Doping of Sn-Based Two-Dimensional Perovskite Semiconductor for High-Performance Field-Effect Transistors

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Abstract—Doping is an important technique for semiconductor materials and devices, yet effective and controllable doping of organic-inorganic halide perovskites is still a challenge. Here, we demonstrate a facile way to dope 2D Sn-based perovskite (PEA)2SnI4 by incorporating SnI2 in the precursor solutions. It is observed that Sn4+ produces p-doping effect on the perovskite, which increases the electrical conductivity by 105 times. This doping technique allows us to improve the mobility of (PEA)2SnI4 field-effect transistors from 0.25 to 0.68 cm2 V−1 s−1. This solution-processed doping technique is promising for flexible and high-performance devices.

I. INTRODUCTION

The low effective mass and intrinsically high carrier mobility of organic-inorganic halide perovskites (OIHPP) semiconductors make them especially attractive as the semiconductor layers in field-effect transistors (FETs) [1]. Among the various perovskite semiconductors, Sn-based two-dimensional (2D) layered perovskites have been the subject of interest for their promising applications in high-mobility FETs [2]. Compared to their 3D analogs, 2D perovskite possesses good environmental stability and suppressed ion migration due to the bulky hydrophobic organic cations. Doping as an essential technique can efficiently adjust the electrical properties of semiconductors in terms of carrier concentration and mobility. Being an emerging semiconductor, (Cs2H5SnI3)2SnI4 ((PEA)2SnI4) provides new opportunities and platforms for studying doping physics and techniques, which will not only help enhance the performance of (PEA)2SnI4 FETs but also expand its applications in other optoelectronic devices. Previously, Qin et al. reported the substitutional doping of (PEA)2SnI4 by Pb2+, which leads to improved environmental stability of (PEA)2SnI4 FETs but depressed hole transport owing to the larger effective mass of Pb in the devices [3]. Reo et al. considered doping of (PEA)2SnI4 thin-films with Cu+ by adding copper iodide (CuI) in the precursor solution [4]. It turns out that the hole transport in (PEA)2SnI4 FETs gets enhanced with the incorporation of CuI due to its outstanding hole-transport property. These studies indicate doping can be a powerful technique to tune the performance of (PEA)2SnI4 devices, but presently effective doping strategies for (PEA)2SnI4 remain to be established.

Herein, we report effective p-doping of (PEA)2SnI4 with Sn4+ through substituting part of the SnI2 with SnI4 in the precursor solution. The doping effect of Sn4+ was confirmed by electrical characterizations. This doping strategy was then employed to fabricate (PEA)2SnI4 FETs, which leads to an increase of average mobility from 0.25 cm2 V−1 s−1 for pristine devices to 0.68 cm2 V−1 s−1 for devices doped with 5 mol% SnI4. This study highlights the great potential of the solution-processed Sn4+ doping technique to be used in 2D Sn-based perovskite for flexible and high-performance devices.

II. EXPERIMENTAL

PEAI was supplied by Xi’an Polymer Light. SnI2, N,N-dimethylformamide (DMF) and γ-butyrolactone (GBL) were purchased from Sigma-Aldrich. N-Methyl-2-pyrrolidinone (NMP) and dimethyl sulfoxide (DMSO) were bought from Alfa Aesar. SnI4 was purchased from Aladdin.

0.1 M (PEA)2SnI4 precursor solutions were formed by mixing PEAI and SnI2 with mol ratio of 2:1 in a mixture solvent of DMF and Lewis base (NMP, DMSO or GBL) with different volume ratios. Sn4+ was introduced by mixing PEAI, SnI2 and SnI4 with mol ratio of 2:1−x:1 (0<x<1) in a mixture of 75% DMF and 25% NMP, where x represents the doping ratio of SnI4. The solutions were heated at 60 °C for 4 h in an Ar-filled glovebox. Then, the precursor solutions were stored for 1 h to cool down to room temperature naturally and filtered. Si/SiO2 substrates with bottom-contact electrodes (Cr/Au: 2 nm/30 nm, L = 160 μm, W = 1000 μm) defined by photolithography were cleaned sequentially by deionized water, acetone and isopropanol, and blow dry by nitrogen gas. The substrates were treated with UV/ozone for 30 min before use. Bottom-gate bottom-contact (BGC) FETs were fabricated by spin-coating the precursor solution on the substrates at 4000 rpm for 30 s and annealing at 100 °C for 10 min in an Ar-filled glovebox.

