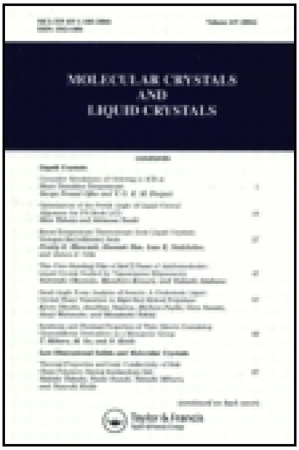

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Molecular Single Crystal Interfaces: Topographical Structure and Crystal Growth

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MOLECULAR SINGLE CRYSTAL INTERFACES: TOPOGRAPHICAL STRUCTURE AND CRYSTAL GROWTH

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Abstract Atomic force microscopy (AFM) reveals that the nanoscopic surface topography, and growth and dissolution mechanisms of molecular crystals are correlated with intermolecular bonding in the solid state. The orientation and growth of topographical features such as steps, ledges and kinks are primarily a manifestation of the enthalpically favored bonding directions within a given crystallographic plane. Hydrogen bonded crystals and charge transfer salts, which exhibit anisotropic solid state bonding, were found to have analogous topographical motifs in terms of surface features oriented along primary bonding directions. The role of these surface features, particularly ledges, in directing the nucleation and growth of secondary crystalline materials is described. Facile nucleation and oriented crystal growth is observed on substrate ledge sites, behavior that is attributed to lowering of the prenucleation aggregate free energy via "ledge directed epitaxy." This involves a lattice match between the substrate and growing phase along the ledge direction, and equivalent dihedral angles of the substrate ledge sites and a pair of aggregate planes whose identity is assigned on the basis of the structure of the mature crystal.

INTRODUCTION

Crystalline solids based on molecular components exhibit numerous properties of fundamental and technological interest, including electrical conductivity, superconductivity, nonlinear optical behavior and ferromagnetism.[1] The principle advantage of these materials is the ability to rationally control their bulk properties through molecular design. Accordingly, "crystal engineering" strategies based on the design of thermodynamically preferred intermolecular interactions in the bulk crystal have developed.[2] However, relatively little effort has been spent examining the formation of molecular crystals in the context of nucleation and crystal growth *processes*

Since nucleation almost always occurs at an interface due to the reduced surface free energy of prenucleation aggregates and crystal nuclei, the structure of a substrate interface can play an important role in the crystallization pathway. Investigations of the nucleation and growth of amino acids[3] and inorganic compounds[4,5] beneath Langmuir monolayers, and ice crystallization on alcohol monolayers has been reported.[6] Further advances in this area would have a significant impact on the formation of molecular crystals in which crystal growth rates, phase selectivity and morphology issues are problematic. This prompted us to examine strategies for molecular level design of solid substrates capable of influencing nucleation of molecular crystals in a rational manner. The molecular surfaces employed in such a strategy may include molecular films such as Langmuir-Blodgett and self-assembled monolayers, or the exposed crystal planes of molecular crystals. The latter approach provides a unique opportunity to examine several fundamental aspects of growth, as the interfacial structure of exposed molecular crystal planes is crystallographically well-defined. In addition, a single molecular crystal can exhibit a variety of crystal planes, with different molecular structures and enantiotopic properties, that can be used as substrates.

Understanding of growth modes on molecular crystal surfaces requires thorough characterization of the chemical and topographical structure of the exposed crystal faces. Studies of epitaxial growth on single crystal substrates generally have ignored the role of topographical features, such as substrate ledges and kinks, in nucleation, even though these features play an important role in single-phase crystal growth.[7] We report herein dynamic *in situ* Atomic Force Microscopy (AFM) studies of molecular single crystals during etching and growth, which illustrate the importance of topographical features in nucleation and growth. In addition, we present an example of the role of well defined topographical ledge sites, present on molecular crystal substrates, in nucleation of secondary organic crystalline phases.

ATOMIC FORCE MICROSCOPY OF ORGANIC CRYSTALS

Glycine crystallizes with the α-modification in aqueous solutions. The mature crystal belongs to the monoclinic space group $P2_1/n$ (a = 5.102, b = 11.971, c = 5.457

Å, and β= 111.7°)[8] and is bipyramidal with three well developed, chemically inequivalent faces. The {110} and {011} family of planes comprise the eight side faces of the crystal bipyramid, with {010} planes capping the ends. The x-ray crystal structure reveals glycine molecules packed into hydrogen bonded sheets within the {010} plane. Each {010} sheet is characterized by N–O contacts of 2.76 and 2.88 Å between molecules along the crystallographic **c**- and **a**-axes, respectively. The zwitterionic glycine molecules exhibit strong electrostatic interactions between pairs of {010} sheets resulting in a bilayer structure.

