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Temperature Dependence of Metal–Organic Heteroepitaxy

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ABSTRACT: The nucleation and growth of 2D layers of tetraphenyl porphyrin molecules on Ag(111) are studied with variable-temperature scanning tunneling microscopy. The organic/metal heteroepitaxy occurs by strict analogy to established principles for metal heteroepitaxy. A hierarchy of energy barriers for diffusion on terraces and along edges and around corners of adislands is established. The temperature is key to activating these barriers selectively, thus determining the shape of the organic aggregates, from a fractal shape at lower temperatures to a compact shape at higher temperatures. The energy barriers for the terrace diffusion of porpyrins and the molecule–molecule binding energy were determined to be $30 \text{ meV} < E_{\text{terrace}} < 60$ and $130 \text{ meV} < E_{\text{diss}} < 160 \text{ meV}$, respectively, from measurements of island sizes as a function of temperature. This study provides an experimental verification of the validity of current models of epitaxy for the heteroepitaxy of organics and is thus expected to help establish design principles for complex metal–organic hybrid structures.

INTRODUCTION

The current interest in ultrathin layers of organic molecules on metal surfaces is fueled by the prospect to be able to synthesize new and improved hybrid materials for applications in next-generation electronic devices, catalysis, chemical sensors, and passivation coatings. Many useful properties arise from interactions at the metal–organic interface. Their study and exploitation depend on the meticulous fabrication of desired organic structures by precisely controlling the interactions between molecules, following the established principles of supramolecular chemistry. The control parameters for the self-assembled growth of organics are the design of the molecules and their functional groups, the stoichiometric ratio of molecules, atoms, and linker clusters, and the temperature. In contrast to solution-based chemistry, the molecular self-assembly on surfaces is limited by the mobility of the adsorbed molecules. The substrate thus becomes an important additional parameter for steering the growth and controlling the architecture of the networks.^{1–3} As such, questions about similarities and differences between metal–organic heteroepitaxy and metal–metal heteroepitaxy arise.

It is well established for the heteroepitaxial growth of metals on metal surfaces that the growth can occur either near the thermodynamic equilibrium or far from equilibrium.² The growth near thermal equilibrium is often correctly predicted by comparing the surface free energies of the film and substrate interfaces,⁴ thereby considering the growth to be a wetting phenomena. Often, though, the growth is far from equilibrium, especially when the deposition rate of atoms or molecules, R , is high and the diffusivity of adsorbed species, D , is low. The latter is temperature-dependent and determines the average distance an

adatom has to travel to nucleate a new aggregate or to attach to an already existing aggregate. If the deposition of molecules is fast compared to their diffusivity, then the individual atomistic processes become important and the growth is essentially determined by kinetics (i.e., thermally activated motion in the presence of diffusion barriers). The size and areal density of adlayer islands are dependent on the ratio R/D .^{1,5,6} As a trend, a large number of small islands are found at low temperatures and high deposition rates, whereas fewer but larger islands are formed at high temperatures and low deposition rates. Fundamental diffusion processes are diffusion on terraces and over steps and, upon attachment on nucleated aggregates, also along adisland edges and across corners. Each of these processes is associated with a characteristic energy barrier. The diffusion across such barriers is thermally activated, with the respective rate depending on the barrier height. The growing aggregates can thus be shaped by selective activation/freezing of certain diffusion processes via the temperature.^{1,2,6}

There are good reasons that these established principles for metal heteroepitaxy may not be applicable to the heteroepitaxy of organics on metal surfaces. Unlike many metal adsorbates, organic molecules are closed-shell systems with energy gaps across the Fermi energy E_F . Usually, interactions between organic molecules and metal surfaces are complex and involve charge donation and back-donation, electronic-level realignment, static surface dipoles, and other factors.⁷ Also, given the

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large size of organic molecules, they often extend over several atomic spacings of the substrate, which makes diffusion barriers on the terraces and at the step edges of the substrate less relevant.

Despite an increasing effort to investigate the structure and properties of ultrathin organic layers, the question remains as to how accurately existing models of nucleation and growth can be applied. In this article, we will study the growth of 2D layers of hydrogenated tetraphenyl porphyrin molecules (2H-TPP) on Ag(111). Porphyrins have become a model system, and a large number of studies addressing the network formation on various metal substrates as a function of metallization and functional groups are now available.^{3,8–13} The 2D networks observed are typically equilibrium structures where the functional groups of the molecules, and not the terrace diffusion, determine the architecture of the networks. We present here a growth study of 2H-TPP as a function of temperature, performed with variable-temperature scanning tunneling microscopy. It is found that nucleation-and-growth-dominated regimes can be distinguished clearly and that the selective activation of edge diffusion and corner crossing by the growth temperature determines the island's shape. Although this result is well known for metals and as such is not very surprising, the value of this study is that it extends the validity of these models to organic heteroepitaxial systems.

