

Air-stable tin-iodide-based perovskite field-effect transistors

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The tin iodide-based hybrid perovskite (C₆H₅C₂H₄NH₃)₂SnI₄ [(PEA)₂SnI₄] is promising as the semiconductor in field-effect transistors (FETs) because of its easy film processability and high carrier mobility. However, the stability of (PEA)₂SnI₄ FETs in air remains a significant issue. In this study, we show that the source of this degradation is oxygen. We observed that the structure of (PEA)₂SnI₄ degraded in the presence of oxygen, along with the formation of gaps between grains. With the aim of suppressing the oxygen-induced degradation, we optimized (PEA)₂SnI₄ spin-coating conditions to increase the grain size and simply encapsulated the (PEA)₂SnI₄ semiconductor with the fluorine-based polymer CYTOP. Adopting these methods led to the greatly improved stability of FET performance in air. Additionally, we fabricated single-crystal (PEA)₂SnI₄ FETs using a lamination method. We saw almost no degradation of single-crystal (PEA)₂SnI₄ FETs even in air because of the grain boundaries.

Metal halide perovskites are attractive materials having tunable bandgaps, high absorption coefficients, efficient photoluminescence, high carrier mobilities, long-range carrier diffusion, and compatibility with simple solution processing or vacuum deposition. These properties allow perovskites to be used for various applications, such as solar cells, light-emitting diodes, and laser devices. Additionally, there has been growing interest in using perovskites as semiconductors in field-effect transistors (FETs). Since the first report of perovskite film FETs by Kagan et al. in 1999 [1], perovskite FET performance has steadily improved as a result of effort by many researchers. We showed that the surface treatment of substrates using a self-assembled monolayer and the adoption of a top-contact, top-gate architecture greatly increased hole mobilities up to 26 cm² V⁻¹ s⁻¹ for FETs with a spin-coated film of 2-phenylethylammonium tin iodide perovskite (C₆H₅C₂H₄NH₃)₂SnI₄ [hereafter, abbreviated as (PEA)₂SnI₄] [2–4]. Zeidell et al. used a solvent vapor annealing method to increase the grain size and passivate the grain boundaries of spin-coated methylammonium lead iodide CH₃NH₃PbI₃ perovskite films, resulting in ambipolar transport in FETs with hole and electron mobilities exceeding 10 cm² V⁻¹ s⁻¹ [5]. (PEA)₂SnI₄ seems to be more suitable for FET application in terms of carrier mobility among reported hybrid perovskites.

However, the stability of (PEA)₂SnI₄ films remains an issue as FETs typically exhibit low stability in air.

It has been reported that tin-based hybrid perovskites, such as MASnI₃ (MA: methylammonium) and FASnI₃ (FA: formamidinium), are unstable in air [6–8]. The main reason for the instability in air is the formation of Sn⁴⁺ from the oxidation of perovskite's Sn²⁺. The oxidation occurs even in an atmosphere containing only a trace amount of oxygen (for example, in a glove box filled with inert gas). The additive SnF₂ has frequently been introduced into tin-based hybrid perovskite films to suppress oxidation [9]. As (PEA)₂SnI₄ FETs fabricated without any additive operate properly [1–4] (PEA)₂SnI₄ may be stronger against oxidation than other tin-based perovskites due to passivation by PEA. Nevertheless, (PEA)₂SnI₄ FET performance quickly degrades in air. It is necessary to improve the air stability of (PEA)₂SnI₄ FETs through the clarification of its degradation mechanisms. In this study, we investigated why degradation of (PEA)₂SnI₄ FETs occurs in air.

The original color of (PEA)₂SnI₄ films was brown. These films gradually became transparent in air, suggesting (PEA)₂SnI₄ degradation. (PEA)₂SnI₄ FET performance also degraded as this color change proceeded. The probable source for the degradation in air was expected to originate from oxygen or water. To make the source clear, absorption spectra of (PEA)₂SnI₄ films were measured in four different atmospheres (dry nitrogen, humid nitrogen, dry nitrogen–oxygen mixture, and humid nitrogen–oxygen mixture). As the result, we found that oxygen will decompose the (PEA)₂SnI₄ structure and negatively impact film morphology while humidity at ~30%RH did not induce degradation. Specifically, gaps between (PEA)₂SnI₄ grains were formed in degraded films. These gaps disrupt current flow and degrade FET performance. This oxygen-induced degradation possibly originates at the grain boundaries as the boundaries have larger available surface areas to react with oxygen.

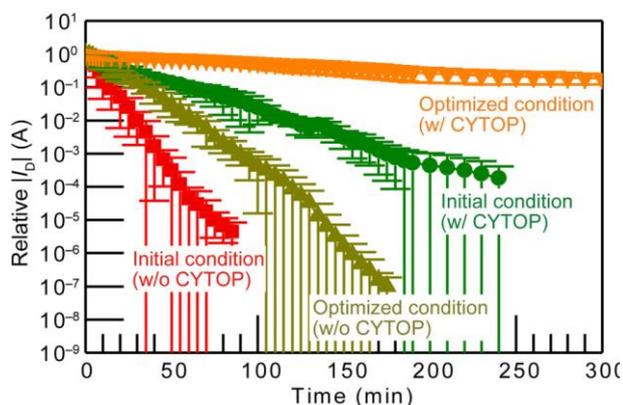
Therefore, we optimized perovskite fabrication conditions to reduce grain boundary density by increasing the grain size. The optimized solvent for spin-coating and annealing temperature were ethanol and 100 °C while our initial solvent for spin-coating and annealing temperature were methanol

and 80 °C. With these optimized conditions, the grain size increased from 30–60 nm to 300–400 nm by approximately ten times, resulting from improved crystallinity. (PEA)₂SnI₄ films fabricated with the optimized conditions had continuous grains without voids or pinholes.

