# Development of High-Performance Metal Halide Perovskite Transistors

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## ABSTRACT

*Despite impressive progress on metal halide perovskites (MHP) based optoelectronic devices, little research has been done for applying them as a semiconducting layer for thin-film transistors (TFTs). Herein, we introduce various engineering to modulate the excessive hole concentrations in three-dimensional $Sn^{2+}$-based halide perovskite film. Optimized $CsSnI_3$ TFTs channel exhibit ultrahigh hole mobilities of 80 $cm^2V^{-1}s^{-1}$ and impressive current on/off ratios exceeding $10^8$ with improved reproducibility and operational stability. Introduction*

## 1. Introduction

Over the past two decades, metal oxide semiconductor-based thin-film transistor (TFT) technology has attracted considerable research interest and great success. Compared with silicon-based and organic materials, metal oxides possess good transparency and balanced electrical performance, mechanical stress tolerance, and spatial uniformity, providing balanced suitability in many aspects. However, all commercially available oxide semiconductors are n-type (electron transporting), with few p-type (hole transporting) counterparts reported (*e.g.*, $Cu_xO$, SnO, and NiO). The next attention has focused on the development of high-performance p-type semiconductors with comparable TFT properties to their n-type counterparts.

The lead (Pb)-based halide perovskite semiconductors have achieved enormous success in the photovoltaics community and show promising p-type charge transport. Nevertheless, Pb toxicity threatens the ecosystem and human health and greatly hinders the market commercialization prospect. Therefore, the pursuit of environmental-friendly alternatives is needed.[1-4] Among these metals, Tin (Sn) is by far the most promising candidate due to its similar or even superior optoelectronic characteristics, *e.g.*, higher hole mobility and lower bandgap.[5-9] Unfortunately, due to the low formation energy of the Sn vacancy ($V_{Sn}$) and easy oxidation of $Sn^{2+}$, $Sn^{2+}$-based perovskite films generally suffer from poor stability and unintentional self p-doping effect with high background hole concentrations of $> 10^{18}$ $cm^{-3}$. Meanwhile, the uncontrollable fast crystallization behaviour results in uneven and poor-quality perovskite films. This fast crystallization detrimentally influences the optoelectronic property of $Sn^{2+}$-based perovskites and the ensuring device performance and reproducibility. A wide range of strategies has been explored to address these drawbacks, including additive engineering, crystallization regulation, ion substitution, and dimensionality modulation.[8,10-17]

The most popular technique nowadays is the addition of tin fluoride ($SnF_2$), which has become an indispensable additive in the $Sn^{2+}$-based perovskite precursors for high-performance devices.[18-22] Although its working mechanism has not yet been clarified exactly, the experiment results demonstrated its beneficial roles in suppressing excessive hole density, alleviating the $Sn^{2+}$ oxidation, and improving the film crystallinity/uniformity. This process, however, generally needs the addition of a relatively large amount of $SnF_2$ (>10 mol%) in the precursors. Due to its poor solubility, excessive $SnF_2$ was found to easily aggregate with the poor morphology and create deep-level traps, which seriously deteriorated the device performance.[23,24] This means that the $SnF_2$ ratio in the precursor should be kept low because the background hole density of the deposited $Sn^{2+}$-based perovskite films is still too high to be applied as a semiconducting layer in various electrical and optoelectric devices. Therefore, it is highly desirable to develop alternative co-additives/strategies to suppress the excessive hole density of $Sn^{2+}$-based perovskites and improve the device performance.

