

Theoretical Study of the Effects of Temperature Slip in LPCVD Systems

A Summary Report to The Electrochemical Society for the 2002 Edward G. Weston Summer Research Fellowship

by Tailai Hu

Low-pressure chemical vapor deposition (LPCVD) is widely used to deposit thin film materials in the microelectronics industry. In most of the previous LPCVD modeling studies,^{1,2} temperature is assumed to be continuous across the gas-surface interface. However, at low pressure, a temperature slip at the growth surface can exist while continuum assumption is still valid in the gas phase, and the magnitude of temperature slip increases as pressure decreases.

Some workers^{4,5} have measured temperature slips that can be more than 100 K under common conditions in LPCVD systems. In our research group, some previous modeling work has been done computationally to study the effects of temperature slip on silicon, silicon carbide, and gallium arsenide LPCVD systems.³ The preliminary results show that, while a temperature slip can in principle result in measurable effects on the mole concentrations of species and the deposition rates, the magnitude of the effects of temperature slip will be much more sensitive in some systems than others. The influencing factors include the magnitude of the temperature slip, the sticking coefficients of important gas-surface reactions, the relative importance of gas-phase reactions and kinetic energy dependent gas-surface reactions, and so on. Hence, we perform a theoretical study of the effects of temperature slip, by using simple models, to study the influences and relative importance of these key parameters on deposition rates.

Two approaches are used in this theoretical study. In the first approach, only a single surface reaction is considered. In LPCVD systems, one of the surface reactions is often rate-determining,³ so this approach is useful in at least a few important cases. The simple surface reaction is assumed to be in the form of $A \rightarrow A(D)$ or $AB \rightarrow A(D)+B$. Gas-phase species (A or AB) impinging onto the surface are deposited, or decomposed and deposited on the surface. This kind of surface reaction is very common in LPCVD systems. In this first approach, the effects of activation energy appearing in surface reactions and temperature slip on deposition rate are highlighted.

Fig. 1. Deposition rate as a function of temperature slip; deposition rates are divided by the deposition rate of the case with zero temperature slip at corresponding activation energies.

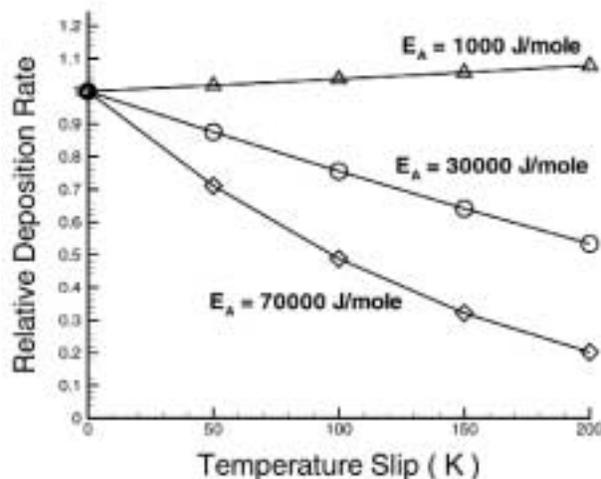
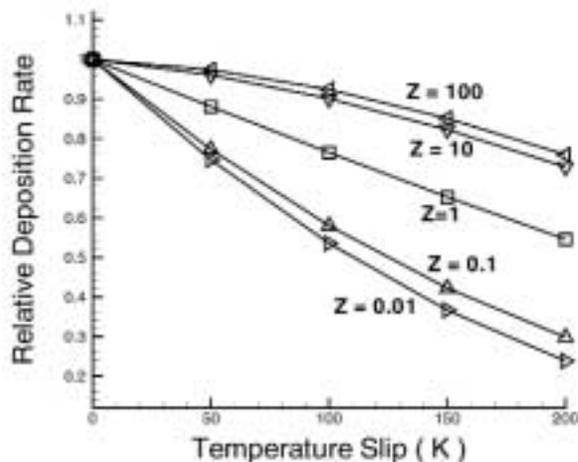


Fig. 2. Deposition rate as a function of temperature slip; deposition rates are divided by the deposition rate of the case with zero temperature slip at the corresponding Z.



