Probing molecular layers with low-energy electrons
Tebyani, A.

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1

Introduction

Molecular materials have been the subject of study in physics and materials science for decades due to their potential applications, particularly in electronics. Countless studies have investigated molecules in crystal form, in thin films and down to single molecules, as well as in hybrids with inorganic elements, for a vast range of properties including electronic, optical, and magnetic characteristics. In particular, charge transport and photovoltaic experiments constitute large portions of physics research in molecular, and more broadly organic, materials. Most of such research has been focused on organic molecules and polymers which possess a conjugated π-electron cloud, such as polycyclic aromatic hydrocarbons (PAHs), due to the higher degree of electron delocalization in this class of organic materials.

A key factor for the interest in organic materials, regarding applications, is the relatively low cost as well as ease of processing and device fabrication, in comparison with inorganic semiconductors. In addition, organic electronic devices can be flexible and lightweight. Another reason for the continued interest in molecular materials, both in fundamental science as well as in applications, is the fact that molecules partially retain their individual properties while at the same time forming van der Waals bonds with other molecules leading to formation of crystals, or crystalline thin films. This is a distinguishing factor between molecular and inorganic materials. This feature has made explanations of some phenomena more challenging. For example, regarding charge transport, deformations of the molecules as a result of movement of electric charge need to be taken into account, requiring use of polaron models rather than single-particle ones [1]. But this feature also offers unique advantages for many applications. For instance, it allows much greater flexibility in photovoltaic devices regarding the range of possible optical bandgaps, as a result of the wide variety of molecules synthesized. Furthermore, specific classes of molecules have unique applications. For example, when fluorescent molecules are embedded as guest impurities within host matrices, they primarily retain their optical properties. However, the host matrix induces slight changes in the fluorescence spectra of these molecules. As a result, fluorescent molecules can be employed as very sensitive probes of local acoustic phonons [2], pressure [3], temperature [4,5], electric field [4,6–10] and charge movement [11,12].

Organic materials have already found applications in commercial products such as organic light-emitting diode (OLED) displays, [13] as well as in important technological processes such as resists for optical [14,15] and electron-beam [16] lithography. In academic research, some notable examples of the diverse properties observed in organic materials include band-like charge transport in molecular and doped polymer films [17–21], Hall effect in molecular crystals [21,22] and molecule-doped polymer films [18], polymer-based memristors [23–26], metallic conduction at organic charge-transfer interfaces [27], various optoelectronic devices based on conjugated polymers [28–32] or molecules [20,33–38] as well as organic-inorganic hybrids [39–41], long-range exciton transport in polymer nanofibers [42], ambipolar polymer-based field-effect transistors with balanced electron and hole mobilities [43,44], negative piezoelectric effect in a ferroelectric polymer [45], long spin relaxation time in organic single crystals [46], polaron spin current transport in conjugated polymers [47] and many more. Meanwhile, conductance measurements across various molecules [48–57], either single molecules in mechanically-controllable break junctions or a few molecules in a self-assembled layer contacted by a conductive atomic tip, have led to observations of negative differential conductance [50,51], electric field control of magnetic anisotropy [52], vibrationally-induced two-level systems [53], spin effects in molecular magnets [51], electron-vibration interactions [54], shot noise [55], quantum interference [56] and humidity-controlled rectification of current [57], among others.

The molecule we have chosen to study is pentacene, a well-known representative of small conjugated PAHs. Pentacene has been the subject of intense study over the years for its electronic as well as optical properties. Some examples of optical properties of pentacene include observations of fluorescence from pentacene molecules embedded as impurities in p-terphenyl crystals [58], and jumps in resonance frequency in the fluorescence excitation spectrum of pentacene molecules in p-terphenyl crystals [59]. Regarding electronic properties, conductance studies have reported charge carrier mobility values above

1 cm^{2}V^{-1}s^{-1} in both single crystal and thin film pentacene devices, [17,60–63] which are notably higher than in typical organic conductors.

