INTRODUCTION TO ORGANIC SEMICONDUCTOR HETEROJUNCTIONS

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Foreword

The book Introduction to Organic Semiconductor Heterojunctions provides a summary of the organic semiconductor heterojunction after many years of profound study in the area of phthalocyanine materials by Professor Yan's group. This book also reflected their knowledge on this area developed in recent years. The main focus of Professor Yan's group is on three aspects. The first is the fabrication of organic semiconductors and heterojunction films, especially the development of the weak epitaxy growth (WEG) method. The WEG technique takes advantage of the self-organization character of disc-like molecules growing on a rod-like molecular base. This method can make large-area, highly oriented, high-quality polycrystalline films on an amorphous substrate with a surface roughness at the molecular level. The second aspect is the study of organic semiconductor heterojunction physics. They have proved by many experiments that the CuPc/F₁₆CuPc interface is an accumulating type heterojunction which is distinguishable from the traditional depleting type inorganic heterojunction. They have observed conductance increase at the interface of accumulating heterojunctions and have explained this phenomenon by electron-thermoemission and energy band models, which has expanded the semiconductor heterojunction theory. The third aspect is the application of organic semiconductor heterojunction devices which have been widely investigated with a focus on organic thin-film transistors (OTFTs). They have gained delightful progress, such as the character of OTFTs based on VOPc fabricated in the laboratory has reached the standard of commercial amorphous silicon which are now widely used, and they are dedicated to putting this into practice.

This book carefully illustrates the fabrication of organic heterojunction films and their characterization process. The charge injection and transport model in organic heterojunction devices is expounded in detail. The authors also give a perspective at the end of every chapter which represents their opinion on the future of each related topic. This book will be a valuable reference to researchers on organic semiconductor materials and devices, and it can also be a textbook for graduate students and staff in this area. I hereby recommend it with honor to all the readers.

Professor Yong Cao Academician of Chinese Academy of Sciences South China University of Technology

Preface

In the late twentieth century, a set of meaningful organic thin film electronic devices began to emerge, such as organic photovoltaic cells (OPV cells), organic light-emitting diodes (OLEDs), and organic field-effect transistors (OTFTs), which are becoming the new members of the electronic thin-film device family. Initially, the active layers of these devices were composed of amorphous or semicrystalline organic/polymer films. The energy gaps of these materials are $1.2 \sim 3.5$ eV with very low conductivity, usually lower than 10^{-8} S/cm. These devices have adopted a basic structure similar to that of inorganic semiconductor devices, especially the organic heterostructure. Their mechanism is also shown to be analogous to inorganic devices.

As the application of these organic thin-film electronic devices is becoming clear and concrete, the stability and functionality of these devices need improvement. This process stimulates the progress of high-mobility organic semiconductors and enriches our knowledge of their electronic structure and transport character. The two major branches of our group are working on organic semiconductor heterostructures and the weak epitaxy growth of organic thin films. These projects are derived from this background.

In November 2006, we were fortunate to be acquainted with Professor Baoxun Du who came to Changchun to give academic lectures.

Professor Du showed great interest in organic heterostructures after he reviewed the work of our group. He pointed out that the content of this part was incomplete and needed to be further verified by a variety of other organic semiconductor materials, but organic heterostructure did deserve expanded research. He suggested for us to compile the recent results into a book, with particular emphasis on the phenomenon, theory and fabrication technique, as well as putting forward what might be the key problems and opportunities in the future, in order to accelerate advances in this area. Professor Du had come to Changchun many times to give us helpful discussions and suggestions during the process of writing this book. His solid academic foundation and precise research attitude have deeply impressed us.

To give a full view of the recent development of organic semiconductor heterostructure, part of the contents were accomplished during the writing process. Some contents still lack abundant experiment, the models are isolated, and the details are immature or even disagree with some published results. In the Perspectives of each chapter, we have brought forward a few problems which need further investigation in the future, and we hope this will give our readers some inspiration.

Chapter 1 gives a general description of the application of organic heterostructures in organic thin-film electronic devices and the recent understanding of their theoretical models. Chapter 2

depicts the growth behavior of vapor phase deposited organic semiconductors and illustrates in detail the weak epitaxy growth technique which has been proven to be suitable for disk-like organic semiconductor molecules. Chapters 3 and 4 focus on the interface electronic structure and the transport character of carriers in the organic heterojunction. The experimental phenomena, heterojunction types, and their characters are also expounded. Chapter 5 introduces the various applications of different types of organic heterojunctions in high-mobility thin-film devices. Chapter 6 presents initial studies on "organic heterojunction semiconductors".

The contents of Chapters 2–6 are supported by the National Natural Science Foundation of China (29 974 031, 20 023 003, 20 035 413, 90 301 008 and 20 474 064) and the Special Funds for Major State Basic Research Projects (2002CB613 400).

The authors acknowledge with gratitude the work of students and colleagues in our group; they have done a great deal to fulfill this book, and their work is greatly valued.

Besides the scientific contribution, the authors acknowledge their considerable debt to Xiujin Wang in our group who has taken the task of manuscript editing, index preparation, and requesting all the permissions required for the illustrations in this book. Finally, we want to express our gratitude to all the people who have assisted our group during the research.

Due to theoretical and technical limits, there must be some deficiencies in this book. We hope this book offers experts and colleagues in this field some introductory points of view that will help to stimulate valuable comments and creative ideas.

> Donghang Yan 20 December 2007

About the Authors

Donghang Yan received his B.Sc. in physics (1985) from Jilin University (China) and his Ph.D. in physical chemistry (1995) from the University of Mainz (Germany). Then he joined the Changchun Institute of Applied Chemistry (China). In December 1997, he was appointed a Full Professor at Changchun Institute of Applied Chemistry, where he leads a research group in the field of organic electronics. At present, the focus of his research is the device physics of organic thin-film transistors and organic photovoltaic cells, the physics of organic heterojunctions, and the growth of highly ordered organic semiconductor thin films.

Haibo Wang received his B.Sc. degree in physics (2001) from Jilin University (China) and his Ph.D. degree in polymer physics and chemistry (2006) from the Changchun Institute of Applied Chemistry (China). His Ph.D. thesis, under the supervision of Professor Donghang Yan, was entitled "Organic heterojunction field-effect transistors". He joined the faculty of the State Key Laboratory of Polymer Physics and Chemistry at the Changchun Institute of Applied Chemistry as an Assistant Professor in 2006 and was appointed as an Associate Professor in 2008. His current interests include the physics of organic heterojunctions, the photoelectron spectrum of organic semiconductors, and ambipolar organic transistors.

Baoxun Du was born in 1936 in Liaoning Province. He graduated from the Harbin Institute of Technology in 1960 and joined the faculty at the Institute of Semiconductors (Chinese Academy of Sciences; CAS). In 1996, he became the Guest Professor at the Changchun University of Science and Technology, the Chief Technology Consultant at the State Key Laboratory of High-Power Semiconductor Lasers and the Associate Director of the Academic Committee. He was awarded second prize by the CAS for advances in science and technology. He wrote a book *The Principle of Semiconductor Lasers*, translated a book *Heterostructure Laser*, and participated in writing the high-technology dictionary as the person in charge of the field of optoelectronic techniques. He is currently engaged in optoelectronic research and teaching, and receives invitations to give lectures at local and overseas institutions.