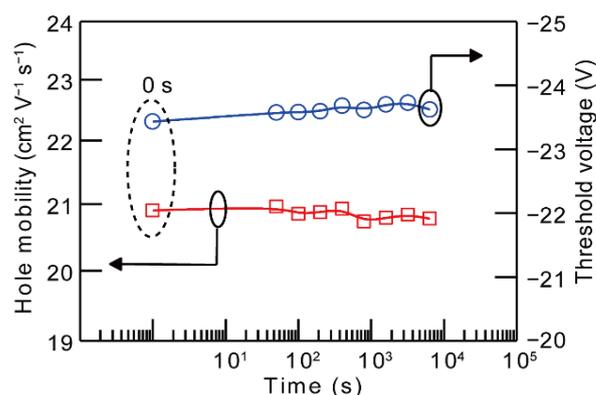
Using the optimized conditions led to an increase in FET hole mobility from $0.40 \pm 0.19 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $7.9 \pm 2.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ by ~ 20 -fold. Additionally, we simply encapsulated FETs with a fluorine-based CYTOP polymer film by spin coating to protect (PEA)₂SnI₄ from oxygen. With these methods, we demonstrated (PEA)₂SnI₄ FETs with greatly improved air stability (see Fig. 1). Our CYTOP encapsulated FETs fabricated using optimized conditions had almost constant drain currents over 5 h

The ultimate sample with less grain boundaries is a single crystal. Therefore, we grew single crystals of (PEA)₂SnI₄ by a solution-cooling method. As-grown (PEA)₂SnI₄ crystal surfaces were inhomogeneous and rough. This may be because the crystals were covered with residue, such as unreacted starting materials and disordered perovskite. To exfoliate this residue layer, a piece of scotch tape was placed on each side of the crystal, and the tape from one side was pulled away. We speculate that this method cleaves the crystal at the interface between two PEA sublayers because these sublayers are weakly bonded by van der Waals interactions. Exfoliated crystal surfaces were much smoother than the as-grown crystal surfaces.

We fabricated FETs by laminating exfoliated single crystals on substrates with source drain electrodes. Although the reproducibility was still low and there was some uncertainty for the mobility calculation, we conservatively estimated that the hole and electron mobilities of our (PEA)₂SnI₄ crystals were $40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ or higher. Hall-effect measurements revealed that the respective electron and hole mobilities of CH₃NH₃SnI₃ perovskite were very high values of $2320 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $322 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in single crystals [10]. Considering that (PEA)₂SnI₄ possesses a SnI framework similar to



Evolution of relative drain current (I_b) for FETs with (PEA)₂SnI₄ semiconductors fabricated using the initial (spin coating from a methanol solution and annealing at 80 °C) and optimized (spin coating from an ethanol solution and annealing at 100 °C) conditions



Plots of calculated hole mobilities and threshold voltages as a function of time for single-crystal FETs operating in air.

CH₃NH₃SnI₃, such high carrier mobilities seem conceivable.

In our single-crystal FETs, the hole mobilities and threshold voltages calculated from the transfer curves measured during the bias stability test did not change significantly over the measurement period of ~ 1 hour. After the bias stability test in vacuum, we introduced air with a relative humidity of $\sim 35\%$ into the probe chamber to evaluate the air stability of the same FET. For this air stability test, no voltage was applied to the FET between the measurements of transfer curves. Surprisingly, the calculated hole mobilities and threshold voltages remained almost constant even in air (Fig. 2). Our single crystal FETs are stable because the crystals have a low density of grain boundaries and defects, and a pristine PEA terminated surface is unlikely to oxidize.

These findings allowed for the fabrication of tin-based hybrid perovskite FETs with improved performance and air stability and will be of great interest to industry and can be used for other tin-based hybrid perovskite devices, such as light-emitting diodes and solar cells.

Acknowledgements

This work was supported by the Japan Science and Technology Agency (JST), ERATO, Adachi Molecular Exciton Engineering Project (JST ERATO Grant Number JPMJER1305); the Japan Society for the Promotion of Science (JSPS), Core-to-Core Program A (Advanced Research Networks); JSPS KAKENHI (grant numbers JP16H04192 and 20H02817); The Canon Foundation; and The Samco Foundation.

References

- [1] Kagan et al., *Science* 286, 945 (1999).
- [2] Matsushima et al., *Adv. Mater.* 28, 10275 (2016).
- [3] Matsushima et al., *Appl. Phys. Lett.* 109, 253301 (2016).
- [4] Matsushima et al., *Appl. Phys. Express* 10, 024103 (2017).
- [5] Zeidell et al., *Adv. Electron. Mater.* 4, 1800316 (2018).
- [6] Stoumpos et al., *Inorg. Chem.* 52, 9019–9038 (2013).
- [7] Dang et al., *Angew. Chem. Int. Ed.* 55, 3447–3450 (2016).
- [8] Wang et al., *Adv. Funct. Mater.* 26, 3417–3423 (2016).
- [9] Koh et al., *J. Mater. Chem. A* 3, 14996–15000 (2015).
- [10] Stoumpos et al., *Inorg. Chem.* 52, 9019–9038 (2013)