In the second approach, we add a single gas-phase reaction in partial chemical equilibrium. Thus, we consider one gas reaction ($AB \leftrightarrow A+B$) and two surface reactions ($A \rightarrow A(D)$ and $AB \rightarrow A(D)+B$). The equilibrium calculation can be first performed for gas-phase mixture. Then, the deposition rates are calculated from the temperature and gas-phase concentrations. In the second approach, the factors that affect the deposition rates in the cases with temperature slip include the ratio of sticking coefficients of the two surface reactions, DG (the change of Gibbs energy in the gas-phase reaction), the activation energy of surface reactions, and so on.

The results in Fig. 1 show the relationship between deposition rate and

temperature slip when choosing different activation energies (first approach). When activation energy is 30 kJ/mole, a modest temperature slip of 100 K can produce more than a 20 percent effect on deposition rate compared with zero temperature slip case. Also, a greater effect of temperature slip on the deposition rate can be seen at larger activation energies.

Fig. 2 shows the effects of the ratios of sticking coefficients on deposition rate in the second approach. In this case, DG is fixed at 20 kcal/mole and $Z = \gamma_{AB}/\gamma_A$ represents the ratio of sticking coefficients for the two surface reactions. When Z is equal to 1, the influencing factor mainly comes from acti-

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vation energy of surface reactions (fixed at 30 kJ/mole in the second approach), which is same as that shown in Fig. 1. When the value of Z is far from unity, the effects on deposition rates are very different than the $Z=1$ case with small values of Z inducing a significantly greater sensitivity of deposition rate to temperature slip.

In sum, we have shown that the effects of temperature slip on deposition rates in LPCVD systems can be sensitive to some important influencing factors, such as the activation energies of surface reactions, the ratios of sticking coefficients, the magnitude of temperature slip, and ΔG of a gas-phase reaction. ■

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Halogenated *Closo*-dodecacarborane Anions: Robust Cation Exchangers for Ionophore-Based Chemical Sensing

A Summary Report to The Electrochemical Society for the 2002 Colin Garfield Fink Summer Research Fellowship

by Shane M. Peper

Polymeric membrane ion-selective electrodes (ISEs) are an important class of chemical sensors that have found widespread use in the areas of clinical diagnostics and environmental monitoring. Traditionally, the sensing phase consists of a plasticized polymer matrix (*i.e.*, poly(vinyl chloride) (PVC)) that is incorporated with an ionophore, which selectively binds the analyte of interest, and an ion-exchanger that facilitates mass transport of the primary ion from an aqueous sample into a hydrophobic sensing phase.¹ The lipophilic tetraphenylborate derivative, tetrakis[3,5 - bis(trifluoromethyl) phenyl]-borate (TFPB) has conventionally been used as a cation exchanger. Under certain sample conditions, however, such as in acidic media, TFPB exhibits less than optimal behavior. It is well known that TFPB undergoes acid hydrolysis,² thus ultimately contributing to the decreased lifetime of chemical sensors being employed under these sample conditions. Toxic heavy metals, such as Pb^{2+} , are a class of analytes that require such acidic sample conditions if one wants to measure total free ion activities.

Very recently, we reported that an undecabrominated *closo*-dodecacarborane anion (UBC) is a suitable alternative to TFPB, offering improved chemical stability while retaining optimal functional characteristics.³ The present work compares several other halogenated carboranes, namely the hexabrominated (HBC), undeca-iodinated (UIC), and the undeca-chlorinated (UCC) derivatives, with the behavior of both UBC and TFPB. Specifically, the chemical stability and/or lipophilicity in acidic media was studied, as well as the unbiased selectivity behavior of bis-2-ethylhexyl sebacate (DOS)-plasticized PVC ISEs containing the Pb^{2+} -selective ionophore tert-butylcalix[4]arene-tetrakis(N,N-dimethylthioacetamide) (Pb^{2+} IV).

The chemical stability/lipophilicity of the ion-exchangers was evaluated using bulk optode thin films as previously described.^{4,5} Films ~ 2 μm in thickness were prepared using a spin-coating device from membrane cocktails containing PVC, DOS, an ion-exchanger, and a chromoionophore

Fig. 1. Leaching profiles of various halogenated carboranes and TFPB in the presence of 0.2 M acetic acid under flowing conditions (1.2 mL/min). Absorbance readings were collected in 60 s intervals and the peak corresponding to the fully protonated form of the chromoionophore (518 nm) was used to determine the extent of ion-exchanger leaching.

