 1397.

(28) Inzelt, G. *Conducting Polymers: A New Era in Electrochemistry*; Scholz, F., Ed.; Springer: New York, 2008; p 265.

(29) Ruiz, R.; Nickel, B.; Koch, N.; Feldman, L. C.; Haglund, R. F.; Kahn, A.; Scoles, G. *Phys. Rev. B.* **2003**, *67*, 125406.

(30) Ye, R.; Baba, M.; Suzuki, K.; Ohishi, Y.; Mori, K. *Jpn. J. Appl. Phys.* **2003**, *42*, 4473.

(31) Guo, D.; Ikeda, S.; Saiki, K.; Miyazoe, H.; Terashima, K. *J. Appl. Phys.* **2006**, *99*, 094502.

(32) Iannotta, S.; Toccoli, T. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 2501.

(33) Meyer zu Heringdorf, F. J.; Reuter, M. C.; Tromp, R. M. *Nature* **2001**, *412*, 517.

(34) Ruiz, R.; Nickel, B.; Koch, N.; Feldman, L. C.; Haglund, R. F.; Kahn, A.; Family, F.; Scoles, G. *Phys. Rev. Lett.* **2003**, *91*, 136102.

(35) Amassian, A.; Pozdin, V. A.; Desai, T. V.; Hong, S.; Woll, A. R.; Ferguson, J. D.; Brock, J. D.; Malliaras, G. G.; Engstrom, J. R. *J. Mater. Chem.* **2009**, *19*, 5580.

(36) da Silvo Filho, D. A. ; Olivier, Y. ; Coropceanu, V. ; Brédas, ; J.-L. ; Cornil, J. In *Organic Field-Effect Transistors*; Bao, Z., Locklin, J. J., Eds.; CRC Press: Boca Raton, FL, 2007; p 1.

(37) Huang, P.; Carter, E. A. *Annu. Rev. Phys. Chem.* **2008**, *59*, 261.

(38) Head-Gordon, M.; Beran, G. J. O.; Sodt, A.; Jung, Y. *J. Phys.: Conf. Ser.* **2005**, 16. Saad, Y.; Chelikowsky, J. R.; Shontz, S. M. *SIAM Rev.* **2010**, *52*, 3.

(39) Car, R. ; de Angelis, F. ; Giannozzi, P. ; Marzari, N. *Handbook of Materials Modeling*; Springer: Dordrecht, The Netherlands, 2005; Chapter 1.

(40) VASP is an acronym for the Vienna Ab-initio Simulation Package. Information on this commercial code for ab initio Molecular Dynamics simulations can be found at http://cms.mpi.univie.ac.at/vasp/, accessed on October 15, 2010.

(41) Gaussian is a roughly 40-year-old ab initio code developed initially by Pople that is commercially available. Information on this package can be found at http://www.gaussian.com/, accessed on October 15, 2010.

(42) de Jong, W. A.; Bylaska, E.; Govind, N.; Janssen, C. L.; Kowalski, K.; Müller, T.; Nielsen, I. M. B.; van Dam, H. J. J.; Veryazov, V.; Lindh, R. *Phys. Chem. Chem. Phys.* **2010**, *12*, 6896.

(43) Elstner, M.; Porezag, D.; Jungnickel, G.; Elsner, J.; Haugk, M.; Frauenheim, Th.; Suhai, S.; Seifert, G. *Phys. Rev. B* **1998**, *58*, 7260.

(44) Elstner, M.; Frauenheim, Th.; Kaxiras, E.; Seifert, G.; Suhai, S. *Phys. Status Solidi* **2000**, *217*, 357.

(45) Zonias, N.; Lagoudakis, P.; Skylaris, C.-K. *J. Phys.: Cond. Matter* **2010**, *22*, 025303.

(46) Pecchia, A.; Latessa, L.; Di Carlo, A.; Lugli, P. *SPIE Proc.* **2003**, *5219*, 25.

