UNCOVERING MOLECULAR MORPHOLOGIES OF C_{60} AND PTCDA ON INSULATORS: DEWETTING IN TWO PROTOTYPICAL ORGANIC SEMICONDUCTORS

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There has been considerable interest in recent years in the use of organic molecules as active electronic and optoelectronic materials for devices. As such, research into the properties and structures of molecular films, crystallites and isolated molecules on surfaces has become an active field, both for the promise of single molecule devices and the prospect of thin film organic electronics. However, despite the importance of insulating materials in typical device structures, there has been minimal study of molecular deposits on insulating surfaces due to difficulties with the use of many traditional surface science tools on such systems. Over the past decade, non-contact atomic force microscopy (nc-AFM) has proven to be a powerful surface science tool on insulators as well as other surfaces, and more recently on heterogeneous samples. Here, we have used UHV nc-AFM as a high resolution tool to study the growth and morphology of two commonly used prototypical molecular semiconductors: C_{60} and PTCDA, on alkali halides. The alkali halides used, KBr and NaCl, cleave well *in situ* with large atomically flat terraces (up to 1 micron) making them ideal for growth studies.

C_{60} deposited on KBr and NaCl forms islands with an unusual branched morphology [1,2]. The mechanism for the formation of branches appears to be related to a dewetting process occurring immediately after growth. The final stages of this process were observed directly in a series of nc-AFM images showing single layer film edges receding to form the types of structures observed at a later time. A transition from compact islands to branched islands was investigated quantitatively, and it is believed that an instability in the dewetting at the length scale where this transition occurs is responsible for for initiating branch formation. Stability of the structures was tested by annealing and growth at elevated substrate temperature. Although compact islands were determined to be the equilibrium morphology from the high temperature growth, the branched islands grown at room temperature are stable under heating. The epitaxy, though different at steps and on open terraces, does not appear to play any significant role in the island morphology, indicating that the substrate plays a minor role in the formation of the island shapes. Disconnected regions of seemingly connected islands have the same orientational relation to the substrate, while such "communication" seems unlikely, in a dewetting scenario these disconnected regions would have originated as one single layer island and only have become separated during dewetting.

PTCDA on NaCl also undergoes a dewetting process, though in a rather different manner. At low coverages, single layer islands are observed in a highly strained epitaxial structure. In areas where there are several substrate steps close together, tall islands with the familiar herringbone arrangement for PTCDA are observed with a depletion in the surrounding single layer islands corresponding to the volume of molecular material in the crystallite. At a coverage of 0.8ML single layer strained islands and tall herringbone crystallites coexist, indicating a coverage induced dewetting transition [3]. To confirm this hypothesis of dewetting, the single layer islands observed at a coverage near the transition were annealed and found to form very large crystalline islands of PTCDA, with no evidence of a monolayer on the substrate.

Dewetting has recently been reported in other molecular systems and found to be a significant factor in growth and morphology [4,5]. These two example systems may indicate that dewetting is also an important consideration in molecule-on-insulator systems as well.

References:

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Figures:

