

## Electrodeposited wide-bandgap semiconducting ZnO and CuSCN thin films and nanowires for interface engineering of polymer solar cells

Cyril Chappaz-Gillot<sup>1,2</sup>, Solenn Berson<sup>1,\*</sup>, Sylvia Sanchez<sup>2</sup>, Raul Salazar<sup>2</sup>, Balthazar Lechêne<sup>1</sup>, Dmitry Aldakov<sup>3</sup>, Vincent Delaye<sup>2</sup>, Stéphane Guillerez<sup>1</sup>, and Valentina Ivanova<sup>2,\*</sup>

<sup>1</sup>CEA, LITEN/DTS, Laboratoire des technologies pour les Modules Photovoltaïques, Savoie Technolac, BP 332, 50 Avenue du Lac Léman, 73377 Le Bourget-du-Lac, France

<sup>2</sup>CEA, LETI, MINATEC Campus  
17 rue des Martyrs, 38054 Grenoble, France

<sup>3</sup>CEA, INAC/SPrAM (UMR 5819 CEA-CNRS-Univ. J. Fourier-Grenoble I), Laboratoire d'Électronique Moléculaire, Organique et Hybride  
17 Rue des Martyrs, 38054 Grenoble, France

\*e-mail: valentina.ivanova@cea.fr; solenn.berson@cea.fr

The polymer solar cells (PSCs) have been developed as a promising low-cost renewable energy source because of their potential for large-area fabrication. The best PSC is composed of a layer of a polymer donor and a fullerene acceptor bulk-heterojunction (BHJ) composite sandwiched between a transparent conductive oxide, such as ITO, and a metal electrode. Different ways to improve the device performances (mainly their efficiencies and stability) have been explored: i) changing the photoactive donor-acceptor system or ii) proposing new device architectures. The conventional BHJ PSC with an active layer sandwiched between a low-work-function Al cathode and a hole transporting layer (HTL) of poly(3,4-ethylenedioxythiophene): poly(styrenesulfonic acid) (PEDOT:PSS) on top of an ITO-covered substrate is the mostly used and investigated configuration (Figure 1). These PSCs, under prolonged exposure to illumination, suffer from rapidly reduced performances. A very effective way for circumventing this problem was proposed with the so-called inverted device (Figure 2). By taking the advantage of the ability to reverse the polarity of charge collection in this configuration, an air-stable high-work-function metal as Ag substitutes the air-sensitive Al as the anodic electrode for hole collection, while metal oxides like TiO<sub>x</sub> and ZnO act as the electroactive interface at the ITO interface. The much higher electron mobility of ZnO results in a better performance because it decreases the electrical resistance of the devices. It was found that to improve the PSC performances, an annealing process of the electron transporting layer (ETL) is required (for both TiO<sub>x</sub> and ZnO). Unfortunately, such a process is not compatible with plastic substrates and a method to deposit high-mobility ZnO films without thermal annealing is challenging. The electrochemical deposition appears a very appropriate technique because it is low cost, low temperature process, compatible with flexible substrates; additionally, the as-deposited materials exhibit good crystalline quality. We developed inverted polymeric photovoltaic devices based on electrodeposited ZnO ETL with power conversion efficiency (PCE) of 3.3% on glass and flexible substrates and remarkably good stability under AM1.5 illumination for an active surface area of 0.28 cm<sup>2</sup> [1]. To the best of our knowledge, this is the first example of highly efficient PSCs exhibiting

significantly good life time on both substrates with an electrodeposited ZnO interfacial layer. Furthermore we developed inverted PSCs with electrodeposited ZnO nanowires (NWs) and a PCE of 2.6% was reached. It should be emphasized that the PCE of such PSCs could be further increased if an optimization of the thickness of the BHJ active layer and that of the HTL is done.

We have also explored the electrochemical deposition for preparation of a p-type wide bandgap semiconductor, the copper thiocyanate (CuSCN), which could subsequently be used as a hole transporting layer in conventional PSCs. Despite the wide utilisation of PEDOT:PSS as thin HTL, its electrical inhomogeneity limits electron blocking capability and its acidic nature produces chemical instability at the ITO/PEDOT:PSS interface. We have very recently developed a template-free electrochemical deposition of CuSCN NWs at room temperature [2]. As-prepared NWs are transparent in the visible spectrum, with a very good crystalline quality and could be deposited on either flexible or rigid substrates. CuSCN NWs have been integrated in conventional PSCs and a PCE of 5.1% with low-bandgap polymer active layer and 0.28 cm<sup>2</sup> active surface area was obtained. In both types of PSC architectures, the optimization of charge collection efficiency and interfacial stability at the organic active layer/inorganic electrode junction is considered to be critically important. Thus, for high-performance PSCs, important key parameters appear to be the appropriate selection of the ETL and the HTL and the method for their preparation. We consider that a big advantage of the electrodeposited thin films and NWs is the fact that they could be further integrated in the PSCs without a subsequent annealing process, a crucial point for the fabrication technology on plastic substrates. An increased interest from the industrial community is expected.

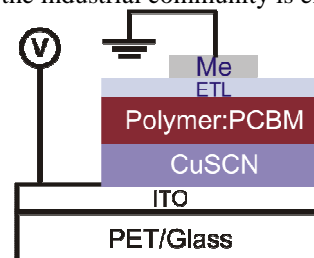


Figure 1. Schema of a conventional polymer solar cell.

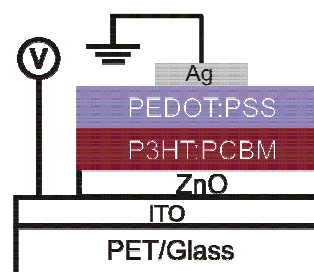


Figure 2. Schema of an inverted polymer solar cell.

## References:

1. S. Sanchez, S. Berson, S. Guillerez, C. Lévy-Clément, and V. Ivanova, Toward high-stability inverted polymer solar cells with an electrodeposited ZnO electron transporting layer, *Adv. Energy Mater.* **2** (2012) 541-544.
2. C. Chappaz-Gillot, R. Salazar, S. Berson, and V. Ivanova, Room temperature template-free electrochemical deposition of CuSCN nanowires, *Electrochem. Commun.* **24** (2012) 1-4.