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Enhanced perovskite phototransistor by multi-step slow annealing strategy

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ABSTRACT

Methylammonium lead halide perovskites have received substantial attention in the research photovoltaic communities, because of excellent optoelectronic properties, including long electron-hole diffusion distance, large absorption coefficients in the UV–Vis spectral region, low-cost, solution-based processing and low binding energy of exciton. However, the crystal defects of perovskite films such as pinholes, defect and grain boundaries lead to carrier capture, trapping and scattering, so that reduce carrier mobility in the channel, which has become the bottleneck of high device performance and limited the application in photo detection. Here we report a simple and straightforward strategy based on a multi-step annealing process, which can effectively improves the coverage, smoothness, uniformity and crystallinity by restraining defects of pinhole formation. The field-effect mobilities of perovskite photodetector treated by one-step (OS) direct annealing method at room temperature shows mobility as 0.256 (0.129) $cm^2V^{-1}s^{-1}$ for holes (electrons), which increase to 2.32 (1.18) $cm^2V^{-1}s^{-1}$ for that treated by muti-step (MS) annealing method. The latter exhibits high figure of merit as detectivity of 8.94×10^{11} Jones, a responsivity of 32 A/W and a short response time of 42 μs. Moreover, it shows better stability with polymethylmethacrylate film covered, which can maintain 90% of initial performance for 10 days in ambient air. These findings demonstrate that MS annealing methods is simple yet effective and feasible to prepared high-efficient perovskite based photo detectors.

1. Introduction

In the past several years, organolead halide perovskites (ABX_3, where A is an organic/inorganic cation, B is a metal cation, and X is a halide anion) with good intrinsic optoelectronic properties have been employed as active layer materials in photovoltaic devices, solar cells, light-emitting diodes, phototransistors and lasers [1–8]. The advantages of perovskite films are large light absorption coefficient in the ultraviolet–visible spectral region, long carrier diffusion length, and solution processability [9–15]. For now, solution process is the most common method to prepare perovskite films because of versatility and low cost. However, solution-processed polycrystalline perovskite films always suffer from crystal defects such as pinholes and grain boundaries, leading to carrier capture, trapping and scattering. Thus, further improvement of their detector performance means fewer defects and higher charge-carrier mobilities [16–18].

Many technological parameters of solution process are regarded as important factors that influence the morphology of the perovskite films, including the annealing temperature and duration, the organic/inorganic precursor ratio, additives, and solvent [19–29]. For widely used one-step solution process of perovskite films (annealing temperature and duration of 100 °C/40–60 min) has been adopted since the work reported by Lee et al. [7]. Then Snaith et al. investigated influence of the thermal processing on the crystallization and performance of perovskite film by the one-step method [30]. Meanwhile, a stepwise ramp annealing method was proposed by Kim et al. and the surface coverage of perovskite films can be tuned by adjusting solvent evaporation rate [31]. Bi et al. revealed that the poor perovskite quality with small grain sizes is owing to the quick reaction between lead halide and the cations during crystallization of perovskite from the precursor solution [32]. Huang et al. compared perovskite films prepared by one-step and multi-step annealing, and the corresponding performances of solar cells [33].

However, the most works focused on perovskite solar cells, ignoring other perovskite optoelectric devices, like phototransistors. Even if they resemble solar cells, there are obvious differences, such as structures, mechanisms, characteristic curves and parameters. Therefore, it is

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irreplaceable and necessary to investigate the influence of film formation process on the performance to phototransistors.

In this regard, we report on the fabrication and characterization of phototransistors of solution-processed perovskite films prepared by two different annealing processes including one-step (OS) direct annealing method and multi-step (MS) slow annealing method. We choose $CH_3NH_3PbI_{3-x}Cl_x$ perovskite as active material of photo detector, due to high smoothness of surface and large grain size [34]. The morphology, structure, optical properties of perovskite films and the effects of gate voltage and light illumination on the transport of the perovskite channels prepared by OS and MS method were investigated.

2. Experiments

2.1. Solution preparation

$CH_3NH_3PbI_xCl_{3-x}$ perovskite precursor solution was prepared by the following protocol. Lead chloride ($PbCl_2$, 0.8 M, 99.999%, Sigma-Aldrich) and methylammonium iodide (CH_3NH_3I, 2.4 M, 98%, Tokyo Chemicals Industry) were mixed in Dimethylformamide (DMF, Analysis purity grade, Chemical Agent Ltd, China). After magnetic stirring (60 °C, 750 rpm for 1 h), all powders were dissolved in DMF. Then the solution was filtered using a polytetrafluoroethylene filter (0.2-μm pore size) and poured into a light resistant container.

2.2. Film preparation and photodetector fabrication

The heavily p-doped Si wafers with 270-nm thick SiO_2 dielectric layers (capacitance of 11.5 $nFcm^{-2}$) were employed as the substrates. The substrates were cleaned ultrasonically in ethanol, acetone, and isopropyl alcohol for 15 min sequentially and followed by a 15 min UV-ozone treatment. The precursor solution was spin-coated on the substrate at 1000–8000 rpm. (film thickness of 80–600 nm) for 40–50s and then treated by two different annealing methods in a glove box. At last, Ti/Au (10 nm/100 nm) source (S) and drain (D) electrodes were deposited by thermal evaporation via a shadow mask, by which the channel length (L) and the channel width (W) were defined as 0.1 mm and 2.5 mm, respectively. To improve device stability, thin PMMA layer was prepared by spin-coating PMMA solution (7 wt% in anisole) onto the photodetector at 5000 rpm for 40 s and baked at 130 °C for 1 min.