(47) Møller, C. ; Plesset, M. S. Phys. Rev. **1934**, *46*, 61. See http://en.wikipedia.org/wiki/Møller-Plesset_perturbation_theory for a wiki summary of the method.

(48) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140*, A1133.

(49) Jones, R. O. In *Computational Nanoscience: Do It Yourself*; Lecture Notes from Winter School at Jülich, Feb 14−22, 2006; Grotendorst, J.; Blügel, S., Marx, D., Eds.; NIC Series; John von Neumann Institut für Computing: Jülich, Germany, 2006; Vol. *31*.

(50) Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1988**, *153*, 503.

(51) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*, 281.

(52) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1990**, *166*(3), 275.

(53) Sæbø, S.; Almlöf, J. *Chem. Phys. Lett.* **1989**, *154*, 83.

(54) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(55) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(56) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200.

(57) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(58) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865. Also note Errata Phys. Rev. Lett. **1997**, *78*, 1396.

(59) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.

(60) Tsetseris, L.; Pantelides, S. T. *Eur. Phys. J. Appl. Phys.* **2009**, *46*, 1.

(61) Silinsh, E. A. *Organic Molecular Crystals*; Springer: Berlin, 1980.

(62) Lany, S.; Zunger, A. *Phys. Rev. B* **2008**, *78*, 235104.

(63) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215.

(64) Wodrich, M. D.; Corminboeuf, C.; Schreiner, P. R.; Fokin, A. A.; von Ragué Schleyer, P. *Org. Lett.* **2007**, *9*, 1851.

(65) Marom, N.; Tkatchenko, A.; Scheffler, M.; Kronik, L. *J. Chem. Theory Comput.* **2010**, *6*, 81. See also Tkatchenko, A.; Scheffler, M. *Phys. Rev. Lett.* **2009**, *102*, 073005.

(66) Dion, M.; Ryberg, H.; Schroeder, E.; Langreth, D. C.; Lundqvist, B. I. *Phys. Rev. Lett.* **2004**, *92*, 246401.

(67) Tkatchenko, A. ; Romaner, L. ; Hofmann, O. T. ; Zojer, E. ; Ambrosch-Draxl, C. ; Scheffler, M. MRS Bull. June **2010**, *35*, 435.

(68) Riley, K. E.; Op't Holt, B. T.; Merz, K. M., Jr. *J. Chem. Theory Comput.* **2007**, *3*, 407.

(69) Foresman, J. B.; Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *J. Phys. Chem.* **1992**, *96*, 135.

(70) Anderson, J. B. *Quantum Monte Carlo: Origins, Development, Applications*; Oxford University Press: Oxford, U.K., 2007.

(71) Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2002**, *117*, 7433.

(72) van der Horst, J.-W.; Bobbert, P. A.; Michels, M. A. J.; Bässler, H. *J. Chem. Phys.* **2001**, *114*, 6950.

(73) Tretiak, S.; Igumenshchev, K.; Chernyak, V. *Phys. Rev. B.* **2005**, *71*, 033201.

(74) Ramasesha, S.; Pati, S. K.; Krishnamurthy, H. R.; Shuai, Z.; Brédas, J.-L. *Phys. Rev. B.* **1997**, *54*, 7598.

(75) Hachmann, J.; Dorando, J.; Aviles, M.; Chan, G. K-L. *J. Chem. Phys.* **2007**, *127*, 134309.

(76) Dorando, J. J.; Hachmann, J.; Chan, G. K.-L. *J. Chem. Phys.* **2007**, *127*, 084109.

(77) Allen, M. P.; Tildesley, D. J. *Computer Simulation of Liquids*; Oxford University Press: New York, 1988.

(78) Verlet, L. *Phys. Rev.* **1967**, *159*, 98.Phys. Rev. **1967**, *165*, 201.

(79) Beeman, D. *J. Comput. Phys.* **1976**, *20*, 13.

(80) Haile, J. M. *Molecular Dynamics Simulation: Elementary Methods*; Wiley: New York, 1992.