The $Sn^{2+}$-based perovskites are highly suitable for the high-mobility p-channel transistors, especially considering the lack of satisfying p-type semiconductors in the current electronics community.[25-28] In addition, a transistor is useful as a platform to investigate the correlation between materials and charge transport properties of emerging perovskite semiconductors.[17,29-34] We recently reported the high-performance inorganic perovskite TFTs based on $SnF_2$ modified $CsSnI_3$-based channel layers, delivering record field-effect hole mobility ($\mu_{FE}$) of ~50 $cm^2$ $V^{-1}$ $s^{-1}$ and on/off current ratio ($I_{on}/I_{off}$) over $10^8$.[35] However, these high-mobility devices operated in a slight depletion-mode (D-mode) with positive threshold voltages ($V_{TH}$) of 12–24 V. This is due

to relatively high hole concentrations in the perovskite channels, and thus large gate voltages are needed to turn off the device. It is undesired for the practical application because of the complicated circuit design and increased power consumption.[28] Although the increase of SnF$_2$ content to 15 mol% could achieve the enhancement-mode (E-mode) operated TFTs, but the TFT $\mu_{FE}$ are seriously degraded due to the notable SnF$_2$ phase segregation and the enhanced impurity scattering.

## 2. Result

Herein we introduce a few different methods to suppress hole concentration to achieve high performance Sn based halide perovskite TFTs. First, we develop new additive. The only 4 mol% new additive achieved a similarly low hole concentration of ~10$^{14}$ cm$^{-3}$ to the CsSnI$_3$-based perovskite films doped with 15 mol% SnF$_2$. To employ the new additive in high-performance perovskite TFTs, the optimized CsSnI$_3$ TFTs exhibited high $\mu_{FE}$ of 65 cm$^2$ V$^{-1}$ s$^{-1}$, high $I_{on}/I_{off}$ over 10$^8$, as well as the improved operational stability. Second we develop replacement of halide atom to a specific pseudo halide to reduce hole concentration.

## 3. Experiment

Preparation of precursor solutions. All chemicals were purchased from Sigma-Aldrich and used directly. The preparation details for SnF$_2$ and CsSnI$_3$-based precursor solutions can be found in our recent report. The new additive solution (0.015M) was prepared by dissolving new additive powder (99.8%) in DMF and followed by the room temperature stirring overnight. The new additive solution was then added to the CsSnI$_3$-based precursors with different molar ratios (with respect to SnI$_2$ and PbI$_2$) and then followed by the 50 °C stirring for 20 min to obtain the solutions for the film/device fabrication. All precursor preparations were carried out in an N$_2$-filled glove box.

Thin-film fabrication and characterization. The film characterization samples were deposited by spin-coating the precursors on different substrates at 5,000 rpm followed by thermal annealing at 100 °C for 5 min in an N$_2$-filled glove box. The film crystal textures were analyzed using XRD with CuKα radiation (Bruker D8 ADVANCE) on glass. The film SEM images were measured using a JSM 7800F on SiO$_2$. The film optical absorption spectra were recorded using a UV-visible spectrophotometer (JASCO V-770). The film XPS analysis was performed using PHI 5000 VersaProbe (Ulvac-PHI, Japan). The film Hall measurements were performed using the van der Pauw method with a 0.51T magnet in an N$_2$-filled glove box at room temperature (approximately 20 °C).

Device fabrication and measurement. Bottom-gate, top-contact TFTs were fabricated on the heavily doped Si substrates with 100-nm thermally grown SiO$_2$ in an N$_2$-filled glove box. The CsSnI$_3$-based channel layers with different dopants were deposited following the above film coating process. The Au source and drain electrodes (40 nm) were deposited on CsSnI$_3$-based channel layers to construct the device using a thermal evaporator placed in an N$_2$-filled glove box. The mask channel length/width was 150/1000 μm. All the TFTs were characterized at room temperature in the dark and N$_2$-filled glove box using a Keithley 4200-SCS. The $\mu_{FE}$ of the TFTs was calculated in the saturation region from the forward transfer curves using equation (1):

$$\mu_{FE} = \frac{2L}{WC_i}\left(\frac{\partial\sqrt{I_{DS}}}{\partial V_{GS}}\right)^2 \tag{1}$$

where $L$, $W$, and $C_i$ are the channel length and width, and the dielectric areal capacitance (34 nF/cm$^2$), respectively. $V_{TH}$ was estimated by linearly fitting $I_{DS}^{1/2}$ with respect to $V_{GS}$. The $SS$ is the inverse of the maximum slope of the $I_{DS}$-$V_{GS}$ plot.

