Available online at www.sciencedirect.com
ScienceDirect
Progress in Surface Science 83 (2008) 490–557
Progress in SURFACE SCIENCE
www.elsevier.com/locate/progsurf

Review

Electron spectroscopy of functional organic thin films: Deep insights into valence electronic structure in relation to charge transport property ☆

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Commissioning Editor: X. Zhu

Abstract

We summarize both historical and recent challenges on angle-resolved and high-energy resolution ultraviolet photoelectron spectroscopy (UPS) of organic thin films. Topics selected for this article are mainly on electron spectroscopic study of the electronic states in relation to charge mobility of organic molecular thin films, especially of weakly interacting organic molecular solids. We describe intramolecular band dispersion in a quasi-one-dimensional molecular chain and intermolecular band dispersion measured with angle-resolved UPS. The latter offers a spectroscopic estimation of the drift hole mobility in organic semiconductors. Furthermore we describe briefly hole-vibration coupling in organic ultrathin films, which dominates the hopping hole mobility and has been recently measured with high resolution UPS. These experiments are thus considered to be a kind of the first-principle measurement of the mobility of organic thin films, which have not yet been realized with electrical measurements. Conduction band dispersion studied with low-energy electron transmission, which is needed in analyzing angle-resolved UPS, ultrafast phenomena appearing in conventional UPS measurements and other interesting work are also introduced.

☆ After completing this article, results of band structure computation on pentacene has been published by Yoshida and Sato [157], which shows clearly that the band structure depends sensitively on polymorph of the crystal structure as described in Section 4.2.1.

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doi:10.1016/j.progsurf.2008.10.002

Keywords: Organic thin film; Organic semiconductor; Organic device; Molecular device; Band structure; Electronic states; Charge mobility; Electron phonon coupling; Electron-vibration coupling; UPS

Contents

1. Introduction

Organic semiconductors, discovered in the mid-20th century [1–3], have larger band gap and smaller band width than their inorganic counter parts; the number of thermally excited carriers in the organic films is not enough to give sufficient current. Thus to obtain sufficient current in organic films, one needs to inject charge carriers effectively from electrodes. As the efficiency of carrier injection is dominated by the charge-injection-barrier height which is the energy difference between the Fermi level (E_F) and the highest occupied molecular orbital (HOMO) state (for hole) or the lowest unoccupied molecular orbital