

# Watching layers of C<sub>60</sub> molecules grow.

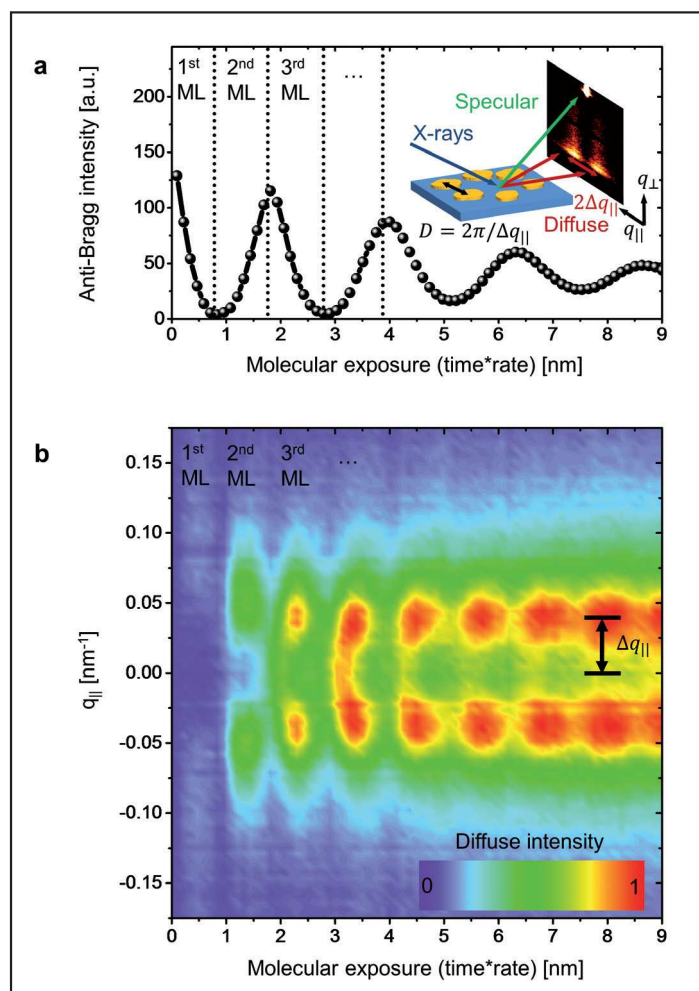
Towards understanding growth on the molecular scale

Assembly of molecular building blocks into functional nanomaterials is increasingly used in devices, but the understanding of molecular film growth on a nanoscopic, molecular level is still in its infancy. We use real-time and *in situ* specular as well as diffuse X-ray scattering in combination with kinetic Monte-Carlo (KMC) simulations to unravel the multilayer growth of the fullerene C<sub>60</sub> in terms of microscopic processes such as surface diffusion, nucleation and step-edge crossing. Particle-resolved dynamics show a lateral diffusion behaviour similar to colloids, but are characterized by an atom-like Ehrlich-Schwoebel barrier. Our results contribute to a fundamental understanding of molecular growth processes for a system which forms an important intermediate case between atoms and colloids.

Understanding the growth of molecular materials, such as the prototypical molecular semiconductor C<sub>60</sub>, is an indispensable prerequisite for the rational design of complex nanomaterials from molecular building blocks. To achieve a molecular scale understanding of nucleation and multilayer growth the three major surface processes during growth have to be considered: (1) surface diffusion of a single molecule, (2) lateral binding of molecules and (3) the step-edge crossing of molecules across island edges.

To address this question, we employ a combination of specular X-ray growth oscillations with real-time diffuse X-ray scattering (see Fig. 1) to simultaneously follow the vertical and lateral morphology during the growth of the fullerene C<sub>60</sub> on the muscovite mica. These challenging experiments are made possible through the high X-ray brilliance, high resolution and advanced detectors with high dynamic range at the MiNaXS beamline P03 at PETRA III.