EXPERIMENTAL PROCEDURE

Our study was conducted under ultrahigh vacuum (UHV) in a multichamber system comprising all tools required for comprehensive in situ sample preparation and characterization. Ag(111) single crystals were prepared by repeated cycles of Ar⁺ sputtering and annealing to 650 K. 5,10,15,20-Tetraphenyl porphine (2H-TPP) molecules, purchased from Frontier Scientific Inc., were deposited by thermal evaporation using a Knudsen cell evaporator. The deposition rate was approximately 0.05 monolayers/min, unless specified otherwise. Images were obtained as a function of temperature using an Omicron variable-temperature scanning tunneling microscope (VT-STM). The deposition of molecules was done directly with the sample resting on the VT-STM sample stage so that imaging could be done during or directly after deposition and at deposition temperature. Where the deposition continued during scanning, the tip was moved between images to prevent shadowing the sample with the STM tip. Some of the studies presented were performed, using the same substrate and molecules, in a separate UHV system with an Omicron low-temperature scanning tunneling microscope (LT-STM). In such studies, the molecules were deposited at room temperature.

GROWTH STUDIES WITH VT-STM

Images of islands of 2H-TPP on Ag(111), taken with a scanning tunneling microscope, are shown in Figure 1. Here, the 2H-TPP molecules were deposited and imaged at 300 K. The images show the well-known 2D networks of 2H-TPP on the terraces of Ag(111)^{3,11,13} and the decoration of the substrate step edges.³ At room temperature, the size and shape of the islands is time-dependent because of a constant flux of detachment and attachment of edge molecules between islands. Figure 1b,c shows the shape of one selected island over a time period of 30 min following deposition. Over the entire course of observation, the molecule count of the shown adisland went from 125 attached molecules to 74, with a new smaller island forming above it (not pictured). The molecules are only weakly bound to the surface and are easily dragged around with the tip of the STM, resulting in visible streaks in the images. When the same sample was cooled to 80 K, the size

Figure 1. (a–c) STM topograph of 2H-TPP/Ag(111) deposited and imaged at room temperature. The images were taken at specified times after the deposition of the molecules. Image size: 23 nm × 23 nm. (d) STM topograph of 2H-TPP/Ag(111) deposited at room temperature and imaged at 80 K. Image size: 100 nm × 100 nm.

of observed adislands increased dramatically as the result of condensation (Figure 1d). Long-term observation of the same system at 80 K showed no significant molecule diffusion.

Next, the island nucleation and growth at low temperatures was studied. The molecules were deposited on the Ag(111) crystal, held at 58 K, and continuously imaged during deposition. In the STM image in Figure 2a, taken after 10 min of deposition, the coverage is $\theta = 0.14$ ML, and after 30 min of deposition, an increased coverage of $\theta = 1.28$ ML was observed (Figure 2b). Here, one monolayer corresponds to a coverage of 0.51 molecules nm⁻², as observed in the densely packed 2D networks formed at room temperature as in Figure 1d. It is apparent from an inspection of the STM images that the nucleated adislands are single monolayers in height and have irregular, fractal-like shapes. With increasing coverage, the islands develop a ramified shape, and nucleation sets in on top of the islands.

The onset of thermally activated motion was studied by depositing molecules on Ag(111) at approximately 55 K and annealing the sample after deposition to specific annealing temperatures, T_A . STM images were then taken at 80 K to suppress molecule diffusion during imaging. Characteristic STM images taken after annealing at different temperatures $T_A < 300$ K are summarized in Figure 3. No significant change in island size and shape with respect to the as-grown morphology was observed upon annealing up to $T_A = 110$ K. The islands remained as small, narrow, irregular structures and were typically 2 ML high. At $T_A = 110–130$ K, the double-layer islands began to disappear and islands showed increased diameters. No 2 ML islands were observed above 150 K, indicating the diffusion of all molecules in the second layer over the organic island edges and on to the Ag(111) surface. The average area of the adislands continued to grow with increasing temperature up to 250 K, and the larger islands exhibited a rather compact shape.