The surface topography of the {010} face of α-glycine crystals, determined by phase measurement interferometric and atomic force microscopies, reveals a terrace-rich surface with terraces bounded by ledges collinear with the **c**- and **a**-axes. The **c**-directed ledges are predominant in solution over length scales of 1 nm to 1mm (Figure 1), while the **a**-ledge population is low. The presence of the **a**-ledge results in the formation of a kink site on the crystal face. The **c**- and **a**-ledges most likely comprise the {110} and {011} planes, respectively, as the observation of these faces in the macroscopic crystal suggests that they are low energy surfaces.

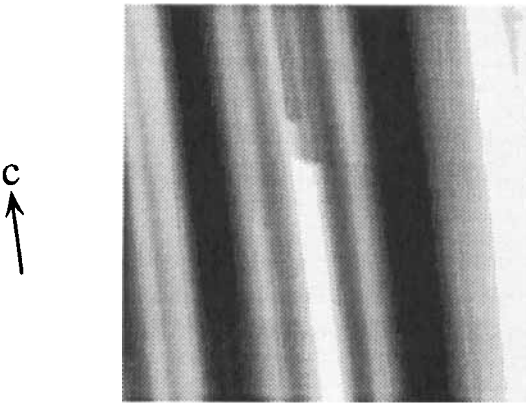

FIGURE 1 Atomic force microscopy image of {010} face of α-glycine in aqueous solution. The vertical scale is approximately 100 nm. The **c**-ledges predominate, although small **a**-ledges can be observed.

In situ observation of {010} terraces indicate that growth occurs with rapid **a**-ledge advancement along the **c**-axis with slow **c**-ledge movement along the **a**-axis. The relative ledge advancement rates result in the predominance of {010} terraces separated by **c**-ledges having step heights ranging from ~10 Å to >200 nm. During growth, the supersaturation is reduced by crystallization and slowly advancing **c**-

ledges gradually merge, reducing both the ledge frequency and step height. The ledge structure of the {010} face reflects the strong hydrogen bonded vectors in the solid state structure. Initial rates of **a**-ledge advancement on {010} typically are on the order of 200 nm/sec at supersaturations of ~25±5% (4.3M). The rate of **c**-ledge advancement is approximately a factor of 5-10 smaller than **a**-ledge advancement under similar growth conditions. Differing **c**-ledge advancement rates have been observed for step heights less than 50 Å (Figure 3a), which can result in ledge coalescence and dissociation. The smallest observed step height of ~10 Å is in good agreement with the height of a single {010} bilayer (~8.9Å).

The organic charge-transfer salt $(TMTSF)_2ClO_4$ (TMTSF = tetramethyltetraselenafulvalene) is a metallic conductor at room temperature, crystallizing in the $P\bar{1}$ space group (a = 7.266, b = 7.678, c = 13.275 Å, and α= 84.58°, β = 86.73°, γ = 70.43°), and exhibiting an acicular crystal habit with the (001) the largest face. AFM of the (001) plane of $(TMTSF)_2ClO_4$ (TMTSF = tetramethyltetraselenafulvalene) reveals a periodic terraced structure along the **b**-axis bounded by ledges extending in the **a**-direction. The periodicity of the ledges is ~200-400 nm while the ledge heights between (001) terraces is 20-100 nm. The ledge orientation along the **a**-axis corresponds to the stacking of the TMTSF molecules in the solid-state. The **a**-direction also corresponds to the fastest growing directionand is coincident with the needle axis of the mature crystal. These **a**-oriented ledges suggest that the growth mechanism involves fast incorporation along **a**.

Dissolution of $(TMTSF)_2ClO_4$ in ethanol results in a flattening of the terrace structure structure. The rate of dissolution can be controlled by the electrochemical potential applied to the crystal. At potentials greater than the reversible potential ($E > E_0 = 0.42$ V versus SCE), the (001) face exhibits large terraces intersected by static **a**-ledges with heights of 13.3 Å (Figure 2), in agreement with the **c** lattice parameter and corresponding to the distance between layers of TMTSF molecules in the (001) face. At more cathodic potentials ($E < E_0$), the relative supersaturation decreases (this is tantamount to electrochemical etching) and **a**-ledges advance along **b**. The macroscopic advancement of **a**-ledges occurs following the formation of small **b**-ledges and **a**/**b**-kink sites. These kink sites, with heights of 13.3 Å and widths ranging from 10 to 50 nm, are unstable and quickly advance in the **a**-direction. The instability of **b**-oriented ledges results in the preservation of **a**-ledges during the dissolution process, which is a manifestation of the strong charge transfer interaction along the **a**-axis and the correspondingly high surface energy of (100) compared to (010) planes. The slow etch sequence illustrates the mechanism of $(TMTSF)_2ClO_4$ dissolution whereby large **a**-ledges flow in the **b** direction. After electrochemical etching, the lattice of the (001) terraces can be discerned with AFM. Dynamic AFM of the growth of $(TMTSF)_2ClO_4$ indicates similar involvement of the ledges and kink sites, with the evolution of unit cell-high terraces via rapid growth at kink sites along the **a** direction. This is manifested in the movement of **a**-ledges in the **b** direction at longer times.