(81) Rapaport, D. C. *The Art of Molecular Dynamics*. 2nd ed.; Cambridge University Press: Oxford, U.K., 2004.

(82) Frenkel, D. ; Smit, B. *Understanding molecular Simulations: From Algorithms to Applications*, 2nd ed.; Academic Press: New York, 2002.

(83) Dougherty, D. B.; Jin, W.; Cullen, W. G.; Dutton, G.; Reutt-Robey, J. E.; Robey, S. W. *Phys. Rev. B* **2008**, *77*, 073414.

(84) Voter, A. F.; Montalenti, F.; Germann, T. C. *Ann. Rev. Mater. Res.* **2002**, *32*, 321.

(85) Montalenti, F.; Voter, A. F. *J. Chem. Phys.* **2002**, *116*, 4819.

(86) Fichthorn, K. A.; Miron, R. A.; Wang, Y.; Tiwary, Y. *J. Phys.: Condens. Matter* **2009**, *21*, 084212.

(87) Best observed from their Web site http://www.cse.scitech.ac.uk/ccg/software/DL_POLY/

(88) Ponder, J. W. Tinker−Software Tools for Molecular Design; Washington University: St. Louis, MO, 2004; described in detail at http://dasher.wustl.edu/tinker/

(89) Allinger, N. L.; Yuh, Y. H.; Lii, J. H. *J. Am. Chem. Soc.* **1989**, *111*, 8551.

(90) Lii, J. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8566.

(91) Lii, J. H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8576.

(92) Tai, J. C.; Allinger, N. L. *J. Comput. Chem.* **1988**, *19*, 475.

(93) Goose, J. E.; First, E. L.; Clancy, P. *Phys. Rev. B* **2010**, *81*, 205310.

(94) Goose, J. E.; Killampalli, A.; Engstrom, J. R.; Clancy, P. *J. Phys. Chem.* **2009**, *130*, 124701.

(95) Cantrell, R. A.; Clancy, P. *Surf. Sci.* **2008**, *602*, 3499.

(96) Cantrell, R. A.; Clancy, P. *Mater. Res. Soc. Symp. Proc.* **2010**, 1263.

(97) Goose, J. E.; Clancy, P. *J. Phys. Chem C* **2007**, *111*, 15653.

(98) Ananth, P. ; Clancy, P. Surf. Sci. **2010**, submitted.

(99) Gonzalez, C.; Lim, E. C. *J. Phys. Chem. A* **1999**, *103*, 1437.

(100) Claes, L.; Kwasniewski, S.; Deleuze, M. S.; Francois, J. P. *J. Mol. Struct.: THEOCHEM* **2001**, *549*, 63.

(101) Claes, L.; Francois, J. P.; Deleuze, M. S. *Chem. Phys. Lett.* **2001**, *339*, 216.

(102) Tai, J. C.; Allinger, N. L. *J. Comput. Chem.* **1998**, *19*, 475.

(103) Dellago, C.; Bolhuis, P. G.; Geissler, P. L. *Adv. Chem. Phys.* **2002**, *123*, 1.

(104) Dellago, C.; Bolhuis, P. G. *Advanced Computer Simulation Approaches for Soft Matter Sciences III*; Holmer, C., Kremer, K., Eds.; Springer: New York, 2008; p 167.

(105) Allen, R. J.; Warren, P. B.; ten Wolde, P. R. *Phys. Rev. Lett.* **2005**, *94*, 018104.

(106) Escobedo, F. A.; Borrero, E. E.; Araque, J. C. *J. Phys.: Condens. Matter* **2009**, *21*, 333101.