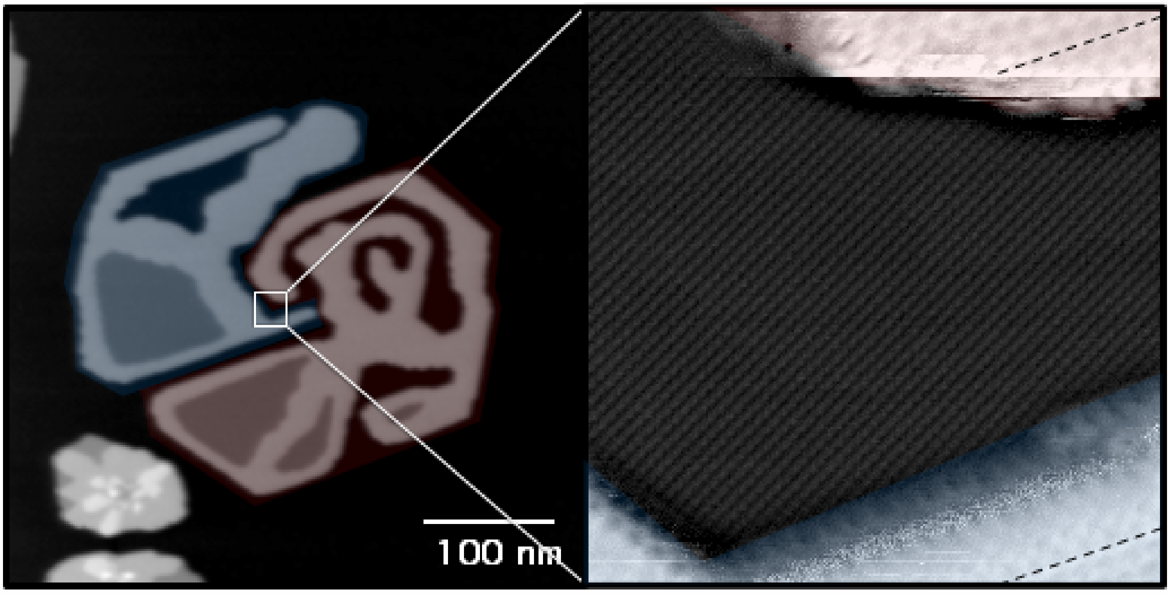

Fig. 1: 2 disconnected regions of a C60 island on KBr separated by dewetting (left), showing the same orientational relation in high resolution (right).

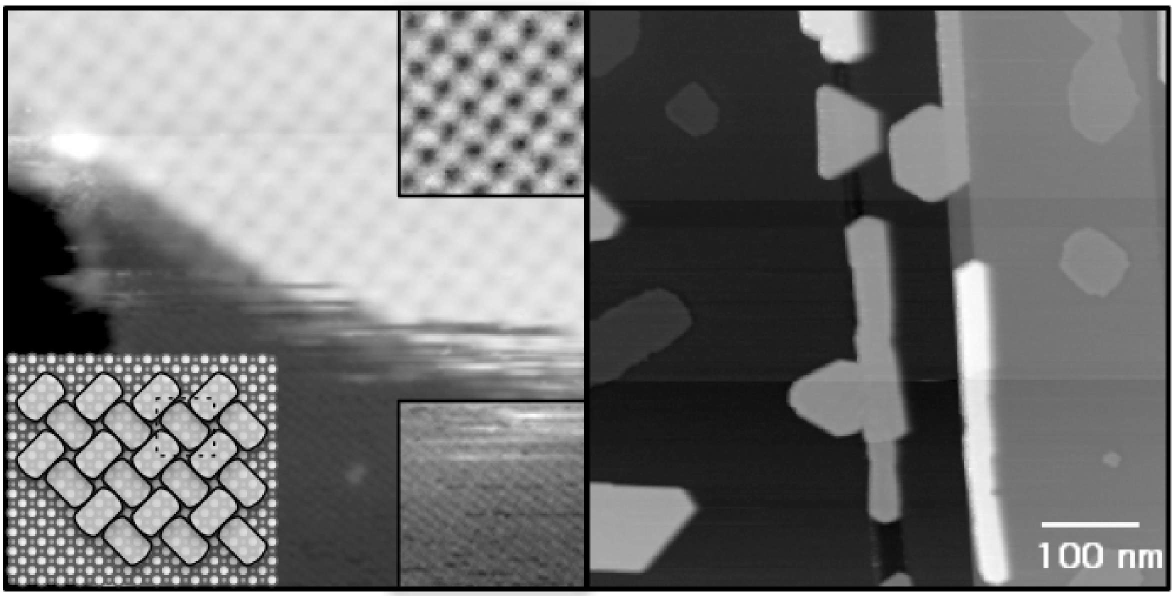

Fig. 2: High resolution nc-AFM on PTCDA overlayer on NaCl with insets adjusted for better contrast (left) used to determine the strained c3x3 epitaxy (lower left inset). Overview image of co-existing monolayer and multilayer islands at 0.8ML coverage (right)