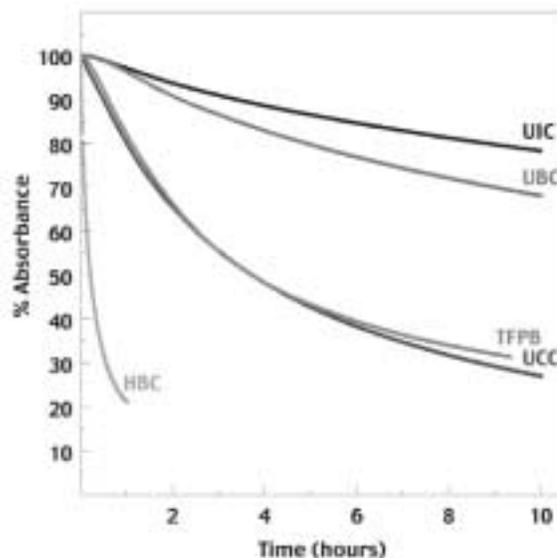
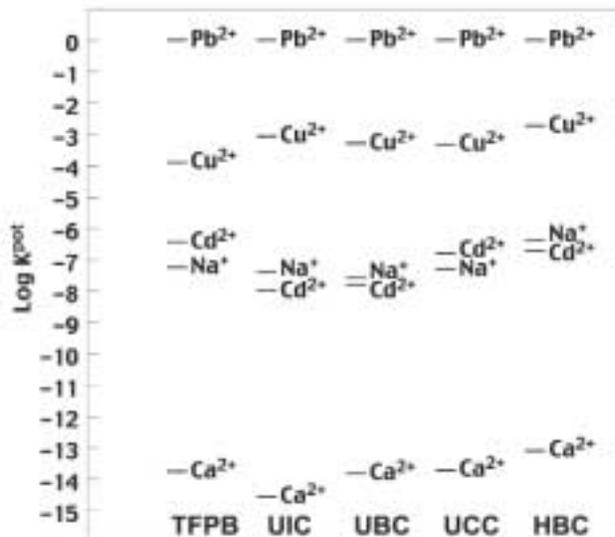


Fig. 2. Unbiased potentiometric selectivity coefficients, $\log K_{\text{Pb}^{2+}}^{\text{pot}}$, for PVC-DOS ISEs containing Pb^{2+} IV and a respective ion-exchanger. Selectivity coefficients were determined using the separate solution method (SSM) and are the mean of five electrodes.



(ETH 5315). The ion-exchanger and the chromoionophore were present in equimolar amounts, such that any loss of ion-exchanger from the film, either due to decomposition or insufficient lipophilicity, would result in deprotonation of the chromoionophore, which could be measured spectroscopically. Figure 1 shows the leaching behavior of the ion-exchangers from films in contact with 0.2 M acetic acid under flowing conditions (1.2 mL/min). It is apparent from the figure that TFPB undergoes rapid hydrolysis and that both UBC and UIC offer significantly improved long-term stability.

Moreover, the best commercially available carborane, HBC, exhibited dramatically poor retention. Interestingly, the rate of leaching of UCC is quite comparable to the rate of decomposition of TFPB. In order to demonstrate functionality, lead-selective ISEs containing lead ionophore IV and a respective ion-exchanger were evaluated in terms of their unbiased selectivity behavior. Unbiased selectivity coefficients are obtained by conditioning the electrodes in a discriminated ion, thus allowing Nernstian response slopes to

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Interfaces Between Organic Semiconductor Materials and Metal Electrodes

A Summary Report to The Electrochemical Society for the 2002 Joseph W. Richards Summer Research Fellowship

by C. Brian France and B. A. Parkinson

Interesting structural organization of organic semiconducting compounds on metal electrodes could influence the electrical properties of new technologically significant devices. We have been investigating the molecular ordering of small molecule organics on Ag(111) and Au(111) films deposited on mica substrates.¹ These metal substrates are prepared in ultra-high vacuum (UHV) and used to simulate a contacting electrode. The metal substrates were prepared with Ar ion sputtering and annealed to produce pristine, terraced surfaces. The molecular semiconductors pentacene and *p*-sexiphenyl (*p*-6P) have been evaporated onto the metal film in UHV then analyzed with a UHV scanning tunneling microscope (STM), temperature programmed desorption (TPD) and photoemission techniques.

