

One-dimensional growth of PTCDA molecular rows on Sn/Si(111) surfaces

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The possibility of including organic semiconductors as active components in the inorganic semiconductor-based devices has increased the interest in these materials in the last years. By exploiting this organic-inorganic approach the advantages are two-fold. On the one hand, one can benefit from well-defined surface structure properties and overall quality of the currently used semiconductors such as Si. On the other hand, a wide range of organic molecules along with their tailorable optical and electronic properties may provide new hybrid devices with enhanced capabilities. Nevertheless the controlled deposition of these organic materials to produce epitaxial thin films, required for optimum functional properties of devices, still represents a considerable challenge, due to the increased reactivity of the semiconductor surfaces.

Improved structural order is observed when reactive semiconductor surfaces are passivated e.g. by reaction with hydrogen atoms in the case of Si substrates [1,2], prior to organic film growth. The passivation induces a reduction of the chemically active sites, mainly by saturating the surface dangling bonds.

In the present work a new approach to passivate semiconductor surfaces has been exploited by adsorbing metal atoms, such as Sn on Si(111) substrates. The adsorption and growth of organic PTCDA (3,4,9,10 perylene-tetracarboxylic dianhydride) molecules on the Sn/Si(111) has been investigated at room temperature by means of scanning tunneling microscopy.

For the deposition of PTCDA on Si(111)-(2√3×2√3)R30°-Sn surface [3] we have observed the formation of a novel molecular PTCDA structure consisting in quasi 1D molecular rows. The evolution of sample morphology with increasing coverage is showed in Fig. 1. The molecular row formation is observed in the initial stage of deposition i.e. 0.2 ML PTCDA. The length and the density of molecular rows increase for subsequent deposition. At 0.5ML PTCDA molecular rows extend homogeneously over the entire surface, creating a highly ordered overlayer with regularly-spaced rows, in a commensurate (4√3×2√3)R30° structure.

The registry of the PTCDA molecule relative to the substrate was determined from high resolution STM images where intramolecular PTCDA features and substrate lattice are resolved simultaneously as shown in Fig. 2. Three symmetry-equivalent PTCDA domains are found. In addition splitting into two domains by a mirror plane exists with the rotation angle $R = \pm 15^\circ$ with respect to the three equivalent surface crystal axis of the Sn/Si(111) substrate.

It is proposed that the molecular anchoring process may be the result of a Sn-O bond formation which stabilizes the molecular rows and promotes the commensurate (4√3×2√3)R30°. The symmetry and orientation of molecular domains suggest that the molecular arrangement is mainly governed by a molecule-substrate interaction.

The studied system, for which unprecedented 1D PTCDA structure has been obtained, may be used as an organic template to further functionalize silicon-based semiconductor surfaces.

References:

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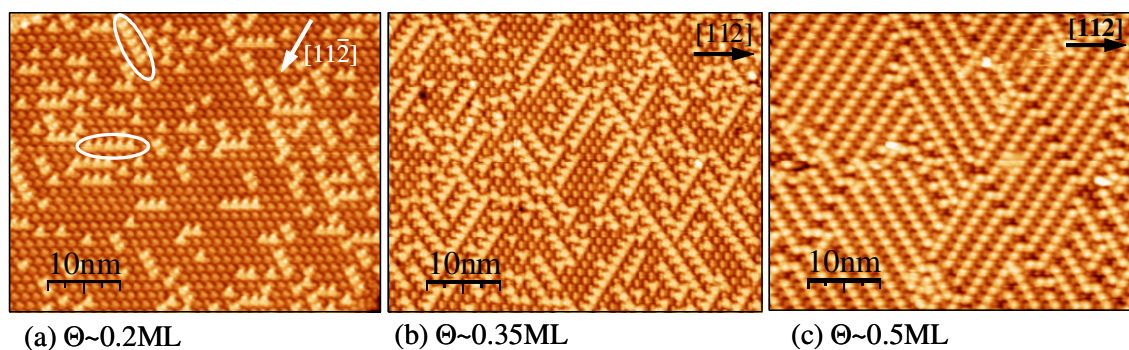


Figure 1 Representative STM images of the Si(111)- $2\sqrt{3}\times 2\sqrt{3}$ -Sn surface after the PTCDA deposition, showing the evolution of sample morphology with increasing coverage. (a) The molecule rows formation is observed starting at 0.2ML. (b) With increasing coverage the length and the density of molecular rows increase. (c) At 0.5ML the PTCDA molecular rows extend homogeneously over the entire surface, creating a highly ordered overlayer with regularly-spaced rows, in a commensurate $(4\sqrt{3}\times 2\sqrt{3})R30^\circ$ structure. Image sizes: 50nm \times 40nm, (a),(b) $V=+2.2V$, $I=0.1nA$. (c) $V=-2.0V$, $I=0.1nA$.

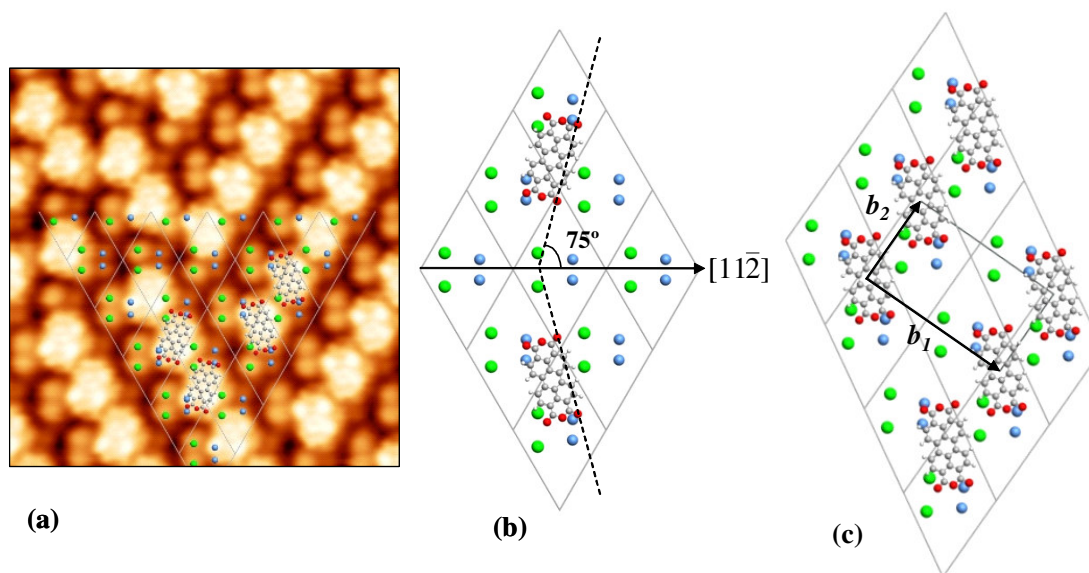


Figure 2 (a) High resolution STM image shows that within each substrate domain, there are two preferential orientations of the molecule related by mirror symmetry relative to the $[11\bar{2}]$ substrate direction (10nm \times 10nm, $V=+2.0V$, $I=0.1nA$). (b, c) Proposed structural models indicate the molecular adsorption geometry and the PTCDA commensurate $(4\sqrt{3}\times 2\sqrt{3})R30^\circ$ structure on the Si(111)- $2\sqrt{3}\times 2\sqrt{3}$ -Sn surface, respectively.