アニール条件による ZnO 系有機フォトダイオードの暗電流安定性の改善
Improvement of dark current stability of ZnO-based organic photodiode by control of annealing condition

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Owing to their inherent mechanical softness and high molecular tunability, organic photodiodes (OPDs) emerged as alternatives to their inorganic counterparts thanks to their competing performance in flexible imagers, healthcare monitors, and near-infrared sensors [1]. However, these OPDs suffer from high noise spectral density which limits their specific detectivity, linear dynamic range, and signal-to-noise ratio. This noise density is reported to be dominated by shot noise which is proportional to dark current [2]. Dark current in OPDs is well-known for its increase upon illumination of strong light, yet its suppression remains understudied. Recently, a strategy to counter the sharp increase of dark current in OPD with ZnO sol-gel electron transfer layer (ETL), a maturely studied ETL, was reported [3]. This study though elaborates origins of the instability, ultimately suggests replacing ZnO with SnO_2 to solve the issue, leaving an important question: how to improve the dark current stability of the ZnO-based OPDs.

In this work, using an inverted structure of bulk heterojunction OPDs, we demonstrated that dark current increase upon light illumination (wavelength 300–1000 nm) of OPDs with ZnO ETL can be effectively suppressed by control of annealing conditions such as temperature (T_{anneal}) and time. The devices with a photoactive area of 0.2×0.2 cm^2 employing layered structure "glass/ITO (70 nm)/ZnO (30 nm)/P3HT:PC_{61}BM (250 nm)/MoO_x (10 nm)/Ag" were fabricated using spin coating and standard evaporation system [Fig. 1(a)]. For all samples, current density-voltage (J-V) characteristics confirm the operation of photodiodes both in the dark and under illumination (white LED, 8.7 mW/cm^2), which upon illumination, the increase of dark current, even as large as two orders of magnitude, was noticeable [Fig. 1(b)]. We successfully decreased the ratio $J_{dark,illum.}/J_{dark,initial}$ of dark current density after illumination to its initial value—a parameter of the dark current stability—from 1.0×10^2 to 0.64 by raising T_{anneal} from 180 to 350ºC [Fig. 1(c)]. These results provide insights into the importance of the annealing condition of ETL to the dark current stability, which will be elaborated on in detail at the meeting.

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References. [1] P. C. Y. Chow & T. Someya, *Adv. Mater.* **32**. 1902045 (2020). [2] J. Kublitski et al., *Nat. Commun.* **12**, 551 (2021). [3] J. Huang et al., *ACS Nano* **15**, 1753 (2021).

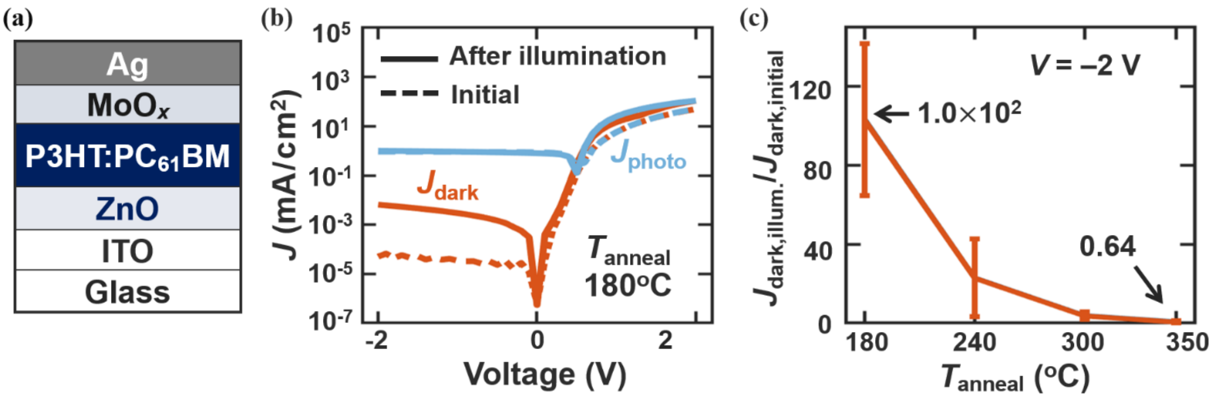

Figure 1. (a) Schematic cross-sectional structure of the inverted P3HT:PC_{61}BM organic photodiodes (OPDs). (b) Initial (dashed line) and after-illumination (solid line) J-V curves of the OPDs. (c) Effect of annealing temperature T_{anneal} on $J_{dark,illum.}/J_{dark,initial}$, the ratio of dark current density after illumination to its initial value.