The interface between Au(111) and pentacene has proved to be more interesting than anticipated, exhibiting a surprisingly large number of coverage dependant ordered structures.²⁻⁴ Low coverages produced 4 polymorphs, while monolayer films produced 4 different row structures. Multilayer pentacene films generated a unique widely spaced periodic row structure, with a 61 ± 5 Å spacing. Ultraviolet photoemission spectroscopy has also been used to determine the energy level alignment of the pentacene and Au(111) interface.⁵ A large interface dipole barrier (0.95 eV) was formed at this heterojunction interface. Two different binding environments for pentacene on Au(111) have been determined utilizing TPD. Monolayer or thinner films show a strong interaction with the Au substrate while thicker films have a smaller binding energy as the pentacene interactions are not dominated by the interface with the Au(111).

Investigations of *p*-6P on Au(111) have also provided useful insights into the organic semiconductor/metal interface. Similar to previous reports, photoemission spectroscopy revealed that the Au(111)/*p*-6p interface has a substantial (0.73 eV) interface dipole.⁶ TPD of thick *p*-6P films (50 Å) revealed the presence of at least two different binding environments. In Fig. 1, peak A and B have desorption temperatures of

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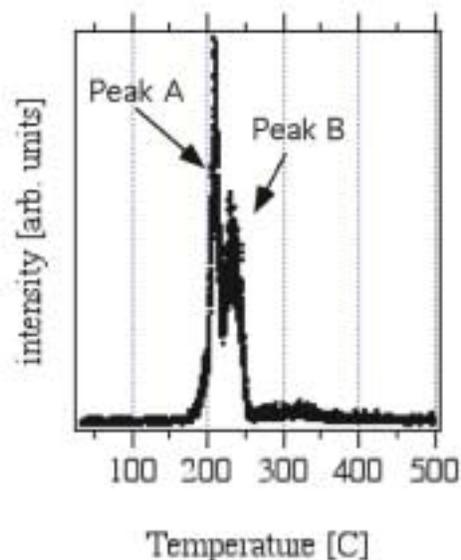


Fig. 1. Temperature programmed desorption of a 50Å *p*-sexiphenyl film on Au(111), heating rate of 15°C/min. Peak A with a peak temperature of 211.2°C (136.4 KJ/Mole) and peak B with a peak temperature of 234.6°C (143.3 KJ/Mole).

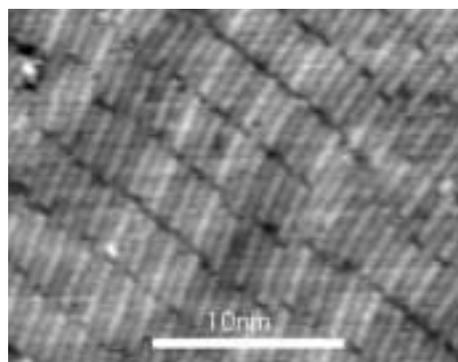


Fig. 2. A 25.4 x 19.7 nm STM image of *p*-6p on Au(111). The Au(111) reconstruction was imaged through the *p*-6p film and three elevated unit cells can be observed in the image. (-0.5 V sample bias, 0.1 nA, max z-height 0.105 nm)

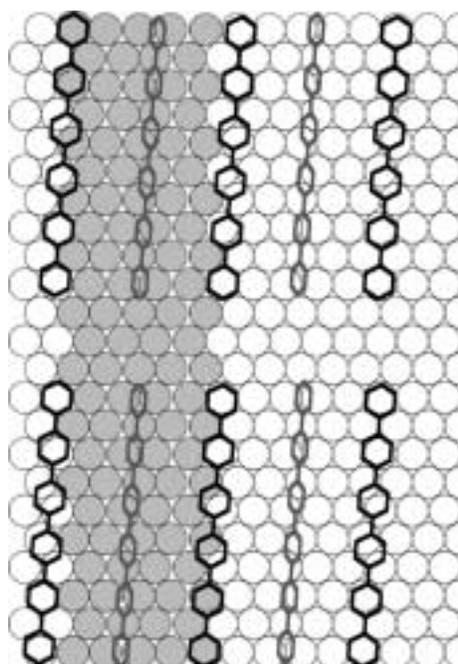


Fig. 3. A proposed model of the *p*-6p film on Au(111). The Au dark substrate atoms represent the $23 \times \sqrt{3}$ reconstruction. The dark *p*-6p molecules signify molecules with their plane parallel to the substrate while lighter molecules represent tilted molecules.

