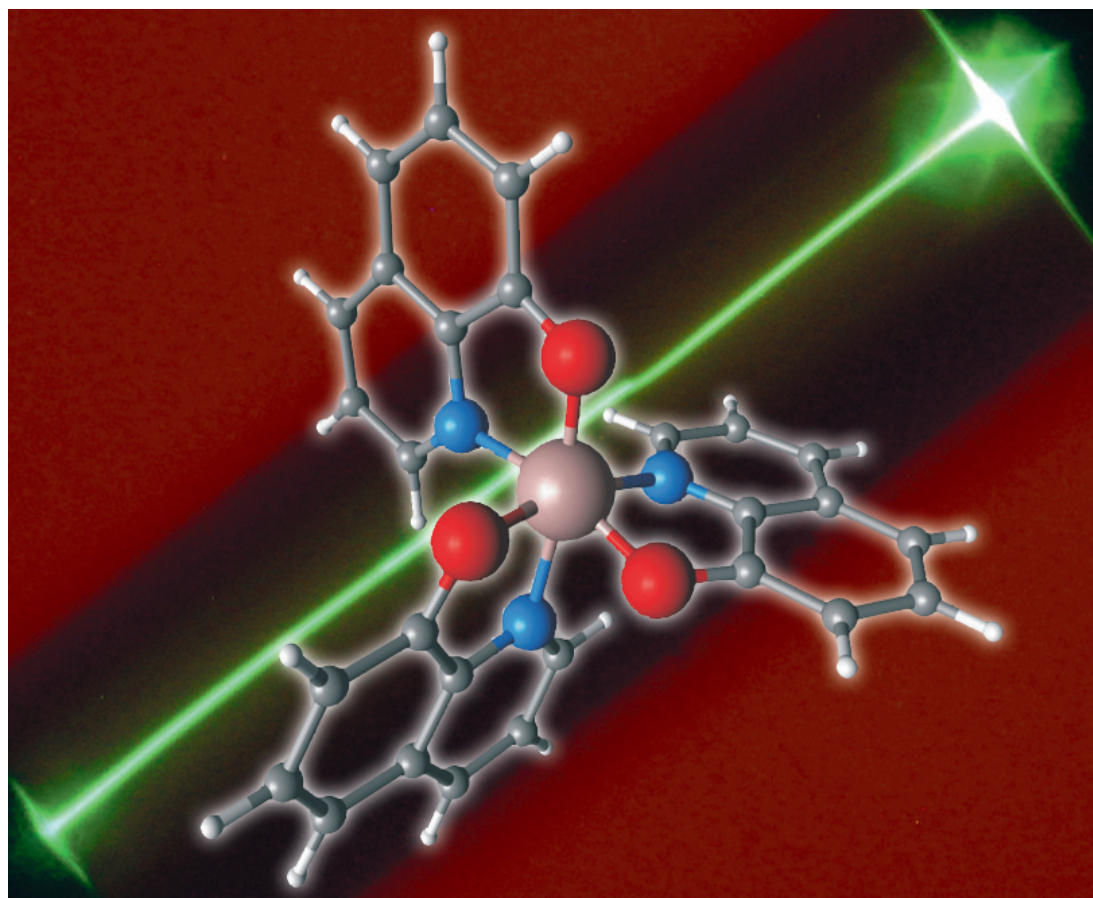


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W. Brütting, Ch. Adachi

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Second, Completely New Revised Edition



Edited by
Wolfgang Brütting and
Chihaya Adachi

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Foreword

Organic semiconductors now provide an important technology base, supported by a rapidly growing body of science. The field is not new; interest in the semiconducting properties of pi-conjugated molecules was already well established in the 1960s and the foundations of their semiconductor science were built then using molecular materials such as anthracene as model systems. As with inorganic semiconductors, the prospect of engineering toward applications has provided several major boosts to the field. The initial drive in the late 1970s was to use organic photoconductors in place of selenium as the photoactive drum in electrophotography applications. Molecular semiconductor “guests” in polymer “hosts” were successfully engineered and are now the ubiquitous technology for this application. They also provided the working systems for the understanding of electronic transport in disordered semiconductors.