2.3. Measurements and experimental set-ups

The UV–vis absorption spectra of the perovskite films were recorded with a Shimadzu uv-3600 UV–Vis spectrophotometer. The X-ray diffraction (XRD) pattern (2θ scans) were obtained from perovskite films deposited on a SiO_2 substrates using a Rigaku D/max 2500 PC X-ray diffraction. The top view images of the deposited perovskite films were confirmed by a LEO 1530 V P scanning electron microscope (SEM). Atomic force microscope (AFM) images and thicknesses of the perovskite films deposited on the Si/SiO_2 substrates and were taken using a Bruker Dimension 5000 Scanning Probe Microscope (SPM) in contacting mode. Steady-state photoluminescence spectroscopy (PL) measurements were acquired using an Ocean Optics USB 4000 fluorescence spectrometer with an excitation laser in wavelength of 365 nm. The devices *I-V* measurements were performed using a Keithley 4200 Semiconductor Parametric Analyzer and a Signotone Micromanipulator PW-400 probe station. The 405 nm semiconductor laser diode was attached to the microscope of the probe station was used as the light source. During the measurements, the samples were kept at room temperature in the ambient atmosphere.

3. Results and discussion

The perovskite films treated by OS and MS in preparation process of photodetector were displayed in Fig. 1(a) and (b). For OS film, annealing temperature was fixed at 100 °C for 1 h. For MS film, a 6-step temperature-rise process was adopted: 65 °C (10 min); 75 °C (10 min); 85 °C (10 min); 90 °C (20 min); 95 °C (20 min); 100 °C (30 min). At first, a transparent yellow film formed immediately since spin-coating of the precursor solution on the SiO_2 substrate had been finished. In the annealing process, the color change of perovskite film treated by OS method was significantly faster than that treated by MS method. The step-wised annealing made the color change slow and gradual, meaning the precursor reaction and byproducts sublimation occurred slower in MS film [35].

The schematic diagram of typical phototransistors was adopted and illustrated in Fig. 1 (c). The X-ray diffraction pattern of samples are displayed in Fig. 1 (d). The diffraction peak positions of the perovskite films treated by two annealing methods are in mutual coincidence. The peaks at 14.2°, 28.5°, 31.8°, 43.3° and 59.5° can be attributed to (110), (220), (310), (330) and (440) diffractions of $CH_3NH_3PbI_xCl_{3-x}$, respectively, confirming the hybrid perovskite films possess the expected orthorhombic crystal structure with high crystallinity [36]. Note that the intensity of diffraction peaks of the perovskite films prepared by the MS method is much stronger than that of OS perovskite films. It indicates the low speed solvent evaporation facilitates atomic rearrangement, so that increases the crystalline fraction, and improves the crystal quality.

Perovskites have been known as direct-bandgap semiconductors with very large absorption coefficients in the UV–visible range [9,37,38]. The UV–vis absorption spectra of perovskite films treated by the two methods are shown in Fig. 1 (e). Both of perovskite films exhibit a 760 nm absorption peak corresponding to the direct band gap transition from the first valence band to conduction band, and a 480 nm absorption peak representing the transition from the second valence band to conduction band, which consistents with previous reports [9]. But the absorbance of MS perovskite film is stronger than that of OS one in entire range (400 nm–800 nm), due to the enhanced film coverage of the MS film with more favorable film growth.

Fig. 1 (f) shows the steady-state photoluminescence (PL) spectra. The improved PL intensity of MS perovskite films demonstrates that the crystal defect is reduced, so that non-radiative electron-hole recombination is restrained. Meanwhile, the migration length of photogenerated carriers is extended, increasing the radiative recombination rate, when crystal defects and trap-states are induced. Accordingly, a lower intensity of OS perovskite film reveals the structural defects increase in number that non-irradiative recombination centers which reduced the PL intensity.

Morphology, film continuity, grain size, and smoothness are all key factors that contribute to high performance of perovskite photodetector. The influence of the different annealing methods on the morphology and structure of the hybrid perovskite films were examined by SEM and AFM. Obviously, the OS film (Fig. 2 (a)) contains many pinholes with different sizes (from hundreds of nanometers to several micrometers) and an incomplete coverage with sharp grain boundaries. While, the MS perovskite film (Fig. 2 (b)) was more uniform and less pinholes. Obviously, the perovskite films with good coverage can be expected a high level of mobility and detectivity. The surface morphology of the perovskite films was also characterized by the AFM measurement as shown in Fig. 2(c and d). They indicate that the perovskite films treated by the OS method have a rather high roughness with a root mean square (RMS) of 36.7 nm while that of the MS film is 12.7 nm. Consistent with the SEM images, the MS film is more compact and shows few pinholes. From the microscopic pictures and optical spectra, a conclusion can be reached that lower temperature and slower annealing process allow a slow reaction between lead halide and the cations during crystallization, which benefits uniformity of crystal with a small number of internal voids and pinholes.

It's worth mentioning that the channel thickness is a key parameter for phototransistor devices. On the one hand, if the semiconducting channel is too thin, it will not absorb sufficient light [13]. Additionally, pinholes in the thin perovskite films can cause inhomogeneous