Predicting Potential-Dependent Electrode–Chemisorbate Vibrational Behavior from Density Functional Theory Calculations

A Summary Report to The Electrochemical Society for the 2002 F. M. Beckett Summer Research Fellowship

by Sally A. Wasileski

Of central interest to electrochemists is understanding the bonding of molecules to electrode surfaces. A major experimental probe for determining electrochemical chemisorbate interactions, and their dependence on the applied potential, is vibrational spectroscopy. *In situ* Raman and infrared spectroscopic measurements are dramatically enhancing the molecular-level understanding of electrode–solution interfaces.¹ From such vibrational spectra, electrochemists can obtain metal- and potential-dependent information on chemisorbate bonding. However, interpreting the vibrational behavior in terms of fundamental changes in bonding properties, such as surface–chemisorbate bond energy, geometry, or charge transfer, is often not straightforward. Augmenting experimental information with a quantum-chemical description of the bonding interaction is important to fully understand these complex systems.

Density Functional Theory (DFT) calculations of surface–chemisorbate systems reproduce binding energies and vibrational frequencies comparable to experiment,² in addition to providing orbital,³ density of state,⁴ and charge polarization^{5–7} descriptions of surface bonding. Modeling the electrode usually involves two strategies: finite cluster and periodic-slab methods. The first is discussed in detail in Ref. 6. The second, utilized here, represents the electrode as a two-dimensional array of metal atoms oriented in a specific surface geometry, such as (111).⁴ Chemisorbates are bound in a repetitive fashion and experimentally relevant, finite-coverage systems can be modeled. Since the periodic electron basis sets utilized in this model more accurately describe metallic band structure, it is the preferred model of electrode–chemisorbate systems.

A primary interest of the fellowship work presented here is to demonstrate how DFT can predict both chemisorbate vibrational frequencies, ν , and the corresponding change in frequency with applied potential (or field), *i.e.*, the Stark-tuning slope,⁵ $d\nu/dF$, as a function of adsorbate coverage. This report describes investigations of such behavior for the archetypical system, atop-bound carbon monoxide on Pt(111) electrodes in comparison with experi-