(107) Allen, R. J.; Valeriani, C.; tenWolde, P. R. *J. Phys.: Condens. Matter* **2009**, *21*, 463102.
(108) Sanz, E.; Valeriani, C.; Frenkel, D.; Dijkstra, M. *Phys. Rev. Lett.* **2007**, *99*, 055501.
(109) Page, A. J.; Sear, R. P. *Phys. Rev. Lett.* **2006**, *97*, 065701.
(110) Borrero, E. E.; Escobedo, F. A. *J. Chem. Phys.* **2007**, *127*, 164101.
(111) Borrero, E. E.; Escobedo, F. A. *J. Chem. Phys.* **2008**, *129*, 024115.
(112) Borrero, E; Contreras, L.; DeLisa, M.; Escobedo, F. A. *Biophys. J.* **2010**, *98*, 1911.
(113) Velez-Vega, C.; Borrero, E. E.; Escobedo, F. A. *J. Chem. Phys.* **2010**, *133*, 105103.
(114) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. *J. Chem. Phys.* **1953**, *21*, 1087.
(115) Voter, A. F. In *Radiation Effects in Solids*; Sickafus, K. E., Kotominin, E. A., Eds.;Springer: New York, 2005.
(116) Fichthorn, K. A.; Weinberg, W. H. *J. Chem. Phys.* **1991**, *95*, 1090.
(117) Biehl, M. In *Multiscale Models of Epitaxial Growth*; Voigt, A., Ed.; Burkhaüser Verlag: Basel, Switzerland, 2005; p 3.
(118) Cantrell, R. A.; Clancy, P. *Proceedings of the 2010 Materials Research Society Fall Meeting*; Boston, Nov 29−Dec 3, 2010; Materials Research Society: Warrendale, PA, 2010.
(119) Biehl, M.; Much, F.; Vey, C.;Voigt, A., Ed.; Burkhaüser Verlag: Basel, Switzerland, 2005; p 41.
(120) Kara, A.; Trushin, O.; Yildirim, H.; Rahman, T. S. *J. Phys.: Condens. Matter* **2009**, *21*, 084213.
(121) Khor, K. E.; Das Sarma, S. *Phys. Rev. B* **2000**, *62*, 16657.
(122) Biehl, M. ; Much, F. In *Quantum Dots: Fundamentals, Applications, and Frontiers*; Joyce, B. A., Ed.; Springer: Dordrecht, The Netherlands, 2005; p. 89.
(123) Kara, A.; Trushin, O.; Yildirim, H.; Rahman, T. S. *J. Phys.: Condens. Matter* **2009**, *21*, 084213.
(124) Nandipati, G.; Shim, Y.; Amar, J. G.; Karim, A.; Kara, A.; Rahman, T. S.; Trushin, O. *J. Phys.: Condens. Matter* **2009**, *21*, 084214.
(125) (a) Schwoebel, R. L.; Shipsey, E. J. *J. Appl. Phys.* **1966**, *37*, 3682. (b) Ehrlich, G.; Hudda, F. G. *J. Chem. Phys.* **1966**, *44*, 1039. (c) Ehrlich, G. *Surf. Sci.* **1995**, *331*, 865.
(126) Northrup, J. E.; Tiago, M. L.; Louie, S. G. *Phys Rev. B* **2002**, *66*, 121404.
(127) Nabok, D.; Puschnig, P.; Ambrosch-Draxl, C. *Phys. Rev. B* **2008**, *77*, 245316.
(128) Gross, L.; Mohn, F.; Moll, N.; Liljeroth, P.; Meyer, G. *Science* **2009**, *325*, 1110.
(129) Mattheus, C. C.; Dros, A. B.; Baas, J.; Meetsma, A.; de Boer, J. L.; Palstra, T. T. M. *Acta Crystallogr., Sect. C* **2001**, *57*, 939.