Figure 2. STM topograph of 2H-TPP/Ag(111) taken at 58 K after (a) 1 min of deposition and (b) 30 min of deposition. (c) Plot of the perimeter vs area relationship of 2H-TPP islands at 58 K.

DISCUSSION

The nucleation and growth of 2D organic layers, as observed for the example of 2H-TPP molecules on Ag(111), show striking similarities to metal heteroepitaxy. As has been demonstrated, the substrate temperature is a key parameter to controlling the growth. We find here for 2H-TPP a comparatively high density of rather small islands of fractal shape at temperatures below 100 K, whereas at higher temperature large, compact islands are formed.

The fractal shape of the islands is evidence of activated diffusion of the molecules on the substrate terraces and along island edges after attachment, but crossing the corners at the adisland perimeter is associated with a higher barrier and thus is not activated at lower temperature. The fractal shape of the islands can be quantified in terms of their fractal dimension, d_f , which relates the scaling of the mass of an object to its size. A common approach to determining the fractal dimension is to calculate the ratio of the island perimeter, P , to the island area, A , from the STM images. The island perimeter and area are related as

$$P \propto A^{d_f/2} \quad (1)$$

As structures become more compact in form, their P/A ratio grows smaller. d_f is calculated from the slope of the plot of the logarithms of the perimeter versus area, which is determined from the STM images (Figure 2). From the data in Figure 3, the fractal dimension is determined to be $d_f = 1.54 \pm 0.03$ at a temperature of 58 K. This value appears to be similar to the

Figure 3. (a–d) STM topographs of 2H-TPP/Ag(111) taken after annealing the system to the specified annealing temperatures. Height profiles of selected islands, (a, b) marked as i and ii and (e, f) plotted, show relative heights of 1 and 2 ML adislands. All data were taken at 80 K.

fractal dimension of metallic nucleates that lack the energy to cross corner boundaries.^{14,15}

The temperature dependence of the fractal dimension is plotted in Figure 4. Clearly, the d_f remains constant until the annealing temperature reaches $T_A \approx 100$ K. Further increasing the sample temperature causes a significant reduction in the fractal dimension to $d_f = 1.21 \pm 0.08$ at $T_A \approx 130$ K, and further annealing up to room temperature does not change the value of d_f further. A phenomenological fit of the data to a sigmoidal function was used to approximate the critical temperature, determined from this plot to be $T_c = 125 \pm 7$ K. This sudden decrease in d_f is related to the observed transition from fractal to compact island shape. This, too, is analogous to the similar transitions in metallic islands, such as those reported for Au/Ru(001)¹⁶ and Ag/Pt(111),¹⁷ where this compaction was ascribed to the activation of the corner crossing of atoms.

In this study, we find that terrace diffusion, associated with an energy barrier E_{terrace} , occurs even at the lowest temperature studied (58 K). The onset of corner crossing, observed at approximately 100–110 K, coincides with the gradual disappearance of islands of double-layer height and with the onset of island ripening (Figure 3). For instance, whereas at the lowest temperatures studied the occurrence of double-layer islands is near 100%, at $T_A \approx 109$ K only about 50% of all islands are of

Figure 4. Calculated d_f as a function of temperature. (Solid red line) Sigmoidal function with $T_0 = 124 \pm 2$ K. (Insets) Characteristic STM images for high and low T_A reflecting the change in d_f .

monolayer height. It is believed that aggregates in the second layer must dissociate first, before diffusing as monomers on the surfaces of single-monolayer islands and descending across the adisland edge. This implies that the barriers for corner crossing, E_c , molecule–molecule dissociation, E_{diss} , and step edge descent, E_s , are all of similar magnitude.

The growth of some of the island at the expense of smaller islands is the familiar Ostwald ripening: adsorbates on the island edges begin to dissociate with increasing frequency and diffuse away until attaching to neighboring larger islands.¹⁸ The ripening of epitaxial systems is well established and described as the growth rate, K , of a circular island over time

$$K = \frac{\Delta r^3}{\Delta t} = \frac{K_0}{k_B T} e^{-(E_A/k_B T)} \quad (2)$$

where K_0 is a measure of the surface energy of the islands and the availability of free molecules,^{4,18,19} k_B is the Boltzmann constant, and the activation energy here is the energy required for a molecule to dissociate from an existant island and diffuse across the surface,^{5,20–22}