## 4. Conclusions

In conclusion, we have demonstrated a new additive as a more efficient hole suppressor compared with the conventional SnF$_2$ for the reduction of the excessive hole concentration in 3D Sn$^{2+}$-based halide perovskites. The strong hole suppression capability enables the small amount of SnF$_2$ feeding in the precursor, eliminating the negative effects of a single SnF$_2$. To achieve high-mobility Sn$^{2+}$-based perovskite TFTs, we further develop a new additive/SnF$_2$ co-doping approach and probe the key roles of SnF$_2$ as the crystallization promoter and the new additive as the hole suppressor. The optimized devices exhibit high $\mu_{FE}$ of 65 cm$^2$ V$^{-1}$ s$^{-1}$, high $I_{on}/I_{off}$ over 10$^8$, and improved operational stability. We expect this efficient hole suppressor, and the novel co-additive approach can provide new opportunities to achieve high-efficiency Sn$^{2+}$-based perovskite optoelectronic devices.

References
[1] Babayigit, A., Ethirajan, A., Muller, M. & Conings, B. Toxicity of organometal halide perovskite solar cells. *Nat. Mater.* **15**, 247-251 (2016)..
[2] Ning, W. & Gao, F. Structural and functional diversity in lead‐free halide perovskite materials. *Adv. Mater.* **31**, 1900326 (2019).
[3] Xiao, Z., Song, Z. & Yan, Y. From lead halide perovskites to lead‐free metal halide perovskites and perovskite derivatives. *Adv. Mater.* **31**, 1803792 (2019).
[4] Lei, H., Hardy, D. & Gao, F. Lead-free double perovskite cs2agbibr6: Fundamentals, applications, and perspectives. *Adv. Funct. Mater.* **31**, 2105898 (2021).
[5] Giustino, F. & Snaith, H. J. Toward lead-free perovskite solar cells. *ACS Energy Lett.* **1**, 1233-1240 (2016).

[6] Jiang, X. *et al.* Tin halide perovskite solar cells: An emerging thin-film photovoltaic technology. *Accounts of Materials Research* **2**, 210-219 (2021).

[7] Xi, J. & Loi, M. A. The fascinating properties of tin-alloyed halide perovskites. *ACS Energy Lett.* **6**, 1803-1810 (2021).

[8] Yan, Y., Pullerits, T., Zheng, K. & Liang, Z. Advancing tin halide perovskites: Strategies toward the asnx3 paradigm for efficient and durable optoelectronics. *ACS Energy Lett.* **5**, 2052-2086 (2020).

[9] Li, M. *et al.* Advances in tin(ii)-based perovskite solar cells: From material physics to device performance. *Small Structures* **3**, 2100102 (2022).

[10] Hao, F. *et al.* Solvent-mediated crystallization of ch3nh3sni3 films for heterojunction depleted perovskite solar cells. *J. Am. Chem. Soc.* **137**, 11445-11452 (2015).

[11] Liao, Y. *et al.* Highly oriented low-dimensional tin halide perovskites with enhanced stability and photovoltaic performance. *J. Am. Chem. Soc.* **139**, 6693-6699 (2017).

[12] Wang, T. & Yan, F. Reducing agents for improving the stability of sn‐based perovskite solar cells. *Chemistry ‐An Asian Journal* **15**, 1524-1535 (2020).

[13] Ye, T. *et al.* Ambient-air-stable lead-free cssni3 solar cells with greater than 7.5% efficiency. *J. Am. Chem. Soc.* **143**, 4319-4328 (2021).

[14] Li, B. *et al.* Tin-based defects and passivation strategies in tin-related perovskite solar cells. *ACS Energy Lett.* **5**, 3752-3772 (2020).

[15] Dong, H. *et al.* Crystallization dynamics of sn-based perovskite thin films: Toward efficient and stable photovoltaic devices. *Adv. Energy Mater.* **12**, 2102213 (2022).