(130) Mattheus, C. C.; Dros, A. B.; Baas, J.; Oostergetel, G. T.; Meetsma, A.; de Boer, J. L.; Palstra, T. T. M. *Synth. Met.* **2003**, *138*, 475.
(131) Parisse, J. D. P.; Ottaviano, L.; Picozzi, S. *J. Phys.: Condens. Matter* **2007**, *19*, 106209.
(132) Bouchoms, I. P. M.; Schoonveld, W. A.; Vrijmoeth, J.; Klapwijk, T. M. *Synth. Met.* **1999**, *104*, 175.
(133) Nabok, D.; Puschnig, P.; Ambrosch-Draxl, C. *Phys. Rev. B* **2008**, *77*, 245316.
(134) Della Valle, R. G.; Venuti, E.; Brillante, A.; Girlando, A. *Chem. Phys. Chem.* **2009**, *10*, 1783.
(135) Van Beest, B. W. H.; Kramer, G. J.; Van Santen, R. A. *Phys. Rev. Lett.* **1990**, *64*, 1955.
(136) Ruiz, R.; Choudhary, D.; Nickel, B.; Toccoli, T.; Chang, K. C.; Mayer, A. C.; Clancy, P.; Blakely, J. M.; Headrick, R. L.; Iannotta, S.; Malliaras, G. G. *Chem. Mater.* **2004**, *16*, 4497.
(137) Zorba, S.; Shapiro, Y.; Gao, Y. *Phys. Rev. B* **2006**, *74*, 245410.
(138) Mayer, A.; Kazimirov, A.; Malliaras, G. G. *Phys. Rev. Lett.* **2006**, *97*, 105503.
(139) Goose, J. E.; Wong, K.; Clancy, P.; Thompson, M. O. *Appl. Phys. Lett.* **2008**, *93*, 183306.
(140) Huang, W. J.; Li, B. Q.; Zuo, J. M. *Surf. Sci.* **2005**, *595*, 157.
(141) Dimitrakopoulos, C. D.; Brown, A. R.; Pomp, A. *J. Appl. Phys.* **1996**, *80*, 2501.
(142) Jin, S. H.; Jung, K. D.; Shin, H.; Park, B. G.; Lee, J. D. *Synth. Met.* **2006**, *156*, 196.
(143) Lee, J.; Kim, J. H.; Im, S. *J. Appl. Phys.* **2004**, *95*, 3733.
(144) Guo, D.; Ikeda, S.; Saiki, K. *J. Phys.: Condens. Matter* **2010**, *22*, 262001.
(145) Amar, J. G.; Family, F. *Phys. Rev. Lett.* **1995**, *74*, 2066.
(146) Tejima, M.; Kita, K.; Kyuno, K.; Toriumi, A. *Appl. Phys. Lett.* **2004**, *85*, 3746.
(147) Choudhary, D.; Clancy, P.; Shetty, R.; Escobedo, F. *Adv. Funct. Mater.* **2006**, *16*, 1768.
(148) Cantrell, R. A. ; James, C. N. ; Clancy, P. **2010**, unpublished results.
(149) Heringdorf, F. J. M.; Reuter, M. C.; Tromp, R. M. *Nature* **2001**, *412*, 517.
(150) Choudhary, D.; Clancy, P.; Bowler, D. R. *Surf. Sci.* **2005**, *578*, 20.
(151) 152 Käfer, D.; Ruppel, L.; Witte, G. *Phys. Rev. B.* **2007**, *75*, 085309.
(152) Ito, Y.; Virkar, A. A.; Mannsfeld, S.; Oh, J. H.; Toney, M.; Locklin, J.; Bao, Z. *J. Am. Chem. Soc.* **2008**, *131*, 9396.
(153) Wöll, C. *Chemical Aspects of Organic Electronics From Fundamentals to Functioning Devices*; Wiley-VCH: Weinheim, Germany, 2009.