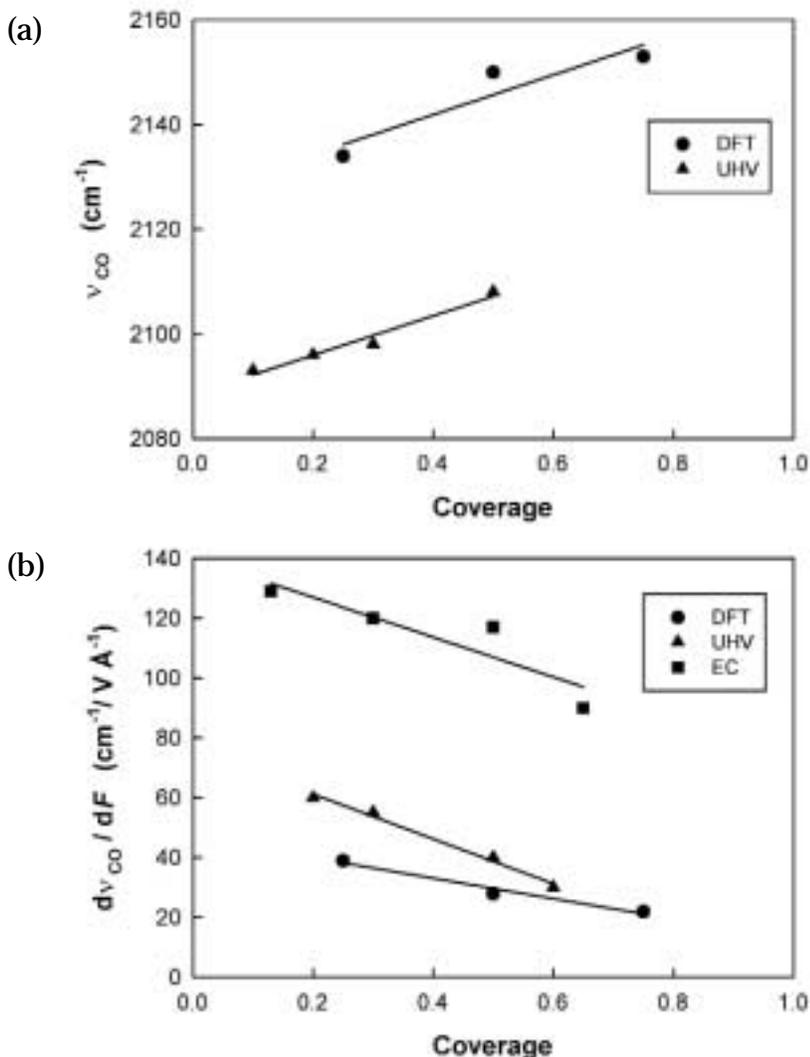


Fig. 1. (a) Intramolecular vibrational frequency for atop-bound CO on Pt(111) versus fractional CO coverage, determined from DFT (circles) and experimentally measured in UHV (triangles). (UHV values extracted from Ref. 8.); (b) Corresponding Stark-tuning slopes versus fractional CO coverage, determined from DFT (circles) and experimentally measured in ultrahigh vacuum (triangles) and electrochemical (squares) environments. (UHV and EC values extracted from Refs. 8 and 9, respectively.)

mental measurements in ultrahigh vacuum⁸ (UHV) and electrochemical⁹ (EC) environments. Plotted in Fig. 1a are C–O intramolecular vibrational frequency, ν_{CO} , vs. CO coverage curves, calculated from DFT using the DACAPO periodic slab code¹⁰ (circles) and measured experimentally in UHV⁸ (triangles). Although the DFT- ν_{CO} magnitudes are approximately 40 cm^{-1} greater than the UHV values, both curves show the marked ν_{CO} increase toward higher coverage, resulting from increased dipole-dipole coupling. Plotted in Fig. 1b are correspond-

ing Stark-tuning slope values, calculated from DFT (see Refs. 5–7 for details) (circles) and measured experimentally in UHV⁸ (triangles) and EC⁹ environments (squares). All three curves demonstrate a decrease in the Stark-tuning slope toward higher coverage (Fig. 1b), resulting from a decrease in C–O bond distance-dependent electron redistribution⁷ with increasing chemisorbate concentration.

It is interesting that the Stark-tuning slopes calculated by DFT match closely

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be obtained for all ions measured and making it possible to calculate more accurate selectivity coefficients.⁶ Potentiometric selectivity coefficients, $\log K_{I,J}^{\text{Pot}}$ are a measure of an ionophore preference for a target ion, I, over an interfering ion, J. The results of the selectivity studies appear in Fig. 2. Interestingly, both UBC and UIC show an improvement in the selectivity over Cd^{2+} by at least a full order of magnitude, meanwhile showing a decreased discrimination of Cu^{2+} . In addition, UIC also shows a modest improvement in the discrimination of Ca^{2+} . HBC, on the other hand, exhibits poor selectivity in comparison to TFPB most likely because of its poor retention in the sensing membrane.

In summary, halogenated dodecaborane derivatives have been demonstrated to be suitable alternatives to TFPB as cation-exchangers in ISEs, with the undecafluorinated derivative being the most retained in leaching studies and also offering in many cases improved selectivity over common interfering ions. Therefore, with new more robust ion-exchangers available further improvements in sensor lifetime and miniaturization become feasible. ■

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211°C and 234°C correlating to a binding energy of 126 and 143 KJ/mole respectively. Scanning tunneling microscopy of near monolayer shows a herringbone structure that is similar to the crystalline packing of this material;⁷ see STM image in Fig. 2. The Au $23 \times \sqrt{3}$ reconstruction is observed through the p-6P film. A proposed model of this organic film is depicted in Fig. 3, where the Au substrate atoms are represented as circles and the darker colored atoms show the locations of the elevated atoms in the Au reconstruction. Darker p-6P molecules represent molecules lying with their plane parallel with the substrate while lighter p-6P molecules are tilted upright. The measured and model unit cell distances agree within 1% deviation, 33.8×14.3 Å and 32.5×14.4 Å respectively.

In summary, the formation of a substantial interface dipole has been confirmed between Au(111) and p-6P. At least two different binding environments have been determined to exist utilizing TPD. Thin film investigations using STM have shown an interesting herringbone structure where each unit cell has one p-6P molecule lining flat on the Au(111) and another tilted on edge. Edge-to-face interactions are maximized in this film structure and are similar to bulk p-sexiphenyl.⁷ ■

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those from UHV, while the EC values are about 2-3 times larger. This unexplained experimental behavior illustrates a significant difference in chemisorbate bonding in EC versus UHV environments. Since the DFT calculations presented here do not include interfacial solvent, chemisorbate solvation may account for this difference. A future project is to model the effect of solvation on the C-O STS using DFT calculations and the periodic-slab model.

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