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Materials, Devices, and Processing of Organic Light-Emitting Diodes

Edited by

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Cover Image. A flexible transparent organic small molecule light emitting panels (see Chapter 6, "Small Molecule Fundamentals" by Xin Xu, Michael S. Weaver). Courtesy of Universal Display Corporation.

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OLED Fundamentals

To my family and to all of the members of the Pacific Northwest National Laboratory OLED team, past and present.

Daniel J. Gaspar

To my parents Tatyana and Vladimir.

Evgueni Polikarpov

Preface

What is an organic light-emitting diode (OLED)? Why should we care? What are they made of? How are they made? What are the challenges in seeing these devices enter the marketplace in various applications? These are questions we hope to answer in this book, at a level suitable for knowledgeable non-experts, graduate students, and scientists and engineers working in the field who want to understand the broader context of their work.

At the most basic level, an OLED is a promising new technology composed of some organic materials sandwiched between two electrodes. When current is passed through the device, light is emitted. The stack of layers can be very thin and has many variations, including flexible and/or transparent materials. The organic material can be polymeric or composed of small molecules, and may include inorganic components. The electrodes may consist of metals, metal oxides, carbon nanomaterials, or other species, though of course for light to be emitted, one electrode must be transparent. OLEDs may be fabricated on glass, metal foils, or polymer sheets (though polymeric substrates must be modified to protect the organic material from moisture or oxygen). In any event, the organic material must be protected from moisture during storage and operation. A control circuit, the exact nature of which depends on the application, drives the OLED. Nevertheless, the control circuit should have very stable current control to generate uniform light emission. OLEDs can be designed to emit a single color of light, white light, or even tunable colors. The devices can be switched on and off very rapidly, which makes them suitable for displays or for general lighting.

Given the amazing complexity of the technical and design challenges for practical OLED applications, it is not surprising that applications are still somewhat limited. Although organic electroluminescence is more than 50 years old, the modern OLED field is really only about half that age—with the first high-efficiency OLED demonstrated in 1987. Thus, we expect to see exciting advances in the science, technology, and commercialization in the coming years. We hope that this book helps to advance the field in some small way.

Contributors to this book are experts from top academic institutions, industry, and national laboratories who provide comprehensive and up-to-date coverage of the rapidly evolving field of OLEDs. Furthermore, this work collects in one place, for the first time, key topics across the field of OLEDs, from fundamental chemistry and physics, to practical materials science and engineering topics, to aspects of design and manufacturing. The chapters together synthesize and put into context information scattered throughout the literature for easy review in one book. The scope reflects the necessity to focus on new technological challenges brought about by the transition to manufacturing. In the first section, all materials of construction of the OLED device are covered, from substrate to encapsulation. In the second section, for the first time, additional challenges in devices and processing are addressed.

This book is geared toward a broad audience, including materials scientists, device physicists, synthetic chemists, and electrical engineers. Furthermore, it makes a great introduction to scientists in industry and academia, as well as graduate students interested in applied aspects of photophysics and electrochemistry in organic thin films. This book is a comprehensive source for OLED R&D professionals from all backgrounds and institutions.

Editors

Daniel J. Gaspar is technical group manager of the Applied Materials Science group at Pacific Northwest National Laboratory (PNNL). Dr. Gaspar earned his PhD in physical chemistry from the University of Chicago in 1998, and his BS from Duke University in 1992. Dr. Gaspar's group concentrates on the discovery and application of new materials for energy applications, including organic light-emitting diodes (OLEDs) for energy-efficient solid-state lighting, energy storage, and separations. Dr. Gaspar leads PNNL's OLED program, setting technical direction and building partnerships with industry, academia, and other national laboratories, in order to advance the goal of accelerating adoption of energy-efficient OLED-based solid-state lighting. Dr. Gaspar's technical contributions include significant expertise in nanoscale materials characterization. Dr. Gaspar has published more than 45 papers and book chapters.

Evgueni Polikarpov is staff scientist in the Applied Materials Science group at Pacific Northwest National Laboratory. He earned his diploma in chemistry from Moscow State University in 1998, and PhD in chemistry from the University of Southern California in 2008 working on dopant materials for OLEDs. Dr. Polikarpov is a coauthor of over 20 research publications. His research interests include materials for photovoltaics and organic light-emitting devices.

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1. Introduction

Evgueni Polikarpov and Daniel J. Gaspar

Electroluminescence of organic molecules has been a well-known phenomenon since the mid-twentieth century. However, it was not until 1987, that organic light-emitting diodes (OLEDs), sometimes called organic light-emitting devices, became promising for practical applications, when Tang and van Slyke demonstrated the first high-efficiency device. Since this discovery, OLEDs have evolved from a scientific curiosity to a commercially viable technology incorporated into hand-held devices for bright, vibrant displays that offer beautiful colors and unmatched viewing angles. Furthermore, recent progress in OLED materials and manufacturing technologies suggests that significant changes such as development of larger displays, specialty lighting, and even general lighting will be possible, once current challenges to longevity and cost are overcome. These novel light sources, not only offer promise of energy efficiency, but also, may enable entirely new approaches to room lighting design due to novel form factors; and for transparent and flexible devices not accessible with other lighting technologies.