(154) Jakabovič, J.; Kováč, J.; Srnánek, R.; Kováč, J., Jr.; Sokolský, M.; Cirák, J.; Haško, D.; Resel, R.; Zojer, E. In *Interface Controlled Organic Thin Films*; Rubahn, H.-G., Sitter, H., Horowitz, G., Al-Shamery, K., Eds.; Springer Verlag: Berlin, 2009; Vol. *129*, pp 185−187.
(155) Kowarik, S.; Gerlach, A.; Schreiber, F. *J. Phys.: Condens. Matter* **2008**, *20*, 184005.
(156) Lee, H. S.; Kim, D. H.; Cho, J. H.; Hwang, M.; Y. Jang, Y.; Cho, K. *J. Am. Chem. Soc.* **20708**, *130*, 10556.
(157) Kim, D. H.; Lee, H. S.; Yang, H.; Cho, K. *Adv. Funct. Mater.* **2008**, *18*, 1363.
(158) Hill, G.; Weinert, C. M.; Kreplak, L.; van Zyl, B. P. *Appl. Phys. A: Mater. Sci. Process.* **2009**, *95*, 81.
(159) Yamamoto, H.; Nishiyama, K.; Ohdomari, I. *J. Phys. IV* **2006**, *132*, 189.
(160) Irving, D. L.; Brenner, D. W. *J. Phys. Chem. B* **2006**, *110*, 31.
(161) Vemparala, S.; Karki, B. B.; Kalia, R. K.; Vashishta, P. *J. Chem. Phys.* **2004**, *121*, 4323.
(162) Bosio, S. B. M.; Hase, W. L. *J. Chem. Phys.* **1997**, *107*, 9677.
(163) Isa, N.; Gibson, K. D.; Yan, T.; Hase, W. L.; Sibener, S. J. *J. Chem. Phys.* **2004**, *120*, 2417.
(164) Day, B. S.; Morris, J. M.; Alexander, W. A.; Troya, D. *J. Phys. Chem. B* **2006**, *110*, 6832.
(165) Day, B. S.; Morris, J. M.; Troya, D. *J. Chem. Phys.* **2005**, *122*, 214712.
(166) Gibson, K. D.; Isa, N.; Sibener, N. *J. Phys. Chem. A* **2006**, *110*, 1469.
(167) Desai, T. V. ; Hong, S. ; Woll, A. R. ; Hughes, K. J. ; Ananth, P.; Clancy, P. ; Engstrom, J. R. *J. Chem. Phys.* **2010**, submitted.
(168) Lukas, S.; Söhnchen, S.; Witte, G.; Wöll, C. *Chem. Phys. Chem.* **2004**, *5*, 266 (Pn on Cu 110).
(169) Witte, G.; Wöll, C. *J. Mater. Res.* **2004**, *19*, 1889 (Pn on Cu 110).
(170) Lukas, S.; Vollmer, S.; Witte, G.; Wöll, Ch. *J. Chem. Phys.* **2001**, *114*, 10123 (benzene, naphthalene, and anthracene on Cu(111) and vicinal Cu(221) and Cu(443)).
(171) Mete, E.; Demiroglu, I.; Danisman, M.; Ellialtioglu, S. *J. Phys. Chem. C* **2010**, *114*, 2724 (Pn on Ag 111).
(172) Käfer, D.; Witte, G. *Chem. Phys. Lett.* **2007**, *442*, 376 (Pn on Ag 111).
(173) Schroeder, P. G.; France, C. B.; Parkinson, J. B. *J. Appl. Phys.* **2002**, *91*, 3010 (Pn on 1 ML Au).
(174) Betti, M. G.; Kanjilal, A.; Mariani, C. *J. Phys. Chem. A* **2007**, *111*, 12454 (Pn on 1 ML Au).
(175) Hu, W. S.; Tao, Y. T.; Hsu, Y. J.; Wei, D. H.; Wu, Y. S. *Langmuir* **2005**, *21*, 2260 (Pn on Au).
(176) Kang, J. H.; Zhu, X. Y. *Chem. Mater.* **2006**, *18*, 1318 (Au).
(177) Zheng, Y.; Wee, A. T. S.; Chandrasekhar, N. *ACS Nano* **2010**, *4*, 2104 (Pn on Au and on oxide).