$$E_A = nE_{\text{diss}} + E_{\text{terrace}} \quad (3)$$

n specifies the critical number of nearest neighbors needed to start island nucleation, taken to be 1 from the very low coverage data at 58 K (not shown). Both the island area and the growth rate were determined from the STM images and are plotted as functions of temperature in Figure 5. The islands become unstable near 300 K, as seen in Figure 1, explaining the kink in the trend in A at that temperature in Figure 5. Upon cooling of the sample to 80 K, the dissociation rates decrease and the islands become stable. K was determined by comparing the size of identical islands in consecutively taken STM images, separated by time intervals Δt . The sharp increase in the island area at a temperature of 110 K is consistent with the onset of the change in the fractal dimension of the islands (Figure 5a), the step edge descent, and compaction of the islands. The intersection of the trend lines for the static and ripening regimes (i and ii, respectively) is located at the same critical temperature from the fractal analysis, 120 K. This is concurrent with the expectation

Figure 5. (a) Temperature dependence of the mean island area. Exponential growth occurs in the range labeled ii between 100 and 250 K. The onset of growth is at ~ 125 K (red dashed line). (b) Island growth rate K , with a fit to eq 2.

that the ripening of the system is controlled by the energy barriers acting against dissociation from the adislands.

The fit over the growth rate of the adislands, K , with both K_0 and E_A held as free parameters, as shown in Figure 5b, provides an estimate of the activation barrier, $E_A = 194 \pm 27$ meV. Although noticeably weaker than the typical terrace diffusion barriers of many metal–metal systems^{17,23,24} with some on the order of 800 meV,²⁵ it is consistent in magnitude with the activation energy of the more weakly adsorbed systems such as Pt/Pt(111) (260 meV),²⁶ Ag/Pt(111) (320 meV),²⁷ and the weakly bound metal–organic system of PTCDA/Ag (130 meV).²⁸

The critical temperature where the system crosses from the static nucleation regime to the ripening regime is clearly near 124 K from Figure 5. This allows for the estimation of E_{terrace} at $k_B T \ll E_{\text{terrace}}$ using the same nucleation model of metal adsorbates and the low temperature data in Figure 2,²⁹ where the nucleation density of dimers is

$$n_x = \frac{1}{4} \left(\frac{4R}{\nu a^2} \right)^{1/3} e^{(E_{\text{terrace}}/3k_B T)} \quad (4)$$

By applying the observed deposition rate $R = 4.97 \times 10^{-4}$ molecules $\text{nm}^2 \text{s}^{-1}$ in this experiment, the nucleation density of $n_x = 4.9 \times 10^{-4}$ islands lattice site^{−1} and the lattice constant for the Ag(111) surface ($a = 2.88$ Å) yield $E_{\text{terrace}} = 30$ –60 meV. The variance is the result of uncertainty in the hopping frequency, which is expected to be in the range of $10^9 < \nu < 10^{12}$. This leaves a dissociation barrier of between ~ 130 and 160 meV for 2H-TPP/Ag(111). Although this is an approximation, it is in reasonable agreement with the diffusion barrier for 2H-TPP from first principles calculations³ and of the same order of magnitude as for weakly bound metal–metal systems with similar attempt frequencies.²⁹

CONCLUSIONS

The nucleation and growth of 2D films of 2H-TPP on Ag(111) occurs by analogy to metal heteroepitaxy. It was shown that existing models accurately describe the surface kinetics of the

2H-TPP/Ag(111) system, despite the incommensurate matching of the film structure with the substrate lattice, the large size of the molecules in comparison with the substrate lattice spacing, weak physisorbed interaction, and van der Waals intermolecular bonding, which all distinguishes organic adsorbates from metallic species. An important reason for this good agreement is that the energy barrier for terrace diffusion is determined by the landscape of the binding energy for the molecules, which has the same symmetry and periodicity as the potential energy landscape for single adatom diffusion, namely, the surface structure of the substrate. However, the effective barrier height is expected to be smaller for the molecules than for single atoms as a result of the lateral size of the molecules, expanding over several substrate lattice spacings, and the increased bond length to the substrate. This is exactly reflected in our measured energy barrier for terrace diffusion. The same hierarchy of diffusion barriers that determines the shape of metallic aggregates also governs the shape of the organic aggregates: with increasing temperature, the terrace diffusion, edge diffusion, corner crossing, and dissociation are successively activated and cause a change in the island shape and size, from small and fractal to large and compact. We expect that our conclusions apply to all of these metal–organic heterostructures where the net force between the supported molecules is attractive. Our experimental verification of the validity of current models of epitaxy is thus expected to help establish design principles for complex metal–organic hybrid structures.

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