Characterization of Step-Edge Barriers in Organic Thin-Film Growth

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Detailed understanding of growth mechanisms in organic thin-film deposition is crucial for tailoring growth morphologies, which in turn determine the physical properties of the resulting films. For growth of the rodlike molecule para-sexiphenyl, the evolution of terraced mounds is observed by atomic force microscopy. Using methods established in inorganic epitaxy, we demonstrate the existence of an additional barrier (0.67 electron volt) for step-edge crossing—the Ehrlich-Schwoebel barrier. This result was confirmed by transition state theory, which revealed a bending of the molecule at the step edge. A gradual reduction of this barrier in the first layers led to an almost layer-by-layer growth during early deposition stage. The reported phenomena are a direct consequence of the complexity of the molecular building blocks versus atomic systems.

Although organic electronics (1) with devices like organic thin-film transistors and organic light-emitting diodes have started to enter the consumer market, there is still—in contrast to inorganic epitaxy—a severe lack of understanding of the basic growth mechanisms. In inorganic epitaxy—mainly of metal films—growth kinetics can substantially determine growth morphologies. In particular, interlayer mass transport is necessary to allow for the layer-by-layer growth mode (2) needed to avoid formation of rough surfaces. Field ion microscopy has revealed that, under certain growth conditions, diffusing adatoms are reflected at descending step edges (3). These dynamics have been explained by the presence of an additional activation barrier for an adatom when crossing a step edge (3–5), which is usually called the Ehrlich-Schwoebel barrier (ESB). For an active ESB, terraced growth mounds form by repeated two-dimensional nucleation of islands of monoatomic thickness (6). In the complete absence of interlayer mass transport, the surface fractions in the individual layers follow a Poisson distribution (7). Moreover, deep trenches form between the mounds that ideally never quite close, and their formation has been referred to as the Zeno effect (8). Interpretation of this effect is based on the presence of a step-edge barrier and allows predictions on quantitative roughness parameters and on the cross-sectional shape of the resulting mounds (8). With the advent of modern scanning probe techniques, this shape can be analyzed in detail and allows for a determination of the ESB (9–11).

In organic thin-film growth, a wide variety of growth morphologies is observed because of the complexity of the building blocks and their interactions. Recently, the formation of mounds in organic thin-film growth (12–14), as well as theoretical efforts to determine the ESB (15), has been reported. In contrast to metal or inorganic semicon-ductor epitaxy, in which single atoms diffuse, a richer spectrum of growth mechanisms is expected in organic film growth because molecules are anisotropic and have internal degrees of freedom that open novel diffusion channels accompanied by changes in the molecular conformation.

We report on the growth processes involved in the formation of para-sexiphenyl (6P) mounds on mica surfaces modified by ion bombardment so that the molecules pack upright on the surface (16). By means of atomic force microscopy (AFM), we evaluate the thickness-dependent evolution of the overall surface roughness, as well as the mound shapes. Using a model developed for inorganic epitaxy, we determined the step-edge barrier for interlayer diffusion of 6P. We emphasize that a diffusion scenario applicable to organic semiconductors differs substantially from classical diffusion mechanisms. Our experiments are supported by transition state theory calculations and molecular dynamics simulations that quantitatively confirm the measured barrier height and illuminate the underlying complex process. Not only do we observe an ESB with an energy of several tenths of an electron volt, we also show its layer dependence.

6P, a blue-light-emitting, π-conjugated molecule, has six phenyl rings connected by single bonds, and van der Waals dimensions of 2.85 nm by 0.35 nm by 0.67 nm. For the film preparation, freshly cleaved mica was inserted into the ultrahigh-vacuum system (base pressure $2 \times 10^{-10}$ mbar) and bombarded with low-energy Ar$^+$ ions to destroy the ordered structure of the surface layer. In contrast, on the freshly cleaved mica, sizable molecule-substrate interactions would lead to a wetting layer and induce the growth of needle-like structures composed of lying molecules (17–19). Sputtering was stopped as soon as low-energy electron diffraction showed no ordered structure (16). Subsequently, 6P was grown in the absence of a wetting layer (20) by means of physical vapor deposition from a homemade Knudsen cell with a growth rate $F$ of 0.3 nm/min at room temperature.

In Fig. 1, A to C, we show AFM images of three 6P films with growing thickness (namely 4, 10, and 30 nm) that demonstrate the formation of mounds with an increasing number of terraces. The cross section of such a single terraced mound, as depicted in the inset of Fig. 1B, reveals that the mounds are characterized by 2.6 ± 0.3 nm–high steps. This value corresponds to the height of a layer formed by nearly upright-standing molecules, as found in the bulk structure (21). As thickness increased, the lateral mound shape changed from ill-defined to roughly polygonal. However, no orientation relation was observed between individual mounds.

Fig. 1. (A to C) Morphological analysis of 6P thin films ($z$ scale: 20, 35, and 50 nm, respectively). The inset in (B) shows a single mound and the corresponding cross section. (D) Normalized averaged cross section of five mounds found in the 30-nm-thick film. The solid line represents the cumulative Poisson distribution used to fit the data. (E) Evolution of the RMS roughness $\sigma$ and (F) of the average mound separation $\lambda$ with film thickness. The error bars correspond to the statistical uncertainty in the data measured by AFM.