[16] Gao, Y. *et al.* Highly stable lead-free perovskite field-effect transistors incorporating linear π-conjugated organic ligands. *J. Am. Chem. Soc.* **141**, 15577-15585 (2019).

[17] Liang, A. *et al.* Ligand-driven grain engineering of high mobility two-dimensional perovskite thin-film transistors. *J. Am. Chem. Soc.* **143**, 15215-15223 (2021).

[18] Kumar, M. H. *et al.* Lead‐free halide perovskite solar cells with high photocurrents realized through vacancy modulation. *Adv. Mater.* **26**, 7122-7127 (2014).

[19] Savill, K. J. *et al.* Impact of tin fluoride additive on the properties of mixed tin-lead iodide perovskite semiconductors. *Adv. Funct. Mater.* **30**, 2005594 (2020).

[20] Chen, Q. *et al.* Unveiling roles of tin fluoride additives in high-efficiency low-bandgap mixed tin-lead perovskite solar cells. *Adv. Energy Mater.* **11**, 2101045 (2021).

[21] Pascual, J. *et al.* Fluoride chemistry in tin halide perovskites. *Angew. Chem. Int. Ed.* **60**, 21583-21591 (2021).

[22] Xiao, M. *et al.* Tin‐based perovskite with improved coverage and crystallinity through tin‐fluoride‐assisted heterogeneous nucleation. *Adv. Opt. Mater.* **6**, 1700615 (2018).

[23] Lee, S. J. *et al.* Fabrication of efficient formamidinium tin iodide perovskite solar cells through snf2–pyrazine complex. *J. Am. Chem. Soc.* **138**, 3974-3977 (2016).

[24] Meggiolaro, D., Ricciarelli, D., Alasmari, A. A., Alasmary, F. A. S. & De Angelis, F. Tin versus lead redox chemistry modulates charge trapping and self-doping in tin/lead iodide perovskites. *J. Phys. Chem. Lett.* **11**, 3546-3556 (2020).

[25] Liu, A., Zhu, H. & Noh, Y.-Y. Solution-processed inorganic p-channel transistors: Recent advances and perspectives. *Mat. Sci. Eng. R* **135**, 85-100 (2019).

[26] Zhao, C. *et al.* Evaporated tellurium thin films for p-type field-effect transistors and circuits. *Nat. Nanotechnol.* **15**, 53-58 (2020).

[27] Salahuddin, S., Ni, K. & Datta, S. The era of hyper-scaling in electronics. *Nat. Electron.* **1**, 442-450 (2018).

[28] Fortunato, E., Barquinha, P. & Martins, R. Oxide semiconductor thin-film transistors: A review of recent advances. *Adv. Mater.* **24**, 2945-2986 (2012).

[29] Senanayak, S. P. *et al.* Understanding charge transport in lead iodide perovskite thin-film field-effect transistors. *Sci. Adv.* **3**, e1601935 (2017).

[30] Paulus, F., Tyznik, C., Jurchescu, O. D. & Vaynzof, Y. Switched-on: Progress, challenges, and opportunities in metal halide perovskite transistors. *Adv. Funct. Mater.* **31**, 2101029 (2021).

[31] Li, Z. *et al.* Understanding the role of grain boundaries on charge-carrier and ion transport in cs2agbibr6 thin films. *Adv. Funct. Mater.* **31**, 2104981 (2021).

[32] Shao, S. *et al.* Field-effect transistors based on formamidinium tin triiodide perovskite. *Adv. Funct. Mater.* **31**, 2008478 (2021).

[33] Zhu, H. *et al.* High-performance and reliable lead-free layered-perovskite transistors. *Adv. Mater.* **32**, 2002717 (2020).

[34] Lin, Y. H., Pattanasattayavong, P. & Anthopoulos, T. D. Metal‐halide perovskite transistors for printed electronics: Challenges and opportunities. *Adv. Mater.* **29**, 1702838 (2017).

[35] Liu, A. *et al.* High-performance inorganic metal halide perovskite transistors. *Nat. Electron.* **5**, 78-83 (2022).