

Layer Growth, Thermal Stability, and Desorption Behavior of Hexaaza-triphenylene-hexacarbonitrile on Ag(111)

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The layer growth, thermal stability, and desorption kinetics of ultrahigh vacuum (UHV)-grown organic discoid molecules (hexaaza-triphenylene-hexacarbonitrile (HATCN)) on Ag(111) have been studied by atomic force microscopy (AFM), thermal desorption spectroscopy (TDS), low-energy electron diffraction (LEED), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). In the initial growth stage (≤ 0.24 nm mean film thickness) a strongly bonded monolayer of face-on oriented molecules is formed which does not desorb upon heating to 900 K, probably due to the formation of paracyanogen. With increasing film thickness the monolayer of face-on oriented molecules transforms at room temperature into a monolayer built up of edge-on oriented molecules, which saturates at a mean film thickness of around 0.8 nm. This layer partially decomposes during heating, and C_2N_2 fragments desorb between 650 and 900 K. On the monolayer of standing molecules a second, metastable, layer forms, which saturates at 1.36 nm. With further increase of the coverage, this metastable layer dewets abruptly upon heating at about 350 K, and all molecules, besides those in the first monolayer, get incorporated into the island-like bulk phase. The formed three-dimensional (3D) islands, which are thermally stable up to 400 K, possess bulk crystal structure, as verified by XRD measurements, but the crystallites are randomly oriented.

Introduction

The performance of organic electronic devices, such as organic field effect transistors (OFETs) or organic light-emitting diodes (OLEDs), depends critically, inter alia, on the energy level alignment between the electrodes and the active layers. The level alignment, and thus the charge injection barrier, can be adjusted by properly tuning the work function of the electrodes involved. This can be achieved by the deposition of thin layers of appropriate organic molecules, prior to the growth of the active layer. In this context cyano-based molecular acceptors like F4-TCNQ¹ have been investigated recently. However, it has turned out that their rather low molecular weight implicates a rather poor thermal stability of the grown structures at room temperature. Therefore, organic molecules with higher thermal stability (which means to a first approximation with higher molecular weight) are desired. One of the promising novel cyano-based molecular acceptors with a significantly higher molecular weight of $m = 384.29$ amu is hexaaza-triphenylene-hexacarbonitrile (HATCN).^{2–5} HATCN is a disk-shaped molecule with the chemical formula $C_{18}N_{12}$. The conjugated heterocycles determine the physical and chemical properties of the molecules and their crystallization. HATCN is a strongly electron-deficient molecule, and a consequence of this is that it avoids π -stacking.⁶ Thus, the crystal structure is characterized by perpendicular $CN-\pi$ interactions, leading to

a quite complex three-dimensional (3D) hexagonal arrangement^{6,7} with 18 molecules in the unit cell.

The electronic properties of organic electronic devices depend strongly on the specific electrode–semiconductor interface. For many model systems it has been shown that the growth of the very first layers determines already to a great extent the structure and morphology of the final film.^{8–10} Previous studies of the thin-film growth of HATCN on different metal surfaces have already demonstrated the delicate dependence of the film formation on the nature of the substrate. On the Au(111) surface¹¹ the first two layers consist of flat-on molecules. The first monolayer turned out to be very mobile and, in contrast to other wetting layers of organic molecules on metallic surfaces,¹² featured a somewhat smaller desorption energy than the multilayer. This was explained by the important contribution of the entropy term in desorption. No low-energy electron diffraction (LEED) pattern could be obtained for this layer, even at liquid nitrogen (LN_2) temperature, due to the high mobility of the molecules on the gold surface. With increasing coverage the second monolayer becomes unstable, and islands form by dewetting of the second monolayer with increasing temperature. The islands exhibit the HATCN bulk structure, according to X-ray diffraction, and it was found that the islands are preferentially oriented with their (143) plane parallel to the Au(111) surface. Surprisingly, it turned out that with further increase of the film thickness the formerly face-on oriented molecules in the first layers also rearrange into the bulk structure, which was proven by thermal desorption spectroscopy. It was proposed that the driving force for this rearrangement was the tendency of the HATCN molecules to avoid π -stacking, which made several layers of parallel oriented molecules energetically unfavorable.

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