In crystal form, pentacene exhibits different polymorphs. [64] The known structures include the Campbell phase [65,66], a different crystal phase observed by Holmes et. al. [67], Mattheus et. al. [68] and Siegrist et. al. [69], as well as a thin film phase. [70,71] In the latter, the molecules adopt a tilted standing-up orientation with respect to the substrate surface, and have a herringbone crystal structure, as illustrated in Fig. 1.1. In this phase, which will be the focus of our study in the next chapters, the pentacene crystal is triclinic with lattice parameters 5.93 Å (o-a in Fig. 1.1), 7.56 Å (o-b in Fig. 1.1), 15.65 Å (o-c in Fig. 1.1), α =98.6°, β=93.3°, γ= 89.8° (angle between o-a and o-b). [70] Or, citing another study, the almost identical values of 5.958 Å, 7.596 Å, 15.61 Å, 81.25°, 86.56° and 89.8°. [71] The molecular long axis tilt from the surface normal for the two independent pentacene molecules in the unit cell are 5.7° and 6.8°, [70] or 5.6° and 6.0° (on amorphous SiO_2 substrate) in another study. [71]

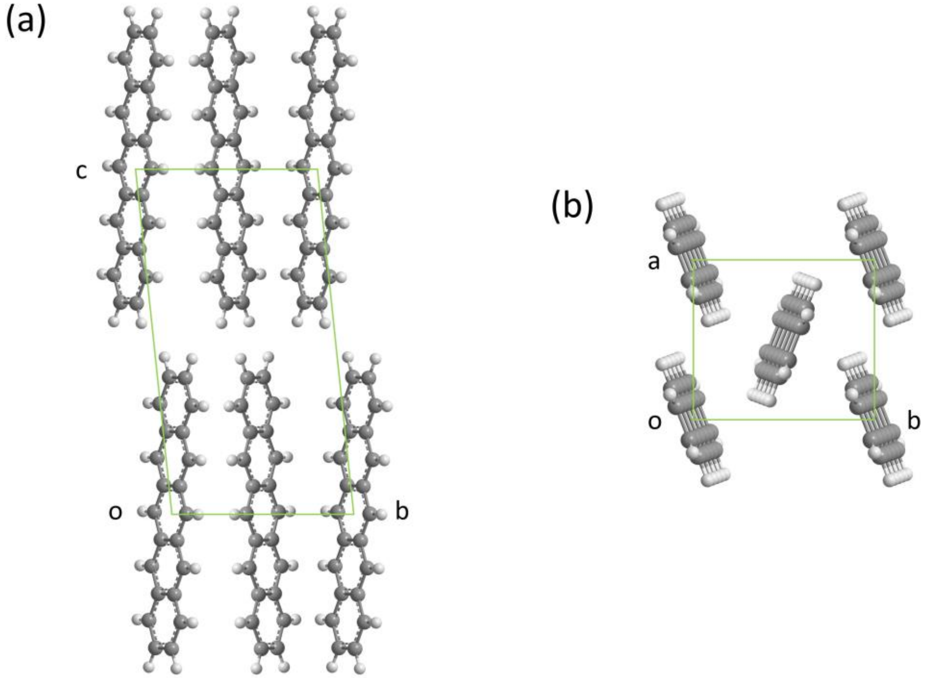

Fig. 1.1 Pentacene thin film (a) side view of two monolayers (b) top view. o-a, o-b and o-c represent the unit cell vectors.

In this thesis, we investigate pentacene crystals near the two-dimensional limit, i.e. in high-quality thin films of one to a few monolayers in thickness. Furthermore, we focus on real-time studies of these layers. We begin with a study of pentacene layer growth on different substrates in real-time using an advanced set-up. We aim to understand the effect of the surface crystal structure and electronic properties of the substrate on the structure of the resulting pentacene layer. Subsequently, we investigate various properties of the pentacene layers *in situ*, and monitor the dynamics of evolution of such properties as a result of controlled changes in the crystal. In particular, we focus on the evolution of the unoccupied electronic band structure of pentacene films as a function of thickness or external stimuli such as electron beam irradiation. The latter can cause controlled structural changes within the layers. We explore such beam-induced changes to the pentacene layers and compare them to other organic materials, and also discuss the implications for electron-beam lithography. Furthermore, we combine our knowledge of the changes in the electronic band structure with real-time measurements of other properties, to provide insights into secondary electron processes such as photo-electron and secondary electron emission.

