Thin Solid Films 649 (2018) 1–6

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Dual functionality of metal-tetraphenylporphyrin in ZnO-based hybrid thin film transistors

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A R T I C L E I N F O

Keywords:
ZnO thin films
Porphyrin
Hybrid film
Thin film transistor

A B S T R A C T

Complementary hybridization of ZnO thin films with aluminum tetraphenylporphyrin (Al(III)TPP), zinc tetraphenylporphyrin (Zn(II)TPP) and H_2TPP (tetraphenylporphyrin) was adopted for tuning the hybrid thin film transistor (TFT) performance and improving their flexibility. After the hybridization with the organic layers, the chemical and structural features of ZnO thin films were well-preserved as compared with those of solely ZnO thin films. The existence of organic layers was monitored by X-ray photoelectron spectroscopy depth profiling. We fabricated the TFT based on ZnO/organic layers, resulting in the on-off ratio and threshold voltage of the devices manipulated by selecting the organic layers. These results can be understood by the performance tuning mechanisms related with the electron charge transfer induced by a work function difference. Remarkably, a significant improvement of the flexibility in the hybrid films was achieved without any significant loss in optical transmittance, which will be high demand in transparent and flexible electronics.

1. Introduction

Transparent and flexible thin film transistors (TFTs) based on metal oxide semiconductors have recently received a great deal of attention to meet emerging technological demands for applications in flexible displays including electronic paper (e-paper) and organic light-emitting diode (OLED) [1–5]. In particular, ZnO is n-type semiconductor with a band gap of 3.37 eV and a high-quality polycrystalline film which can be deposited at room temperature. Thus, there is a good compatibility with plastic substrates in terms of their processing temperature for flexible electronics. However, it is widely recognized that three issues for applying ZnO-based TFTs have been emerged: (i) insufficient device performance including on-off ratio and carrier mobility compared to those of conventional poly-crystalline silicon based TFTs, (ii) the requirement for improved flexibility of ZnO TFTs, and (iii) the lack of threshold voltage-tuned TFTs for developing a basic inverter. To solve these problems, tremendous efforts have been devoted: (i) Li-doped ZnO-based TFTs with high electron mobility using a ZrO_2 dielectric layer were fabricated by ambient spray pyrolysis [6]. And the fabrication of solution-processed ZnO thin films and chemical vapor deposition-grown graphene hybrid two-dimensional TFTs was also presented, exhibiting an outstanding electron mobility and a high on-off ratio [7]. (ii) The hybridization of carbon nanotubes (CNTs)-ZnO TFTs and graphene-ZnO TFTs provide an appropriate solution for improving their flexibility because CNTs and graphene are promising materials for flexible and transparent electronic applications [7,8]. (iii) Various metallic capping layers such as Ca, Ti, Cu, and Au were employed for the realization of indium-gallium-zinc-oxide (IGZO) based TFTs with a tunable threshold voltage [9]. And chemically-derived graphene oxide (GO) and Au-decorated GO flakes were hybridized with solution-processed ZnO TFTs in order to manipulate the threshold voltage [10]. However, an alternative strategy to overcome three deficiencies simultaneously still remains elusive. Here, we developed a facile methodology for improving the flexibility of the ZnO thin films as well as achieving the performance tuning of the devices. It is undisputed that porphyrin possesses invaluable properties which enable to manipulate their electrical properties by selecting its central metal atoms, such as Ni, Co, Cu, Zn, Pt, Al and Mn [11–15]. In our previous work, we

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https://doi.org/10.1016/j.tsf.2018.01.017
Received 7 April 2017; Received in revised form 28 December 2017; Accepted 11 January 2018
Available online 12 January 2018
0040-6090/