(178) Marchetto, H.; Groh, U.; Schmidt, Th.; Fink, R.; Freund, H.-J.; Umbach, E. *Chem. Phys.* **2006**, *325*, 178.
(179) Eremtchenko, M.; Bauer, D.; Schaefer, J. A.; Tautz, F. S. *J. Mater. Res.* **2004**, *19*, 2028.
(180) Hänel, K.; Söhnchen, S.; Lukas, S.; Beernink, G.; Birkner, A.; Strunskus, T.; Witte, G.; Wöll, Ch. *J. Mater. Res.* **2004**, *19*, 2049–2056.
(181) Oehzelt, M. ; Berkebile, S. ; Koller, G. ; Haber, T. ; Koini, M. ; Werzer, O. ; Resel, R. ; Ramsey, M. G. In *Proceedings in Physics*; Rubahn, H.-G., Sitter, H., Horowitz, G., Al-Shamery, K., Eds.; Springer Verlag: Berlin, 2009; Vol. *129*, p 19.
(182) Lipton-Duffin, J. A.; Miwa, J. A.; Kondratenko, M.; Cicoira, F.; Sumpter, B. G.; Meunier, V.; Perepichka, D. F.; Rosei, F. *Proc. Natl. Acad. Sci.* **2010**, *107*, 11200.
(183) Al-Mahboob, A.; Sadowski, J. T. *Surf. Sci.* **2009**, *603*, L53–L56 (Pentacene on C_{60}).
(184) Simeoni, M.; Picozzia, S.; Delley, B. *Surf. Sci.* **2004**, *562*, 43 (Pentacene on Al 100).
(185) Lee, K.; Yu, J. *Surf. Sci.* **2005**, *589*, 8 (Pentacene on Au (001)).
(186) Li, H.; Duan, Y.; Coropceanu, V.; Brédas, J.-L. *Org. Electron.* **2009**, *10*, 1571 (Pentacene on Au (111)).
(187) Müller, K.; Kara, A.; Kim, T. K.; Bertschinger, R.; Scheybal, A.; Osterwalder, J.; Jung, T. A. *Phys. Rev. B* **2009**, *79*, 245421 (Pentacene on Cu (110)).
(188) Yamane, H.; Yoshimura, D.; Kawabe, E.; Sumii, R.; Kanai, K.; Ouchi, Y.; Ueno, N.; Seki, K. *Phys. Rev. B* **2007**, *76*, 165436 (Pentacene on Cu (110)).
(189) Toyoda, K.; Hamada, I.; Yanagisawa, S.; Morikawa, Y. *Appl. Phys. Express* **2010**, *3*, 025701 (Pentacene on Cu (111)).
(190) Baldacchini, C.; Mariani, C.; Betti, M. G.; Vobornik, I.; Fujii, J.; Annese, E.; Rossi, G.; Ferretti, A.; Calzolari, A.; Di Felice, R.; Ruini, A.; Molinari, E. *Phys. Rev. B* **2007**, *76*, 245430 (Pentacene on Cu 119).
(191) Sun, X.; Suzuki, T.; Yamauchi, Y.; Kurahashi, M.; Wang, Z. P.; Entani, S. *Surf. Sci.* **2008**, *602*, 1191 (Pentacene on Fe (100)).
(192) Toyoda, K.; Hamada, I.; Lee, K.; Yanagisawa, S.; Morikawa, Y. *J. Chem. Phys.* **2010**, *132*, 134703.
(193) Watkins, N. J.; Yan, L.; Yongli, G. *Appl. Phys. Lett.* **2002**, *80*, 4384.
(194) Sadowski, J. T.; Nagao, T.; Yaginuma, S.; Fujikawa, Y.; Al-Mahboob, A.; Nakajima, K.; Sakurai, T.; Thayer, G. E.; Tromp, R. M. *Appl. Phys. Lett.* **2005**, *86*, 073109.
(195) Wang, J. Z.; Sadowski, J. T.; Xiong, Z. H.; Fujikawa, Y.; Xue, Q. K.; Sakurai, T. *Nanotechnology* **2009**, *20*, 095704.