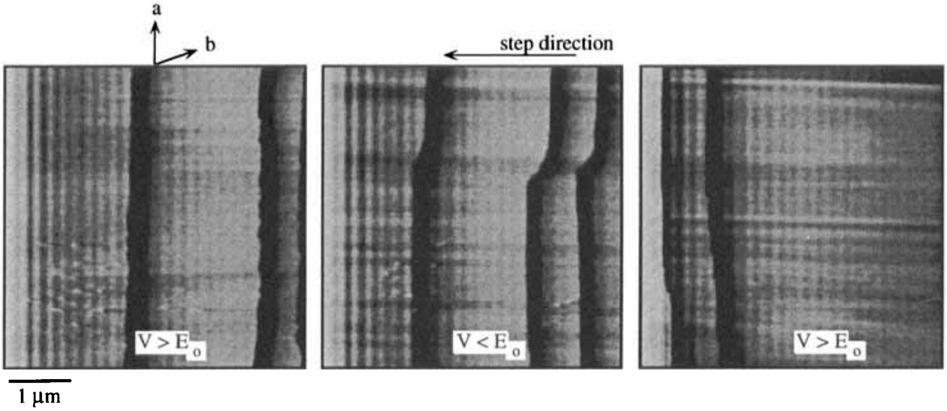

FIGURE 2 *In situ* AFM of the {001} face of $(TMTSF)_2ClO_4$ showing dissolution under potential control. During dissolution (*middle*), steps oriented along **a** flow in the **b**-direction. The step flow can be arrested by increasing the electrochemical potential (*left* and *right*). The step heights are 1.3 nm.

In addition to their role in growth and dissolution, topographical features, such as ledges, can also play an important role in the nucleation of secondary crystalline phases. Consideration of conventional nucleation theories suggests that ledges can provide two surfaces for interaction with molecules that form a nucleus, in contrast to two-dimensional nucleation modes in which only one interface is available for nucleation. Under conditions where this interaction at the ledge is favorable, nucleation will occur at lower supersaturations than on sites where ledges are absent.

This has been demonstrated by the nucleation and growth of benzoic acid on succinic acid substrates. Succinic acid crystallizes in the monoclinic space group $P2_1/c$ (a = 5.519, b = 8.862, c = 5.101 Å, and β = 91.6°).[9] The crystal structure of succinic acid reveals hydrogen-bonded succinic acid chains arranged in sheets parallel to $\{010\}_{sa}$, with the chains oriented along the $[10\bar{1}]_{sa}$ direction. Single crystals can be cleaved readily by applying a small force with a sharp razor blade or microtome along $[001]_{sa}$ perpendicular to the $(100)_{sa}$ face, providing freshly prepared, clean $\{010\}_{sa}$ surfaces with typical dimensions of 3 mm x 9 mm. These faces possess linear features along $[10\bar{1}]_{sa}$, which are observed readily by optical microscopy. AFM indicates that the features along $[10\bar{1}]_{sa}$ are macroscopic ledges with heights > 5 nm. AFM experiments indicated that the minimum dihedral angle between $(0\bar{1}0)_{sa}$ terraces and the step planes separating the terraces was 113° which agrees with the $(0\bar{1}0)_{sa} \cap \{111\}_{sa}$ dihedral angle determined from the crystal structure (112.6°). Both the $\{010\}_{sa}$ and $\{111\}_{sa}$ crystallographic planes have high molecular packing densities, and comprise layers of hydrogen-bonded chains. These planes can be characterized as low energy surfaces as there is strong hydrogen bonding between succinic acid molecules *parallel* to these planes and minimal molecular corrugation. Strong hydrogen bonding along the succinic acid chains parallel to $[10\bar{1}]_{sa}$ favors cleavage along planes containing this direction. Weak van der Waals forces between $\{010\}_{sa}$ and $\{111\}_{sa}$ layers are responsible for the predominance of the $\{010\}_{sa}$ and $\{111\}_{sa}$ planes in the cleaved crystal. *The structure and microscopy results therefore support a surface topography principally consisting of* $[10\bar{1}]_{sa}$ *ledges containing the* $(0\bar{1}0)_{sa} \cap \{111\}_{sa}$ *planes.*

