

Characterization and engineering of hybrid polymer-oxide semiconductor heterointerface

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<https://doi.org/10.15017/1398360>

出版情報：九州大学, 2013, 博士（工学）, 課程博士
バージョン：
権利関係：全文ファイル公表済

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学 位 の 種 類	博士 (工学)
学 位 記 番 号	工博甲第2273号
学位授与の日付	平成25年9月24日
学位授与の要件	学位規則第4条第1項該当 工学府 物質創造工学専攻
学 位 論 文 題 目	Characterization and engineering of hybrid polymer-oxide semiconductor heterointerface (ポリマー・酸化物半導体ハイブリッド材料のヘテロ界面のバンド構造の特性評価と界面エンジニアリングに関する研究)
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論 文 内 容 の 要 旨

In recent years, hybrid organic/inorganic semiconductor heterostructure has been investigated for several emergent applications such as organic field effect transistors (OFET), hybrid photovoltaics (HPV), and organic/inorganic light emitting diodes (OLED). The hybrid heterostructure is expected to have both advantages of organic and inorganic materials at the same moment. Organic materials have the key advantage of simple and low-temperature thin film processing through inexpensive techniques such as spin coating, ink-jet printing, or stamping. In addition, they provide high light absorption coefficient, flexibility, structural diversity. Inorganic materials, on the other hand, offer the potential for substantial mechanical hardness, and thermal stability as well as a wide range of electronic properties which are enabling the design of insulators, semiconductors, and metals. The complementary properties of organic and inorganic materials possess a great potential to make up for limitation of individual inorganic/inorganic or organic/organic junctions.

The most important issue regarding device operation is related to the hetero interface. Nevertheless, there is a lack of research about the hybrid organic/inorganic semiconductor heterointerface. Most of studies often explained band structure at the hybrid interfaces with the electron affinity rule. However, the vacuum level bends

during the formation of the heterointerface. Furthermore, the electrical states are affected by electrical transportation and defects at the interface, meaning that the interface will exhibit band bending behavior. Therefore, it is necessary to understand the actual band alignment based on the Fermi level. The better understanding will give us effective approaches to control the band alignment to enhance device performance.

This dissertation provides a better understanding and engineering of hybrid organic/inorganic interfacial band structures. Here, I adopted a poly(3-hexylthiophene-2,5-diyl) (P3HT) and a poly(styrenesulfonate) doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS) as organic components because of their great potential in optoelectronic application. P3HT is a p-type semiconducting polymer which has been widely employed in HPV, because P3HT has an optical band gap (1.9-2.0 eV) corresponding absorption overlaps well with the strongest spectral components of incident sunlight. PEDOT:PSS has been often employed as a Schottky photo detector and hole transport layers in OLED, because of its high hole conductivity and high work function (~5.2 eV). For inorganic component, I adopted zinc oxide (ZnO), because ZnO is an environmental friendly material with a number of advantages including easy fabrication of various nanostructures, higher quantum efficiency, greater resistance to high-energy radiation, a low growth temperature, and suitability for wet chemical etching.

This dissertation includes four chapters. Chapter 1 describes general introduction including background, problems, strategies, and materials for this work.

Chapter 2 gives the discussion of the hybrid interfacial band structures. Here, I employed a hard X-ray photoelectron spectroscopy (HX-PES) which is a powerful tool for investigating a heterostructure interface because it has a longer mean free path than conventional XPS. By combining angle-resolved measurements (AR-HXPS), HX-PES allows us to measure rough depth profiles at the interface. The band structure of PEDOT:PSS contact on a Zn-polar ZnO single crystal was discussed in chapter 2.1. The results revealed somewhat different band alignment of PEDOT:PSS/ZnO interface from that of conventional metal/oxide semiconductor interface. The detected ZnO bulk region showed flat band structure, meaning that the PEDOT:PSS doesn't deplete ZnO layer strongly. The upward band bending of the ZnO layer was observed at the interface within a few nanometers. The upward band bending formed the charge injection barrier of 0.8 eV, resulting that the PEDOT:PSS contact showed Schottky contact property.

In chapter 2.2, the band alignment of Ag/P3HT/ZnO photovoltaic structure was discussed. At the P3HT/ZnO interface, a band bending of P3HT and a short surface depletion layer of ZnO were observed. The offset between the highest occupied molecular orbital of P3HT and the conduction band minimum of ZnO at the interface contributed to the open circuit voltage (V_{oc}) was estimated to be approximately 1.5 eV, which was bigger than that of the electrically measured effective V_{oc} of P3HT/ZnO photovoltaic devices, meaning that the P3HT/ZnO photovoltaic structure has the potential to provide improved photovoltaic properties.

Chapter 3 demonstrates hybrid photovoltaic devices as one of applications. Here, two promising approaches have been investigated to improve the short circuit current density (J_{sc}) and the open circuit voltage (V_{oc}), respectively. Chapter 3.1 demonstrates the fabrication technique for large-scale uniformly ordered ZnO NRs via nanoimprint lithography and hydrothermal growth, and discusses how effective of them for increasing J_{sc} . The growth conditions were examined by comparing nanorod growth on different transparent conductive oxide layers, namely, aluminum-doped zinc oxide (AZO) and indium tin oxide (ITO). Structural characterization revealed that the crystallinity and flatness of the ZnO seed layer were key factors in improving uniformity as regards the diameter, height, and orientation of the ZnO nanorods. Uniform ordering of ZnO NRs increased the donor-acceptor interface area, which is directly related to J_{sc} . The J_{sc} was consequently five times bigger than that of a planar heterojunction.

Chapter 3.2 discusses another approach which is surface treatment of inorganic component to engineer interfacial band structure. For the treatment, I employed a nitrogen plasma treatment in which the discharge

pressure was kept at near-atmospheric pressure (NAP). Such high-pressure plasma produces high-density active nitrogen species and allows effective plasma treatment even at room temperature. As a result, nitride passivation can be achieved with fewer defects. The electronic structure of the NAP-treated ZnO surface was investigated by a combination of soft X-ray photoelectron spectra and dark current-voltage measurement. The results revealed NAP treatment compensated carriers to form a highly resistant interlayer at the ZnO surface, which reduced carrier recombination and, as a result, increased the open circuit voltage (V_{oc}) up to 0.71 V.

Finally, chapter 4 summarizes this dissertation.

論文審査の結果の要旨

本研究は有機-無機ハイブリッド材料のヘテロ界面電子状態の解析と新しいヘテロ界面設計法の確立に取り組んでいる。電子状態については様々な光電子分光法と電気測定法を系統的に用いることにより詳細に解析している。ヘテロ界面の設計方法として検討した窒素プラズマ処理とナノインプリント法はいずれも高い有用性と汎用性を示している。これらの成果はヘテロ界面におけるキャリアプロセスの基礎的な理解に寄与すると同時にデバイス特性の向上に向けた材料設計や界面制御に関する指針を与え、有機-無機複合機能材料科学の基礎的知見に大きく寄与し価値ある業績と認める。