The explosion of interest, dating from the late 1980s, was triggered by the observation of relatively efficient electroluminescence in thin-film diode structures, in both molecular semiconductors and solution-processed polymeric semiconductors. Though electroluminescence had been observed in single-crystal semiconductors in the 1960s, it was the prospect of practical materials processing to deliver useful devices such as pixelated displays that drew industrial and commercial attention, and this has supported a vibrant global research community. Besides light-emitting diodes, now in products such as smart phone displays, other devices have been brought to realistic levels of performance: field-effect transistors today match the performance of thin-film silicon, and solar cells offer realistic energy conversion efficiency, at 10%.

The level of device performance has been achieved on the back of a wide range of scientific and engineering breakthroughs. Perceived obstacles to performance (such as limits to solid-state luminescence efficiency or to field-effect carrier mobility) have been pushed aside and a remarkable landscape of new science and new phenomena is now revealed. This is captured by the excellent series of chapters in this book that cover both the richness of the physics-based science and the global reach of the field, with authors from leading research groups across North America, Europe, and Asia.

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Richard Friend

Preface

With the invention of the transistor around the middle of the last century, inorganic semiconductors like Si or GaAs began to take over the role as dominant materials in electronics from the prevailing metals. At the same time, the replacement of vacuum tube-based electronics by solid-state devices initiated a development that by the end of the twentieth century led to the omnipresence of semiconductor microelectronics in our everyday life. Since the beginning of the twenty-first century, we are facing a new electronics revolution that has become possible due to the development and understanding of a new class of materials, commonly known as *organic semiconductors*. The enormous progress in this field has been driven by the expectation to realize new applications, such as large area, flexible light sources and displays, low-cost printed integrated circuits, or plastic solar cells from these materials.

Strictly speaking, organic semiconductors are not new. The first studies of the dark and photoconductivity of anthracene crystals (a prototype organic semiconductor) date back to the early twentieth century. Later on, triggered by the discovery of electroluminescence in the 1960s, molecular crystals were intensely investigated by many researchers. These investigations could establish the basic processes involved in optical excitation and charge carrier transport. Nevertheless, in spite of the principal demonstration of an organic electroluminescent diode incorporating even an encapsulation similar to the ones used in nowadays commercial display applications, there were several drawbacks preventing practical use of these early devices. Since the 1970s, the successful synthesis and controlled doping of conjugated polymers established the second important class of organic semiconductors. Together with organic photoconductors (molecularly doped polymers), these conducting polymers have initiated the first applications of organic materials as conductive coatings or photoreceptors in electrophotography. The interest in the semiconducting properties of molecular materials revived in the 1980s due to the demonstration of an efficient photovoltaic cell incorporating an organic heterojunction of “p- and n-type” semiconductors as well as the first successful fabrication of thin-film transistors from conjugated polymers and oligomers. The main impetus, however, came from the demonstration of high-performance electroluminescent diodes from vacuum-evaporated molecular films and from conjugated polymers. Owing to the large efforts of both academic and industrial research laboratories

during the past two decades, organic semiconductor devices have progressed rapidly and meanwhile led to first commercial products incorporating displays and light sources made of organic light-emitting diodes (OLEDs), logic circuits utilizing organic field-effect transistors (OFETs) or solar energy harvesting modules on the basis of organic photovoltaic cells (OPVs).

This book focuses on the fundamental physics behind this rapidly developing field of organic electronics. It ties in with the previous edition of “Physics of Organic Semiconductors” published in 2005. Due to the big success of the first edition and the rapidly developing and still growing field, a new edition with completely restructured contents and new contributing authors was put together in order to include novel exciting developments over the past 6 years. In spite of the appearance of first commercial products, there is still a large interest in fundamental issues in the field of organic semiconductors. This book, therefore, tries to bridge the gap between textbook knowledge largely based on crystalline molecular solids on the one side (see, for example, Pope & Swenberg, *Electronic Processes in Organic Crystals and Polymers*, or Schwoerer & Wolf, *Organic Molecular Solids*) and other books focusing more on device applications.

The editors want to thank all contributing authors for writing high-quality up-to-date chapters of their work, including the state of the art in the respective field. Without their efforts this book would not have been possible. Furthermore, we want to thank Russell J. Holmes (University of Minnesota) who acted as consultant editor in the early stages of this book project. We are also indebted to our academic teachers, Prof. Em. Markus Schwoerer (Bayreuth University) and Prof. Em. Tetsuo Tsutsui (Kyushu University), who brought us in touch with this fascinating subject more than 20 years ago.

