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Hybrid perovskite solar cells (PSCs) have rapidly emerged as a promising candidate for the next generation photovoltaics with power conversion efficiencies (PCEs) up to 22%. Low temperature solution processing, low cost raw material and relative insensitivity to intrinsic point defects are some of the attractive qualities of this emerging class of devices. But one of the major obstacles for the commercialization of PSCs lies in the long-term stability of the perovskite films subjected to different environmental conditions such as temperature, humidity and illumination.

In this work, we focused on experimental evidence of halide ion migration in $CH_3NH_3PbI_{3-x}Cl_x$ based solar cells and its effect on current-voltage hysteresis for which various mechanisms have been proposed. The inverted planar structure adopted for the PSCs was: glass/ITO/PEDOT:PSS/perovskite/PCBM/Ag. The perovskite thin films were deposited by 1-step spin-casting process and the organic PEDOT:PSS (hole-transporting layer) and PCBM (electron-transporting layer) layers were deposited by spin-coating process.

Firstly, the PCE under 1 sun equivalent illumination reached 12.7% for the best cell of a series of 10 samples with an active area of 0.28 cm^2. The J-V hysteresis effect was small (less than 2.5%) between the reverse and the forward direction, consistent with the results reported in the literature. Secondly, using glow discharge optical emission spectrometry (GD-OES), a spectroscopic technique allowing direct determination of major and trace elements, we have shown that halide ions migrate inside the perovskite films under an applied bias during 2 minutes in both directions. Furthermore, no migration of lead and nitrogen ions was observed in the same time scale. Thirdly we observed the hysteresis of current-voltage characteristics under dark conditions (thus without any photo-generated carriers) versus voltage scanning rate and temperature. The activation energy value of 0.253 eV derived from the Nernst-Einstein relation above 264 K, for which the perovskite phase is tetragonal, indicates that the conduction is dominated by the ions (instead of electrons for conventional semiconductors) and furthermore confirms that the conduction is ascribed to the migration of anion vacancies, which is well known in the perovskite-type halides such as $CsPbCl_3$ or $CsPbBr_3$. These experiments prove that there is a direct link between halide ion migrations in $CH_3NH_3PbI_{3-x}Cl_x$ based perovskite thin films and current-voltage hysteresis.