During relatively short history of OLEDs, the materials and technology have advanced rapidly. In just over 20 years, quantum efficiency (or the fraction of charge that is converted into light) has increased more than 20-fold, approaching the theoretical limit for internal quantum efficiencies. Despite these advances, the search continues for stable and efficient materials and device architectures, and for tackling increasing important challenges that have come to the fore in manufacturing technology: substrate and electrode processing, light extraction, and cost. Research and development efforts have focused on decreasing manufacturing costs while maintaining needed performance for large-area OLED devices and light sources in order to be competitive in the marketplace, while enhancing device stability and maintaining efficiency, nonetheless.

OLEDs are a unique technology, based on the use of organic molecules to conduct large amounts of charge, which recombines to emit light that is bright enough for displays or general lighting. Successful application of organic luminescence in light-emitting devices required materials and device structures that overcame the intrinsically high resistivity of the organic materials while achieving balanced charge injection from electrodes into organics. The first indication that these limitations could be addressed was cited in a paper by C. W. Tang and S. vanSlyke, which mentioned using a thin film heterostructure (stacked thin films). In a heterostructure OLED under operation, holes and electrons are injected from electrodes (usually inorganic) into organic layers, where they are then transported to the emissive layer (EML). The opposite charges form an exciton, which decays to electronic ground state while emitting a photon. This emission process can be fluorescent or phosphorescent, depending upon the emitting molecule. Individual layer thicknesses of 50 nm or less enable low drive voltages, typically <10 V, and, currently in many cases, close to theoretical limit determined by exciton energy. Furthermore, separate hole and electron conducting layers provide efficient charge injection and recombination by permitting optimization of electron, hole injection, and transport, simultaneously. The device developed by Tang and vanSlyke used an EML consisting entirely of emitting molecule. Shortly, after the introduction of thin film heterostructure-based OLEDs, two-component EMLs consisting of emitter molecules doped into an appropriate host matrix were demonstrated—leading to a great increase in device efficiency. This efficiency improvement was the result of an increased charge recombination and exciton confinement in an EML. Dispersing the emitter in a matrix also reduced self-quenching of the emitting dopants. In the late 1990s, a new family of emissive dopants was introduced that generated marked increase in OLED efficiency. These new high-efficiency emitters were based on utilization of triplet excitons (where quantum mechanical spin quantum number is 1, accounting for 75% of excitons). Efficient harvesting of triplet excitons requires a phosphorescent dopant, where both singlets and triplets lead to emissive recombination. In order to reduce degradation and ensure efficient radiative recombination relative to nonradiative recombination, phosphorescent dopant should have a radiative lifetime on a microsecond timescale. Currently, the only known way to achieve both high phosphorescence efficiency and a microsecond radiative lifetime is to incorporate a heavy metal atom into the dopant, whose spin–orbit coupling efficiently promotes, intersystem crossing between singlet and triplet states. Thus, the most efficient OLEDs involve phosphorescent precious metal complexes, particularly iridium (whose name stems from "iridescent"); small amount of these exotic materials suffice to produce extra-large areas of coating. Despite their cost, these materials are not source of current high cost of OLEDs. The challenges lie in scaling down all OLED manufacturing process steps, such as—cost of substrate manufacturing, organic film deposition, and electrode deposition. All these must be decreased for OLED-based televisions, lighting, and other large-area applications in order for OLEDs to achieve their full potential, especially in low-cost markets such as lighting.

Currently available OLED products are nearly all displays. Given the higher value and price offered for displays, they have been the main focus of OLED development, in their history. OLED-based lighting, on the other hand, has yet to overcome its unique set of challenges. For lighting applications, products must simultaneously achieve lifetime, color quality, uniformity, brightness, and efficiency acceptable to a consumer. In particular, the definitions for what constitutes "white" light are very stringent. To save energy and money for consumers, efficiency demands are also very challenging. Fortunately, resolution, pixel pitch, and ambient contrast requirements are relaxed as compared to displays. However, the biggest challenge to OLEDs for lighting from the perspective of device materials is combining high efficiency with longevity.

The two most notable features of OLED field are (1) rapid progress and (2) high degree of integration of different disciplines: OLED research encompasses expertise in electrical engineering, synthetic chemistry, optics, electrochemistry, mechanical engineering, and materials science. These two characteristics create the need for an up-to-date monograph that covers the current state of progress in OLED research with emphasis on technical aspects necessary for the development of viable OLED products, that is, from fundamentals to practical considerations of device manufacturing. The primary focus of this book is to cover this spectrum from beginning to end. To date, topics that are of increased interest to those developing OLED-based lighting solutions—comprising encapsulation, light extraction, deposition methods, and tools—have not been addressed