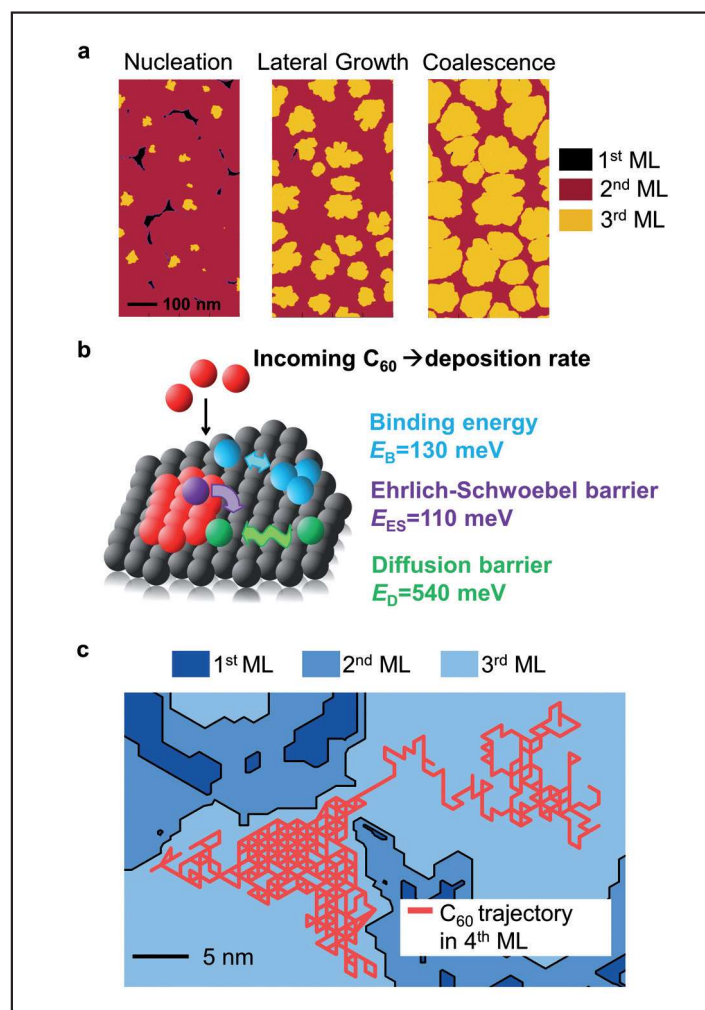
The time-dependent specular X-ray reflectivity as a function of molecular exposure is shown in Fig. 1a for a substrate temperature of 60 °C and a deposition rate of 0.1 ML min<sup>-1</sup>. The scattered intensity at the so-called anti-Bragg point, which lies at half of the Bragg angle, oscillates with a period of two monolayers (ML), as the X-rays are reflected from consecutive C<sub>60</sub> layers and alternately interfere destructively and constructively. The X-ray growth oscillations provide information about the vertical layer filling during growth and are indicative of layer-by-layer growth. While the diffuse scattering is weak, it nevertheless contains important lateral information. Figure 1b shows a map of the diffusely scattered intensity as a function of  $q_{\parallel}$  and molecular exposure. For each C<sub>60</sub> layer, the diffusely scattered intensity has two maxima along  $q_{\parallel}$ , because the characteristic average island distance  $D$  causes an increase in the diffusely scattered intensity at  $\Delta q_{\parallel} = \pm 2\pi/D$ . The peak positions enable us to quantitatively describe the nanostructure



**Figure 1**

(a) Specular X-ray growth oscillations during the growth of the fullerene C<sub>60</sub> (inset: X-ray scattering geometry). The distinct growth oscillations are indicative for layer-by-layer growth. (b) Diffuse X-ray scattering (GISAXS) during the growth of the fullerene C<sub>60</sub>. For each C<sub>60</sub> layer, the diffusely scattered intensity has two maxima along  $q_{\parallel}$ , because the characteristic average island distance  $D$  causes an increase in the diffuse scattered intensity at  $\Delta q_{\parallel} = \pm 2\pi/D$ .

through the island density  $N \propto 1/D^2$  [2, 3]. To understand the morphological evolution on a molecular level the experimental data have been evaluated using kinetic Monte-Carlo (KMC) simulations [1]. From simulated growth morphologies, the vertical and lateral structure during growth is deduced. In



**Figure 2**

(a) Kinetic Monte-Carlo (KMC) simulated film morphologies: Three different growth stages are observed: (1) nucleation, (2) lateral island growth and (3) coalescence. (b) Surface processes in  $C_{60}$  growth. The diffusion barrier  $E_D$ , binding energy  $E_B$  and Ehrlich-Schwoebel barrier  $E_{ES}$  determine island nucleation and interlayer transport in multilayer growth. Included are numerical values determined by fitting the experiment using KMC simulations. (c) Trajectory of a single  $C_{60}$ -molecule.

Fig. 2a three different simulated growth stages, (1) nucleation, (2) lateral island growth and (3) coalescence, are shown.

By comparing the experimentally observed vertical and lateral structure information with KMC simulations we determine a complete set of energy parameters describing the intra- and interlayer diffusion processes of  $C_{60}$ . This comparison yields an effective step-edge crossing, so-called Ehrlich-Schwoebel barrier of  $E_{ES} = 110$  meV, a surface diffusion barrier of  $E_D = 540$  meV and a binding energy of  $E_B = 130$  meV (see Fig. 2b). The high value of the surface diffusion barrier arises due to a simplified triangular lattice used in the simulation which means a diffusion step goes across two sites of the real hexagonal lattice.

Beyond an explanation of the experimental data, the KMC simulations allow us to study particle-resolved dynamics (see Fig. 2c for a trajectory of a single  $C_{60}$  molecule), which reveal similarities and differences between atomic, molecular and colloidal systems during growth. When comparing the average surface free diffusion times,  $C_{60}$  is able to diffuse much longer than an atomic species before immobilization on the surface, which we attribute to the colloid-like short range of  $C_{60}$ -interactions. Both  $C_{60}$  and soft-matter colloids can form bonds only with the immediate vicinity due to the short interaction range of  $C_{60}$  van der Waals forces and colloidal interactions. Nevertheless, we find that the step-edge crossing process for  $C_{60}$  differs from colloidal systems. In contrast to  $C_{60}$ , for which we find a truly energetic Ehrlich-Schwoebel barrier, colloidal epitaxy exhibits a flat energy landscape at the step-edge.

Since  $C_{60}$  features aspects of both atomic and colloidal systems, our findings will help to gain insight into island nucleation and surface growth processes for molecules between the length scales of atomic and colloidal systems. This quantitative, scale-bridging understanding enables predictive simulations and a rational choice of growth conditions, which, together with molecular design and synthesis, ultimately leads to a systematic understanding of growth of molecular and soft materials. For more details see the original publication.

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## Original publication

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