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Enhancement of Optoelectronic Properties of Organic-Inorganic Hybrid Perovskite Photodiode by Engineering Electron Transport Layer

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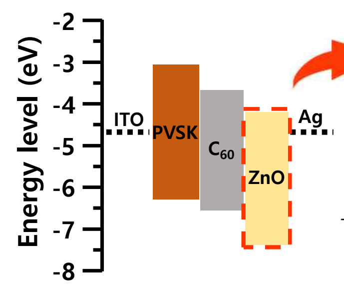
Introduction

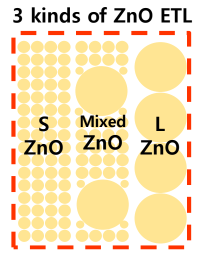
Organic-inorganic halide perovskites (OIHPs) is one of the strong candidates for the next generation photodetector material, because they have attractive properties such as tunable band gap, high light absorption, high carrier mobility, and compatibility with flexible substrates.

In this study, we report the improved performance of OIHP photodiode (OIHP PD) by engineering electron transport layer (ETL). We adopted ZnO nanoparticles (NPs) as an electron transport layer (ETL) material. Because the grain itself or the grain boundaries of ZnO NPs serve as conduction channel or depletion region respectively, it can be easily inferred that the ETL with relatively large ZnO NPs would show better charge transportation properties due to the reduction of grain boundaries. However, the both enhancement of dark current and bright current is not always advantageous in achieving high performance PDs, because the detectivity (D*) of PD is directly associated with the current on-off ratio. So, we tried to optimize the performance of OIHP photodiodes by adopting ZnO ETL NPs with inhomogeneous size distribution. This approach successfully enhanced the external quantum efficiency and detectivity of photodiodes.

Result & Discussion

- Band scheme of OIHP PD





- The thickness of ZnO ETL was fixed to be 50nm
  - i) small ZnO (S ZnO) : Average diameter is 10 nm
  - ii) large ZnO (L ZnO) : Average diameter is 50 nm
  - iii) Mixed ZnO : Mixture of S ZnO and L ZnO NPs

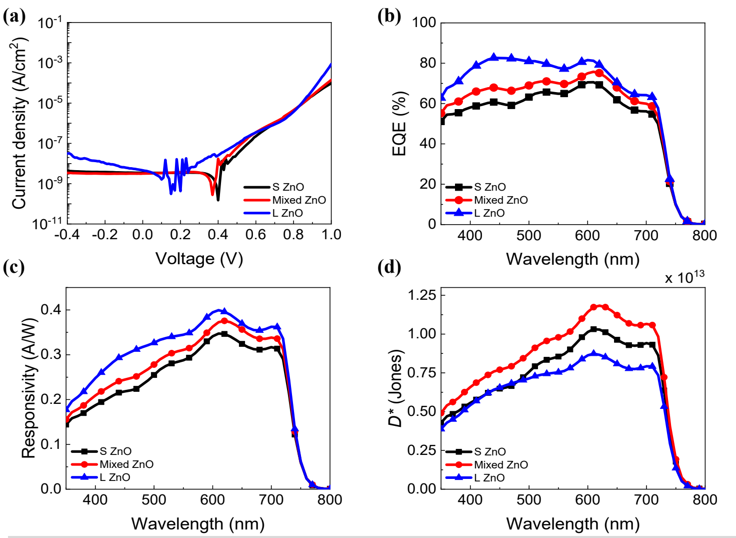
· We fabricated OIHP PDs with a structure of ITO/$MAPbI_{2.55}Br_{0.45}$/C_{60}/ZnO/Ag

· C_{60}/ZnO double layer was adopted as ETL.

· In order to engineer the ETL, we varied the size of ZnO nanoparticles, which constitute ETL.

· We examined 3 kinds of ZnO ETL with different ZnO NP size ; S ZnO, L ZnO, and mixed ZnO

- Characteristics of OIHP photodiode.