For this aim, we use an experimental technique called Low Energy Electron Microscopy (LEEM). LEEM satisfies several important criteria for our research. First, in LEEM, the energy of the electrons used for imaging and spectroscopy is usually just a few electron Volts (eV). This leads to a low mean free path, [72,73] making LEEM suitable for studies of surfaces and ultrathin films. Second, because the entire field of view is illuminated at once with electrons (or photons), as opposed to scanning probe techniques, real-time monitoring of changes in the sample is possible, starting with the *in situ* preparation of the samples. Third, nanometer-resolution imaging [74] of the sample offers the ability to exclude local inhomogeneities from affecting the measured properties, by selecting sub-micrometer homogeneous areas to perform measurements on. This is in contrast to some common experimental techniques, such as charge transport measurements, that probe the properties of the sample as a whole. Fourth, typical electron energies in LEEM (0-20 eV) are particularly relevant for studying chemical processes and physical properties such as electronic band structure and crystal excitations. Fifth, due to the low energy of the electrons, beam irradiation damage to the molecular layers can be minimal for the lowest range of energies, depending on the material (chapter 4). Irradiation damage is a very important topic in research on organic samples. While some common microscopy techniques such as Transmission Electron Microscopy (TEM) or Scanning Electron Microscopy (SEM) offer high-resolution and real-time imaging, electron energies used in these techniques are typically tens or hundreds of keV, resulting in destruction of the organic sample during measurement. In contrast, minimal irradiation damage makes LEEM particularly favourable among microscopy techniques for studying organic materials. Finally, LEEM offers the ability to prepare samples *in situ* and perform all the measurements within one piece of equipment, all at ultrahigh vacuum (UHV) pressures, avoiding exposure of the sample to ambient conditions that can alter sample properties during transfer between different equipment.

In this thesis, we utilize the interaction of low-energy electrons with the molecular layers for two purposes. On the one hand, to learn about the properties of the layers, such as their crystal structure via diffraction. On the other hand, we employ low-energy electrons as an external stimulus to create controlled changes in the chemical and physical properties of the sample (chapters 4 and 5). Applying the variety of measurement techniques available in LEEM, we obtain insights from experiments on pentacene layers that can be generalized to wider classes of materials. In more detail, we discuss the following topics in the next chapters.

In chapter 2, we explain the primary experimental technique, i.e. LEEM. We introduce the instrument, how it works and the various measurement techniques available in LEEM. Such techniques include imaging in real-space and Low-Energy Electron Diffraction (LEED), use of apertures for bright-field, dark-field and µLEED imaging, PhotoElectron Emission Microscopy (PEEM), Electron Energy Loss Spectroscopy (EELS), LEEM-IV (intensity vs. voltage) spectroscopy and Angle-Resolved Reflected-Electron Spectroscopy (ARRES).

In chapter 3, we begin our exploration of molecular layers with an in-depth study of their growth. Growth of small aromatic molecules on surfaces has been the subject of several studies in the past. Here, we compare the growth of pentacene layers on graphite and hexagonal boron-nitride, two very different members of an emerging class of substrates, i.e. van der Waals materials.

In chapter 4, we study the low-energy electron chemistry initiated in the molecular layers as a result of exposure to a beam of very low-energy electrons. We measure electron beam irradiation damage cross-sections for incident electrons in the 0-40 eV range. We also investigate the effect of irradiation damage on the electronic and structural properties of the layers. Furthermore, we compare and contrast our results with similar studies on different classes of organic materials such as polymers, and discuss the implications for important technological processes such as electron-beam lithography.

In chapter 5, we study the evolution of the unoccupied electronic states of pentacene films via LEEM-IV spectroscopy, from one monolayer up to four monolayers. The results obtained for the unoccupied states are then correlated with measurements on (the energy-dependence of) secondary electron processes, specifically with PEEM and EELS measurements. Our results demonstrate the critical, and often overlooked, role of unoccupied states above the vacuum level on secondary electron processes, such as photo-electron and secondary electron emission. Our conclusions are generalizable not only to other organics, but to all classes of materials.

In chapter 6, we delve deeper into the unoccupied band structure of pentacene films above the vacuum level. Using ARRES, we measure the relation between energy and in-plane momenta for unoccupied states in pentacene layers, and remarkably find considerable dispersion. We compare the results for two and three monolayer films and also follow beam irradiation damage with ARRES band structure plots.

In chapter 7, we present an important advancement in LEEM, i.e. the extension of available sample temperatures from room temperature down to 15 K. We explain the design of a cryogenic sample chamber incorporated into the LEEM instrument at Leiden University, and show the first results obtained in the cryogenic chamber on a three-monolayer pentacene film. Specifically, we study electron beam irradiation damage and LEEM-IV spectra at various temperatures between 300 K and 52 K.

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