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Part One
Film Growth, Electronic Structure, and Interfaces

1

Organic Molecular Beam Deposition

Frank Schreiber

1.1 Introduction

Organic semiconductors exhibit a range of interesting properties, and their application potential is rather broad, as seen in many other chapters in this book. For the crystalline “small-molecule” systems, grown by organic molecular beam deposition (OMBD), the subject of this chapter, it is generally agreed that the structural definition is important for the functional properties. The following list should serve to illustrate the various aspects:

- 1) The definition of interfaces (degree of interdiffusion and roughness)
 - a) Organic–organic (e.g., in organic diodes)
 - b) Organic–metal (e.g., for electrical contacts)
 - c) Organic–insulator (e.g., in transistors, insulating layer between gate and semiconductor)
- 2) The crystal structure
 - a) Which structure is present? (Note that polymorphism is very common in organics).
 - b) Are different structures coexisting?
 - c) Orientation of the structure (epitaxy)?
 - d) Is the structure strained (epitaxy)?
- 3) Crystalline quality/defect structure
 - a) Mosaicity (note that in a thin film one has to distinguish between quality in the xy -plane and in z -direction (surface normal)).
 - b) Homogeneity within a given film (density of domain boundaries etc.)
 - c) Density of defects (and their nature), which also impacts the electronic properties.
- 4) Issues related to multicomponent systems
 - a) Phase segregation versus intermixing; size of “domains.”
 - b) Possible new structural phases of the mixed system; superstructures?
 - c) Tuning of properties by graded concentration profiles?

Since the structure has a strong impact on the functional properties, understanding the structure formation, that is, the growth process, and finding ways to optimize the structural definition is a prerequisite for technological progress. Moreover, understanding the physics of the growth process raises several fundamental challenges.

We will mostly focus on “thicker” films, their growth modes, and the evolution of the morphology for thickness ranges that are typically employed in organic semiconductor applications. We will discuss only to a limited extent the work on the first monolayer, although as the “seed layer” for the following layers this is obviously important. Thus, some of the classical surface science issues, such as binding distances and associated interface dipoles, although very important [1, 2], epitaxial relation, and so on, are not the focus of this chapter. For these issues and also for information on the history of the field, we refer to Refs [3–15]. Also, we will not discuss issues related to chirality, although they are undoubtedly intriguing [11, 16–18].

In terms of growth technology, the equipment is essentially the same as for inorganic molecular beam epitaxy. Evaporation cells on a vacuum chamber are used to provide a flux of molecules at the substrate surface (typically some range around $1 \text{ \AA}/\text{s}$ to $1 \text{ \AA}/\text{min}$), and ideally the growth can be monitored *in situ*. Virtually, all surface and interface techniques have been used for OMBD-grown films, and we refer to standard textbooks for details of the experimental methodology.

This chapter is organized as follows. We first present some of the general issues in thin film growth and then what is specific and potentially different for organics (Section 1.2). In Section 1.3, we give an overview of the most popular systems. Section 1.4 contains a number of case studies, trying to highlight the issues that we feel are particularly relevant and typical for OMBD. The case studies are based on a few selected compounds and are not intended as an exhaustive list. They are organized according to the (inorganic) substrates, covering, insulators, metals, and semiconductors. In Section 1.7, we briefly indicate the issues for organics-based heterostructures, inorganic–organic, and organic–organic. Some conclusions are given in Section 1.8.

In a review with limited space such as the present one, it cannot be our goal to give a complete and exhaustive overview. Instead, the examples are centered mostly around our own work, which we try to discuss in the context of the general field. This selection is obviously unbalanced, and we apologize for omissions of other important work.

We note that this chapter is an updated version of the 2005 edition of this book and related to Ref. [13]. Important developments since then are, *inter alia*, the precision determination of binding distances of organic semiconductors on metal contacts along with the associated electronic properties (e.g., Refs [1, 2]), the further development of real-time monitoring of growth (e.g., Ref. [19]) and an increased understanding of organic–organic heterostructures, as reviewed at the end of this chapter.