Crystallization of benzoic acid on a freshly cleaved succinic acid crystal substrate at sublimation temperatures between 35-60°C produced *oriented* single crystals of benzoic acid crystals on the $(0\bar{1}0)_{sa}$ face growing from the $[10\bar{1}]_{sa}$ ledges, with nucleation frequencies approaching 50 mm^{-2} (Figure 3). Crystallographic analysis revealed that the benzoic acid crystals were oriented such that the $(001)_{ba}$ plane was in contact with $(0\bar{1}0)_{sa}$, with the $[010]_{ba}$ axis oriented at an angle of 46°± 1.7° with respect to $[10\bar{1}]_{sa}$. The $[100]_{sa}$ makes a 42° angle with $[10\bar{1}]_{sa}$, therefore, $[010]_{ba}$ is <u>not</u> coincident with $[100]_{sa}$.

The orientation of benzoic acid on succinic acid involves $[001]_{ba}$ parallel to $[001]_{sa}$ and $[010]_{ba}$ nearly parallel to $[100]_{sa}$. *This is contrary to expectations based upon a simple two-dimensional (or even one-dimensional) epitaxy model,* as there exists an exact one-dimensional lattice match of $[100]_{ba}$ and $[100]_{sa}$ and only a small 0.8% mismatch between the $[010]_{ba}$ and $[001]_{sa}$. Rather, growth from the succinic acid ledge sites is attributed to lowering of the prenucleation aggregate

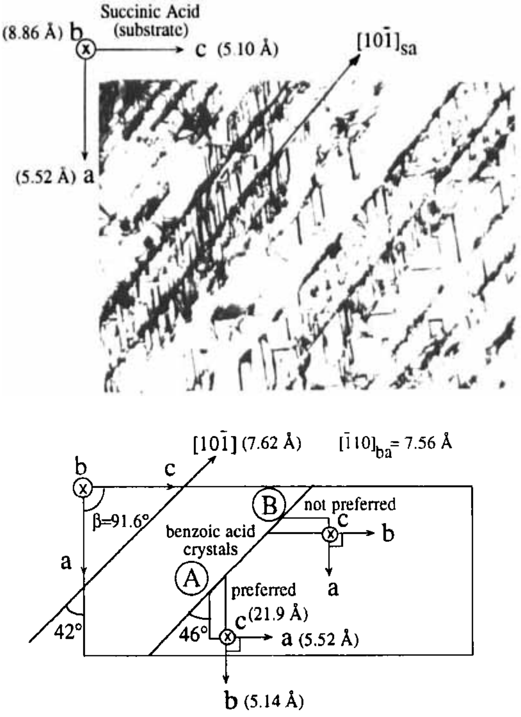

FIGURE 3 Oriented benzoic acid crystals grown from the gas phase onto $(0\bar{1}0)_{sa}$. Bottom, schematic representation of the orientations of benzoic acid on $(0\bar{1}0)_{sa}$. The preferred orientation represents >80% of the mature crystals, and almost 100% of benzoic acid crystals initiated from $[10\bar{1}]_{sa}$ steps. The lattice parameters and directions for succinic acid and benzoic acid are also depicted.

free energy via "ledge directed epitaxy." This involves a lattice match between the substrate and growing phase along the ledge direction and equivalent dihedral angles of the substrate ledge sites and a pair of aggregate planes, whose identity is assigned on the basis of the structure of the mature crystal. The $[10\bar{1}]_{sa}$ ledge has a 1.0% lattice mismatch with the [110] direction of benzoic acid and a difference of only 0.6° between the ledge dihedral angle and the dihedral angle of the $(001)_{ba} \cap (1\bar{1}2)_{ba}$ planes. Based on the crystal structures, these interfaces consist of "molecularly smooth" low energy planes, favoring stabilization of the prenucleation aggregates by dispersive interactions. As a consequence of these epitaxial effects and the crystallographic symmetry of the monoclinic space groups of the substrates and benzoic acid, benzoic acid growth is highly oriented. It is noteworthy that only one of the possible orientations (see Figure 3) is observed. This is a consequence of the crystallographic inequivalence of these two orientations because of the monoclinic symmetry of the succinic acid substrate. This behavior also has been observed for other substrate-crystal systems.[10]

These results indicate that the topographical structure of molecular crystals can be instrumental in nucleation and growth, particularly when strong anisotropy is present. Further studies, including extension of these principles to nucleation and growth in solutions, will provide substantial insight into crystal growth seeding, crystal morphology, and selectivity toward polymorphs during the crystal growth process.

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