III. RESULTS AND DISCUSSION

Solvent engineering by adding Lewis bases into the perovskite precursor solutions can facilitate the formation of the intermediate phase during spin-coating, which can modify the crystallization [2]. Therefore, we try to mix different Lewis bases with DMF to improve the carrier transport and crystalline quality of spin-coated (PEA)2SnI4 films. The transfer characteristics of FETs prepared from NMP, DMSO and GBL with different volume ratios were exhibited in Fig. 1a-c. The device configuration of BGC FETs was shown in the inset of Fig. 1a. The comparison of mobilities with different solvent
engineering was concluded in Fig. 1d. Devices with 25% NMP solvent exhibited the highest average mobilities, which is related to the slow evaporation speed caused by the high boiling point and low vapor pressure, as well as its good wetting property with the substrate due to the low viscosity [2].

Fig. 2a illustrates the structure of (PEA)2SnI4. Previously, it was reported that SnI2 in Sn-based perovskites are easily oxidized to Sn4+, which are metastable and can thermodynamically evolve to the Sn2+ releasing two holes and leading to the p-doping of the perovskite, i.e., Sn4+ → Sn2+ + 2e− [5, 6]. These results motivate us to intentionally incorporate Sn4+ into (PEA)2SnI4 for controllable p-doping. The average electrical conductivity (σ) of the pristine films, which were prepared from 5% NMP solutions without SnI2 dopant, is 2.6×10−6 S cm−1, and it is enhanced as the doping ratio increases, reaching a maximum average value of 2.1×10−4 S cm−1 at the doping ratio of 30 mol%, which is direct evidence showing the doping effect of SnI2 on (PEA)2SnI4 perovskite.

Encouraged by the prominent doping effect of SnI2 on (PEA)2SnI4 films, we sought to leverage these benefits to enhance the device performance of (PEA)2SnI4 BGBFETs. The devices show typical p-type FET behaviors (see Fig. 2a) due to the low formation energy of tin vacancies which can lead to self-doping effect [7]. The saturation mobility (μ) of 0.25 ± 0.08 cm2 V−1 s−1, threshold voltage (Vth) of −21 ± 1.6 V and on/off ratio (Ion/Ioff) of 104 were obtained in the pristine devices.

As shown in Fig. 2a, by doping the films with SnI2 in the doping range of 1-5 mol%, we observed a significant enhancement of the device current, indicating the improvement of device performance. However, the current begins to decay when the doping ratio is higher than 10 mol%. The variation of performance parameters as a function of doping ratio is presented in Fig. 2b, which shows the devices exhibit μ of 0.68 ± 0.16 cm2 V−1 s−1, Vth of 10 ± 5.6 V, and Ion/Ioff of 105 at the optimized doping ratio of 5 mol%. One thing notable is the increased hysteresis in the doped device, which is probably attributed to the extra I− brought by SnI2 in the films, causing enhanced ion migration. In spite of the slightly increased hysteresis, these results still show that doping (PEA)2SnI4 films with SnI2 is a promising way to achieve high-performance FETs.

Fig. 3. Fabrication and characterization of (PEA)2SnI4 FETs. (a) Transfer curves (Vgs = −40 V) of FETs with different doping ratios. (b) Mobilities, threshold voltages and on/off ratios extracted from transfer characteristics.

IV. CONCLUSIONS

In conclusion, we have reported an effective doping technique by utilizing SnI2 as a dopant for p-doping (PEA)2SnI4. By adopting the doping technique, we were able to enhance the device mobilities of (PEA)2SnI4 FETs dramatically from 0.25 cm2 V−1 s−1 to 0.68 cm2 V−1 s−1. Overall, our work provides a viable doping technique for (PEA)2SnI4, and this solution-processed method is promising for flexible and high-performance devices.

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