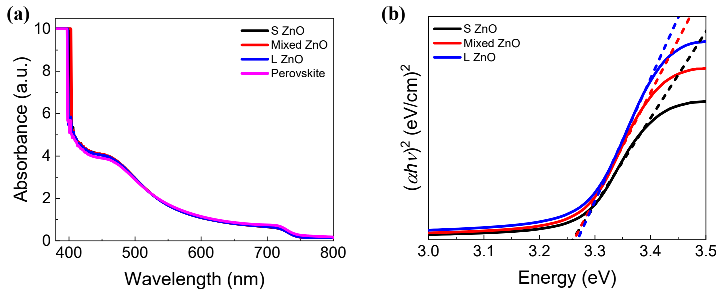


· Figure (a) and (b) show that the dark current (J_d) and EQE of the OIHP PDs increases as the content ratio of large ZnO NPs increase. But the J_d of PD with Mixed ZnO ETL rarely changed.

· Figure (c) shows the responsivity of OIHP PDs. Because the responsivity is calculated based on the EQE, it resembles the EQE spectra.

· Figure (d) shows that the highest detectivity was obtained in the PD with mixed ZnO.

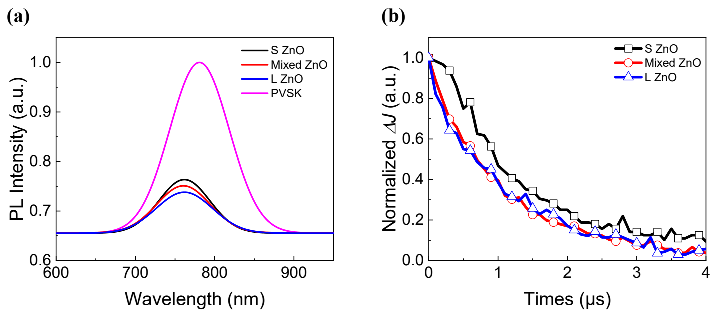
- Optical properties ; absorbance of OIHP PDs and band gap of ZnO films.



· Figure (a) shows absorbance of perovskite film and OIHP PD with three kinds of ZnO ETL. There are no significant differences in absorbance between perovskite film and full-structured PD.

· Figure (b) is tauc plots for absorbance of three kinds of ZnO film. They all have the same energy band gap of 3.26 eV. This empirical data shows that the J_d and EQE increase of OIHP PD with L ZnO does not originate from the variation of energy band gap depending on the size of ZnO NPs.

- Charge extraction characteristics of ZnO ETL



· Figure (a) shows steady-state fluorescence (PL) spectra of perovskite film and OIHP PDs with three kinds of ZnO ETL. The PL quenching is attributed to charge extraction from perovskite to ETL. C_{60}/ZnO ETL had a significant quenching effect for the florescence of perovskite layer. The photodiode with L ZnO ETL shows the lowest peak intensity.

· Figure (b) shows the transient photocurrent of OIHP PDs with three kinds of ZnO ETL. The faster charge transportation results in faster fall time. Fall times of OIHP PD with S ZnO, Mixed ZnO, L ZnO ETL are estimated to be 2.71, 2.16, 2.04 μs respectively. It means the response time gets faster as the content ratio of large ZnO NPs increases.

· The grain or the grain boundaries of ZnO NP serve as conduction channel or depletion region, respectively. Figure (a) and (b) show empirical data which confirm charge extraction is enhanced as the content ratio of large ZnO NPs increases.

Conclusion

- We engineered the ETL by varying the sized distribution of ZnO NPs and investigated its effect on the performance improvement of OIHP photodiode.
- The ETL with large ZnO NPs can extract charge more effectively than the ETL with small ZnO NPs, because the ETL with large ZnO NPs has less grain boundaries which serve as depletion layer.
- The characteristics of OIHP photodiode could be optimized by adopting ZnO ETL with specific ratio of small and large size ZnO NP.

Acknowledgement

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