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## Probing molecular layers with low-energy electrons

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# Summary

Molecular materials have been a subject of interest in both fundamental research as well as applications for decades, and have been studied as bulk crystals, (thin) films and as individual molecules. The differences in the physical, chemical and mechanical properties of molecular materials as well as the large variety of these properties among different categories of molecules, allow for tunability of material properties for a desired functionality or application. This dissertation explores pentacene crystals near the two-dimensional limit, i.e. in films of one to a few monolayers, a range of thickness less explored in the literature. Specifically, this dissertation focuses on real-time studies of such pentacene layers, starting with dynamics of layer growth, and including changes in the film's electronic and optical properties as a result of varying thickness or external stimuli. Pentacene was chosen as a representative of small polycyclic aromatic molecules.

For this purpose, an experimental technique called Low Energy Electron Microscopy (LEEM) is employed, since it satisfies several important criteria. LEEM probes at most the top few nanometers of the sample, and hence it is suitable for studying ultrathin films. Furthermore, it allows for real-time imaging and spectroscopy, provides high spatial and spectroscopic/energy resolution, and the range of electron energies is relevant for studying both electronic properties as well as chemical processes. Chapter 2 of this dissertation describes the LEEM instrument and the various measurement techniques it provides.

In the growth of molecular layers, the substrate has significant influence on the crystal structure as well as various properties of the adlayer. In chapter 3, we study the growth of crystalline pentacene layers on hexagonal boron-nitride (hBN) and graphite flakes, two members of an emerging class of substrates, i.e. van der Waals materials. These two substrates have nearly identical atomic surface lattices that closely match the aromatic ring structure of pentacene, yet graphite is a conductor while hBN is an insulator. We observe that on both substrates, pentacene first forms a flat-lying wetting layer due to a templating effect by the substrates. Next, however, pentacene grows in a standing-up thin film phase on hBN, but forms tilted recumbent (i.e. pentacene molecules lying down) crystalline domains on graphite. We ascribe this to the differences in the electronic properties of the substrates, which result in a stronger electronic interaction between pentacene and graphite, compared to hBN. This chapter highlights the multi-faceted way in which substrate properties, such as surface lattice, electronic properties, as well as cleanliness, affect the growth of the molecular adlayer.

## *Summary*

In chapter 4, we study chemical changes in molecules as a result of interaction with low energy electrons. This topic is of immense importance in various applications, such as electron-beam lithography, or for reduction of damage to organic or biological matter as a result of exposure to ionizing radiation. Here, we study the cross-section for damage to crystalline pentacene layers as a result of exposure to an electron beam with tuneable energies between 0 eV and 40 eV. We investigate the damage primarily by means of changes in the diffraction pattern of the pentacene layers, as well as changes in their electronic band structure. We conclude that different mechanisms describe electron interaction and damage at different electron energies. Namely, at energies of only a few eV, (dissociative) electron attachment is the key mechanism, while at higher energies, impact ionization dominates. We observe that beam damage decreases as the energy of the incident electrons is reduced. The reduction in damage cross-section is particularly rapid below 10 eV, such that near 0 eV, beam damage is virtually nil. This is in contrast to lithography resists such as PMMA or tin-oxo cages, which in similar experiments show beam damage upon interaction with incident electrons of all energies down to 0 eV. This difference can be of relevance for lithography. Specifically, it implies that the use of aromatic materials as e-beam resists could reduce the effects of secondary electrons in resist exposure, given that these electrons usually have energies of only a few eV.

In chapter 5, we study the influence of unoccupied electronic states above the vacuum level on the emission of photo-electrons and secondary electrons, using thin crystalline pentacene films as a model system. These states are known to play an important role as intermediate states from which an electron is emitted to the vacuum, yet, they are often overlooked or not independently investigated, mostly due to the lack of proper spectroscopic techniques. Monitoring the growth of pentacene layers on a silicon substrate using UV photons, we observe a decrease in photoemission intensity from the pentacene film with the growth of each additional layer. Given an absence of increase in the ionization energy for thicker films, or change in the crystal structure of the layers, the reduction in intensity is explained by suppression of the photoemission process. The suppression can be directly connected to a reduction in the density of available intermediate states in thicker films. Since electrons first need to transition into these intermediate electronic states above the vacuum level before leaving the material, a reduction in the availability of these states directly results in lower photoemission intensity. The density of unoccupied electronic states above the vacuum level can be directly measured in LEEM via electron reflectivity spectra, in which lower density of electronic states at any given electron energy results in higher electron reflectivity. Furthermore, we demonstrate the influence of the unoccupied electronic states on the emission of secondary electrons. Using electron beam irradiation, we cause controlled

changes in the structure of the pentacene films, which result in concomitant changes in their unoccupied electronic density of states, observable in LEEM electron reflectivity spectra. Electron energy spectra measurements reveal that these changes directly affect the energy distribution of secondary electrons. The observations in pentacene films regarding the role of unoccupied electronic states in electron emission processes can be generalized to all materials, and highlight the importance of knowledge of these states for correct interpretation of electron emission experiments. In chapter 6, we further explore the unoccupied electronic states of crystalline pentacene layers above the vacuum level. In particular, we obtain LEEM electron reflectivity spectra not only as a function of energy, but in addition, also as a function of in-plane momenta. These measurements provide a fuller picture of the unoccupied density of states, and are relevant for the discussion above, regarding emission of electrons that are ejected at an angle with respect to the surface normal.

Finally, we describe the design of a cryogenic sample chamber for LEEM in chapter 7. The design is based on the IBM/SPECS aberration-corrected LEEM instrument, with modifications that include mechanisms for cooling the sample and its surroundings, and minimization of the various sources of heat load. Using both a liquid nitrogen dewar connected to the sample stage and the superconducting objective lens, as well as a liquid helium flow cryostat cooling the sample and its vicinity, controllable sample temperatures down to 15K have been achieved. We also present the first scientific measurements obtained from a pentacene film at various temperatures between 300K and 52K. These measurements show a reduction in electron beam irradiation damage cross-section at lower temperatures, as well as changes in LEEM electron reflectivity spectra upon cooling the sample. The cryogenic chamber enables novel LEEM experiments addressing questions in surface science and condensed matter physics.