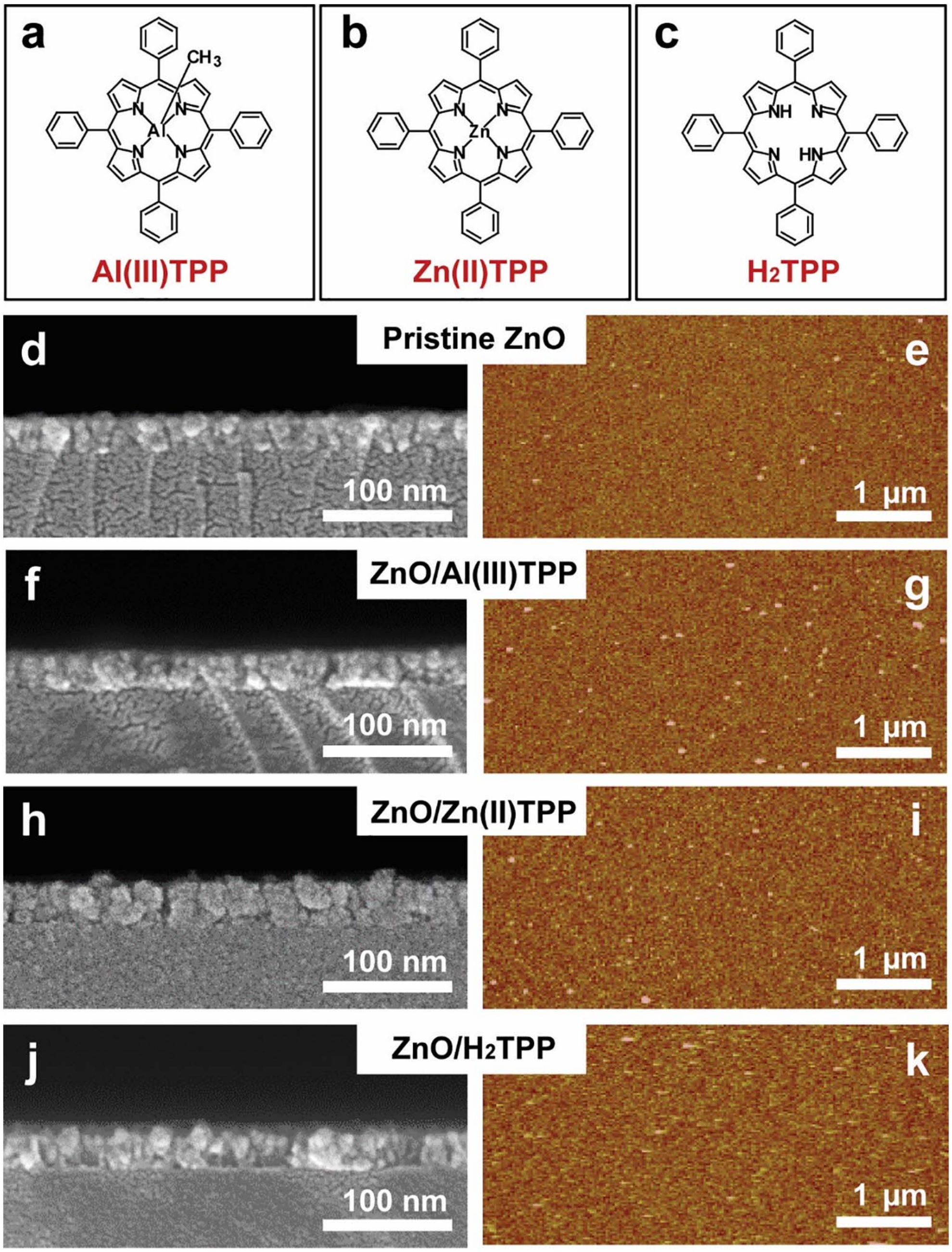

Fig. 1. Chemical formula of (a) Al(III)TPP, (b) Zn(II)TPP, and (c) H_2TPP. Cross-sectional SEM images and AFM images of ZnO thin films on (d, e) SiO_2 (300 nm)/Si(100), (f, g) Al(III)TPP/SiO_2/Si, (h, i) Zn(II)TPP/SiO_2/Si and (j, k) H_2TPP/SiO_2/Si substrates.

established the facile methodology for multi-stacked metalloporphyrin thin films using the hybrid deposition system combining thermal evaporation (TE) and atomic layer deposition (ALD) [16]. Here, we adopted the hybridization of ZnO thin films with metalloporphyrin including aluminum tetraphenylporphyrin (Al(III)TPP), zinc tetraphenylporphyrin (Zn(II)TPP), and tetraphenylporphyrin (H_2TPP) films for tuning the electronic structure of the ZnO thin films. These organic layers allow tuning the device performance of ZnO-based TFTs induced by reliable control of the concentration of carriers in ZnO thin films as well as improving the flexibility of ZnO thin films due to high flexibility in the organic layers. The mechanism of the electrical interaction between the ZnO thin film and organic layers was explored systematically.

2. Experimental details

Complementary hybridization of ZnO/organic thin films (Al(III)TPP, Zn(II)TPP and H_2TPP) were implemented by the hybrid deposition system [16]. An Al_2O_3 layer (50 nm) as a gate dielectric was deposited on highly doped *p*-Si(100) substrates by ALD. The deposition process for ZnO/organic hybrid films was performed as follows: Firstly, the H_2TPP layer was deposited on the Al_2O_3 surface by TE. Next, the synthesis of metalloporphyrin on the Al_2O_3 surface was performed by hybrid deposition system combining a TE and vapor phase metalation. Initially, the Al_2O_3/Si substrate was placed onto a rotatable sample holder in the hybrid deposition chamber. A 0.35 nm-thick H_2TPP films were deposited on the Al_2O_3 surface under 1.33×10^{-4} Pa with the growth rate at 0.06 Å/s by opening the main gate valve after the sample holder was rotated downward. Afterwards, the main gate valve was closed during the sample facing upward. Al(III)TPP (or Zn(II)TPP) film was formed onto the monolayer H_2TPP film by introducing trimethyl aluminum (TMA) (or diethyl zinc (DEZ)) under 1.8×10^1 Pa for 5 s (or 40 s). After the completion of metalation reaction, the system was purged with a liquid nitrogen gas flowing at 500 sccm for 30 s. The thickness of Al(III)TPP (or Zn(II)TPP) film was easily manipulated by