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Controlled growth of ZnPc thin films for photovoltaic applications

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Abstract

The growth of ultra-high-vacuum evaporated ZnPc films was discussed in detail. The effects of growth rate and substrate temperature on the film morphology are investigated by atomic force microscopy. It is clear that growth conditions play a very important role in the surface morphology. High substrate temperature leads to the formation of larger grain. The relationship between ZnPc morphology and organic photovoltaic properties is discussed. PCE of the device using ZnPc grown at 90 °C and 0.12 Å/s is enhanced by a factor of 71% relative to the device using ZnPc grown at 0.02 Å/s. Moreover, the devices prepared at room temperature exhibit relatively higher PCE due to the significant improvements in photocurrent, open-circuit voltage. These results directly imply that controlled growth of the organic films plays a crucial role in further improving the device performances.

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Keywords: organic photovoltaic; ZnPc thin film; vacuum evaporation; surface morphology

1. Introduction

Organic photovoltaic (OPV) devices based on small molecules and polymer have been attracting considerable interests as a potentially useful source of renewable energy due to their important advantages including low weight, low-cost production and flexibility [1]. Significant progresses have been achieved since first efficient donor/acceptor (D/A) heterojunction bilayer device was reported in 1986, and the power conversion efficiency (PCE) of OPV devices reaches about 6% [2-4]. However, PCEs of the devices by using various materials and device structures are still not sufficient for practical application. Generally, light absorption in organic materials always leads to the generation of mobile excitons. The diffusion of excitons into the D/A interface is necessary to dissociate themselves

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into electrons in acceptor and holes in donor. The light-induced current will be generated only these electrons and holes collected by using electrodes. Thus, PCE is limited by several instinct factors such as the light absorption, exciton diffusion, charge collection and charge transfer efficiencies [5]. Many experimental and theoretical investigations imply that the organic materials, the thickness, the morphology and crystalline order of organic thin films play crucial roles in these efficiencies [6]. Since the structure has strong impact on the functional properties, it is very important to understand the growth process of organic films, and find ways to optimize their surface morphology and molecular order (grain formation). As well known, the covalent bonds play an important role in the grain formation of inorganic materials, the relative weak van der Waals force of organic materials has less constraint on the morphology. It is possible the interaction with substrate type and surface, growth temperature as well as the growth rate influences the grain size and structural characteristics. Therefore, it remains challenge to find out suitable process in order to better control the growth of organic materials for device application.

In this paper, we investigate the growth of zinc phthalocyanine (ZnPc), thin films by an ultra-high-vacuum (UHV) – evaporation system. The substrate temperature and the film growth rate were varied during the film growth. Significant variations in the surface morphology are observed in ZnPc films under different growth conditions. The effects of growth conditions on the grain size are discussed. The performances of OPV devices using ZnPc thin films with very different surface morphology are also studied.

2. Experimental

Glass and commercial prepatterned indium-tin-oxide (ITO) coated glass were used as substrates. Prior to deposition, the substrate was treated by oxygen plasma for 30 minutes. 95%-purity ZnPc (Sigma-Aldrich) were further purified three times by gas flow sublimation method before use. 20 ± 1 nm ZnPc thin films were prepared by an UHV evaporation system under a deposition pressure of about 1×10^{-6} Pa. A quartz-crystal oscillation monitor was used to monitor the thickness and growth rate. The film thickness was also verified by Dektak 8 surface profiler (Veeco). The growth rates were varied from 0.02 to 0.25 Å/s by well controlling the Knudsen-cell temperature. The substrate temperatures were adjusted from room temperature to 150 °C. The growth characteristics of ZnPc films including surface morphology were studied with atomic force microscopic (AFM, SII) with dynamic mode.

To avoid the structural variations in C60 films, after deposition of ZnPc films, the samples were transported to another vacuum system, in which C60 films and electrodes were evaporated on 4 different substrates at one time. 80 ± 5 nm C60 film was deposited at room temperature with a growth rate of 0.20 Å/s on the surface of ZnPc film to fabricate planar ZnPc/C60 heterojunction. 0.1 nm LiF and 100 nm Al layers were deposited as cathode. The typical cell area was 0.04 cm². The current density versus voltage (*J-V*) characteristics of the cells were measured in the dark and under simulated AM 1.5G solar illumination by using a Keithley 2400 Digital Source Meter at room temperature. Incident power was adjusted by using a calibrated silicon photodiode to match 1-sun intensity (100 mW/cm²).

3. Results and Discussion

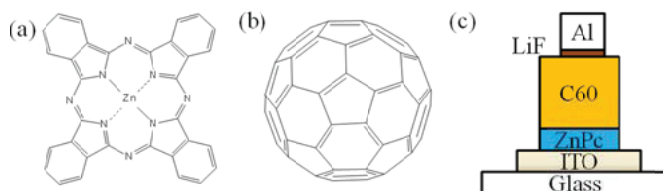


Figure 1. Chemical structures of (a) ZnPc and (b) C60, and (3) OPV device structure.

Figure 1 (a) and (b) show the chemical structures of ZnPc and C60. ZnPc contains highly conjugated macrocycles, consisting of four isoindol units connected by nitrogen atoms in the wing position. ZnPc has a flat and symmetrical molecular structure. As well known, the arrangement of the molecules plays an important role on their own electrical and optical properties.

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