(196) Hatch, R. C.; Sanchez, C. W.; Höchst, H. *Appl. Phys. Lett.* **2010**, *97*, 093303.

(197) Zheng, Y.; Wee, A. T. S.; Chandrasekhar, N. *ACS Nano* **2010**, *4*, 2104.

(198) Weiss, P.; Abrams, M.; Cygan, M.; Ferris, J.; Kamna, M.; Krom, K.; Stranick, S.; Youngquist, M. Y. *Anal. Chim. Acta* **1995**, *307*, 355.

(199) Bogicevic, A.; Strömquist, J.; Lundqvist, B. I. *Phys. Rev. Lett.* **1998**, *81*, 637.

(200) Stumpf, R.; Scheffler, M. *Phys. Rev. B* **1996**, *53*, 4958.

(201) Xiang, S. K.; Huang, H. *Appl. Phys. Lett.* **2008**, *92*, 101923.

(202) Fendrich, M.; Krug, J. *Phys. Rev. B: Condens. Matter* **2007**, *76*, 121302.

(203) Hlawacek, G.; Puschnig, P.; Frank, P.; Winkler, A.; Ambrosch-Draxl, C.; Teichert, C. *Science* **2008**, *321*, 108.

(204) Weckesser, J.; Barth, J. V.; Kern, K. *J. Chem. Phys.* **1999**, *110*, 5351.

(205) Schunack, M.; Linderoth, T. R.; Rosei, F.; Lægsgaard, E.; Stensgaard, I.; Besenbacher, F. *Phys. Rev. Lett.* **2002**, *88*, 1561021.

(206) Otero, R.; Hümmelink, F.; Sato, F.; Legoas, S. B.; Thostrup, P.; Laegsgaard, E.; Stensgaard, I.; Galvão, D. S.; Besenbacher, F. *Nat. Mater.* **2004**, *3*, 779.

(207) Dobbs, K. D.; Doren, D. J. *J. Chem. Phys.* **1993**, *99*, 10041.

(208) Trevethan, T.; Shluger, A. L. *J. Phys. Chem. C* **2008**, *112*, 19577.

(209) Trevethan, T.; Shluger, A. L.; Kantorovich, L. *J. Phys.: Condens. Matter* **2010**, *22*, 084024.

(210) Murphy, A. R.; Fréchet, J. M. *J. Chem. Rev.* **2007**, *107*, 1066.

(211) Lehnherr, D.; Tykinski, R. R. *Materials* **2010**, *3*, 2772.

(212) Horowitz, G. *Adv. Mater.* **1999**, *10*, 365.

(213) Witte, G.; Wöll, Ch. *J. Mater. Res.* **2004**, *19*, 1889.

(214) Liu, H.; Lin, Z.; Zhigilei, L. V.; Reinke, P. *J. Phys. Chem. C* **2008**, *112*, 4687.

(215) Bishop, K. J. M. ; Wilmer, C. E. ; Siowling, S.; Grzybowski, B. A. Small **2009**,

(216) McMahon, D. P.; Troisi, A. *Chem. Phys. Chem.* **2010**, *11*, 2067.

(217) Puschnig, P.; Nabok, D.; Ambrosch-Draxl, C. In *Interface Controlled Thin Films*; Rubahn, H.-G., Sitter, H., Horowitz, G., Al-Shamery, K. Eds; Springer-Verlag: Berlin, 2009.

(218) Wu, Z.; Kanai, Y.; Grossman, J. C. *Phys. Rev. B* **2009**, *79*, 201309.

(219) Grossman, J. C.; Mitas, L. *Phys. Rev. Lett.* **1997**, *79*, 4353.

(220) Drummond, N. D.; Needs, R. *J. Phys. Rev. Lett.* **2007**, *99*, 166401.

(221) Sorella, S.; Casula, M.; Rocca, D. *J. Chem. Phys.* **2007**, *127*, 014105.

(222) Petrosyan, S. A.; Rigos, A. A.; Arias, T. A. *J. Phys. Chem. B* **2005**, *109*, 15436.